SESTEC - 2024

XI DAE - BRNS BIENNIAL SYMPOSIUM ON EMERGING TRENDS IN SEPARATION SCIENCE AND TECHNOLOGY

July 10 - 13, 2024
HSNC University, Mumbai, India

Organised by
Bhabha Atomic Research Centre, Mumbai
in association with
HSNC University, Mumbai
&
Association of Separation Scientists and Technologists (ASSET)

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व
सचिव, परमाणु ऊर्जा विभाग
Chairman, Atomic Energy Commission
&
Secretary, Department of Atomic Energy

MESSAGE

I am pleased to learn that the XIth DAE-BRNS Biennial Symposium on "Emerging Trends in Separation Science and Technology" (SESTEC-2024) is being organized at HSNC University, Mumbai, India during 10 -13July 2024.

Separation science and technology plays a pivotal role in various stages of the nuclear fuel cycle, from recovering uranium and thorium from ores in the front end to efficiently retrieving fissile materials from the spent fuels in the back end. Depending on the natural resource availability, different countries opt for either open (without recycling) or closed (with recycling) nuclear fuel cycles. The Indian nuclear power program is committed to the closed fuel cycle approach and has developed schemes for the recovery of valuable radionuclides from the spent fuel thereby maximizing the use of natural uranium and thorium resources.

Innovative, efficient, selective, cost-effective, environmentally benign, and commercially viable separation schemes and related technologies are crucial for reprocessing spent nuclear fuels and extracting fissile materials from natural resources. Separation science and technology also plays a key role in producing highly pure radioisotopes for medical and other societal applications. The scalability of laboratory-scale R&D to commercial implementation is heavily influenced by chemical engineering considerations.

I understand that a good number of participants are from overseas countries will be presenting their research work at the symposium. SESTEC-2024 will provide a vital platform for researchers and engineers in the field of Separation Science and Technology to interact, share their insights, and address real-world challenges related to separation processes.

I am confident that SESTEC-2024 will comprehensively cover robust and efficient separations in the nuclear fuel cycle, as well as novel separations in diverse fields such as energy, bio refinery, water purification, wastewater treatment, solvent synthesis, and purification.

I extend my best wishes to all participants of SESTEC-2024.

Ajit Kumar Mohanty
(Ajit Kumar Mohanty)

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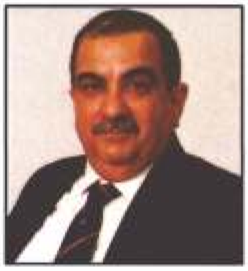

MESSAGE

I am glad to know that the XIth DAE-BRNS Biennial Symposium on "Emerging Trends in Separation Science and Technology" (SESTEC-2024) will be held at HSNC University, Mumbai, India, from July 10th to 13th, 2024.

Separation science plays a pivotal part in many areas of science and technology including nuclear science. India's nuclear power program is based on a three-stage closed nuclear fuel cycle, where reprocessing of the spent nuclear fuel poses significant challenges due to the complex nature of the dissolver solution and the associated radio-toxicity. Presently, the PUREX process is the primary process for separating Uranium and Plutonium from the dissolver solution. Management of the high level waste is another challenging step in the back end of the nuclear fuel cycle. In recent years, non-aqueous reprocessing involving dissolution of spent fuel in molten salt/ionic liquids followed by preferential electrochemical separation has emerged as a novel and viable approach and poise to play a significant role in ambitious Indian nuclear energy program. Solid adsorbent based treatment of large-volume low-radioactivity waste solution is cost effective procedure. Environmental remediation of contaminated sites requires robust understanding of environmental chemical behaviour of long lived actinides and fission products. Research and development of efficient and selective adsorbents for various radionuclides will thus be crucial for a safe nuclear energy program.

Outside the nuclear industry, separation science and technology also plays an important role in waste water treatment where membrane based separation methods are routinely employed. Other sorbents like activated carbons, composite nanomaterials with specific functionalities are being increasingly employed by researchers worldwide. Apart from these, 'green' separation methods using deep eutectic solvents and other methods like electro coagulation find applications for the separation of heavy metals from industrial effluents.

SESTEC-2024 technical program covers a wide range of presentations on various aspects of separation science and technology. I am delighted to note the overwhelming participation from various DAE units, CSIR labs, IITs and universities. A good number of distinguished overseas speakers, renowned pioneers in their fields, will deliver presentations. I am confident that the deliberations at this symposium will inspire young researchers and will provide excellent opportunities for networking, sharing ideas, and fostering innovation which can positively impact India's efforts in achieving Amritkaal goals.

I wish SESTEC-2024 a grand success.

Vivek Bhasin

01.07.2024

(Vivek Bhasin)

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HSNC University, Mumbai

A State Public University

Prof.(Dr.) Hemlata K. Bagla
Co-Chairman, SOC,
SESTEC-2024
Vice Chancellor
HSNC University, Mumbai

I am delighted to welcome all participants to the Eleventh DAE-BRNS Biennial Symposium on "Emerging Trends in Separation Science and Technology" (SESTEC-2024), which will be held at HSNC University, Mumbai, India, from July 10th to 13th, 2024. The symposium is jointly organized by Bhabha Atomic Research Centre, Mumbai, in collaboration with HSNC University, Mumbai, and the Association of Separation Scientists and Technologists (ASSET).

I am confident that the symposium will serve as an excellent platform for scientists and engineers to discuss recent advances in separation science and technology, encompassing membrane technology, reactive separations, chromatographic separations, wastewater remediation, and separations related to nuclear fuel cycle activities. This symposium has effectively facilitated such discussions over the past several years.

Hosting this prestigious event at HSNC University, Mumbai, provides a unique opportunity for our young researchers to engage with leading national and international scientists in the field of separation science and technology, and to actively contribute to the symposium's organization. The significance of separation processes in chemical synthesis operations, particularly in terms of cost and technology advancement, cannot be overstated. The special session on **“Wealth from Waste: Recycling Perspectives”** promises to be particularly enlightening.

On behalf of HSNC University, I extend my best wishes to all participants and invite them to explore our facilities and engage with my colleagues during their visit. I also wish to express my sincere gratitude to our supporters whose generous and timely contributions have been instrumental in ensuring the success of SESTEC-2024.

HKBagla

Prof. (Dr.) Hemlata K. Bagla

Message from Director, RC & I G

I am delighted that the Eleventh DAE-BRNS Biennial Symposium on "Emerging Trends in Separation Science and Technology" (SESTEC-2024) will be held at the HSNC University, Mumbai, India, from July 10th to 13th, 2024, with the participation of around 300 delegates including a good number of overseas participants. We have curated an engaging and stimulating technical program that reflects the latest advancements in the field of separation science and technology.

SESTEC-2024 will feature approximately 230 contributory papers covering a wide range of topics relevant for separations including the synthesis of solvents, resins, and membranes; separations in the nuclear fuel cycle; green separations; chromatography, electrochemical, and pyro-chemical separations; separation in industries; wastewater remediation; membrane science and technology; radiochemical separations; speciation studies; and computational studies in separation processes.

The SESTEC series of symposia has consistently attracted separation scientists and engineers, providing a valuable platform for young minds to interact with experts in their respective fields relevant to the nuclear fuel cycle. From mining of U to the reprocessing of spent nuclear fuel, separation science and technology remains integral to the nuclear fuel cycle. R&D efforts have been focused to exploring new alternative separation methods relevant to the nuclear fuel cycle, particularly directed towards innovative management of radioactive wastes.

Separation science and technology also plays a crucial role in modern industries. To highlight its impact on wastewater remediation, a special session has been dedicated with presentation from delegates from different institutes. Additionally, a symposium session will underscore the importance of separation science in the operations of the Heavy Water Board for isotopic separations.

On behalf of the Organizing Committee of SESTEC-2024, I extend a warm welcome to all delegates attending this Symposium. I am confident that this event will prove invaluable for exchanging innovative ideas and forging collaborative work program between different research groups.

(P.K. Mohapatra)
Director, RC & I Group

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Proceedings of 11th DAE – BRNS Biennial

Symposium on Emerging Trends in Separation Science and Technology (SESTEC – 2024)

**Hyderabad (Sind) National Collegiate (HSNC) University,
Mumbai, India**

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Organized by

Bhabha Atomic Research Centre, Mumbai

Co-organized by

**Association of Separation Scientists and Technologists (ASSET)
&
Hyderabad (Sind) National Collegiate (HSNC) University**

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Advanced polymer-based membranes with tailored adsorptive and catalytic properties

Mathias Ulbricht

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Membrane technologies have been established in a wide range of industrial applications; the most successful processes are nowadays realized in very large scale. Organic polymers are the dominating materials, and intense research and development is focused on innovations leading to advanced membranes with higher separation performanceadapted to specific requirements of important applications [1].One key approach for scalable manufacturing of porous polymeric membranes is casting of polymer solutions followed by controlled phase separation (“phase inversion”), with the option to obtain a wide range of pore structures from the same casting solution (e.g. [2]). The modification or functionalization of the membrane surface can be used to further tailor properties toward specific requirements (e.g. [3]).

In this presentation we will discuss approaches to novel porous polymer-based membrane with integrated adsorber or catalytic properties. Porous membrane as flow-through adsorber can be obtained by reactive coating of established filtration membranes [3] or by integrating adsorber particles during membrane casting via phase inversion [4]. Recently we had established a platform for the fabrication of porous polymer-based multi-composite membranes that can have very high loading of functional additives. The first case study revealed remarkable synergies between nickel nanoparticles and carbon particles as additives in polyethersulfone-based membranes, regarding both, processability and catalytic activity of nickel in reduction reactions [5]. The scope of functionalities and potential applications is currently extended to photocatalytic materials [6], the *in situ* fabrication of catalytic nanoparticles in the polymer solution before casting and phase inversion [7] as well as reactive deposition of metal nanoparticles in functional porous (electrically conductive) polymer membranes. The application potential of the novel functional membranes will be demonstrated in studies on flow-through catalytic degradation of micropollutants in water [5-7],and the utilization of porous carbon-loaded polymer membranes as catalytic electrodes for electrochemical reactions such as, for example, carbon dioxide reduction.

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Closed nuclear fuel cycle strategy in Russia

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The nuclear power is the only large-scale source of energy that is independent on the external conditions like wind, sun or tide. It is responsible for c.a. 30% of green energy production worldwide with the tendency to increase. However, the limiting issue of nuclear energy generation is nuclear wastes that are generated at all steps of the nuclear fuel cycle. The most challenging technological task is the management of spent nuclear fuel or high-level wastes (HLW) from the reprocessing of this fuel. The geological disposal of high-level wastes is one of the options for HLW management that requires safety assessment for >100.000 years. The other option is partitioning and transmutation that enable burn-up of long-lived radionuclides like actinides in fast neutron reactor. This enables to decrease the safe disposal to c.a. 300 years.

The options for partitioning of rare-earth elements and minor actinides using various extraction systems are addressed in the presentation. The studies involve quantum chemical predictive calculations for various molecules, synthesis of the most promising candidates and their studies under various conditions. The record high values of separation factors for Eu/Am and Am/Cm is achieved by diamides of phenanthrolinedicarboxylic acids that also demonstrate high radiation and hydrolytic stability.

Using literature data as well as experimental data the model to calculate separation factors as well as solubility and lipophilicity is developed based on the machine learning methods. This model has a good predictive power enable effective ligand design.

These studies are used for the new strategy development based on the combination of thermal neutron reactors with cheap energy generation and fast neutron reactors for recycling of fissile materials and burn-up long-lived radionuclides from wastes (e.g. Am-241).

Keywords: partitioning, high-level wastes, geological disposal

Commissioning Experience of Demonstration Fast Reactor Fuel Reprocessing Plant

K.Rajan
Associate Director, Reprocessing Group
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The Demonstration Fast reactor fuel Reprocessing Plant (DFRP) has been constructed and successfully commissioned at IGCAR, Kalpakkam. The main objective of this plant is to process spent fuel discharged from FBTR on regular basis (Carbide & Oxide) and to demonstrate the reprocessing of spent fuel from PFBR. The process and equipment design is based on the extensive operating experience gained from CORAL (COmpact Reprocessing of Advanced fuels in Lead cells). The valuable feed back from DFRP will be useful in optimizing the design of future fast reactor reprocessing plants, namely the Fast Reactor Fuel Cycle Facility (FRFCF).The commissioning of this facility was carried out in stages as per regulatory requirements viz, pre commissioning checks and tests, water-acid run, acid-TBP run, uranium run and hot run. This paper brings out the strategies followed in commissioning the facility and the experiences gained during the same.

In the Stage – I of commissioning, the pre-operational checks and tests were performed, including physical verification of all the systems (pipelines, equipment), calibration of process equipment and tanks, along with the checking of the operability of associated instrument systems, settings of process interlocks/alarmsetc. This stage of commissioning has a significant role in ensuring the consistency between design requirements and as-built status of the systems including their proper identification. The operational status of all the process and utility systems of the plant were checked. A procedure was established for controlling temporary changes to plant and equipment. The activities and reviews carried out at this stage were very important to establish the as-built status of the plant and in planning the subsequent commissioning activities.

The next stage, Stage – II, Water/ Acid Run was carried out with the objective of obtaining the initial operational data on equipment ensuring the compatibility of operation with the interfacing systems and to verify the performance of these systems. The major activities in this stage include - acid flushing of all tanks, equipment and pipelines, performance testing of liquid transfer systems, performance testing of Dissolver& Evaporators and leak Testing of the cells/ Containment boxes (achieving acceptable leak rates meeting international standards) to ensure the integrity of the cells for handling radioactivity. The reports and results were submitted to Regulatory authorities for review towards obtaining the clearance for the next stage of commissioning. During this stage, it was ensured that the performance of all the systems were meeting their design intent. In case of any deficiencies, the same were rectified and retested, before proceeding to the next stage.

Acid/ Solvent Run Stage – III of the commissioning program was carried out for the hydrodynamic testing of the solvent extraction contactors, solvent wash equipment and diluent washers. Also the performance testing of the liquid transfer system associated with the solvent, performance testing of sampling system, were done during this stage. In this stage of commissioning, the solvent was introduced for the first time in the tanks and the process piping in the cells. So, it was ensured that the process cells were free of all sources of ignition and combustible material before introduction of the solvent into system. Also, all the modifications were to be completed before this. Erection of lead bricks& RSWs, followed by the Radiometry Testing for the cells, to evaluate the shielding adequacy of the cells was carried out. The Pre-Service Inspection of dissolver equipment was also completed.

The cold feed run, Stage – IV of commissioning was carried out with an objective of demonstrating the performance of all the key plant equipment and systems of the head end (chopping, dissolution, and clarification), mass transfer performance of process (solvent extraction contactors, evaporators) and performance of Uranium reconversion system using uranyl nitrate solution. At this stage review towards the design criteria for radiological protection of the plant– Zoning/ barriers, Radiation Monitoring requirement aspects and security aspects of the facility were also carried out. Procedures and Compliance for obtaining waste authorization approval from regulatory body were initiated. Necessary steps were taken to carry out the Dose budgeting for the activities planned in hot commissioning of the plant. Also, training and licensing/qualification of the operation and maintenance personnel of various levels, was carried out to ensure availability of qualified manpower for hot operations.

Stage – V of commissioning, namely Limited Hot feed run is the last milestone activity which completes the commissioning phases with introduction of radioactive material i.e. spent fuel into the plant and marks the start of the operation of the plant. This stage was started after complying with the relevant radiological and other operation safety requirements for plant operation viz., stack monitoring, and adequacy of off gas / ventilation system. The plant has been hot commissioned with the processing of the first batch of spent fuel from FBTR with a burnup of 155 Gwd/ton. All the process and support systems have performed as intended and the product has been successfully recovered meeting all the specifications. Additionally, the waste streams such as the raffinate and lean organic had very less Pu losses and have qualified for disposal to the waste management agency. With the successful commissioning of this facility, we have moved a step closer to realizing a robust commercial scale reprocessing of fast reactor spent fuel.

Integrated Electrocoagulation and Membrane Distillation for Treating Hydraulic Fracturing Produced Water

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Water is a very valuable natural resource. Maximizing reuse of wastewater is essential to meet increasing demands for fresh water. Hydraulic fracturing is used to recover oil and gas from tight rock formations. While this is an effective method to recover oil and gas from these non-conventional resources, a significant amount of highly impaired flow back and produced water is results. Currently this water is often deep well injected into geologically isolated formations. Maximizing recovery of this water for beneficial uses is essential to promote a circular economy. Further it has been shown that deep well injection of large amounts of produced water can lead to earthquakes.

Given the highly impaired nature of this produced water, multiple unit operations are needed if these wastewaters are to be recovered for beneficial uses. Electrocoagulation is considered a promising pretreatment technology. Herein, we have investigated the use of aluminium electrodes for electrocoagulation as a pretreatment operation. The effects of electrode arrangement applied current, reaction time, pH, and inter electrode distance on the quality of the treated water have been investigated.

The results obtained here indicate that electrocoagulation can obtain good removal of turbidity (95%), total suspended solids, TSS (90%), and total organic carbon, TOC (69%) by carefully choosing the reaction conditions. The performance of the electrocoagulation process depends strongly on the quality of the feed water. The viability of a practical continuous electrocoagulation process will depend on the volume (footprint) of the reactor which in turn will depend on operating conditions and the quality of the feed water.

Microfiltration using submerged membranes was used to rapidly separate the sludge from the supernatant. Next membrane distillation was used to remove non-volatile inorganic salts. Based on laboratory data, a 1,000L per day pilot scale unit was built and evaluated.

We show that combining membrane distillation with a crystallizer can maximize wastewater recovery. Crystallization in the feed tank was used to suppress scale formation on the membrane distillation membrane. By treating and reusing PW, preservation of surface and groundwater forming 80% of the water utilized in hydraulic fracturing could be achieved. In addition, treating PW will reduce the amount of PW directly disposed in Class II disposal wells, which further address the main cause of earthquakes. However, addition of a crystallizer will lead to increased operating costs.

The commercial viability of membrane distillation for treating hydraulic fracturing produced water depends on ensuring the membrane dose not wet leading to failure of the process. Here electrocoagulation was shown to be an effective pretreatment process for removal of dissolved organic compounds that can foul the membrane and lead to passage of water through the membrane pores. However, development of more robust membranes that are resistant to wetting will be essential and can help reduce the level of pretreatment required. Recent work on modification of the membrane surface in order to impart fouling resistance will also be presented.

Production and Applications of Radioisotopes at RIKEN RI Beam Factory – Search for New Elements through Therapy of Cancer

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At RIKEN RI Beam Factory, Wako, Japan, we have been developing production technologies of radioisotopes (RIs) and conducting RI application studies in the fields of physics, chemistry, biology, engineering, medicine, pharmaceutical and environmental sciences [1,2]. With light- to heavy-ion beams from the AVF cyclotron, we produce more than 100 RIs from ^{7}Be (atomic number $Z = 4$) to ^{262}Db ($Z = 105$). In chemistry of super heavy elements (SHEs), chemical properties of Rf ($Z = 104$) in aqueous solutions were investigated in collaboration with Osaka Univ., Kanazawa Univ., and JAEA [3–5]. In nuclear medicine, we have been developing a production technology of ^{211}At in the ^{209}Bi(α,2n)^{211}At reaction for targeted α-particle therapy (TAT) [6].

RIs of a large number of elements (multitracer) are simultaneously produced from metallic targets such as ^{nat}Ti, ^{nat}Ag, ^{nat}Hf, and ^{197}Au irradiated with a 135-MeV/nucleon ^{14}N beam from RIKEN Ring Cyclotron (RRC) [7]. The multitracer is useful to trace the behavior of many elements simultaneously under an identical experimental condition. Recently, we have devised a large-scale ^{211}At production system with a rotating ^{209}Bi target and a dry distiller for chemical separation of ^{211}At on the beam line of RRC [6]. ^{225}Ac has also been produced in the ^{232}Th(^{14}N,$xnyp$)^{225}Ac reaction for TAT [8].

An isotope of element 113 was synthesized in the cold fusion reaction of ^{209}Bi(^{70}Zn,n)^{278}113 using the gas-filled recoil ion separator (GARIS) at the RIKEN Linear ACcelerator (RILAC) facility [9]. The name nihonium and symbol Nh were approved for the new element to complete the 7th period of the periodic table [10]. A synthesis experiment of new element 119 is ongoing in the ^{248}Cm(^{51}V,xn)$^{299-x}$119 reaction using GARIS-III at the upgraded superconducting RILAC facility (SRILAC) [11]. We installed a gas-jet transport system to GARIS as a novel technique for the SHE chemistry [12]. Long-lived SHE RIs of ^{261}Rf, ^{262}Db, ^{265}Sg ($Z = 106$), and ^{266}Bh ($Z = 107$) useful for chemistry experiments were produced in the heavy-ion induced reactions on a ^{248}Cm target and their decay properties were investigated in detail using a rotating wheel apparatus for α and spontaneous fission spectrometry [12,13]. After the successful chemical synthesis of Sg(CO)$_6$ led by the Univ. Mainz and GSI groups [14], a detailed experiment to investigate the stability of the metal carbon bond in Sg(CO)$_6$ is in progress with a thermal decomposition setup led by the PSI group [15]. Also syntheses and properties of Tc, Ru, Rh, and Re carbonyls were studied with the ^{252}Cf fission source at IMP and GARIS for future studies on Bh, Hs ($Z = 108$), and Mt ($Z = 109$) carbonyls [16–18].

Keywords: Radioisotope production, Heavy-ion accelerator, Superheavy elements, Targeted α-particle therapy

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Application of Micro Polymer Inclusion Beads for Zn(II) Separation

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The recovery of Zn(II) from industrial wastewater is advantageous by reducing the metal discharges into the environment and promoting resource recycling. The present study reports a promising approach for recovering Zn(II) from acidic wastewaters (i.e. electroplating solutions) using polymer inclusion beads (PIBs) within the size range suitable for industrial applications (i.e., > 500 µm diameter). This was achieved via modification of our previously developed microfluidic system for the fabrication of micro polymer inclusion beads (i.e., < 100 µm diameter) and re-optimisation of the PIB fabrication parameters such as fabrication flow rates and desolvation conditions. PIBs with average diameter of 620 ± 32 µm containing 30:70 wt% ratio of poly(vinyl chloride) and di-(2-ethylhexyl)phosphoric acid) were fabricated, exhibiting a smooth and spherical appearance, with a loading capacity of 48.3 mg Zn/g PIBs. These PIBs achieved Zn(II) extraction of over 93% and back-extraction efficiency of 99% from 30 mg L^{-1} Zn(II) solution at pH 3.0 and 1 M HCl, respectively, and were reusable for at least seven complete extraction/back-extraction cycles under batch conditions. High selectivity for Zn(II) over copper(II) and nickel(II) was demonstrated. The PIBs were characterised by optical microscopy and thermogravimetric analysis (TGA) and were successfully applied to the separation of Zn(II) from electroplating solutions. Also, a column packed with these PIBs was demonstrated to be suitable for Zn(II) separation.

Intensified separations using ultrasound focusing on extraction, leaching and crystallization

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Passage of ultrasound through a liquid medium under specified conditions of frequency and intensity results in generation of cavitating conditions. Cavitation can be in general defined as generation, growth and subsequent collapse of the cavities releasing large quantum of energy locally with overall conditions remaining as ambient. The spectacular effects of cavitation viz. generation of highly reactive free radicals, local hotspots and liquid circulation associated by intense turbulence make application of ultrasound a lucrative technique for separations. The present work will initially highlight the different aspects of ultrasound based reactors including mechanism of generation of cavitation, reactor designs and optimum operating parameters.

Experimental case studies based on the research work at Institute of Chemical Technology will also be presented. It has been conclusively shown that controlled application of ultrasound is able to intensity the extraction, leaching and crystallization without affecting the recovered products. Specifically the expected benefits in the case of extraction and leaching are higher yields and reduced time whereas in the case of crystallization, the expected benefits include uniform particle size distribution, lowering of induction time and metastable zone width as well as lower mean size of obtained particles. The effect of important operating conditions such as power dissipation, duty cycle and time of irradiation in addition to specific application related parameters will also be discussed along with the reactor designs suitable for large scale operations.

Overall, it appears that the use of ultrasound result into a significant increase in the productivity as demonstrated using number of studies at laboratory and pilot scale of operations. Proper optimization of the operating parameters should result in a substantial savings in the treatment costs without affecting the final product quality.

Covalent Organic Framework Membranes for Molecular Separations and Beyond

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Membrane-based separation is vital in various industrial processes because of its low energy consumption, compact design, and ease of operation. The advancement of this technology hinges on the development of innovative membrane materials. While polymer-based membranes have been used for a long time, their efficiency is limited by the trade-off between permeability and selectivity. Thus, the quest for novel membrane materials is a primary focus for academia and industry. Nanoporous materials, such as zeolites, metal-organic frameworks (MOFs), and covalent organic frameworks (COFs), based membranes provide better separation performance due to their ordered porous structures.

COFs, in particular, are promising for advanced gas and liquid-phase separation processes because of their crystalline nature, well-defined porosity, tunable functionalities, and versatile architectures.[1] Since the first COF membrane (COFMs) for gas separation was introduced in 2015, there has been rapid progress in their development, underscoring their potential in membrane-based separations of gas mixtures (CO_2/N_2; CO_2/CH_4; H_2/N_2 etc.), molecular separation (ions and dye separation), solvent nanofiltration, oil-water separationand more.[2]Not limited to molecular separation, recently, COFMs have also been emerged as potential semiconducting materials for photonics and optoelectronic device applications.[3]In my talk, I will discuss two of our recent works on optical conductivity of free-standing 3D COFMs using terahertz (THz) spectroscopy and nonlinear optical (NLO) response of free-standing COFMs along with molecular separation potentials of our inhouse developed COFMs.

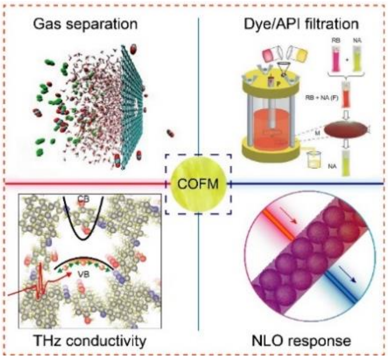

Figure 1. Schematic of the distinct applications of COFMs for molecular separation and light-matter interaction.

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Multiple Ligand and Selective Oxidation Based Approach for Am/Cm Separation

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Both the intergroup separation of trivalent actinides and lanthanides and separation of Am and Cm is an essential step in the back end of the nuclear fuel cycle for the long term sustainability of the nuclear energy program. A large number of ligands have been developed by different research groups around the world for intergroup separation of trivalent actinides and lanthanides. Separation of two consecutive 'f' block elements in the same group which are present in the same oxidation state is the most difficult job for the separation scientists due to their very close ionic potential. Separation of Am^{3+} and Cm^{3+} seeks special attention to the separation scientists in view of their very similar complexation and extraction behaviour. Two different approaches are explored for the mutual separation of these two consecutive '5f' elements.

In one case, the cooperative effect of the marginal and opposite selectivity of two different ligands is exploited by taking these two ligands in two different phases. Diglycolamide (DGA) based ligands shows marginal selectivity for Cm^{3+} over Am^{3+} due to marginally smaller ionic radus of Cm^{3+} as compared to Am^{3+}. Tetradentate hydrophilic 'N' donor heteropolyclyclic ligands, on the other hand show preference for Am^{3+} over Cm^{3+} probably due to marginally higher softness of the former resulting in marginally higher covalent interactions between Am^{3+} and 'N' donor heteropolyclyclic ligands. We could successfully improve the separation efficiciency by combining lipophilic DGA and hydrophilic 'N' donor heteropolyclyclic ligands.[1,2] Interestingly reversal of selectivity was observed by suitably changing the ligand combination.[3]

In another case, however, selective oxidation of Am is adapted to develop the separation strategy of Am and Cm. This oxidation based separation methods give much higher selectivity as compared to the previously described method. Sodium bismuthate is evaluated by many researchers around the world for the oxidation of americium. There are, however, many contradictory reports in the literature on the oxidation behaviour of Am by this well known oxidant and the mechanism of the Am oxidation, viz. whether the oxidation occurs in the solution or at the surface is not clear till date. We, therefore, revisited the Am oxidation study more systematically by the bismuthate ion and suggested an inter layer ion exchange assisted oxidation mechanism. We could achieve a separation factor of $>10^4$ between Cm and Am through the selective oxidation of americium.[4]

In this talk, I will share our experience on Am/Cm separation at Radiochemistry Division, BARC using both the separation strategies, viz. exploitation of cooperative selectivity of two ligands and selective Am oxidation based separation of Am and Cm.

Keywords: Am/Cm separation, Cooperative selectivity, Am oxidation, Sodium bismuthate

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Probing the possible building blocks of Fe^{3+} and Fe^{3+}-As^{3+} containing natural minerals for permanent decontamination

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Iron oxyhydroxide, a natural nanophase of iron found in the environment, plays a crucial role in regulating surface and groundwater composition. Recent research proposes that within the nonclassical prenucleation cluster growth model, subnanometer-sized clusters (olation clusters/Fe_{13} δ-Keggin oxolation clusters) might act as the prenucleation clusters (PNCs) of ferrihydrite or iron oxyhydroxide solid phase. However, these clusters are difficult to characterize as they are only observable momentarily in low-pH, high-Fe concentration solutions before agglomerating into extended solids, keeping the controversy over the true nature of the PNCs alive. Based on our previous observation [1], we introduce large quantities of zinc acetate salt (ZA) into iron chloride solutions at the olation−oxolation boundary (3.6 mM Fe^{3+} at pH

$\sim$2.6). Remarkably, this manipulation is found to alter the structural arrangement of these subnanometer clusters before blocking them in isolation for hours, even at pH 6, where extended iron oxyhydroxide phases typically precipitate [2]. On the other hand, understanding the chemical interactions prevalent between Fe^{3+} and As^{3+} ions in aqueous medium leading to nucleation of ionic clusters/solids, followed by aggregation and growth of stable solid phases, is of great environmental significance. Therefore, we also attempt to probe the nucleation process of Fe^{3+}-As^{3+} clusters in solutions of various concentrations and pHs using a combination of experimental and theoretical techniques. Interestingly, our study reveals nucleation of primary FeAs clusters in nearly all of them independent of concentration or pH. Theoretical studies employed density functional theory (DFT) to predict the primary clusters as stable Fe_4As_4 units. The surprising resemblance of these clusters with known Fe^{3+}-As^{3+} minerals at the local level was observed experimentally, which provides an important clue about solid-phase growth from a range of Fe^{3+}-As^{3+} solutions [3]. Experimental techniques such as synchrotron-based small-angle X-ray scattering, X-ray absorption spectroscopy, high-resolution transmission electron microscopy (TEM), and cryoTEM, along with density functional theory (DFT) calculations, have been employed in carrying out these studies.

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Multiscale Modeling of Metal-Ion-Ligand Complexation and Decomplexation Phenomena in Solvent Extraction

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The recent trend towards renewal of attention in nuclear power as a futuristic energy alternative is driven by the goal of net zero carbon emission. However, widespread acceptance of nuclear power necessitates an effective spent fuel reprocessing approach for safe management of nuclear waste. The reprocessing using the concept of closed nuclear fuel cycle can reduce the high-level solid waste along with creation of the renewed fuel for nuclear reactor of 2nd generation. The large scale reprocessing of spent fuel is mostly performed by solvent extraction and hence is dictated by the efficiency of the liquid-liquid extraction (LLE) processes. In LLE process, the radionuclide are separated from acidic aqueous solution by a molecular extractant resides in an organic solvent. The selection of solvent and molecular extractant is mostly done by myriad of trial experiments. Additionally their thermophysical and dynamical properties are also experimentally determined for interpretation of the experimental results. Overall, selection of solvent-ligand system for preferential complexation and selective extraction for a specific radionuclide by performing experiments is a tedious and costly affair. Moreover, many spatial and temporal characteristics of the chemical species within the experimental system is either very difficult to measure experimentally or not possible at all.Due to inherent difficulty, the understanding of molecular details at liquid–liquid interface using only experimental technique is inadequate to establish the interfacial behaviour. This is mostly due to the fluidity of the interface and its concealed environment, which restricts the experimental facts.

Multiscale modeling (MM) consisting of electronic structure calculations, statistical mechanics, ab-initio and classical molecular dynamics simulations with the aid of supercomputational facility and machine learning can capture the complex molecular phenomena in LLE process at different spatial and time scales. Therefore, MMwill expedite to reach a reasonable conclusion in minimum no of trials of experiments and thus reduce the cost as well as time. The present talk will focus on the fundamental understanding of structural, thermo-physical and dynamical properties of the liquid-liquid extraction system in bulk and at the interface using ab-initio and molecular dynamics simulations. Additionally, elucidation of the decomplexation and reverse migration mechanism of radionuclide from loaded organic phase to the aqueous phase using large time scale molecular dynamics simulation and density functional theory will be presented.

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IT-05

Innovative Approaches for Sustainable Manufacturing of Functionalized Membranes for Metal Extraction and Recovery

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Functionalized polymeric membranes offer an attractive and straightforward solution to address the urgent demand for sustainable metal extraction methods. They can efficiently extract raw materials from waste sources and fulfill the imperative need to protect the environment from toxic elements. However, for these membranes to be considered a viable solution for industry applications, enhancements in their formulation are required. This involves focusing on more sustainable manufacturing practices in terms of material selection, as well as exploring novel routes to produce highly stable and reusable membranes.

In this study, we investigate various approaches to achieve greener manufacturing of functionalized polymeric membranes. We introduce novel materials for producing polymer inclusion membranes (PIMs) and explore the utilization of polymerized ionic liquids. The resulting membranes have been used to treat different type of waters contaminated with metals such as Hg, Pd, Cd, and Cr.

In the case of polymeric membranes including an specific extractant (as PIMs), the polymers traditionally used are cellulose triacetate (CTA) and poly(vinyl chloride) (PVC). They are dissolved in a suitable organic solvent, such as chloroform and THF. However, to enhance sustainability and avoid harmful solvents, a shift towards utilizing more eco-friendly alternatives is mandatory. This is the case of the polymer poly(caprolactone) (PCL), a biodegradable and flexible polyester used, for example, in medical applications. PCL has shown to be compatible with extractants such as Aliquat 336 and the task-specific ionic liquid trioctylmethylammonium thiosalicylate (TOMATS), providing useful membranes for the extraction of Cd ions in sea water or the recovery of Pd. Other components of PIMs include plasticizers, which are added to improve both the mechanical and transport characteristics of the membrane. Traditionally, phthalates like DEHP and DBP have been extensively used as plasticizers, but growing concerns over their health and environmental impacts have led to exploration of alternative options. Butyl stearate (BTS) is a synthetic, oil-based ester with a significantly lower cost compared to other plasticizers. It has recently emerged as an attractive alternative for manufacturing PIMs aimed at removing Hg from natural water. BTS has proven to be a suitable plasticizer for both PVC- and CTA-based PIMs, using TOMATS as an extractant. Membranes prepared with BTS exhibit hydrophilicity and mechanical properties similar to those prepared with traditional plasticizers.

Furthermore, the use of polymerized ionic liquids (PILs) in manufacturing polymeric membranes offers a novel method to incorporate specific functional groups in a highly stable manner. By incorporating imidazolium-polymerized ionic liquids (PILs), the resulting membranes are mechanically stable and useful for the extraction of Cr(VI). Stability tests have shown that these membranes can be reused multiple times without degradation, even after exposure to alkaline solutions (used as stripping solution). Notably, these membranes do not require regeneration or activation treatments, making continuous Cr(VI) recovery through membrane permeation feasible. Moreover, the imidazolium PIL-based membrane has demonstrated high efficiency in recovering chromate from industrial wastewater samples, indicating its practical suitability for environmental remediation and highlighting the potential of PIL-based membranes as sustainable and efficient materials for water treatment applications.

Keywords: Functionalized polymeric membranes, Greener manufacturing, Polymerized ionic liquids, metals.

Acknowledgments: *Ministerio de Ciencia, Innovación y Universidades through project PID2022-140312NB-C22 funded by MICIU/AEI/10.13039/501100011033/FEDER, UE is acknowledge for the financial support.*

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Separation Science at the Core of Environmental Remediation of Contaminated Sediments

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Differential affinity of pollutants to sorbents has been integral to the design of engineered environmental process, which is most apparent in the field of water treatment. Transport of toxic pollutants in the natural environment, such as in aquatic sediments and groundwater aquifers is also controlled by sorption processes. The biggest challenge in describing the sorption mediated separation processes in the sediment/aquatic porous media is adequately defining the behavior of a highly heterogeneous natural field matrix. Environmental problems are often poorly defined due to complexities in geochemical composition and in addition confoundment by biogeochemical alterations. In this presentation we describe two case studies where careful considerations of biogeochemical processes enabled effective modeling of pollutant transport and design and implementation of remedies in the field.

The first case study involves large-scale beneficial use of lightly contaminated aquatic sediments from maintenance dredging of the Baltimore Port which generates about 5 million cubic yards of dredged material per year. Motivated by the principles of circular economy, research was performed to evaluate options of using the sediments for shoreline restoration programs with layered placements that prevent the upward migration of toxic organic and metal pollutants into the surface water. Sorption capacities of a range of locally-available potential sorbent materials were tested in the laboratory and used as inputs in a pollutant transport model to evaluate the effectiveness of different layered placement options. The model demonstrated that the placement of a 10 cm layer of sorbent-amended sediment can be effective in preventing the release of pollutants from a 1 m thick layer of dredged sediments placed under it for at least 100 years. A large-scale wetland restoration effort in Baltimore is currently using the same principle to control migration of toxic pollutants from underlying sediments through an engineered sediment cap.

The second case study involves mercury as a pollutant. The transport of several metals like mercury in the environment is complicated by geochemical transformations of the metal or associated ligands. Mercury is largely associated with chloride or dissolved organic matter ligands that control transport in the aquatic environment, but the microbiologically transformed species of mercury, monomethyl mercury, is the one primarily responsible for bioaccumulation in the food web and exposure to humans. Understanding these natural processes of transformation and ligand-association is critical to mechanistically explain transport in the natural environment and for designing effective engineered systems for separation and remediation. In this research we performed laboratory-scale studies to evaluate capping options to mitigate transport of mercury from contaminated sediments into surface water. Novel equilibrium passive samplers were used to provide a fine-scale measurement of dissolved methylmercury concentrations in sediment porewater across the sediment-water interface. We show that for mercury, it is critical to understand and control the zone of mercury transformation to enable not only effective retardation of mercury transport but also minimize biological transformation into monomethylmercury by sulfate reducing bacteria present in sediments.

Synthesis of Functional Molecules, Polymers & Resins for Separation Chemistry

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Polymers are playing a key role in catalysis, synthesis, drug-delivery, and separation chemistry. Synthetic polymers have a special role in material chemistry applications. Polymer-anchored catalysts can be recycled and reused with ease. The new class of poly(ionic liquids) also known as polyelectrolytes has a striking advantage of poly(ionic liquids) in their "tunable properties". For instance, the solubility of these PILs can be reversibly changed as a function of their counter anion. At the same time, chirality can be introduced into these PILs at various stages either through covalent linkage or via ionic means.

We have prepared mesoporous cross-linked polymers bearing carbamoylmethyl-phosphine oxide (CMPO) pendant groups with an ethylene glycol dimethacrylate (EGDMA) backbone which exhibited an excellent adsorption selectivity and affinity towards U(VI) over the Th(IV) and Am(III). Sequential and selective separation of U(VI) and Th(IV) was demonstrated by extraction chromatography. Phosphoramidate anchored resins were synthesized by covalently linking diethyl (3-(1H-imidazol-1-yl)propyl)phosphoramidate group to chloromethylated polystyrene- divinyl benzene resin. Batch studies of the fabricated polymeric resin was showed that its having more sorption affinity towards Th(IV) than U(VI) with a very high separation factor of Th(IV)/U(VI) indicating a possible separation of Th(IV) over U(VI) from a mixture of these two metals.

During the presentation, synthesis of various tailor made functionalized small molecules, Ionic liquids, poly(ILs) and functionalized resins and their usage in catalysis, gas separation, drug delivery and separation chemistry.

Keywords: Functional molecules, Poly(ionic liquids), Resin, Ggas separation, Uranium, Thorium

IT-08

N-heterocyclic ligands for separation of trivalent f-elements

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Nuclear energy is the most concentrated and one of the safest sources of energy. This year marks 70 years since 1954, when the first grid-connected nuclear power plant (Obninsk NPP, Russia) was commissioned. Nuclear reactors and the nuclear industry have come a long way since then. But even today, nuclear fuel's potential is not fully exploited. Closing the nuclear fuel cycle, i.e. extracting and reusing valuable components from spent nuclear fuel, will increase the performance factor of natural uranium and thorium. There are more than 50 chemical elements in spent nuclear fuel. Extracting and separating the individual elements therefore requires the development of efficient and selective industrial chemical processes.

One of the most challenging chemical tasks is the complete separation of the trivalent f-elements, in particular americium and curium, due to their close chemical properties, electronic structures, and ionic radii. One of the most suitable industrial methods for the separation of soluble components is liquid extraction. The extraction systems (extractant + diluent) must meet many requirements: high selectivity, high radiation resistance, high thermal stability, etc. It is therefore important to find an extractant that not only has the highest selectivity and efficiency, but also has sufficient solubility as well as chemical and radiolytical stability.

After conducting extensive research, it has been demonstrated that extraction systems based on phenanthroline dicarboxylic acid diamides exhibit high efficiency, selectivity, and stability when separating trivalent felements. The combination of steric effects of the substituents at nitrogen atoms of amide groups, together with electronic effects of substituents in the phenanthroline core, can help achieve very high separation factors for Am/Ln and Am/Cm pairs. These effects also play a valuable role in the solubility and protonation of such extractants.

During the presentation, we will discuss recent results on the development of extraction systems for the separation of Am/Ln and Am/Cm pairs and their use in pilot-scale experiments.

Keywords: trivalent f-elements, americium, curium, lanthanides, solvent extraction, N-heterocyclic ligands

Advanced Oxidation Methods for Treatment of Industrial Wastewater

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Abstract

Advanced oxidation processes (AOPs) are receiving significant attention of researchers worldwide primarily due to stringent wastewater discharge and recycling norms. In the presentation, the performance of various advanced oxidation processes alone or in combination is presented for various industrial effluents such as spent caustic (oil refineries), spent wash (alcohol distilleries), pulping and bleaching effluents (pulp and paper mills). Using these processes, recalcitrant and hazardous organic pollutants can be oxidized into short chain molecules mainly carboxylic acids which improves their biodegradability. The treated wastewater can be used to recover biogas or the carboxylic acids can utilize as carbon source in downstream biological processes. The adoption of such processes improves the performance of effluent treatment plant substantially. Moreover, the significant reduction in sludge generation can be achieved.

Deep Eutectic Solvent: Promising alternative for the recovery of metal values from waste through hydrometallurgical route

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Deep eutectic solvents (DESs) due to their unique properties like non flammability, low vapor pressure, high heat capacity, high solvating power, thermal stability are nowadays considered as promising alternative to traditional solvents and ionic liquids in the field of separation science in order to achieve sustainability [1]. The term “DES” means a eutectic mixture comprising a hydrogen bond donor (HBD) and an acceptor (HBA) [2] attains the lowest melting point than the constituents. Moreover, huge number of various compounds which could be selected for their preparation has been helpful in regulating their properties consistent with requirements and use. The increasing amount of waste products comprising valuable metals are growing concern from the environmental point of view. It also intensifies the diminution of natural metal resources. Hydrometallurgical options like leaching and solvent extraction are usually the leading procedures for the efficient separation and recovery of metals from values from battery, magnets and other post-consumer waste products. Chloine chloride based DESs have been extensively used for extracting cathode materials from spent LiBs by leaching followed by solvent extraction. In most cases the cobalt was extracted preferentially over lithium. Aliquat 336-Hexanoic acid based DES diluted with kerosene was used to extract Li,Co and Ni from synthetically prepared battery waste solution [3]. Better selectivity was observed towards Ni as compared to Li and Co. Chloine chloride based DESs have also been employed to leach metals such as Nd, Sm ,Dy, Fe and Co from magnet waste. Hydrophobic DESs are used to recover the metals from leached solution through solvent extraction. Our group has reported extraction and separation of Nd/Fe and Sm/Co from simulated magnet waste solution using Aliquat336-glycerol DES [4] which revealed quantitative extraction of Nd and Sm. Iron extraction was less and cobalt was not extracted at all. Further investigation is required on the effectiveness of fascinating hydrophobic DESs produced from non-toxic chemicals for recovery of valuable metals from various waste products.

Keywords: Deep Eutectic Solvent, Hydrometallurgy, Waste, Metal Recovery

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Radiation Engineered Advanced Materials: Pioneering Sustainable Solutions for Water Pollution Remediation

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Over the last few decades, there has been a significant increase in wastewater production due to rapid population growth and the continuous expansion of the industrial sector. This has led to a major environmental issue, with textile dyes and toxic metal ions being the primary pollutants found in water sources, necessitating urgent, effective and sustainable treatment solutions. Utilizing gamma radiation and plasma for material processing provides eco-friendly, efficient, and adaptable techniques for modifying both bulk and surface properties of polymers and nanomaterials. The key aspect of these methods is their operation under normal reaction conditions, without the need for harmful initiators, chemical reductants, or organic solvents as well as offering improved process control, thereby making them suitable for customizing high-performance functional materials.

The talk will present the basic and applied aspects of gamma radiation and plasma-induced surface modification processes in developing innovative functional materials for addressing water pollution. It is essential to have a comprehensive understanding of the process parameters in order to optimize the degree of functionalization required for specific applications. The optimization of process parameters and characterization of developed functional materials using FTIR, XPS, NMR,TGA, DSC, SEM, EDX, , ED-XRF, etc., will be presented. The talk will highlight our recent R&D activities in the field of radiation and plasma-engineered advanced functional materials for environmental purposes, particularly in the remediation of water pollution. These encompass the production of a variety of radiation-grafted functional polymer adsorbents for the purification of industrial textile wastewater, removal of toxic metal ions from water streams, and development of recyclable catalytic systems through the immobilization of enzymes/metal nanoparticles onto surface-engineered functional supports for water pollutant remediation [1-4].Some of these research outcomes have been translated into water purification technologies, which are transferred to private licenses.

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Non-nuclear Applications of Heavy Water/Deuterium

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Enlargement of the mandate of HWB includes identification and promotion of non-nuclear applications of heavy water / deuterium for industrial and medical applications. Non-nuclear an application of heavy water has picked up momentum in recent years as various applications are being harnessed commercially viz. NMR solvents, in medicinal chemistry, in optical fiber, in semiconductor industry etc.

HWB has entered into collaborative agreement with two Indian Parties, M/s Clearsynth, Hyderabad and M/s SyNMR, Bengaluru for development of deuterated NMR solvents, reagents, APIs and other value added products. Recently HWB signed agreement with M/s Sigma Aldrich Chemicals Pvt Ltd. for long term supply of Heavy Water for manufacturing of deuterated compounds.

HWB has taken up development of D-labeled compounds specifically NMR solvents. With the aim to reduce import, a small scale facility has been set up at HWBF, Vadodara for in-house developments of few deuterated compounds viz. $CDCl_3$, DMSO-d6, acetone-d6, acetonitrile-d3, benzene-d6, etc. This facility is being utilized for synthesis of deuterated NMR solvents under applied R&D and products are being marketed through Board of Radiation & Isotope Technology (BRIT), DAE. An augmented facility for production of deuterated compounds is also being set up at HWBF, Vadodara.

In the recent times, demand of Heavy Water in both domestic as well as global market is showing a sharp increasing trend and India has become the largest exporter of Heavy water to many developed countries viz. USA, Switzerland, Germany, France, S. Korea, Japan etc and nearing to achieve monopoly status in global supply. During last year revenue generated through sale (domestic & export) of HW for non-nuclear applications to the tune of hundreds of crore which is all time high.

As the global market for heavy water is witnessing continuous growth, enormous scope exists for taking up various research & developmental activities with deuterium in non-nuclear filed by Indian research institutes and Indian industries and HWB, through collaboration can catalyze various developmental activities in this direction.

Isotopic Separations at Heavy Water Board

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Heavy Water Board (HWB) primarily engaged in separation of Deuterium from Hydrogen and its enrichment for production of Deuterium oxide, commonly known as Heavy Water, used as coolant and moderator in Pressurised Heavy Water Reactors (PHWR).

Isotope separation methods commonly consist of Diffusion, Distillation, Centrifugation, Thermal Diffusion, Exchange reactions, and Electrolysis, which are employed on case-to-case basis to achieve sizable degree of separation and further enrichment. HWB is engaged in separation of isotopes of Hydrogen, Boron and Oxygen and employed processes like Distillation, Chemical exchange and Electrolysis on industrial scale, as the other viable processes were not found economical on larger scale industrial facilities. HWB also employed multiple isotopic separation techniques to achieve extraction and enrichment of given isotope based on optimized Separation duty. Accordingly, cascade theory is adopted for designing and operation of isotopic separation facilities.

Hydrogen is having three isotopes, i.e. Hydrogen, Deuterium, and Tritium, where Hydrogen and Deuterium are stable isotopes and Tritium is radioactive. Heavy Water i.e. Deuterium oxide is available in nature along with Hydrogen with isotopic concentration of around 150 ppm D/(D+H) a/a Isotopic purity (IP). Accordingly river water, which is less contaminated with ionic load and dissolved solids, converted to de-mineralized water (DMW) and exposed to chemical exchange with H_2S gas for extraction of Deuterium from feed water and enrichment, using G-S process. After achieving the sizable IP, the product of Chemical Exchange section is fed into Vacuum Distillation for final enrichment upto Nuclear grade HW.

Boron is having two stable isotopes i.e. B-10 and B-11, where B-10 natural abundance is around 20 % a/a IP. Since many of the Boron compounds are in solid form in ambient conditions, it is necessary to select certain specialty compound for achieving isotopic separation of B-10 and B-11 through conventionally available Isotope separation methods. Accordingly, Boron trifluoride-diethyl ether complex, commonly known as BF_3 complex is employed for isotopic separation and further enrichment. HWB is equipped with facilities for converting the BF_3 complex into useful B-10 enriched compounds required for Fast Breeder Reactor program.

While, B-10 enriched compounds finds application in Nuclear field, B-11 which is getting simultaneously enriched during B-10 enrichment, finds applications in the field of Semi-conductor industry. HWB is exploring potential to support Indian Semi-conductor industry by sourcing the B-11 compounds for production of B-11 enriched BF_3 gas required for doping of semi-conductor chips and other such applications. Isotopic separation technique utilized is Exchange Distillation of BF_3 complex. HWB is equipped with facilities for converting the BF_3 complex into useful B-11 enriched compounds required for Semi-conductor industries.

Oxygen is having three stable isotopes i.e. O-16, O-17 and O-18 with their natural abundance as 99.763%, 0.037%, and 0.200% respectively. O-17 has application in biomedical research where determination of cerebral metabolic rate of oxygen utilization is monitored by assessing the changes of metabolically generated $H_2{}^{17}O$ in brain tissue from inhaled ^{17}O-labeled oxygen gas. O-18 enriched water also finds application in the field of nuclear medicine and biomedical research. 10 % O-18 enriched water finds applications in human metabolism studies and > 96 % O-18 enriched water is used as precursor of F-18, used in detection and staging of cancer using Positron Emission Tomography (PET) scanning. It is observed that while enrichment of Deuterium in vacuum distillation unit, O-18 also gets enriched above its natural concentration to a degree equivalent to relative volatility under given conditions. Vacuum distillation of water is continued further for achieving desired concentration of O-18 isotope. The product water at end of distillation cascade is in the form of $D_2{}^{18}O$. The Deuterium is replaced with Hydrogen using combination of electrolytic splitting & catalytic re-combination.

Special contacting devices are necessary for Isotope separation technology, since there is limitation w.r.t. degree of freedom, narrow difference in chemical & physical properties, etc. and usually such processes are too energy intensive and demands higher separation duties. Hence, novel processes and combination of various isotopic separation techniques are usually employed.

Keywords: Isotope, Distillation.

IT-14

Recovery of valuable metals at Heavy Water Board

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Heavy water under the enlarged mandate is entrusted with development and deployment of new process, technologies, systems & equipment in frontier areas of relevance to Department of Atomic Energy's programmes. Recovery of valuable metals having applications in medical diagnosis, Electronic industry, Defence, space and strategic purpose has been an area of importance in DAE. The cost and availability of such valuable metals has become a matter of concern for countries relying on import to cater their requirement. Therefore, research and development into state-of-the-art technologies for the recovery of these metals from primary / secondary sources is absolutely necessary. Metals obtained from secondary sources can be an import substitute and also ensure judicious utilization of resources.

Heavy Water Board (HWB) is closely associated with Bhabha Atomic Research Centre (BARC) for development of various technologies for recovery of some valuable metals, for example Rare material (RM) recovery from Wet Phosphoric Acid (WPA) of fertilizer plants, Cobalt and Nickel recovery from MDN alloy scrap of MIDHANI and Gallium recovery from Bayer Liquor of NALCO. In order to recover valuable metals, with small concentrations, highly selective separation methods, such as hydrometallurgical routes, are needed. Hydrometallurgical processes are also seen as more environmental friendly, and they have lower energy consumption, when compared to pyro-metallurgical processes.

For industrial deployment of these technologies, in-house technology development forms an important pre requisite since the required information is specific and desired details are not available in public domain. Developments in these fields need to cover all relevant areas such as development of critical equipment/systems identifying suitable material of constructions, safety and environmental aspects, etc. A RD^3 model followed for technology development comprises of Research, Development (Bench scale), Demonstration (Pilot scale) and Deployment (Industrial scale). The scientific research is carried out by BARC and the 3D's are carried out by HWB with close coordination with research institutes / organizations like BARC / IGCAR / ICT and host industrial units.

HWB has established the technologies for the above mentioned materials by conducting exhaustive trials at HWB Facilities. The RM recovery from WPA was demonstrated at HWB Facility Mumbai by continuous operation in synergy with WPA plant of host Fertilizer Company for a period of six years without having any effect on quality of end product (phosphatic fertilizer). During the course of demonstration various Liquid-Liquid extraction equipment were tested this resulting in development of Asymmetric Rotating Impeller Column (ARIC) for the extraction operation. HWB now plans to set up industrial scale plant for recovery of Rare material from WPA.

After the successful demonstration of RM recovery technology, HWB has taken up recovery of Cobalt and Nickel from MDN alloy scrap of MIDHANI in collaboration with MP&CED, BARC. Presently, there is no production of cobalt in the country due to lack of primary sources. The entire demand of cobalt is met through imports. The process is a combination of Hydro and pyro metallurgy. The hydrometallurgical process is established by carrying out multiple trials on bench at HWB Facility Mumbai. The bench scale trials for the pyro metallurgical part are under progress. HWB has completed the engineering work for hydrometallurgical part of process and procurement for the setting up pilot scale plant with a capacity of 5 Mt/annum of Cobalt is in progress.

HWB has also taken up recovery of Gallium from Bayer liquor of NALCO in collaboration with BARC and NALCO. Gallium does not occur as a free element in nature. It usually occurs as a trace component in Zinch & Bauxite ores. Worldwide Gallium is recovered mostly from the Bayer liquor obtained in alumina process during Aluminium production. Presently all the Gallium demand is met through imports. BARC and HWB have jointly developed a technology for recovery of Gallium from Bayer Liquor. The process mainly comprises of Ion Exchange, Solvent extraction and Electrolysis. BARC has carried out scientific research for the process. HWB has carried multiple bench scale trials at HWBF, Mumbai resulting in improved resin performance. Based on the results of bench scale trials HWB has finalized the design and operation philosophy of the process. HWB is now planning to set up pilot scale demonstration facility in the premises of NALCO at Damanjodi, Odisha with a capacity of 15 kg/Annum of Gallium metal.

Keywords: *Hydrometallurgy, Solvent extraction*

High-loading Immobilization of ultra-selective nano-sorbents in water filters for fast cesium and ammonium removal

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Background. Cesium (Cs) removal from natural water is critical in alleviating radioactive pollution. Effective removal of ammoniacal nitrogen (NH_3-N) is crucial in various applications, from domestic and industrial wastewater treatment to aquaculture water management, pharma, and biotech applications. To tackle these challenges, we developed a reusable polyethersulfone (PES) mixed-matrix microporous membrane embedded with unprecidentially high-loading (50%w) of Zinc hexacyanoferrate nanoparticles (ZnHCF). This microporous filter offers several advantages over existing ammonium and Cs removal technologies. Unlike zeolite-based filters and adsorbents, it remains highly effective even in the presence of other ions and highsalt solutions, such as seawater. Additionally, adsorbed ammonium can be recovered during regeneration (using 4M NaCl), and the regenerated membrane can be reused for multiple cycles. Furthermore, unlike ZnHCF-PES beads, this membrane showed superior ammonium removal kinetics.

Experimental/methodology. Ammonium and Cs removal and recovery experiments were performed in a dead-end filtration setup with an effective membrane area of 21.85 cm^2. Ammonium (30 to 70 mg/L) or Cs spiked different ionic strength NaCl solutions (0.01 to 0.5 M), brackish water, and seawater were used as feed solutions. Permeate fluxes during filtration experiments were kept at 40 to 140 $l.m^{-2}.h^{-1}$.

Regeneration /ammonium recovery from the spent microfilter was carried out using a 4M NaCl solution.

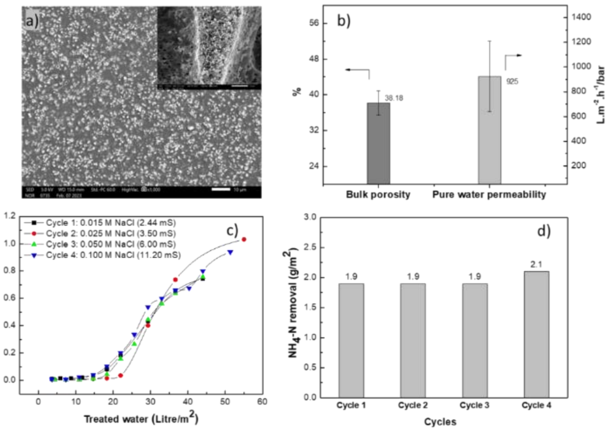

Figure 1. a) Top surface and cross-sectional SEM image b) Bulk porosity and pure water permeability of membrane c) Graph illustrating the reusability of the membrane and its performance under varying ionic strengths across four cycles. During this permeate flux was ~ 45 $L.m^{-2}.h^{-1}$. d) Ammonium removal capacities of the membrane across four consecutive cycles.

Results and discussion. The membrane's molecular weight cut-off (MWCO) and pure water permeability were determined to be ~ 360 K Da and 925± 280 $L.m^{-2}.h^{-1}$/bar, respectively. Uniformly dispersed and high loading (~ 50 %) of immobilized ZnHCF nanoparticles (Fig.1a) inside the membrane matrix leads to higher ammonium removal capacities (~ 1.9 g NH_4-N/m^2 of membrane) for different ionic strength NaCl solutions (fig. 1c) across four consecutive removal/recovery cycles. Moreover, the microporous filter had a removal capacity of ~ 1 g NH_4-N/m^2 and 1.65 g NH_4-N/m^2 for seawater and brackish, indicating its applicability for high ionic strength solutions. We tested the filter at a larger surface area (0.7 M^2) and obtained similar and consistent performances, indicating good scalability. Furthermore, the saline eluent solution was recycled using membrane contactors, which recovered ammonium fertilizer. Preliminary Cs removal experiments revealed that Cs can be removed effectively and rapidly in the presence of other ions. This invention can potentially improve readiness for radioactive water pollution events and enhance the sustainability of nitrogen removal.

Addressing Questions of Sustainability in Advanced Nuclear Fuel Cycles

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As part of the UK's Advanced Fuel Cycle Programme (AFCP: 2017-2023) a broad-based research and development programme was initiated that developed options for advanced recycling of spent nuclear fuels (SNF) in future fuel cycles. This built on decades of UK experience in the reprocessing and recycling of SNF as well as progress made under international collaborations. Of particular importance has been progress made since the early 2000s through projects that were funded by European Framework Programmes (FP); *e.g.* GENIORS (GenIV Integrated Oxide fuel Recycling Strategies) and PUMMA (Plutonium Management for Maximum Agility).

The scientific and technical direction of the AFCP advanced recycle theme was framed around enhancing the sustainability of nuclear energy generation by addressing the three pillars of sustainable development, *i.e.* environmental impacts, social impacts and economic impacts. The programme encompassed aqueous and pyro-chemical separation processes as well as waste management processes. Additional work packages covered evaluating nuclear fuel cycle options and impacts of innovative technologies at the plant scale. Alongside the technology development and scientific impact, substantial importance was placed on meeting various 'strategic outcomes' that will deliver future economic benefits to the UK nuclear industry; for instance, the development of skills, commissioning new R&D facilities and collaborating internationally.

This presentation will review some of the key outcomes of the Advanced Recycle and Sustainability theme of AFCP by summarizing the highlights in three relevant areas:

1. Critical reviews of environmental and economic impacts of open and closed fuel cycles [1-2]
2. The development of future separation and waste treatment processes for aqueous recycling of SNF [3]
3. Solvent extraction-based processes developed in Europe for the homogeneous recycling scenario [4]

The focus will be on how SNF recycling can increase the overall sustainability of nuclear energy as well as how advanced separation and waste treatment processes could reduce the environmental and economic costs of future reprocessing plants *per se*.

Keywords: Sustainability, Recycling, Reprocessing, Minor Actinides, Partitioning, AFCP, GANEX

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Processing of Uranium Ore at UCIL Mill's of India

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Chief Superintendent (Mill)

Uranium Corporation of India Ltd (UCIL) plays a key role in the nuclear fuel cycle. The available U ore grade in our country is lean in nature; to sustain 3 stage nuclear power program of our country, we are processing the same. Ore is mined, crushed, ground, thickened, leached through atmospheric- acidic /pressurised alkaline route, filtered, clarified, concentration of U in liquor is increased through Ion exchange or re-dissolution of concentrate and precipitated with reagents to form different types of Uranium Concentrate and supplied to Nuclear Fuel Complex for further processing.

PROCESS DESCRIPTION

The Run of Mine (ROM) Ore sized from 150 to 500 mm is reduced to 74µ (200Mesh) particle size by deployment of series of comminution equipment's such as Jaw, Standard & Short Head Cone crusher, Rod & Ball Mill with Hydro-cyclone Size classifier. The solid consistency of Hydro-cyclone overflow is 25-35% (w/w), which is increased by using thickener and Horizontal Vacuum Belt Filter (HBF). Filter cake is repulped with weak U liquor obtained from the HBF used in post leaching section and pumped to leach reactor, were optimum reagent/lixivant concentration, Temperature, Pressure and residence time is maintained for effective leaching of U solute from the solid matrix. Prior to the leaching, $U_{natural}$ is present in reduced tetravalent insoluble form, during leaching process it get oxidized gets converted into hexavalent form and entering into leach Liquor in Uranyl ion form. Leached slurry is filtered in HBF with 3 to 4 stages of countercurrent washing for removal of soluble U adhering to gangue mineral surface by displacement wash method; the filtrate contains 1000-2000 PPM of suspended solid, which is removed through clarifier and Precoat vacuum drum filter. The clear filtrate is passed through Ion exchange (IX) column in case of acidic route for hiking the concentration of U reporting to precipitation or precipitated directly by addition of NaOH were alkaline leach route is adopted , U concentration is hiked by addition strong liquor generated through re-dissolution method. Impurities present in the strong liquor produced via IX are removed through selective precipitation cum separation by sedimentation and the impurity free liquor containing Uranyl sulphate is precipitated through addition of H_2O_2 and NH_4OH. The precipitate obtained in both the route is washed in HBF, repulped, spray dried and finally calcined in rotary kiln. Uranium ore concentrate is dispatched to NFC.

Leached cake is repulped, neutralized with lime to increase pH of slurry and maintain in between 9.5 to 10.5 to prevent re-solubilization of heavy metal. Neutralised slurry is disposed into double lined system containing 2 mm HDPE liner and impervious clay/earth lined dam having permeability of 10^{-9} m/s. The solid settles and the liquor decants through spillway and gets collected in collection pond which is subsequently treated in Effluent treatment plant for fixing Radium and other metallic ion through addition of $BaCl_2/Ba(OH)_2$ and $Ca(OH)_2$ respectively. The precipitate thus obtained is removed in thickener and disposed of in tailings dam. The effluent is discharged to the environment were the parameters are well within inland discharge limit. Tummalapalle (TMPL) mine and Mill operate with Zero discharge scheme.

The ore mined from Singhbhum shear zone is consumed by Mill's of Jaduguda and Turamdih contains high SiO_2 content and low acid consuming gangue, thereby lead to selection of atmospheric acid leaching in Pachuca and CSTR with MnO_2 as oxidant. Required Mesh of Grind in Mill is 60% of ore particle passing 200 Mesh is sufficient for sustaining maximum leaching efficiency. IX is used to increase the U concentration in liquor and impurities in strong liquor such as ferric and sulphate ion are removed through addition of $Ca(OH)_2$ to form Iron Gypsum cake and subsequently U is precipitated, washed, spray dried , calcined and dispatched.

The host rock of TMPL deposit is siliceous dolomitic phosphatic limestone, which contains 83% Carbonate leading to excessive consumption of H_2SO_4, led for opting autoclave leaching in alkaline medium at elevated Pressure and Temperature with direct injection of gaseous O_2 and Na_2CO_3. Mesh of Grind in Mill is 85% passing 200 Mesh as the reagent will be able react with the U at the surface of particle only.

From Concept to Reality: Zwitterionic Polymeric Membranes Revolutionizing Separation Technology

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Zwitterionic entities contain equimolar quantities of positive and negative charges on the same molecule. Hence zwitterionic moieties can form a hydration layer via hydrogen bonding with water molecules. This hydration layer prevents the accumulation of molecules around the components possessing the zwitterionic moiety. Therefore the nanoparticles containing these moieties have been widely utilized for drug delivery purposes, since the hydration layer prevents the attack by the body’s immune system and thereby improves the blood circulation time ensuring effective treatment. Since zwitterionic nanoparticles are well known for their antifouling properties, it has been theorized that their incorporation into polymeric membranes could improve the membrane properties; especially its antifouling property apart from its hydrophilicity and permeability. There is scope for experimental work regarding this area and the efficiency of these modified membranes in the rejection of natural organic matter (NOM), dyes, heavy metals, pesticides and pharmaceuticals. Apart from the application of these nanoparticles in water treatment, they have also been used as biosensors, antifouling coatings, coating of biomedical implants and in cell imaging.

Uranium Hexafluoride Chemistry in Ionic Liquids: Innovations for Nuclear Fuel Cycle Applications

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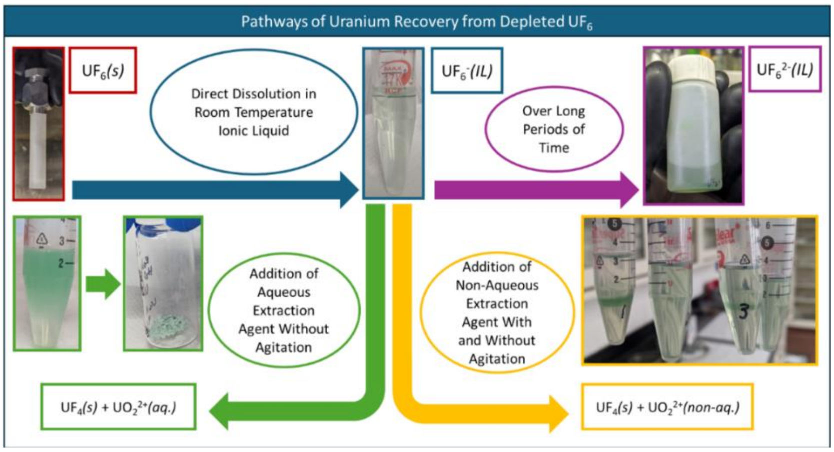
The US nuclear fuel cycle is anticipated to undergo significant changes with the development of reactors using High Assay Low Enriched Uranium (HALEU), requiring enrichment levels exceeding 5% ^{235}U. These novel reactor fuels will necessitate modifications in ^{235}U enrichment strategies, deviating from current systems and likely resulting in increased stocks of depleted UF_6. Uranium hexafluoride, a corrosive material with significant vapor pressure, is presently stored but holds potential as a resource for new reactor systems that do not rely on enriched uranium. Consequently, converting UF_6 into a more chemically stable uranium compound is beneficial for material handling and optimizing the nuclear fuel cycle. This method also has significant applications in nuclear forensics and safeguards, offering a means to collect, transport, and analyze UF_6 from enrichment systems.

Recent advancements in the use of room temperature ionic liquids (ILs) have introduced promising methods for UF_6 stabilization and uranium recovery. The dissolution of UF_6 in ILs, particularly bis(trifluoromethanesulfonyl)imide, causes the reduction of uranium, eventually rendering the material chemically inert. Over time, precipitates of the reduced uranium coordinated with the IL cation form. A more rapid uranium recovery was achieved by adding aqueous and nonaqueous extraction agents. Vigorous mixing of the uranium/IL solution with the extraction agent initiated a competing reaction, resulting in uranium recovery in a mixed valency state. This process partially reduced uranium to solid UF_4, while the remaining portion was oxidized to a uranyl ($UO2^{2+}$) species in the extraction agent phase. This innovative approach not only accelerates uranium recovery but also enhances the efficiency and safety of handling UF_6.



Eliminating the agitation step after adding the extraction agent increased the UF_4 yield and revealed that solid UF_4 precipitation occurred at the IL/extraction agent interface. Uranium concentrations were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The solid UF4 was characterized by powder X-ray diffraction (pXRD) and thermal gravimetric analysis (TGA). Reaction kinetics were investigated by monitoring UF_4 production with UV-visible spectroscopy. The experiment was also repeated at various temperatures to calculate the reaction's activation energy. These comprehensive analyses provide a deeper understanding of the underlying mechanisms and optimize the conditions for large-scale applications.

This presentation provides an overview of near-term advances in US nuclear reactor technology, emphasizing impacts on the nuclear fuel cycle, particularly uranium enrichment. It discusses the implications of UF_6 reactions in ionic liquids for nuclear forensics and security. Furthermore, the research highlights the influence on uranium utilization in near-term and future fuel cycles. By addressing the challenges and opportunities associated with HALEU and UF_6 management, this work contributes to the sustainable development of nuclear energy.

Seaweed-derived innovative materials for sustainable environmental remediation

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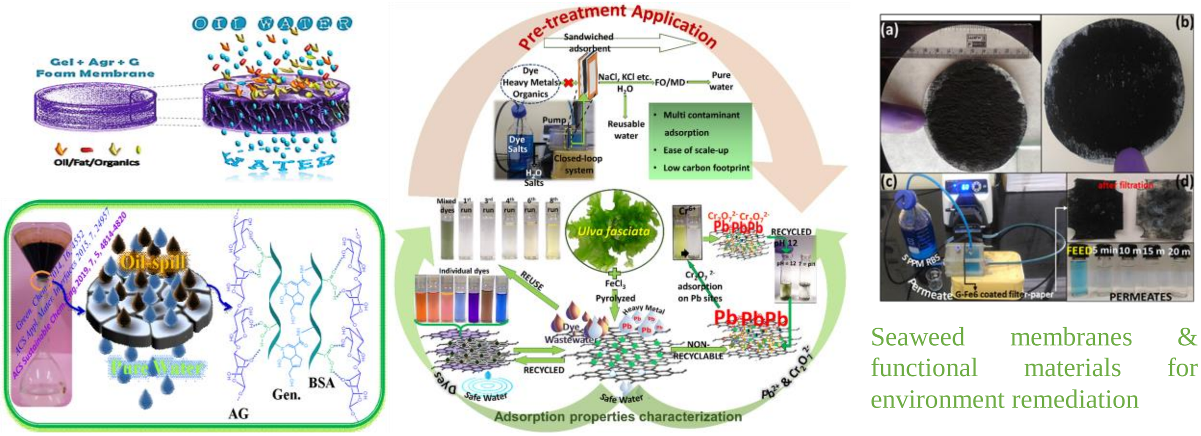
Abstract: India has a coastline of 7516 Km touching 13 States and Union Territories (UTs). Seaweeds are an integral part of coastal ecosystems and offer invaluable ecosystem services supporting the life of many marine forms. The economic value of seaweeds significantly contributes to the sustainable development of rural coastal regions. Seaweeds mainly utilized for production of phycocolloids across the globe, with an estimated value of more than one billion US$. In India, my group (CSIR-CSMCRI) working on the value addition of Indian seaweed biomass. Under this program, we have developed several seaweed-processing technologies for the commercial production of phycocolloids and biostimulants from Indian seaweed biomass. These technologies transferred to more than 30 industries & products are available in the market for commercial uses. About 840 seaweed species are growing in India, among these ~40 seaweeds are commercially important. Hence, we utilized unexplored (~800) seaweed species and their polysaccharides for the production of sustainable materials for industrial applications. In this direction, my group has developed green and eco-friendly methods for the production of porous membrane for separation of oil-water; emulsion; organic-water; and waste garage/cooking oil from contaminant water. In recent, sustainable materials such as biodegradable films, beads, nanocomposites, super adsorbents, nanomaterials, functional carbon, etc. developed for food & agriproducts packaging, dye degradation & removal, toxic metal removal, and fluoride removal. This talk briefly appraises the status of Indian seaweed processing technologies and their commercialization. It also highlights the utilization of seaweed derived sustainable materials for environmental remediation to achieve sustainable development goals.



Seaweed membranes & functional materials for environment remediation

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Rare Earths Resource Processing for Establishing Value Supply Chain

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Rare earth elements (REEs), a group of 17 elements, have become essential enablers of technologies for global clean energy initiatives as well as the gadgets and electronics that are integral to modern life. These elements are vital in various modern technologies, including smartphones, electric vehicle motors, wind turbines, and advanced military equipment, providing crucial functionality to these devices. Despite their usage in relatively small quantities, REEs are indispensable in hundreds of technologies, materials, and chemicals across commercial, industrial, social, medical, and environmental applications.

Rare earth permanent magnets, for instance, are found in a wide range of devices from home appliances to sophisticated machines like wind turbines, electric vehicles, satellites, radars, and defense equipment. These magnets are valued for their ability to deliver high magnetic flux in compact sizes, facilitating device miniaturization while maintaining high performance. The growing demand for REEs is significantly driven by the electric vehicle and renewable energy sectors, both of which are critical for climate control and the pursuit of a greener planet, not just in India but worldwide. Due to their increasing demand in green and energy-saving applications, coupled with limited resources, certain REEs such as Neodymium (Nd), Europium (Eu), Yttrium (Y), Terbium (Tb), and Dysprosium (Dy) have been categorized as critical elements. The deployment of energy technologies in wind turbines and electric vehicles could create an imbalance in the supply and demand of these key materials, leading to vulnerabilities in the REE value chain. Countries with abundant REE deposits have thus become pivotal players in the industry and crucial components of international supply chains.

Sustaining the rare earth industry within a country is vital for achieving energy security and is a significant driver for a low-carbon economy. Ensuring resource sustainability is essential to bridging the gap between the supply and demand of these critical elements, especially given their projected demand in the energy sector. This discussion will address the challenges associated with the processing of rare earth resources and the development of technologies necessary to establish a robust value supply chain within the country.

Structurally Engineered Porous Monolith Materials as Solid-State Naked-Eye Ion-Sensors and Visible Light-Induced Photocatalysts for Environmental Decontamination Applications

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The growing environmental and health issues from surging inorganic/organic pollutants have become a dangerous menace in the twenty-first century. With the recent technological advancements, a new generation of smart materials is on the rise for environmental decontamination applications related to real-time monitoring/capturing or dissimulating persistent toxic organic/inorganic pollutants from environmental samples. In recent years, ordered mesoporous silica monoliths featuring unique properties of ordered porous network structure(2-50 nm), larger surface area, and flexible structural forms proved promising as a new class of solid-state optical sensors. Importantly, tuning the structure and porosity through process-controlled synthesis facilitates tailor-made exclusive applications. Likewise, porous polymer monoliths of percolating macro-porous networks and accessible mesopores are becoming attractive alternate materials for separations, catalysis, and biomedical applications.

In recent years, solid-state optical sensors using these porous structures have been envisaged by pairing chromo-ionophoric probes with functionalized coordination centers for metal ion complexation, thereby offering satisfactory solutions to toxicity issues. The combinatorial array of inorganic-organic hybrids through physical entrapment or sheltering of organic probes reveals a bimodal behavioral system for metal ion optical sensing and preconcentration. The unique structural features of these hybrid systems make them more referable considering the benefits of long-term stability, reusability and eco-friendly approach. In addition, the propensity of hyper-conjugated supramolecular designs and nano-toxicological nanoparticles are the significant limitations of liquid-based colorimetric ion sensing that can be avoided by structurally customized porous monolith materials, which our research group has studied extensively.

Similarly, the photo-induced catalytic oxidation processes have gained considerable attention for wastewater treatment of organic (textile dye/pharmaceutical) pollutants. Porous materials with well-defined, tailor-made structural and surface properties are new-age materials that offer positive features for heterogeneous photocatalysis. Porous polymer monoliths supported by heterojunction nanocomposites and photoactive metal-organic frameworks contribute intensely to environmental and energy-related applications. Based on our research activities, my talk will highlight the advantages of improved scattering and adsorption of light, abundance reaction sites, large specific surface areas, and enhanced mass and charge transfer using hybrid porous materials as visible light-responsive photocatalysts and solid-state optical sensors.

Aqueous reprocessing of metallic alloy fuels at IGCAR

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U-Zr and U-Pu-Zr alloys are considered as advanced fuels due to their better thermo physical properties over other types of ceramic fuels. The fuel compositions generally used are U-Zr and U-Pu-Zr alloys in which Pu and Zr contents vary from 15 to -19 and 6–10%, respectively. A ternary alloy of U-19%Pu-10%Zr has been used worldwide. Pyro-chemical reprocessing based on electro-refining is the best suitable method for reprocessing of spent metallic fuels. As an interim process, the feasibility of using aqueous based PUREX process has been explored in our laboratory for reprocessing of spent metallic fuels in order to close the fuel cycle. PUREX process can be broadly classified in to two parts, dissolution and solvent extraction. Dissolution of spent nuclear fuels in nitric acid medium without any residues is an important step in PUREX process. If the metal fuels has to be reprocessed by aqueous route, *i.e* by PUREX process, the spent fuels has be dissolved in nitric acid medium. But it is reported in literature that direct dissolution of U-Zr alloys in nitric acid medium results in the formation of UZr_2 delta phase which reacts violently with nitric acid medium. In addition, presence of sodium in metallic fuels further complicates the dissolution of metallic fuels due to sodium water reaction. Therefore, sodium needs to be removed prior to dissolution, to avoid violent reactions of sodium and water. After sodium removal, metallic alloy fuels should be converted to either oxides or nitrides, carbides for safe dissolution because direct dissolution involves exothermic reactions. Therefore in our studies metal fuels are converted into oxides and nitrides and its dissolution behavior was investigated. After dissolution studies, solvent extraction studies were carried out with TBP and TiAP based solvents in cross-current and counter-current mode. The talk presents overview of aqueous reprocessing of metallic alloy fuels. Various studies carried out for the aqueous reprocessing of metallic fuels such as oxidation behavior of sodium bonded U-Zr alloys with clad T91 followed by their dissolution, dissolution behavior of T91 clad, the dissolution behavior of nitrides of Zr, U, U-Zr and U-Pu-Zr alloys, continuous counter-current mixer settler runs with U-Zr and U-Pu-Zr feed solutions using 1.1 M TBP/n-DD solvent, mixer-settler runs with U–Zr feed solutions using 1.1 M TiAP/n-DD, mixer-settler runs for the recovery of zirconium with 1.47 M TBP/DD from 6 M HNO_3 using an ejector mixer-settler facility etc will be discussed.

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Speciation of actinides with various complexing agents (Aqueous chelators, Deep eutectic solvents and Electrodic materials) and their relevant applications

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Speciation of actinides is a fundamental chemical aspect associated with the various activities of the nuclear fuel cycle. The solution processes viz., redox dynamics, complexation, dissolution, solubility, sorption, and precipitation mainly depend on the solvation environment, i.e., speciation, of the metal ion. In addition, the various environmental processes such as redox, complexation, sorption, precipitation, and bioavailability of actinides affect the aqueous speciation and retards or enhance their migration. Actinides are the most dangerous heavy metals in the environment due to their radiological and toxicological effects. These elements enter the environment because of several technogenic processes and their high concentration in the environment is known to pose serious health hazard to mankind. The actinides are redox sensitive and have different oxidation states from (III) to (VII) and their stability is strongly dependent on physiochemical conditions viz. pH and complexing conditions. In the environment, these elements are found at low concentration level. Therefore, solution speciation of actinide ions has been of substantial recent interest with an objective (i) to predict its migration in the aqueous phase and to understand the chemistry of unusual oxidation states, (ii) to understand their chemical behaviour and reactivity in the non-aqueous media and (iii) to monitor their presence at low concentration level. The advancement of sensors for speciation and monitoring at low concentration level of actinides is essential to understand the mobility and reactivity of actinides in the environment

Carboxylate and phosphonate based moieties are omnipresent chelators in abiotic and biotic environmental conditions. Thus, based on these function groups the chelators viz., Citrate, Phenylphosphonate and Phosphonocarboxylate are taken for aqueous speciation of actinides. These chelators are highly aqueous soluble and ionizable in physicochemical circumstances. In addition, the above chelators can be considered as a model system for understating the interaction of actinides with humic acid, glyphosate, and microbe. Deep eutectic solvent (DES) is a neoteric green and sustainable chemical media of the 21st century and is considered a promising alternative to organic solvents and ionic liquids. The chemical behaviour and reactivity of a metal ion in DES depends on their speciation which controls key aspects of metal processing and electrochemical behaviour such as solubility, interaction, coordination and redox. Probing of the speciation of actinides in DES is important for their dissolution, analysis, and separation. Due to high solvation potential, the Malonic acid based DESs were chosen to gain speciation of actinides. The cohesive studies on redox and molecular speciation of actinides with aqueous soluble chelators and DES are carried out using multi-technique approach. As an electrodic material, the 2D-MXenes [$M_{n+1}X_nT_x$ (n = 1~3), where M represents an early transition metal, X is C and/or N, and T_x refers to surface-terminating functional groups (such as O, -OH or -F)]and boron based nano-particle have high electrical conductivity, excellent hydrophilicity, good chemical and thermal stability, high surface areas, tuneable, abundant surface functionalities, and highstability in the cathodic potential window. Therefore, these electrodic materials can work as a promising sensing material for actinides and to catalyse the O=An bond of $[O{=}An{=}O]^{n+}$.

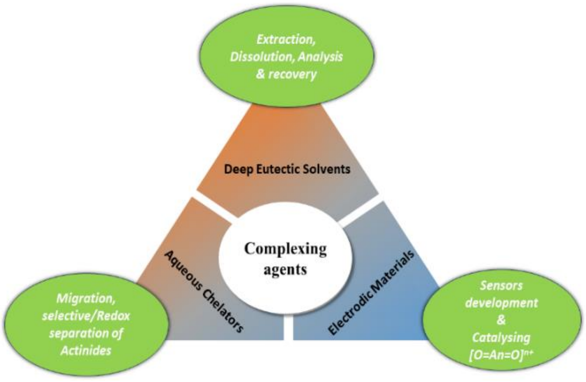

Figure 1. ***Speciation of actinideswith various complexing agents***

Production and electrochemical separation of rare earth radiometals for formulation of theranostic radiopharmaceuticals

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With recent advances in novel approaches to cancer imaging and therapy, the application of theranostic techniques in personalized medicine has emerged as a very promising avenue of research inquiry in recent years. Interest has been directed towards the theranostic potential of Rare Earth (RE) radiometals due to their closely related chemical properties which allow for their facile and interchangeable incorporation into identical bifunctional chelators or targeting biomolecules for use in a diverse range of cancer imaging and therapeutic applications without additional modification, i.e., a “one-size-fits-all” approach. Electrochemical separation is an emerging approach towards obtaining clinical-grade RE radiometals after irradiation of targets in research reactor or cyclotron facilities for preparation of a wide variety of radiopharmaceuticals. In this talk, a comprehensive summary of the electrochemical processes developed for the separation of radiometals that could be used for diagnostic or therapeutic applications in nuclear medicine will be provided. For using electrochemistry as a tool for the separation of radiometals, intricate knowledge is essential to understand the basic parameters of electrochemical separation processes which include applied potential, selection of electrolyte, choice of the electrode, the temperature of the electrolyte, pH of the electrolyte and time of electrolysis. The advantages of the electrochemical separation approach over the other conventional methodologies such as solvent extraction, column chromatography, sublimation, etc., shall also be discussed. The latest research and development from our laboratory on electrochemical methodologies developed for separation of ^{90}Y from ^{90}Sr; ^{43}Sc, ^{44}Sc,^{47}Sc from Ca;^{45}Ca from ^{46}Sc;^{153}Sm from ^{154}Eu;^{169}Er from ^{169}Yb;^{177}Lu from Yb and $^{132/135}$La from Ba shall be highlighted. In all the cases, the final product is obtained either in a ‘no-carrier-added’ (NCA) form or free from inextricable impurities and thus found suitable for formulation of radiopharmaceuticals.

Recent Advances in Liquid–Liquid Extraction: Equipment and Control Philosophy

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Metals such as Uranium, Zirconium, Niobium, Tantalum, Hafnium, Plutonium etc., are important for the nuclear industry in their purest forms. At Nuclear Fuel Complex (NFC), reactor grade (RG pure) Uranium Oxide, Zirconium and Niobium are produced at tonnage scale adopting Liquid – Liquid Extraction, commonly known as 'Solvent Extraction' purification technique. The main challenges in extracting these metals are (i) the input feed solution to the extraction equipment contain un-desirable emulsifying agents along with suspended solids hindering phase-separation, (ii) stringent requirements on the product quality for achieving purity up to PPM level, (iii) requirement of expensive solvent and chemicals resulting in higher production costs and (iv) the extraction efficiency is affected by many parameters such as acidity, metal concentration in feed, solvent concentration, solvent to aqueous solution ratio and temperature.

During the past five decades, opportunities offered by the above challenges coupled with several other constraints necessitating use of lower grade ores as feed stocks, energy efficient processes, strict environmental requirements, reduced product costs; paved way to realize several innovations in the solvent extraction field. These innovations could be successfully demonstrated at industrial scale and were aimed at developing (a) simplified, efficient, ease-to-operate-maintain type of novel solvent extraction equipment and (b) simple and effective process model and control philosophy where-in the *difficult-to-measure* process variables are estimated with the help of *easy-to-measure* variables coupled with an appropriate process model for effective solvent extraction process monitoring and control.

This talk details the construction of novel and ease-to-operate-maintain version of mixer-settler units. It also focuses on the latest advances at NFC towards developing innovative data based process model and control philosophy for the critical solvent extraction operation at large scale.

Uranium deposit of India along with current status of UCIL mines and future roadmap; An overview

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Superintendent (Geology), UCIL.

India's mining and processing of low grade uranium deposits begun long back in 1950s. M/s.Uranium Corporation of India Limited (UCIL), a Public Sector Undertaking (PSU), has the mandate to mine and process Uranium ore of the country to meet fuel requirement of first stage nuclear power programme of the country.

The ~200-km-long intensely deformed Singhbhum Shear Zone (SSZ) in eastern India hosts India's largest U and Cu deposits and related Fe mineralization. Uranium mineralization of the SSZ may be described as veins or disseminated type and strata-bound at places but the economically exploited ore body is formed through shear controlled as it is indicated by micro-folding and other related structural features. SSZ is having the occurrence of different minerals like, copper, uranium, gold, molybdenum, tungsten, phosphate etc. This vein type hydrothermal uranium mineralization includes many of the uranium deposits as well as running Uranium mines of India namely: Bagjata, Jaduguda, Bhatin, Narwapahar, Turamdih, Banduhurang and Mahuldih. However, other potential deposits/occurancelike, Kanyaluka, Jaduguda-Baglasai-Machua, Banadungri, Garadih, Kumari-Kamalpur, Basurdha-Dudra, where sub-surface drilling and/or other pre-mining activities are going on now-a-days.

Tummalapalle Uranium deposit is situated in the YSR district of Andhra Pradesh. Geologically the area is in the south western part of the Cuddapah basin, close to the Archean basement. The mineralization lies within Vempelle formation of Papaghni group of Cuddapah Super Group. The host rock is characterized by impure, siliceous, phosphatic, dolomitic limestone with stromatolites, ripple marks and mud cracks thus also named as dolostone. The radioactive minerals identified in the ore zone are pitchblende, coffinite, and U-Ti complex. Here, the associated minerals are pyrite, chalcopyrite, molybdenite and collophane.

The new upcoming project activities for opening of Uranium mine is going on intensely in the country. The projects are namely, Tummalapalle Extension and Kannampalle project of Andhra Pradesh, Gogi-Kanchankayi project of Karnataka, Rohil exploratory mining project of Rajasthan, Jajawal project of Chhattisgarh and Garadihand Banadungri project of Jharkhand.

Bioremediation of uranium contamination with enzymatic uranium mineralization

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Uranium (U) can be hazardous to humans due to radiotoxicity and chemical toxicity and therefore, bioremediation strategies are required to alleviate U contamination. This talk will highlight the potential of a bacterium, namely *Chryseobacteriumsp.* strain PMSZPI isolated from a U ore deposit, for biomineralization of uranium (U) in contaminated environments. The bacterium demonstrated superior ability to sequester and precipitate uranium from aqueous solutions that is critical for reducing uranium contamination. The free cells exhibited efficient U binding (~90% of 100 µM U) and U bioprecipitation (~93–94% of 1 mM U at pH 5, 7 and 9) loading up to~225.5 mg U/ g dry wt. [1]. For effective separation of U from contaminated solutions, the bacterial cells were immobilized within calcium alginate beads or polyacrylamide gel in order to facilitate their handling and application in remediation efforts. Under batch system, high efficiency in uranium removal was demonstrated with ~ 98-99% of uranium precipitation from 1 mM U solution within a 24-hour at pH 7in presence of glycerol-2-phosphate substrate (Fig. 1). Various biophysical techniques, including scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD), were employed to locate and characterize the biogenically formed uranyl phosphate mineral (Fig 2). The Ca-alginate immobilized biomass retained its uranium precipitation ability and phosphatase activity even after storage for 90 days at 4°C, indicating its potential for long-term use. The feasibility of employing the immobilized lyophilized biomass immobilized in polyacrylamide gel in continuous flow system was investigated that showed significant uranium loading capacity of 0.8 g U/g of biomass at pH 7 using 1 l of 1 mM uranyl solution[2]. This investigation established the feasibility of practical application of the immobilized biomass of *Chryseobacterium* sp. strain PMSZPI in remediating uranium-contaminated environments.

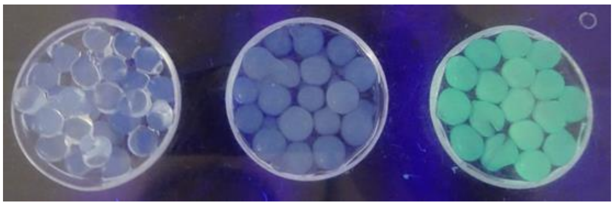

Fig.1: Visualization of PMSZPI biomass entrapped in Ca-alginate beads following U precipitation. Calcium alginate beads without biomass (Blank beads) or with biomass unexposed or exposed to U for 24 h visualized under UV light and photographed. The beads exposed to U exhibited green fluorescence characteristic of uranyl phosphate mineral (meta-autunite) resulting from U precipitation that was entrapped in the beads.

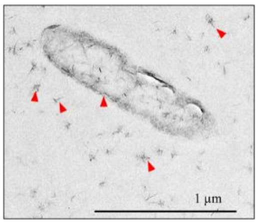

Fig.2: Transmission electron micrograph (TEM) of bead section containing immobilized biomass exposed to 1 mM U. Uranyl phosphate precipitates shown as electron dense spicules formed on the surface or around the cells represented by red arrows.

Keywords: Uranium, Immobilization,bioprecipitation, bioremediation

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Role of Supported Liquid Membrane for Actinide assay in Nuclear Fuel Cycle

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Membrane based separation processes have emerged as one of the most researched and rapidly expanding separation techniques of the century. Membrane based separation provides several advantages over conventional separation processes like fast and high-efficiency separation, high mechanical strength, reduced solvent usage, lower energy consumption, possible utilization at ambient temperature and moderate pressure, low process cost and at the same time also offers scalability. A supported liquid membrane (SLM) is one of the three-phase liquid membrane systems in which the membrane phase (liquid) is held by capillary forces in the pores of microporous polymeric or inorganic film. Usually SLMs are based on hydrophobic organic solvent immobilized in a polymeric membrane separating two aqueous solutions, viz. the feed solution and the strip solution – such that the SLM allows selective transport of analyte from the feed solution to the strip solution. In a way, SLM-based separation combines the solvent extraction and stripping processes (re-extraction) in a single step. Though SLMs are most commonly applied for transport of various metal ions and impurities, we have explored a very different application of supported liquid membranes.

Precise and accurate determination of actinides is necessary at different stages of the nuclear fuel cycle, e.g., input accountability of nuclear fuel, material accounting in the dissolver solution, burn-up determination, and most importantly for nuclear forensics. Our lab in Fuel Chemistry Division, BARC is involved in the quality control of nuclear fuel samples that requires precise determination of both isotopic composition and concentration of various actinides e.g. U, Pu, Am etc. We have developed and reported SLMs immobilized with various phosphate and amide-based ligands that offered dual functions: (i) matrix elimination and/or preconcentration of actinides from complex aqueous samples and (ii) direct assay of the actinide pre-concentrated on SLM by thermal ionization mass spectrometry (TIMS) or alpha spectrometry (AS), without involving any leaching/stripping [1-4].

The liquid extractants tris(2-ethylhexyl) phosphate (TEHP) and bis(2-ethylhexyl) phosphoric acid (DEHPA), in different molar proportions, were physically immobilized by capillary force in the pores of commercially available, microporous poly(propylene) (PP) and poly(ethersulfone) (PES) membranes – these SLMs were found to be highly selective towards Pu(IV) and U(VI) compared to Am(III) and other trivalent lanthanides in nitric acid medium [1]. Another SLM (DOHA-RTIL@PP) was prepared by physical immobilization of the hydrophobic, a solution of the liquid extractant N,N′-dioctyl-αhydroxyacetamide (DOHA) in a RTIL viz. 1-hexyl3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C6mim][NTf2] within the pores of PP membrane. DOHA concentration in DOHA-RTIL@PP membrane can be tuned aiming either for selective preconcentration of Pu from an aqueous matrix or for bulk removal of actinides [2-4]. The SLM, impregnated with 2M DOHA in RTIL, the membrane showed strong affinity for actinides and was successfully employed for the removal of bulk actinides from aqueous samples with more than 96% recovery. On the other hand, when impregnated with 0.2M DOHA in RTIL, the SLM showed very high selectivity for Pu(IV) in acidic medium, in the presence of other competing actinides, viz., Am(III), U(VI) and Np(V). Also, the use of RTIL instead of the conventional dodecane solvent not only makes the process greener but also improves the separation factor for Pu(IV) and increases the equilibrium uptake capacity significantly. We have developed and demonstrated direct loading of the SLMs on Re filament for the isotopic analysis of Pu by TIMS [1]. The DOHA-RTIL@PP membrane have been successfully employed for efficient and selective solid-phase separation of Pu(IV) from (U,Pu)C and fuel dissolver solution samples [2,4]. We have also developed a novel method for the extraction of Pu from acidic samples using SLM, followed by preparation of alpha source by direct decomposition of the SLM on a metal planchet for the quantification of Pu by alpha spectrometry.

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Conducting molten salt electrorefining of Uranium metal at 10 kg per batch scale: Challenges and recent achievements

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A pyrochemical process, known as Pyroprocess, is an advanced nuclear reprocessing method, being studied in many countries as an alternate to PUREX process. It is a non-aqueous, high temperature process, based on molten salt electrorefining. Pyroprocess offers several advantages over PUREX, such as the ability to process short-cooled high burn-up fuel, intrinsic minor actinide recycling, less criticality problems and negligible liquid waste volume. This process is highly suitable for reprocessing spent metal fuels. In India’s three-stage nuclear power program, metal fuel Fast Breeder Reactors paired with pyroprocess can provide very low overall doubling time, a very significant advantage. IGCAR is therefore pursuing a metal fuel cycle program in this direction. Pyrochemical reprocessing studies, focused on molten salt electrorefining, began at IGCAR’s Radiochemistry Laboratory in the 1990s.These studies have been carried out using U/Pu alloys simulating spent fuel in inert atmosphere glove boxes. Although these studies proved the process's feasibility, but for setting up reprocessing plants based on pyroprocess required scaled up demonstration of the process. The technology know-how for PUREX is not directly applicable to pyroprocess based reprocessing plants due to significant differences between the two processes. To develop and demonstrate the engineering technology required for setting up pyroprocess plants, a facility called PyroProcess Research and Development Facility (PPRDF) has been set up in IGCAR.

For the process demonstration, PPRDF will use natural uranium alloys containing non-radioactive isotopes of typical fission products, to simulate spent metal fuel. The facility's primary goal is to demonstrate electrorefining and cathode product consolidation, two major process steps, for a batch size of 10 kg of uranium alloy, simulating spent metal fuel. PPRDF will also provide crucial experience in remote operation and maintenance of process equipment, maintaining argon atmosphere with controlled purity, pressure and temperature in a large containment box, and integrated instrumentation and control systems.

PPRDF is provided with a 500 m^3 argon atmosphere containment box (CB). High Temperature Electrorefiner (HTER), for electrorefining, and Automated Vacuum Distillation & Melting System (AVDMS), for cathode product consolidation, are the main process equipment housed inside CB. PPRDF has been commissioned, and the first uranium electrorefining run was successfully completed. The talk will cover the activities undertaken to reach this milestone, the challenges faced, the significance of the achievement, and future plans.

Mechanisms of actinide and lanthanide extraction by polydentate N,O-donor ligands

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The isolation of actinide elements from spent nuclear fuel represents the most significant step in closing the nuclear fuel cycle. Developing new extraction systems to accomplish this is a challenging interdisciplinary task that draws on the expertise of radiochemistry, organic chemistry, physical chemistry, and coordination chemistry. One promising class of ligands for selective isolation of americium is N,O-donors, which exhibit a high rate of equilibrium establishment and the potential for a wide range of synthetic modifications. One important feature of this class of ligands is the use of highly polar aromatic solvents such as meta-nitrobenzotrifluoride (F-3), which significantly affects the form of complex compounds that pass into the organic phase as well as the likelihood of ion pair formation therein.

This report will focus on the possible extraction mechanisms of various subclasses of N,O-donor ligands, such as tri-dentate ligands using the example of pyridine diphosphonates as well as various tetradentate diamides of 2,2'-bipyridyl-6,6'-dicarboxylic acid, 1,10-phenanthroline-2,9-dicarboxylic acid and 1,10-phenanthroline-2,9-diphosphonates. As an integral part of the extraction system, the extraction of nitric acid and its effect on the kinetics of extraction will be discussed.

The various forms of complex compounds, including $Am(NO_3)_3$, $Ln(NO_3)_3$, $UO_2(NO_3)_2$, and Np, which are obtained both in the solid state using SC-XRD and spectroscopic methods, such as UV-Vis, XANES, EXAFS, and NMR, applied directly to organic phases will be discussed. Based on this data, we will discuss how the composition of these complex compounds affects the trends in extraction efficiency and selectivity. Additionally, the effect of organosoluble additives such as ionic liquids and chlorinated cobalt dicarbollide on the main extraction parameters and the forms of the complex compounds will be presented.

It has been summarized that polydentate extractants, which are believed to have solvation extraction mechanisms, can extract 5f- and 4f-elements by various mechanisms depending on the conditions (nitric acid concentration, initial form of element, type of substituent) in polar solvents. These elements can be extracted through various mechanisms, such as hydrate/solvate extraction, cation exchange, and anion exchange.

Acknowledgments: This work was supported by Russian Scientific Foundation (grant № 20-73-10076.)

Keywords: Actinides, lanthanides, solvent extraction

Key Aspects in the Development of Analytical Methodologies for Radiopharmaceuticals in High Performance Liquid Chromatography

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One of the main challenges for the development of analytical methods in the quality control of radiopharmaceuticalsis the short time available to finish the analysis due to the limited half-life of radiomolecules. To evaluate the success and quality of radiolabeling, it is necessary to determine the radiochemical purity and chemical purity of the radiomolecules under study. In simple molecules, e.g. [^{18}F]FDG or [^{99m}Tc]DTPA, are easily determined using thin-layer chromatography (TLC). Nevertheless, for new diagnostic and therapeutic agents with complex precursors and more radiolabeling steps, better analytical separations are crucial to identify impurity peaks, which are only detectable using higher sensitivity methods such as high-performance liquid chromatography (HPLC). This implies an increase in the complexity of analytical methodology development. For the proper development of the method, it will be necessary to select an analytical column with an appropriate stationary phase and dimensions for the analyte, along with a mobile phase of suitable composition. Additionally, it is necessary to determine some analytical parameters not used in TLC, such as the correct construction of a calibration curve, determination of the linearity range, selectivity, limit of detection (LOD) and limit of quantification (LOQ).

This work presents practical examples of method optimization, reducing analysis times as shown in Figure 1. In A, a retention time of 10.8 minutes is observed for [^{18}F]PSMA-1007[1], while with the same stationary phase and changes in the physical dimensions of the column, it is possible to reduce it to 2.6 minutes without losing selectivity with the OH-PSMA impurity[2], as shown in B. Additionally, the determination of the main parameters necessary for the validation of an analytical method will be reviewed, increasing sensitivity in modern radiopharmaceuticals used routinely.

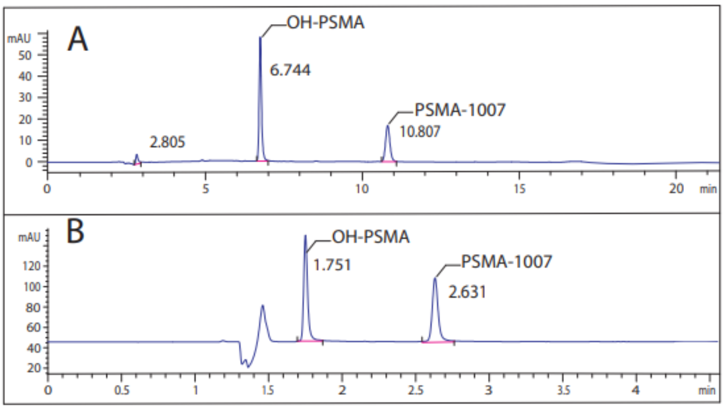

Figure 1. Comparison of two columns with the same C18 stationary phase. Panel a has dimensions of 250 x 4.6 mm x 5 µm, and panel B has dimensions of 150 x 4.6 mm x 2.6 µm.

Keywords: Radiopharmaceuticals, High Performance Liquid Chromatogrphy, Quality Control

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Pickering emulsion assisted synthesis of functionalized graphene oxide-polystyrene composite microspheres for the selective removal of Zr from acidic solutions

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The remarkable adaptability of graphene oxide, as well as its vast surface area, have fuelled research into the use of functionalized graphene oxides for metal ion recovery. Graphene oxide is an oxidized variant of graphene that is generally generated by oxidation-assisted graphite powder exfoliation utilizing the well-known Hummers' oxidation technique. The selective removal of Zr from acidic aqueous waste of U-Pu-Zr metallic fuel is of importance since U-Pu-Zr may be reprocessed through an aqueous approach. The difficult aqueous chemistry of zirconium demands its separation, and solid phase adsorbent technologies, particularly tailored graphene-based materials, have demonstrated their potential usage due to intrinsic benefits such as greater chemical stability, surface area, and so on. The Zr-selective adsorbent, amide functionalized graphene oxide (GO)-polystyrene composite was prepared and characterized by FT-IR, XRD, Raman and SEM analyses. Graphite powder was oxidized to graphene oxide wherein an amide functionality was incorporated using chemical modification. The above material was used as a template while the styrene was polymerized to make a GO-polystyrene composite material. Fig.1, SEM images, showed the micrometer sized polystyrene beads sandwiched between the GO sheets. The adsorbent had displayed a good selectivity of Zr over the trivalent lanthanides and even uranium at all the acid conditions. Fig. 2 shows the adsorption behavior of Zr by the adsorbent. The study also has pointed towards the use of a solution consisting of 0.1 M nitric acid and 0.5 M citric acid for the quantitative removal of adsorbed zirconium from the adsorbent material. The demonstration of the Zr adsorption from the simulated solution corresponding to the PUREX liquid aqueous raffinate originated from U-Pu-Zr also have showed the potential and the possible use of functionalized GO-styrene composite for Zr removal.

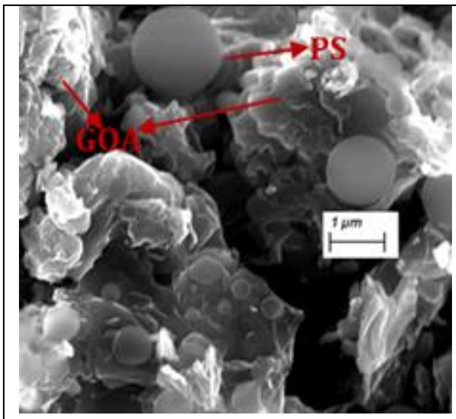

Fig. 1 SEM image of amide functionalized graphene oxide (GO)-polystyrene composite.

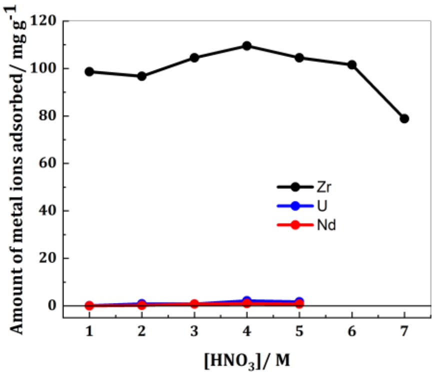

Fig. 2 Adsorption of Zr, U and Nd by amide functionalized graphene oxide (GO)-polystyrene composite.

Keywords: Zirconium, Graphene oxide, SEM, Extraction, Polymer.

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An engineered Graphene oxide for the removal of palladium from nuclear waste

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Graphene oxide (GO), an oxidized version of graphene prepared by the oxidation of graphite, finds various applications in separating metal ions, notably due to its vast surface area and tunable nature. The flexibility to introduce diverse functional groups by chemical modification has additional advantages as different metal ion selective ligands could be chemically attached to the GO and make them task-specific. Palladium, one of the platinum group metals with a substantially lower abundance of 10^{-6} %, is one of the quintessential elements in the electronic and chemical industry. Recent applications in hydrogen storage, photovoltaic materials, hydrogen sensor applications, and so on also add to the massive industrial demand for palladium. Conversely, the nuclear fission reaction produces vast amounts of palladium as a fission product. However, the practical problem with harnessing this palladium is the presence of ^{107}Pd, which has an abundance of ~ 17 %. Therefore, utilizing the reactor-produced palladium may not be possible. Nevertheless, considering the long half-life of ^{107}Pd and its being a soft beta radioactive, it can be used for various applications in the nuclear industry wherein palladium is required, particularly hydrogen isotope separation, etc. Therefore, palladium separation from nuclear waste attracts interest. Additionally, palladium separation from the waste stream makes it amenable for vitrification, as the former could invite additional trouble.The palladium adsorptive performance of pristine GO, an amine modified GO and an amide modified GO has been studied. The GO was prepared by oxidation of graphite powder. Further, GO was modified in to an amide modified GO by treating with thionylchloride followed by reaction with diethylenetriamine. Fig. 1 shows the FTIR of GO and amide modified GO. Fig. 2 shows the adsorption behavior of palladium by GO and amide modified GO. Amide modified GO showed higher adsorption of Pd as compared to pristine GO. The studies indicated the possibility of employing the above GOs for removing Pd from the radioactive wastes.

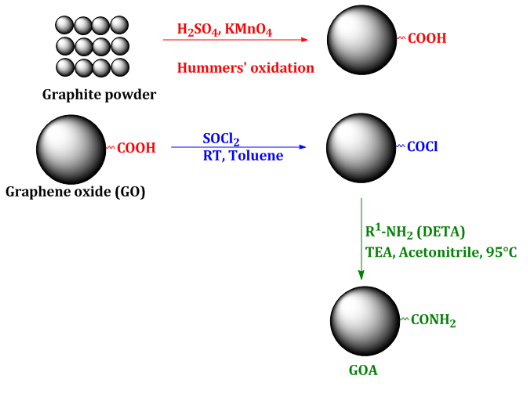

Fig. 1 Sematic representation of the preparation of amine functionalized graphene oxide

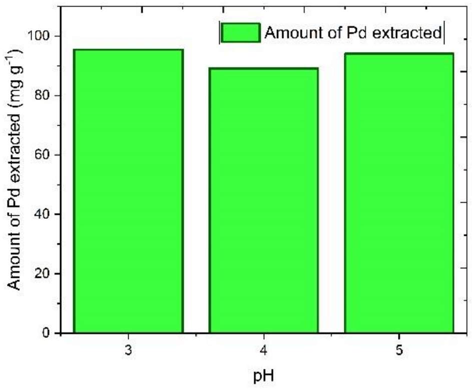

Fig. 2 Adsorption of Pd by amide functionalized graphene oxide

Keywords: Hummers' oxidation, Graphene oxide, Purification, Extraction, Palladium.

References

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Use of GO-polymer composite for uranium removal

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Enhanced demand for uranium in nuclear reactors with the increased energy requirement associated with massive industrialization and population rise has mooted the research on looking into alternate sources of uranium other than the conventional earth crust-based igneous rocks. Separation of uranium from the seawater, though the total reserves are more significant than the land-based sources, is challenged by poor abundance. Solid phase adsorbents are considered for separating uranium from seawater owing to its poor abundance and viewing the competitive separation by other interfering ions. High selectivity, larger capacity, and separation efficiency are the few desirable features that are looked into in solid-phase adsorbents, and GO-based adsorbents offer superior advantages to meet the above. GO provides a sheet-like structure made of sp2 hybridized carbon atoms that are pronounced by carboxylic acid and epoxy groups. An amine-functionalized GO-polymer composite was considered for the uranium separation applications.GO was prepared by oxidizing graphite powder, and several carboxyl and epoxy functional groups are supposed to be produced during this process. The oxidizing conditions are optimized to suit the production of maximum epoxy groups compared to carboxyl groups. The epoxy-functionalized GO was further modified to an amine-functionalized GO by reacting with diethylene triamine. Subsequently, an in situ polymerization of styrene was carried out in the presence of the above amine GO, using AIBN as a free radical initiator. The polymer amine GO composite (PS-GOam) was employed for testing uranium separation capability under different conditions such as pH of the aqueous phase, contact time of adsorbent with the aqueous phase, uranium concentration, etc. Fig. 2 shows the uranium uptake as a function of pH that displays increased adsorption with increase of pH with maximum uptake at pH 5. Stripping studies that were carried out using 0.1 M nitric acid resulted in 100 percent U recovery from PS-GOam within three contact stages. The study pointed to the possibility of using PS-GOam for uranium separation from diluted uranium-bearing feed solutions. Additionally, the studies can be extended to uranium pre-concentration applications and uranium separation from other feed solutions containing submicron levels of uranium.

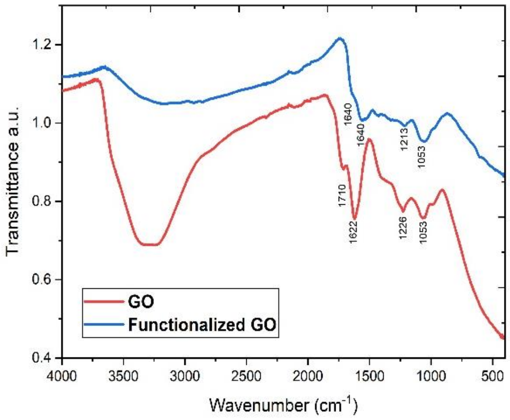

Fig. 1. FTIR spectra of Graphene Oxide (GO) and Amine functionalized Graphene Oxide

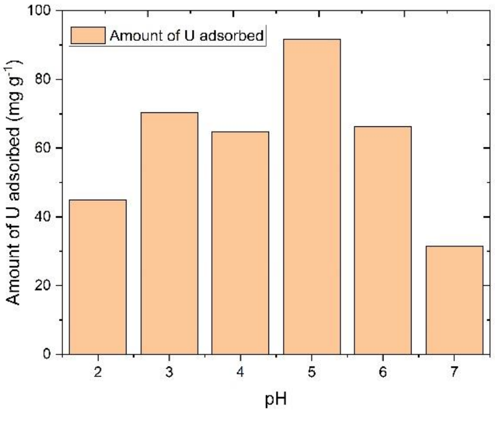

Fig.2. Adsorption of U by amine functionalized polymer amine GO composite

Keywords: Zirconium, Graphene oxide, SEM, Extraction, Polymer.

References

1. A.S. Suneesh, P.A. Manojkumar, P.A., B.R. Selvan, C. Ghosh, R. Mythili, S. Chandra, N. Ramanathan, Mater. Sci. Eng.: B, 295 (2023) 116609.

Gamma radiation induced synthesis of 2-mercaptobenzimidazole functionalized poly-propylene fabric for removal of aqueous Ag(I)

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A 2-mercaptobenzimidazole-functionalized poly-propylene non-woven fabric adsorbent was synthesized in two steps. The first step is the grafting of glycidyl methacrylate (GMA) onto polypropylene (PP) non-woven fabric. The subsequent step was the chemical modification of the GMA-grafted PP fabric with 2-mercaptobenzimidazole. Grafting was carried out using the gamma-irradiation-induced simultaneous graft polymerization method. Cut sections of the commercially available PP non-woven fabric were refluxed with ethanol at 80°C for 6 hours to remove dirt and organic impurities. The resultant PP fabric was dried in a hot air oven at 60°C overnight. Previously weighted clean and dry PP non-woven fabric was taken in dry stoppered glass test tubes. 10 ml of a monomer (GMA) solvent mixture was added to it and vigorously purged with N2 for 15 minutes to remove the oxygen dissolved (from the monomer solution) or trapped (in the PP fabric). The test tubes were sealed immediately with Teflon tape and paraffin film to prepare the samples before subjecting them to gamma irradiation. All the samples prepared during the course of this work were irradiated in a 60Co gamma irradiator indigenously developed by BRIT (Board of Radiation and Isotope Technology), India, with a dose rate of 5.1 kGyh-1. PP fabric was weighted before (Wi) and after irradiation, followed by drying (Wf). The percentage grafting (%G) was calculated from gravimetric analysis using the equation %G = [(Wf-Wi)/Wi] ×100. The effects of various experimental parameters on percentage grafting, such as solvent medium, water content in the solvent medium, monomer concentration (Fig. 1), dose, and dose rate, were investigated through systematic studies to obtain an optimum percentage grafting. The GMA-grafted PP fabric was chemically modified further with 2MBI in 10% water in THF medium at 55°C for 8 h under reflux conditions. The resulting material was analyzed with scanning electron microscopy (SEM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR) (Fig. 2), and Raman spectroscopy techniques to investigate various characteristic properties such as topography and morphology, thermal stability, functional group identification, etc. The percentage conversion of the functionalization reaction with 2MBI was also optimized by using various solvents (such as THF, acetonitrile, etc.) and different concentrations of 2MBI. The synthesized adsorbent was subjected to sorption and kinetics studies with an aqueous Ag(I) solution. The adsorbent was found to have a maximum sorption capacity of ~150 mg/kg and very fast kinetics, such that >90% of the sorption capacity was achieved within 15 min. (Fig. 3)

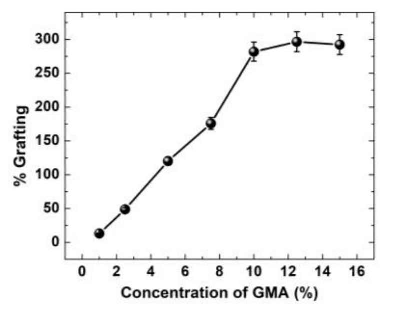

Fig. 1. Effect of concentration of monomer (GMA) on % grafting

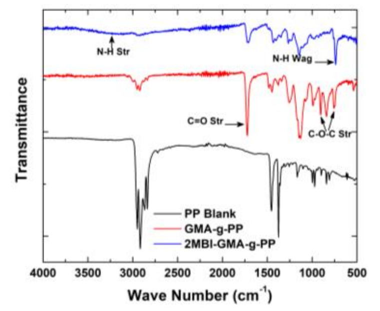

Fig. 2. FTIR spectra of the adsorbent

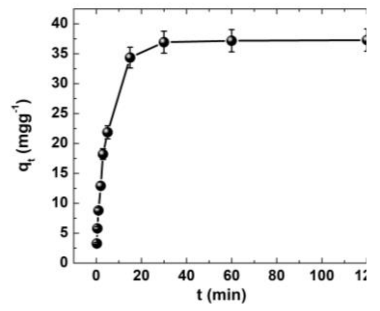

Fig. 3. Kinetics of sorption of Ag(I) by 2MBI-GMA-g-PP

Keywords: Poly-propylene, Glycidyl Methacrylate, Grafting, Sorption, Kinetics, Ag(I)

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Development of membrane based pre-concentration technique in combination with TXRF for the determination of mercury in water samples at ultra trace level

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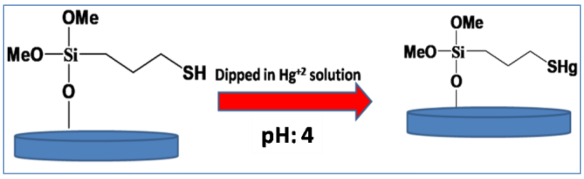
Total reflection X-Ray Fluorescence (TXRF) is a well established technique for the determination of both metals as well as non metals in various types of sample matrices down to ultra trace level. However this technique cannot be directly utilized for the determination of toxic elements like Hg due to its high vapor pressure and low boiling point, which leads to the loss of Hg during the drying of the sample solution on quartz reflector **[1]**. To overcome this problem we have developed a membrane based pre-concentration technique combined with TXRF. This methodology not only overcomes the drying problem, but also improves the detection limit of Hg down to ppt level. In this work 3 Mercaptopropyl trimethoxy silane has been functionalized on quartz sample supports. The –SH functionality present in this molecule has a very good affinity towards divalent Hg^{+2} at some specific pH. FTIR study confirmed the binding of –SH group with sample supports. Fig. 1a shows the schematic of binding of Hg^{+2} species to the membrane formed by 3 Mercaptopropyl trimethoxy silane, immobilized on quartz sample supports. The TXRF spectrum recorded to analyze Hg (Fig.1 (b)) shows clear peaks of Hg L lines after the pre-concentration. The S-Kα peak coming from the membrane itself has been used as in-situ internal standard for the calibration purpose. Different parameters like pH of the medium, membrane concentration, equilibration time etc. were optimized to get maximum adsorption. It was seen that maximum adsorption occurs at pH 4. All the TXRF measurements were carried out using Low Z High Z TXRF spectrometer, with Rh target in air. The area under each elemental line was determined using PyMca software package. This simple membrane based pre-concentration methodology combined with TXRF gives detection limit for Hg 90 ppt.

a



b

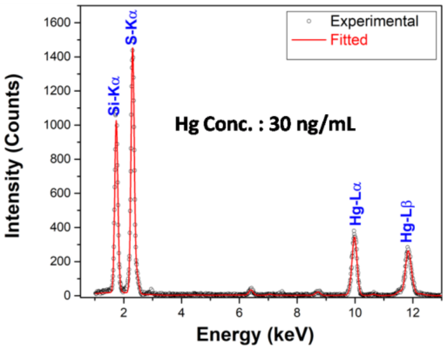


Fig. 1a: Schematic of the immobilization of 3 Mercaptopropyl trimethoxy silane on quartz sample supports,
Fig. 1b: PyMca fitted TXRF spectrum obtained after pre-concentration of a solution having Hg concentration 30 ppb.

Keywords: TXRF, Pre-concentration, Immobilization, Mercury, Detection limit

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Simple, precise and inexpensive method for the synthesis of mesoporous γ-Al_2O_3 nanoparticles for its application in the remedial solution of LLW nuclear solutions

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Liquid-solid extraction is the preferred process to treat large volume solutions for its decontamination from hazardous contents. In the nuclear field inorganic sorbent is a better choice due to its radioactive stability. In this category several metal oxides such as such as MnO_2, Fe_3O_4, Al_2O_3, calcium silicate, hydroxyapatite, etc. have been used for the liquid-solid extraction of long-lived minor actinides from LLW nuclear waste solutions. The main disadvantage observed with these inorganic sorbents is low uptake and poor sorption kinetic. To overcome these issues a continuous search in the modification or development of new inorganic adsorbent is in progress. Use of nano size particles or sorbents are of great use to overcome the problem of low process kinetics and sorption capacity. Alumina exists in several polymorphs i.e α, χ, η, δ, κ, θ, γ, and ρ) [1]. α-alumina is identified as the most thermodynamically stable phase in bulk form. The transformation of γ-Al_2O_3 (density ρ = 3.56 g cm–3) to α-Al_2O_3 (ρ = 3.98 g cm–3) is accompanied by a volume reduction of about 10% and proceeds through a metastable phase of θ-Al_2O_3 [2] .In present investigation solid state mechanochemical approach is used for the synthesis of γ-Al_2O_3. This method of synthesis is highly precise, simple and with high yield of mesoporous γ-Al_2O_3 nanoparticles. Alumina particles obtained in process were characterized to corelate their potential utility for the extraction of metal ions from bulk aqueous solutions. The XRD pattern of resulted alumina particles (Fig 1) revealed the average crystallite size of alumina nanoparticles is 2−3 nm, which was calculated from the full width at half maximum of the (400) peak at 2θ = 45.81 using Debye− Scherrer's equation. To determine the surface area, pore size, and pore volume of the samples at a temperature of 77 K, Brunauer-Emmett-Teller (BET) method was adopted(Fig.2 and 3). The surface area of the synthesized alumina is 371.64 m^2 g^{-1} and the pore volume derived as 0.49 cc/g. The adsorption average pore diameter of the 5-8 nm is calculated using the NLDFT method. The IR spectrum of synthesized close similarity with the same for γ-alumina in literature. To understand the phenomenon of sorption which is a surface phenomenon that occurs due to partial electrostatic charge of attraction between the ion and the sorbent surface, Zeta potential measurement was carried out of the sorbent under different pH conditions. In these studies, the isoelectric point was found to be 6.7. Further the practical utility of this sorbent under required chemical conditions was ascertain by dipping solid particles in the solutions of applicable pH range of 1 to 10 for longer durations and practically negligible dissolved content of Al were observed in the supernatant solutions. The preliminary experiments of solid-liquid extraction of uranium(VI) from nitrate solutions showed promising results (about18 mg g^{-1} of the extraction of U). Further work is progress for detail extraction studies of metal ion extractions relevant to LLW nuclear solutions.

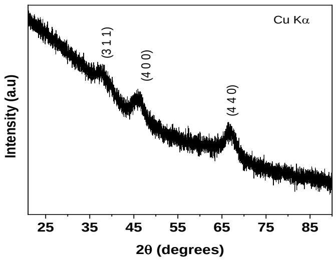

Fig.1 XRD pattern of alumina prepared

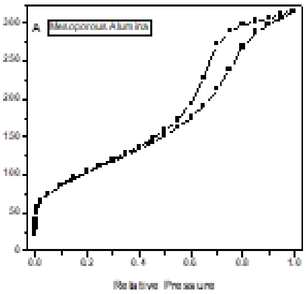

Fig.2 Surface analysis of alumina

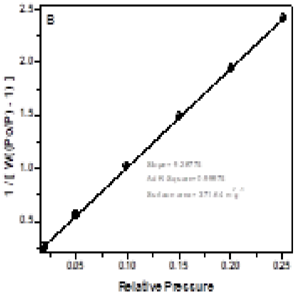

Fig.3 Pore analysis of mesoporous alumina

nanoparticles of Al_2O_3 shows

Keywords: Nanoparticles, γ-Al_2O_3, *Solid-liquid extraction*

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Extraction of Plutonium into tetra-butyl ammonium nitrate baseddeep eutectic solvents

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In view of the importance of actinide separations in the backend processes and the deleterious nature of thedegradation products of TBP, a green and sustainable hydrophobic solvent is required as an alternative to TBPfor the liquid-liquid extraction (LLE) of actinides [1]. One potential replacement for the VOCs is thought to beionic liquids (ILs). The main drawbacks of ILs, however, are their high viscosity, toxicity, high cost, numerouscompeting extraction mechanisms, and loss of ionic liquid into the aqueous phase while operating in the cationexchange mode, which restricts their applications in the extraction of actinides. On the contrary, DeepEutecticSolvents(DESs),anovelclassofdesignergreensolventswithpromisingsolventcharacteristics,easeofsynthesis,lowcost,etc.havegainedalotofattentioninarangeofelectrochemicalandseparationapplications[2] making them viable substitutes for the conventional diluents for LLE of actinides.In the current work, tetra-butyl ammonium nitrate (TBAN) was used as the H-bond acceptor anddecanoic acid (DA) as the H-bond donor in their 1:2 mole ratio to prepare a low viscous TBAN-DA DES. Inaddition, it was used as a diluent for tributyl phosphate (TBP; 30%). Previously we have done the LLE of uranylusing TBA-DA DES while the present study aims to evaluate its extraction efficacy for Plutonium from acidicaqueous feeds. The LLE of Pu from the aqueous medium was carried out with varying acidity (0.2 to 7 M; Fig.1) and time of equilibration (15 min to 90 min.). In the case of TBAN-DA, the D values initially decrease withacidity up to 2 M beyond which increases and becomes statured at 5 M whereas in the case of TBAN-DA-30%TBPtheDvaluesincreaseupto4Mandappeartohavesaturatedathigheracidconcentrations.Theextractionof Pu was found to be higher in TBAN-DA-30% TBP than the TBAN-DA. Extraction kinetics study suggestedthat 30 minutes were sufficient for the attainment of equilibrium (Fig. 2). Using cyclic voltammetry the redoxpeak potential, diffusion coefficient (D0), transfer coefficient (α) and electron transfer rate constant (k0) of theextracted Pu(IV) in both the DESs were determined for its electrodeposition. It was found that approximately98% of Pu(IV) from the above DESs were stripped with 1M oxalic acid in a single contact.

Fig. 1: Variation of D values with acidity of Pu extraction

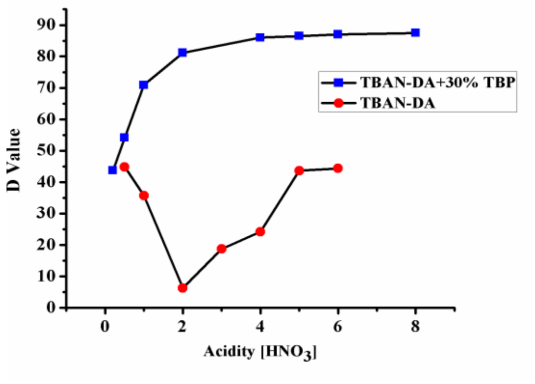
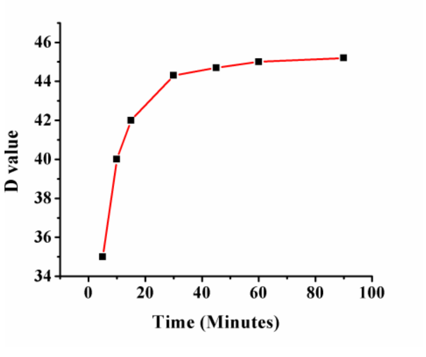


Fig. 2: Kinetic data for Pu extraction



Keywords: *Plutonium, Deep eutectic solvents, Liquid-liquid extraction, cyclic voltammetry*

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Diluent free solvent extraction studies of Pu(IV) with 1:2 TOPO DEHPA based eutectic media

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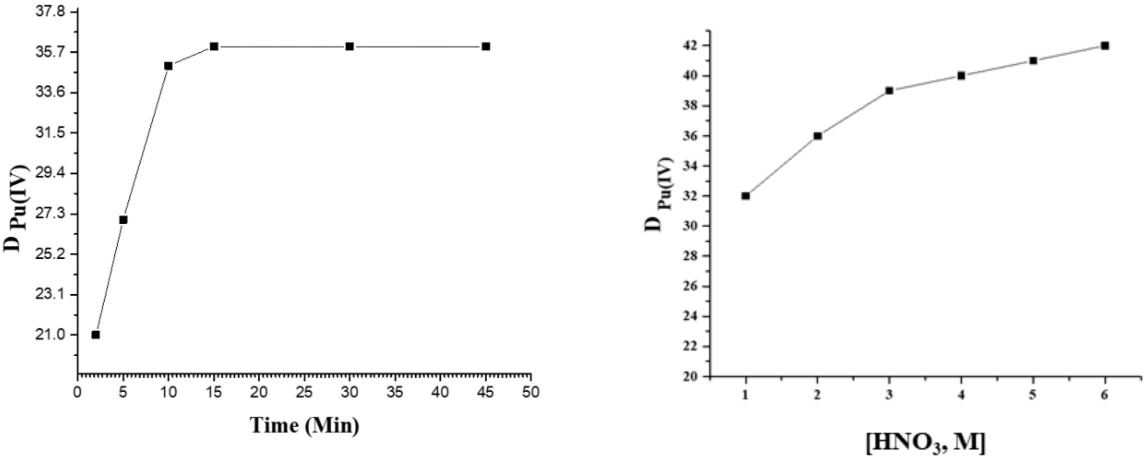
Deep Eutectic Solvent (DES) exhibits similar tunable properties as that of Ionic Liquids (ILs) and serves as a superior counterpart of conventional ionic liquids owing to their low-cost components and ease of synthesis [1-2]. DES emerging as newer solvent systems which found applications in several areas, especially in electrochemistry and separation studies. DES is prepared by combining or mixing a hydrogen bond donor (HBA) and hydrogen bond acceptor (HBD) in a proper ratio which results in a liquid with a melting point lower than either of the components [1-2]. Hydrophobic DES can be explored as diluent-free solvent media in the recovery of actinides from nuclear waste solutions generated at various reprocessing streams. In the present study, DES has been prepared by mixing TOPO and DEHPA in a 1:2 mole ratio. The resulting solvent was directly (without any diluent) employed for the extraction of plutonium from the nitric acid medium. The Stock solution containing ^{239}Pu tracer in nitric acid of required acidity was used for extraction experiments. Pu(IV) state was adjusted by adding a pinch of $NaNO_2$ crystals. The extraction experiment was carried out by equilibrating equal volumes of aqueous phase containing ^{239}Pu tracer with the hydrophobic TOPO: DEHPA eutectic solvent. ^{239}Pu was monitored by the alpha liquid scintillation counting. The distribution ratio is computed as the ratio of the activity of ^{239}Pu in organic and aqueous phases. The kinetics of extraction shows (Fig.1a) that 15 minutes is sufficient to attain equilibrium for Pu liquid-liquid extraction. The effect of acidity reveals that extraction of Pu(IV) increases with an increase in acidity from the 1-6 M range (Fig.1b) and the experimentally observed D value is 42 at 6 M. The extracted Pu(IV) can also back extracted (>95%) from the DES phase by using 0.05M oxalic acid solution.



(a) **(b)**

Figure 1. (a) D value with increasing times (Kinetic plot) (b) D value with varying acidity

Keywords: *Plutonium, Deep eutectic solvents, Liquid-liquid extraction, cyclic voltammetry*

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A-09

Synthesis and Evaluation of Zr-based Metal-Organic Framework immobilized on Activated Sand for the Removal of Cs(I) ion

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Removal of monovalent ions from neutral or mild acidic condition is always a challenging task. Metal cyanoferrates, crown-ethers, calix-crown are well known reagents for alkali or alkali-earth metal ion extraction from acidic as well as basic media**[1-3]**. In view of importance of Cs(I) ion removal concerning nuclear waste management as well as environmental issues, this research work introduces a method to develop new adsorbent for eliminating Cs(I) ions from aqueous solutions. The synthesis involves integrating a sulfonic acid-functionalized Zr-based metal-organic framework (MOF) onto activated sand, resulting in a composite material with Cs(I) ion adsorption capabilities.

The Zr-based MOF is synthesized using a hydrothermal approach, ensuring the creation of a stable framework with notable surface area and porosity**[4]**. The subsequent functionalization of the MOF with sulfonic acid groups improves its affinity for Cs(I) ions, promoting selective adsorption**[5]**. Immobilizing this functionalized MOF onto activated sand enhances mechanical stability and facilitates the practical deployment of the composite material. Structural and morphological properties of the composite material were evaluated using techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), and Brunauer-Emmett-Teller (BET) surface area analysis. The results confirm successful incorporation of the MOF onto the activated sand substrate, highlighting a uniform distribution of active sites. Batch adsorption experiments were also performed to assessCs(I) ion removal efficiency of the synthesized composite material. The adsorption data was studied with Freundlich isotherm and the presented in figure 1. In conclusion, this approach offers a sustainable and efficient strategy for synthesizing a composite adsorbent capable of selectively extracting Cs(I) ions from water.

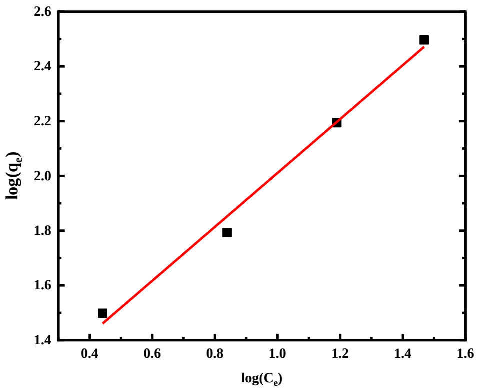

Fig. 1: Freundlich isotherm curve for Cs(I) adsorption on Zr-MOF@activated sand

Keywords: MOFs, Cesium, Zirconium, activated sand

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Selective extraction of trivalent ions using multi DGA-functionalized silica based sorbent

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Diglycolamides such as Tetraoctyldiglycolamide (TODGA) and Tetra(2-ethylhexyl)diglycolamide (T2EHDGA) are widely explored for the extraction of actinides and lanthanides from acidic nuclear waste streams [1]. However, extraction of fission product Sr along with actinides and lanthanides in these diglycolamides makes the partitioning of actinides & lanthanides more complicated. Recently, preorganization of diglycolamide arms over different supramolecular frame work such as calixarenes and aza macro cycle crown ether with –NH terminal has been emerged as anefficient technique to improve the extraction efficiency and selectivity of diglycolamide towards actinides and lanthanides with respect to fission product such as^{90}Sr. In fact several functionalized ligands like C-4-DGA and C-2-DGA etc. are reported in the literature which shows high extraction efficiency as usual like DGA for lanthanides &actinides without extracting Sr in contrast to DGA [2]. The effect of preorganization on extraction performance of DGA arms are also replicated when they are chemically funcationalised over solid materials like silica [3]. Thus, in this work,asilica based DGA-functionalised solid phase material (SiO_2-APTES-DGA(Oct)$_2$), for selective extraction of trivalent ions like Am^{3+}, Eu^{3+}, and Y^{3+},has been synthesized in our laboratory whose structure is shown in **Fig. 1(a).** The synthesised material has been characterized by FTIR, ^{13}C (CP/MAS) solid phase NMR, TGA-DSC and BET etc. techniques. The extent of grafting of DGA fragments on the solid phase of silica evaluated by TGA measurement as 17.2% corresponds to 0.425± 0.01mmol/g. The sorption ability of the solid phase material is evaluated on batch scalefrom nitric acid medium and expressed in terms of K_d(ml/g) value.

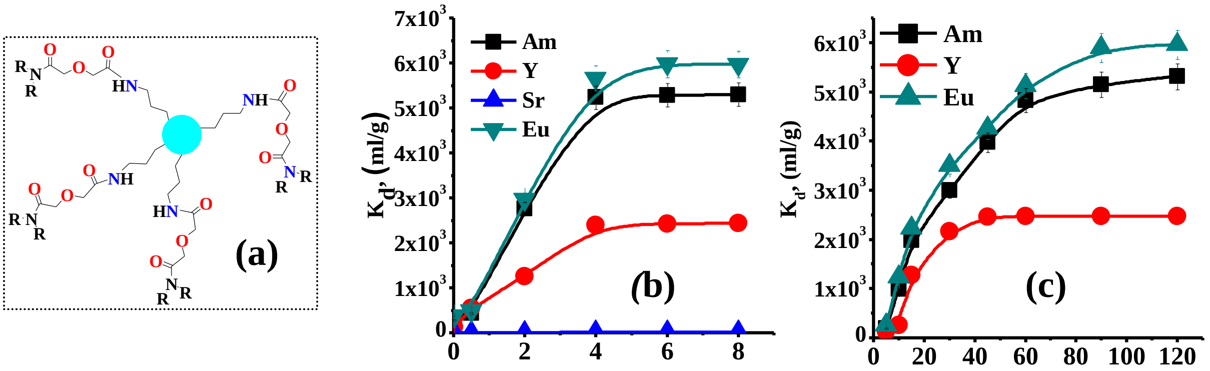

Fig.1:(a) Chemical structure of SiO_2-APTES-DGA(R)$_2$, (R=Oct), (b) Variation of K_D with [HNO_3] (c) Extraction kinetics

Fig. 1(b) reveals that the DGA-functionalised solid phase material shows very high K_d for Eu^{3+}, $Am^{3+}$and Y^{3+} as a function of the nitric acid concentration whereas very low $K_d$for Sr^{2+}. It is due to the preorganization of the DGA arms in SiO_2-APTES-DGA(Oct)$_2$, which prohibitsthe attainment of six atom donor crown ring type arrangement occurring during Sr extraction with free DGA. The solid phase material SiO_2-APTES-DGA(Oct)$_2$exhibit moderately faster sorption kinetics as shown in **Fig. 1(c).**Water soluble complexing agent namely Tetraethyldiglycolamide (TEDGA) has been explored for the elution of loaded metalions from SiO_2-APTES-DGA(Oct)$_2$. Three batch contacts with 0.2 M TEDGA/4MHNO_3 medium are found to be sufficient to regenerate the solid phase material. The minimal change in sorption efficiency of Am for the γ–radiationexposed SiO_2-APTES-DGA(Oct)$_2$highlights the good material stability of the synthesized material.

Keywords: diglycolamides, functionalization, strontium,supramolecule.

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Development of a cesium specific inorganic ion exchanger based on sodium titanophosphate

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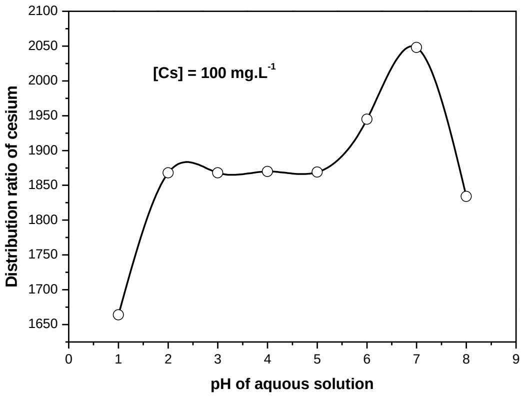
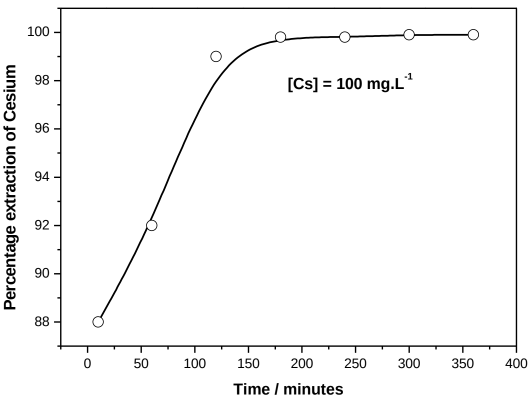
The separation of cesium from any radioactive waste is significant due to its radioactive nature. There are two main isotopes of cesium which are responsible for the radioactivity. They are ^{135} Cs and ^{137} Cs, with half-life of 2.3 million years and 30.2 years, respectively [1]. Different processes are used to dispose of nuclear waste depending on the quantity of radioactivity and radionuclides present. Among the several fission products, radioactive cesium is a significant concern due to its high specific activity. The fission of uranium and plutonium produces substantial quantities of cesium. Because of its volatile nature, immobilizing cesium-bearing waste poses several challenges. As a result, attempts have been made to separate cesium, which might cause difficulties in the waste matrix [2]. The separated cesium is also used as a gamma radiation source. Inorganic ion exchangers are the better candidates compared to organic based ion exchangers due to radiation stability. In this context, sodium titanatophosphate has been prepared and studied as a possible cesium selective inorganic ion exchanger. Sodium titano phosphate was prepared by the reaction between sodium carbonate, meta titanic acid and ortho phosphoric acid. The preparation involves, sodium carbonate and nanocrystalline anatase powder in the form of metatitanic acid ($TiO_2•H_2O$) were taken in a glass beaker and 88% ortho phosphoric acid was slowly added and stirred well. The slurry was heated to dryness at 130°C over a hot plate under constant stirring. The dried product was taken for the extraction studies. Several studies for cesium uptake were performed from pH 1 to pH 8.The maximum distribution ratio of 2100 was observed at pH 7. A fast kinetics is observed for the extraction of cesium by sodium titano phosphate.





Keywords: Sodium titano phosphate, inorganic ion exchanger, cesium.

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Amide Grafted Polymeric Resin for Uranium Recovery from Effluents

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Nuclear energy is a clean, cost effective and non-carbon emitting source compared to fossil fuels. Rapid demand of global energy increases the need of nuclear energy. In past few decades the research had been done intensively on nuclear energy. International Atomic Energy Agency (IAEA) suggests nuclear power becomes the long term sustainable energy source. Uranium is most important in nuclear energy as a nuclear fuel. Mining of uranium from terrestrial ores, produces variety of nuclear wastes contains radiological and non-radiological waste. Discharge the mining effluents into water bodies possessing an adverse effect on environment. There are various techniques for removing of lean uranium from liquid effluent including, chemical precipitation, solvent extraction, membrane separation, ion exchange and adsorption, biological methods and electro coagulation. Various solid phase extraction methods based on grafted polymers have been developed for selective uranium separation. In this work, we propose a solid phase extraction material (polymeric resin). A new polymeric resin developed functionalized by amide moiety and backbone was styrene divinyl benzene framework. Polymeric resin developed by commercially available polymer. Advantage of using amide functional group is because of their harmless degradation product, elimination of secondary wastes, incinerability and economy.

This work reports the characterization of amide grafted resin by ^{13}C Solid State NMR,FT-IR, SEM-EDX, and TGA. After characterizing successfully, evaluation studies were done on batch and column mode with synthetic lean aqueous uranium solution contains nitrate ions in acidic pH range. It was found that the optimum condition for uranium adsorption onto grafted resin was 2M ammonium nitrate at pH 2-3 range.

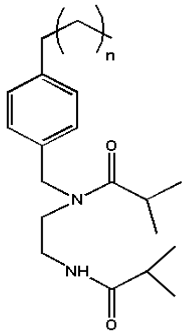

Figure 1. Structure of Diisobutyl diamide resin.

Table 1. Uptake of Uranium various feed acidity.

S.No.	Feed acid HNO_3	% Sorption of Uranium	
		Without NH_4NO_3	With NH_4NO_3
1.	0.25 M	Nil	nil
2.	pH 1	5	5
3.	pH 2	2	96
4.	pH 3	11	90
5.	*pH 4	7	nil

*Precipitation was observed at pH 4 and above so experiment not conducted in this pH range.

Keywords: Nuclear Energy, Uranium, Solid Phase Extraction, Amide grafted resin.

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Development of an optical sensor for the accurate measurement of acidity of solutions

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The uranium and plutonium from spent nuclear fuel are separated by a liquid-liquid separation process known as PUREX, using tri-*n*-butylphospate (TBP) in *n*-dodecane as an organic solvent. For this purpose, the spent nuclear fuel will be dissolved in concentrated nitric acid (10-12 M), and the separation of uranium and plutonium will be carried out from nitric acid after adjusting the feed acidity to 4 M. The recovery of extracted metal ions from TBP requires a lower nitric acid condition (~ 0.5 M). From a large-scale plant perspective, the accurate measurement of acidity in different streams of PUREX is necessary. Online measurement of the acidity of the solution would enhance the efficiency of the process, and it would be highly beneficial for the operation of reprocessing plants handling radioactive solutions. An optical sensor based on chromazurol-S dye was developed to meet this objective [1]. Chromazurol-S dye shows different absorbances at different acidities; therefore, the absorbance variation can be correlated to the acidity values. A glass plate coated with chromazurol-S was employed for the practical deployment of the method. Chromazurol-S was impregnated with polybenzimidazol (PBI), which forms hydrolytically stable transparent coatings on glass [2]. The dissolved polymer mixture was coated to a glass plate by dip coating procedure. Initially, the glass plate was pre-coated with silane with the help of 3-chloropropyltriethoxysilane, for conditioning of the glass surface with polar silane groups, enabling a smooth formation of PBI coating. The polymer coated glass plates were cured by controlled vacuum heating at 120^{0}C. Fig.1 shows the UV-VIS spectra of 0.05% (w/v) chromazurol-S in aqueous medium at different acidities. It can be seen that chromazurol-S shows two absorption maxima (λ_{max}) centered at 464 nm and 542 nm at different acidities. The peak at 464 nm was found to be gradually shifted to 542 nm at higher acidities. Fig. 2 compares the UV-VIS spectra of glass plate coated with chromazurol-S-impregnated PBI membrane at different acidities. The λ_{max} of peaks were found to be shifted to 502 nm and 550 nm in this case. There was a linear increase in the absorbance of 502 nm peak till the aqueous phase acidity was 6 M. Thereafter the peak was found to be shifted to 550 nm. The peak differences at higher aqueous phase acidities were prominently visible when chromazurol coated glass plates were used. Further studies were performed to confirm the reproducibility and stability of the membrane under different aqueous phase acidities. Overall, the study's results confirm the possibility of using chromazurol-S PBI-coated glass plates for online acidity measurements.

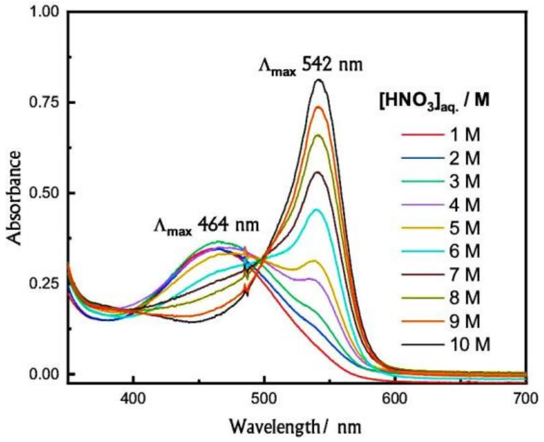

Fig. 1 UV-VIS spectra of Chromazurol-S (0.05%) at different nitric acid concentrations

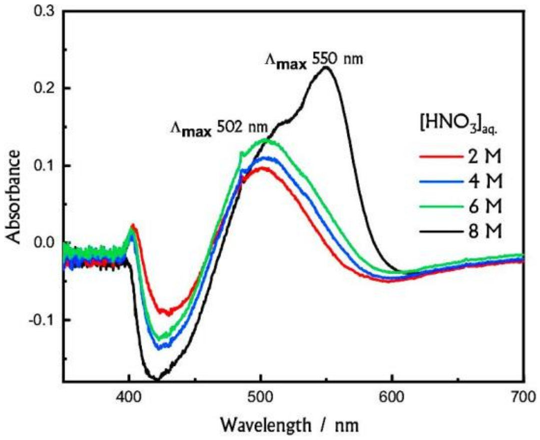

Fig. 2 UV-VIS spectra of Chromazurol-S impregnated PBI coated glass plate at different acidities

Keywords: optical acidity sensor, chromazurol-S, PBI membrane, on-line acidity measurement.

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Novel applications of Imino-di-acetamide (IDA) grafted polymeric resin for metal separation from aqueous process streams

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This work throws light on the practical advantages of utilizing co-ordinate complexation mechanism of the in-house synthesized imino-di acetamide functionalized polymeric resins for separations among the divalent cations. Most cation exchangers, be it singular functional or chelating, show appreciable uptake of Ca^{2+} in the pH 1 to pH 3 range acidic streams, be it sulfate, acetate or chloride. In presence of excess Ca^{2+}, uptake of other heavy metal cations like Lead (Pb^{2+}) or the uranyl cation (UO$_2$)$^{2+}$gets suppressed. It is common to have transition metals coming along with Ca^{2+} ions in industrial streams, like presence of Pb^{2+} with excess Ca^{2+} in lead acid battery waste effluent of sulphuric acid medium or presence of excess of Ca^{2+} along with traces of Uranyl in acetate medium in nuclear fuel cycle. In comparison to imino-di-acetic acid based chelating cation exchanger, it's amidic counterpart IDA functional group does not interact at all with Ca^{2+} providing clean removal of complexing metals with little to no adjustment of pH. The kinetics of Pb^{2+} uptake is fast and follows pseudo-2nd order. Moving towards metals relevant to urban mining, separation between transition metals (Co^{2+}, Ni^{2+} and Cu^{2+}) or between Pb^{2+} and Cu^{2+}can be carried out in the range of pH 1 to 2itself using IDA group whereas the most widely used imported chelator bis-picolylamineworks well mainly near pH 3, providing a wider window for pH dependent metal separation. The technology for the synthesis of IDA grafted polymeric resins and one main application on its recovery of Copper oxide nanoparticles from depopulated printed circuit board have already been transferred and are in the final stages of implementation. This work highlights some more practical applications of the IDA grafted resin for uranyl and lead removal in presence of excess calcium, and the inter-separation among 3d transition metals relevant to urban mining.

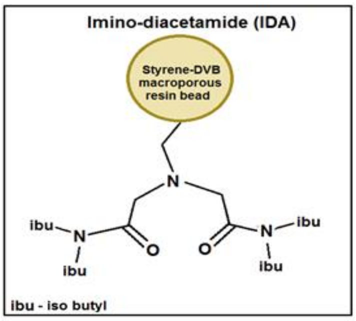

Figure 1 Structure of IDA grafted resin

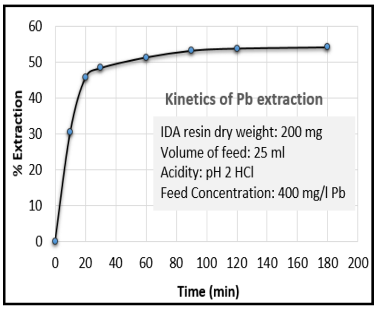

Figure 2 Kinetics of Pb uptake by IDA resin in pH 2 HCl

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Preparation of NCA^{90}Y resin microsphere from FBTR irradiated fuel dissolver solution

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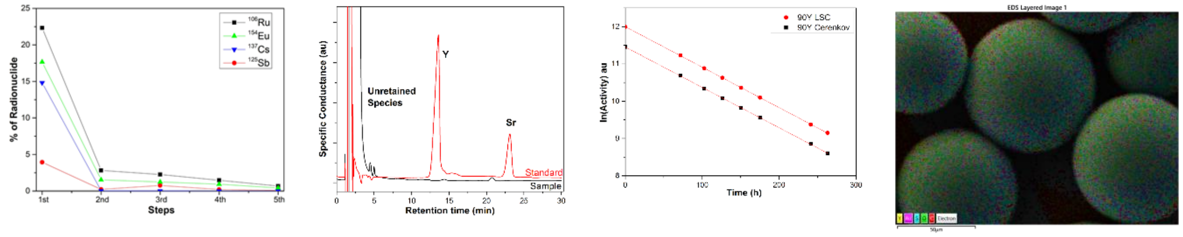
^{90}Y, due to its strong β-max of 2.2MeV,is one of the well-known radioisotopes for the therapeutic application of radioactivity. Among various other modalities, ^{90}Y resin microsphere as a brachytherapy source has its application for liver cancer [1,2]. In the present study, NCA^{90}Y was recovered from ^{235,238}U, ^{239}Pu(n_{fast},f)^{90}Sr(β^-)^{90}Y using Sr selective crown ether followed by quick purification using the Ion Chromatography technique. The dissolver solution of Fast Breeder Test Reactor (FBTR) irradiated mark 1-grade mixed carbide (U-Pu-C) fuel, with burnup of 105 GWd/t, wasequilibrated with 0.1M DtBuCH18C6/ Octanol medium inside hotcell**(Fig.1a)**. The scrubbed back-extracted aqueous phase, sufficiently older than t_{max}, was injected into the Ion Chromatography (IC) system using Dosino. Nucleosil strong cation exchange column with 10mM α-HIBA, 2mM EDA eluent was used with a 0.9 mL/min flow rate to separate Y and Sr fractions. Unretained species were eluted out within the first 4 minutes of elution**(Fig.1b)**. Initially, the experiment was carried out with Sr and Y inactive standards, and retention times were recorded.

Fig.1: Various stages of ^{90}Y resin microspherepreparation



a. Profile of impurity radionuclides during various steps of solvent extraction.

b. IC Chromatogram containing Y and Sr fractions of Std and Sample, respectively.

c. Decay pattern of ^{90}Y by both LSC and Cerenkov Counting, au: arbitrary unit

d. SEM-EDS image of stable Y resin microsphere

A fraction of both ^{90}Sr and ^{90}Y fractions were collected and analysed by the HPGe detector for gamma impurities and by the LSC/ Cerenkov counting**(Fig.1c)** mode to estimate theradionuclidic purity of ^{90}Y. This step is necessary to qualify the sample for further processing. The purification process was carried out in duplicate.The purified ^{90}Y was labelled in strong cation exchange resin to form ^{90}Y resin microsphere**(Fig.1d)**. Various quality control parameters, e.g., water solubility, chemical, radionuclidic purity, and half-life, were verified using Gamma spectrometry, Cerenkov, and LSC techniques. The obtained half-life was 64.05h**(Fig.1c)**, which is in excellent agreement with the literature and is indirect evidence of the very high radionuclidic purity of the sample.

Keywords: ^{90}Y microsphere, Crown ether, ^{90}Sr(^{90}Y), Ion Chromatography, Brachytherapy for liver cancer

Acknowledgement

The authors gratefully acknowledge the assistance received from FBTR and the RML team for irradiation and post-irradiation processing of irradiated fuel. We acknowledge Ms A. Lali and Dr Manish Chandra for the SEM-EDS analysis and the hotcell team comprising of T Kalaiarasu, D Bola Sankar, S Rajeswari and the Director of MC&MFCG and the Director, IGCAR, for their constant support and encouragement.

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Evaluation of extraction profile of Np(IV) into TOPO:DEHPA Deep Eutectic Solvent

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Recovery of minor actinides during the reprocessing of spent nuclear fuel is a principal objective for nuclear waste management [1]. The separation of long-lived actinides like Np and Am is very crucial during the Actinide partitioning step in the processing of HLW generated during PUREX process. The hydrophobic deep eutectic solvents (HDES) appeared as cost-effective alternatives in the solvent extraction of metal ions due to the avoidance of the usual organic phase diluents. Deep eutectic solvent (DES) is a type of eutectic mixture consisting of a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD) with a melting point lower than the individual components [2]. In the present work, DES was prepared by mixing a 1:1 mole ratio of TOPO and DEHPA and kept it at 50°C for 60 minutes until a homogeneous and transparent solution was formed. DES prepared was found to exhibit good liquidus range (23-30ºC). The prepared DES was cooled at room temperature (26ºC) and directly employed for liquid-liquid extraction of Np(IV) from nitric acid medium. During the experiment, 1M HNO3 containing ^{237}Np tracer was added with a few drops of 0.5mM Ferrous sulphamate solution followed by its extraction into TTA in xylene to prepare a stock solution of Np(IV). In liquid-liquid extraction experiments, a required volume of aqueous containing ^{237}Np(IV) and DES phase was taken and equilibrated. The extraction efficiency was evaluated by assaying Np(IV) in the aqueous phase before and after the equilibration by using alpha liquid scintillation counting. As shown in Fig. 1 rapid extraction of Np(IV) with (TOPO: DEHPA) DES was observed as the reaction reached the equilibrium within 10-12 minutes. The influence of the phase ratio (DES: Aqueous) on the extraction performance was investigated (Fig. 2). It reveals that the synthesized DES possess excellent extraction ability for Np(IV) with a wide range of volume ratio from 1:1 to 1:10, however, the extraction efficiency was found to decrease rapidly below 1:20 volume ratio.

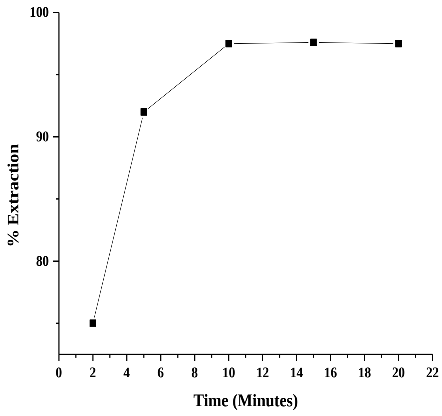

Fig. 1. The extraction of Np(IV) with Time

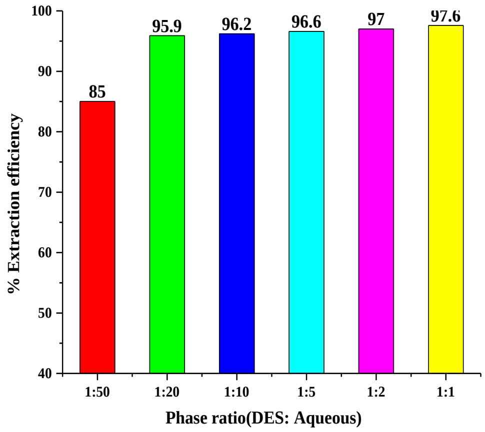

Fig. 2. Effect of phase ratio on the extraction of Np(IV)

Keywords: *Neptunium, Deep eutectic solvent, Liquid-Liquid extraction*

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Development of an engineered GO-magnetite composite for uranium recovery

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Challenges in separating uranium from different solutions containing it in sub-micron levels demand sophisticated solid-phase adsorbents having high selectivity. Graphene oxide, an oxidized form of graphene, is a suitable choice for the above, considering its high surface area, flexibility to form different composite materials, etc. In the context of uranium separation, a magnetite-GO composite was prepared to overcome the fine nature of GO that prevents its applicability in large-scale separation. GO was prepared by the oxidation of graphite by a traditional oxidation-based approach known as Hummers' oxidation. During this process, the carboxylic acid moiety is generated on GO's surface, enabling ion-exchange separation of metal ions. Due to its higher ionic potential, Uranium has a higher preference than other metal ions. Additionally, the magnetite part of MGO enables faster physical separation of the adsorbent phase from the aqueous solution, thus offering a magnetic-assisted solid phase separation. As mentioned above, the amount of carboxylate groups is the key to governing the ion exchange property of GO. This paper deals with the development of MGO and optimization of the GO by a modified Hummers' oxidation process.

Three different batches of MGO (Batch-1, Batch-2, and Batch-3) were prepared by introducing variation of the amount of KMnO4 used and the duration of reaction in the Hummers' method. The response of each set of samples (MGO) for uranium absorption is shown in Table 1. The third batch of MGO demonstrated the highest adsorption values of U (120 mg g-1) and adsorption efficiency of more than 95 %. The FT-IR analysis (Figure 1) shows that change in relative intensity of peaks corresponding to the broad spectral band at 3350-3250 cm-1 is attributed to the presence of enhanced amount of carboxylate groups, produced by the modified Hummers' method. All the adsorption studies were performed with MGO from Batch-3 to yield maximum adsorption performance. Overall, the study indicated that number of carboxylate groups in GO is tailored by increasing the duration of oxidation on MGO composite that has the direct implication on uranium adsorption.

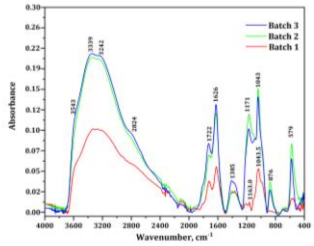

Fig. 2 FT IR of GO prepared at different batches with varied conditions.

Table 1. Preparation conditions of GO prepared under different experimental conditions and their uranium adsorption performance.

Batches of GO	KMnO$_4$/g	H$_2$SO$_4$/ mL	H$_3$PO$_4$/ mL	Duration/ hrs	U adsorbed/ mg g^{-1}	Percentage adsorption
Batch -1	3.5	90	10	2	75	75.4±0.8
Batch -2	4.5	90	10	2	90	80.4±0.1
Batch -3	4.5	90	10	12	120	95.0±0.9

Keywords: Uranium, Magnetic adsorbent, Exfoliation, Extraction, Graphene oxide.

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Metal ion mediated crosslinking of carboxymethyl chitosan using epichlorohydrin as the crosslinker

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One of the important radionuclides that is encountered during the dilute chemical decontamination of nuclear reactors is ^{60}Co. Selective removal of this radionuclide in presence of large excess of non-active ferrous ions can considerably reduce the radioactive waste volume generated during the process. So, there is an increased interest in developing cobalt selective sorbents or resins. This need has driven our earlier reports on synthesis of Co selective sorbents through techniques such as metal ion imprinting and functionalization of chitosan[1,2].

In this report we reveal the synthesis of a chitosan based cobalt selective sorbent through a new methodology. The chitosan derivative chosen was carboxymethyl chitosan, which was synthesized fromchitosan through functionalization using chloroacetic acid and sodium carbonate[1]. The water soluble carboxymethylated chitosan derivative was crosslinked using epichlorohydrin, a common crosslinker used for chitosan, under alkaline conditions. A new methodology -metal mediated crosslinking of the carboxymethyl chitosan - was attempted for this purpose. Crosslinking of the metal-complexed carboxymethyl chitosanderivative will result in fixing of the binding site geometry in the crosslinked matrix. This can result in increase in metal ion uptake capacity as well as selectivity for the templateand its analogues.The epichlorohydrin crosslinked carboxymethyl chitosan thus prepared was studied in detail for their metal ion uptake characteristics. The polymer was found to possess higher Co(II) uptake (295 µmol/g) compared to the chitosan based Co(II) sorbents reported by us earliernamely, glutaraldehyde crosslinked carboxymethyl chitosan[1] (265 µmol/g) and epichlorohydrin crosslinked cobalt (II) imprinted chitosan[2](92 µmol/g).

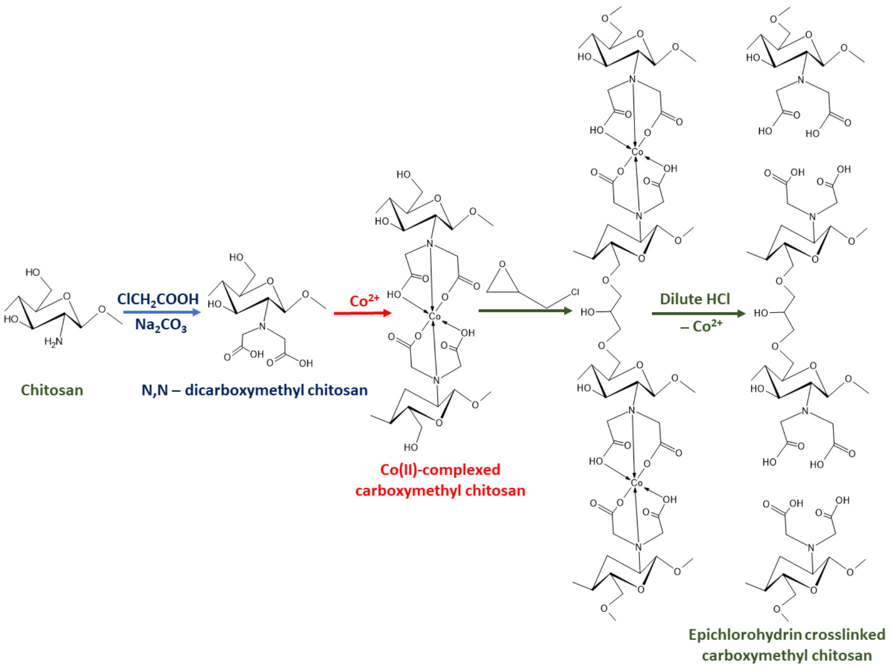

Figure 2. Synthesis of epichlorohydrin crosslinked carboxymethyl chitosan

Keywords: Carboxymethyl Chitosan, Co(II), epichlorohydrin, metal ion imprinting, selective removal

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Uranyl sensing Optode Film in Aqueous Solution

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Due to anthropogenic activities, erosion of rocks, soil, and weathering effects, ultra-trace concentrations of uranium are consistently present in the environment. Various stages of the nuclear fuel cycle introduce minute amounts of uranium into natural aquifers [1]. Uranyl sensing optode film was based on a membrane supported pre-concentration methods which can be customized for concentrating uranium in aqueous solution. Optode consist of hydrophobic Deep Eutectic Solvent (HDES) as a carrier. HDES was prepared using TOPO as HBA and DA as HBD. This HDES was employed for highly efficient and selective extraction of U(VI) from aqueous solutions. A uranium-selective optode was custom-made using CTA as the polymeric base, TEHP as a plasticizer, TOPO:DA HDES as the extractant, and Br-PADAP as the indicator, which responds to UV-Visible spectrometry in proportion to the uranium concentration. To know the chemical interaction between TOPO, DA and HDES as well as blank optode and U- loaded optode, their FTIR studies were carried out. The FTIR spectra are presented in Fig.1(a) & 1(b) respectively. The FTIR spectra shown in Fig.1(a) revealed that, the prominent C–H bands at around 2926 cm^{-1}(CH_3/CH_2 asymmetrical stretching vibrations) and 2852 cm^{-1} (CH_2 symmetric stretch) were consistent in DES with those in the individual FTIR spectra of TOPO and DA, indicating that; none of these groups were involved in any chemical reactions. However, the bands corresponding to C=O (DA) and P=O (TOPO) were significantly shifted in DES in comparison to the FTIR spectra of the individual components, indicating their mutual interaction preferably resulted in hydrogen bonding. For instance, the C=O peak of DA at 1687 cm^{-1} shifted to 1720 cm^{-1} in the spectrum of TOPO:DA DES. This red shift suggests that, the dimer of DA, with C=O groups involved in hydrogen bonding, was disrupted during DES formation, as P=O groups also formed hydrogen bonds with the -OH group of DA. The strong peak corresponding to the P=O stretch at 1148 cm^{-1} of TOPO shifted to 1124 cm^{-1} in DES, indicating its hydrogen bonding with DA. The FTIR band of P-octyl at 1464 cm^{-1} in TOPO also shifted slightly to 1455 cm^{-1} in DES. Fig. 1(a) shows that, the broad O–H stretching band centered at 3000 cm^{-1} and O–H bending at approximately 1400 cm^{-1} of the COOH in DA were stifled in TOPO:DA DES, which is because of hydrogen bonding [2]. An overlaid comparison of the FTIR spectra of Blank optode film {CTA, (TOPO:DA) DES, TEPH and Br-PADAP} and U(VI)-loaded optode film having similar composition is shown in Fig. 1(b). It indicates that, the peaks corresponding to C=O remained unchanged in U(VI)-loaded DES based film compared to that of pristine DES based film, suggesting the non-involvement of C=O group in complex formation with uranyl ions. However, the intensity of the P=O peak increased and shifted downward, indicating the direct interaction of the uranyl group with the phosphoryl group of DES by disrupting the hydrogen bonding.

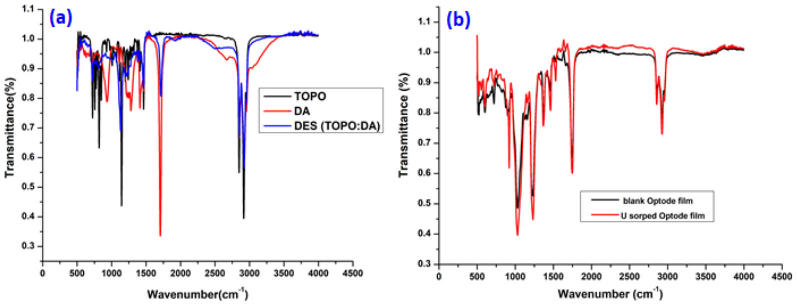

Fig. 1 (a)FTIR spectra of TOPO, DA and their corresponding DES, (b)Blank optode film consist of CTA, (TOPO:DA)DES, TEPH and Br-PADAP & U(VI)-loaded optode film (c).

The synthesized membrane shows potential for application as Uranyl Sensor.

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N-heterocyclic ligands for separation of trivalent f-elements

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Nuclear energy is the most concentrated and one of the safest sources of energy. This year marks 70 years since 1954, when the first grid-connected nuclear power plant (Obninsk NPP, Russia) was commissioned. Nuclear reactors and the nuclear industry have come a long way since then. But even today, nuclear fuel's potential is not fully exploited. Closing the nuclear fuel cycle, i.e. extracting and reusing valuable components from spent nuclear fuel, will increase the performance factor of natural uranium and thorium. There are more than 50 chemical elements in spent nuclear fuel. Extracting and separating the individual elements therefore requires the development of efficient and selective industrial chemical processes.

One of the most challenging chemical tasks is the complete separation of the trivalent f-elements, in particular americium and curium, due to their close chemical properties, electronic structures, and ionic radii. One of the most suitable industrial methods for the separation of soluble components is liquid extraction. The extraction systems (extractant + diluent) must meet many requirements: high selectivity, high radiation resistance, high thermal stability, etc. It is therefore important to find an extractant that not only has the highest selectivity and efficiency, but also has sufficient solubility as well as chemical and radiolytical stability.

After conducting extensive research, it has been demonstrated that extraction systems based on phenanthroline dicarboxylic acid diamides exhibit high efficiency, selectivity, and stability when separating trivalent f-elements. The combination of steric effects of the substituents at nitrogen atoms of amide groups, together with electronic effects of substituents in the phenanthroline core, can help achieve very high separation factors for Am/Ln and Am/Cm pairs. These effects also play a valuable role in the solubility and protonation of such extractants.

During the presentation, we will discuss recent results on the development of extraction systems for the separation of Am/Ln and Am/Cm pairs and their use in pilot-scale experiments.

Keywords: trivalent f-elements, americium, curium, lanthanides, solvent extraction, N-heterocyclic ligand

Isolated bubble rising in a pulsatile flow field: Impact on drag

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Air pulsed columns are the workhorse of spent (thermal) fuel reprocessing in many countries. Hydrodynamics inside the column is quite complex. Air is injected inside the column for interface/density measurement. Dynamics of a gas bubble in a pulsatile flow of the continuous phase is not reported in literature. In this work we report on the dynamics of a single bubble rising in an air induced pulsatile flow field for the first time. Pulsatile flow of desired amplitude (A) (15 mm and 27 mm) and 1 Hz frequency (f) is generated using a 3-way solenoid valve, a digital timer (duty cycle 30%) and compressed air. The setup is a glass U-tube manometer (1-inch diameter) filled with tap water. Gas (air) is injected through a side port at 35 mL/min using a precise and calibrated peristaltic pump. A CCD camera is used to capture the movement of bubble under static and pulsatile flow field. Corresponding Y-velocity (vertical) is determined from image analysis. Fig. 1 shows the snapshots of a typical bubble rising in a pulsatile flow field (Axf=27 mm/s). Fig. 2a show the Y-velocity under pulsatile and static flow field. X-axis is the time of travel of the bubble in non-dimensional form for an entire pulsing cycle (1 s). It can clearly be seen that in presence of pulsatile flow, escaping tendency of the bubble rises significantly (~an order of magnitude). Experiments are done in duplicate to ensure repeatability (COV ~ 25 % for estimate of C_{DA}). Rise velocity under pulsatile condition is higher than that in static condition. Moreover, rise velocity seems to follow the pulsing cycling as is evident from crest and trough in the time profile of Y-velocity. This means the bubble is accelerating/decelerating. The acceleration is evaluated and used to determine unsteady state effective drag coefficient (C_{DA}) acting on the bubble. Under accelerating conditions, buoyancy (driving force), drag, virtual mass and Basset (memory) (restraining) force acts on the rising bubble. C_{DA} encompasses the effect of net restraining forces (drag, virtual mass and Basset force) [**1**]. Fig. 2b shows variation of C_{DA} as the bubble rises in pulsatile vis-à-vis static continuous phase. C_{DA} is seen to be lower for pulsatile flow.

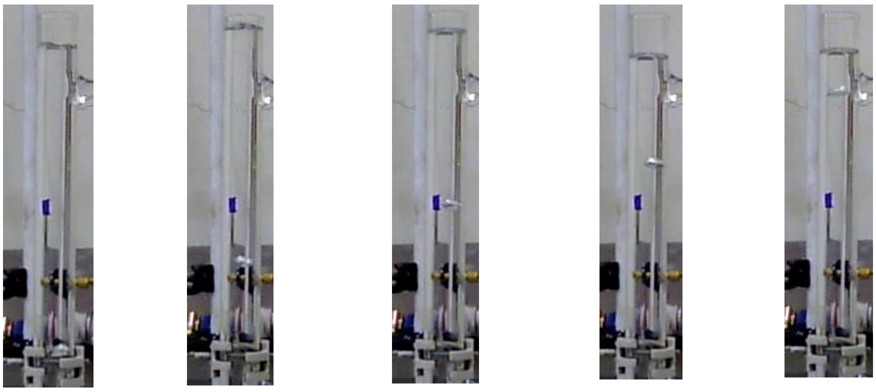
θ=0 *θ=0.25* *θ=0.5* *θ=0.75* *θ=1*

Figure 1: Snapshots of time a bubble rising in a pulsatile flow filed (Af=27 mm/s)

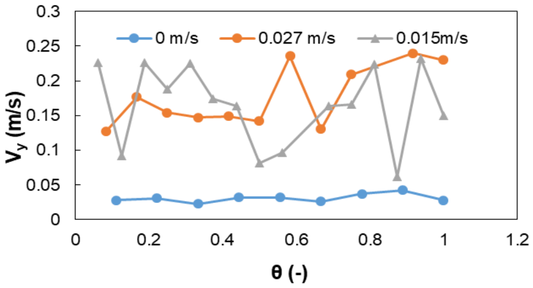

Figure 2a: Time v/s Y-velocity under pulsatile and static flow field.

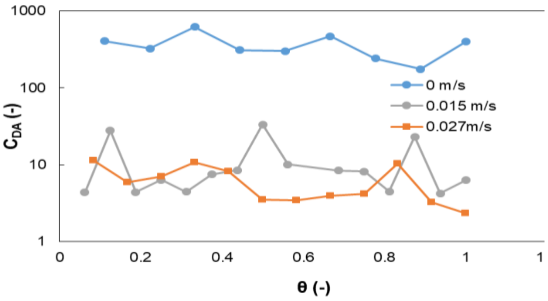

Figure 2b: Temporal variation of unsteady state drag coefficient (C_{DA}) under pulsatile and static flow field

Keywords: *Air pulsed column, bubble, drag coefficient, pulsatile flow, and unsteady state*

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Determination of Equivalent Boron Contents in Plutonium Product of Fast Reactor Fuel Reprocessing

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Spent fuels of high burn up (155GWd/t) and short cooled (2 years) discharged from Fast Breeder Test Reactor (FBTR) are being reprocessed in Compact Reprocessing of Advanced fuels in Lead shielded cell (CORAL), Kalpakkam, India. A Modified PUREX process with high acid flow sheet is deployed for the recovery of Uranium and Plutonium leaving bulk of fission products into high level wastes. Since, specification of plutonium oxide powder is highly stringent and lanthanide's contamination on PuO_2 product severely affects fuel performance, its concentration must be determined and expressed in term of equivalent boron content (EBC). The term EBC is described in equation (1). This paper explains procedure for the determination of concentration of lanthanides and other neutron poisons present in PuO_2 product and finding the EBC value of different nuclei. Weighed quantity of PuO_2 obtained was dissolved in nitric (11.0 M) and hydrofluric acid mixture (0.1 M) at 85-90℃ in teflon beaker. The impurities present in dissolved Pu product was separated by solvent extraction method using tri-n-Octyl phosphine Oxide (TOPO) in Xylene as an extractant. In this method, bulk of Pu present in the dissolved product was selectively extracted into TOPO by equilibration for 10 minutes. Resultant raffinate was quantitatively transferred into standard measuring flask. The loaded organic phase was scrubbed with nitric (4.0 M) and scrubbed acid was mixed with raffinate in the standard measuring flask and made up to known volume. The recovery of lanthanides and cadmium in aqueous phase was tested and it was found to be > 99.9 %. The concentration of impurities in aqueous phase was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) after complete removal of Pu by solvent extraction. Total EBC of PuO_2 is determined by the summation of individual EBC values of impurity and results are presented in Table 1.

$$\text{EBC of impurity} = (\text{EBC factor})(\mu\text{g of impurity/g of PuO}_2)\ldots\ldots.(1)$$

$$\text{EBC factor} = \frac{(\text{atomic mass of boron})\ (\sigma_a\ \text{impurity})}{(\text{atomic mass of neutron poisons})\ (\sigma_a\ \text{boron})}$$

σ_a = neutron absorption cross section in barns

Table 1. Calculation of EBC value for PuO_2 obtained from reprocessing of FBTR spent fuel

Elements	EBC factor	µg of impurity per g of PuO_2	EBC of impurity
B	1	0.5 ± 0.02	0.50
Cd	0.317	0.2 ± 0.01	0.06
Sm	0.534	0.2 ± 0.01	0.11
Eu	0.425	0.1 ± 0.005	0.04
Gd	4.399	0.5 ± 0.02	2.20
		Total EBC	2.91

Extraction of UO_2^{2+}, Pu^{4+} and Am^{3+} from hydrochloric acid medium by ammonium based ionic liquids: effects of structural variations

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Ionic liquid has been considered as one of the potential 'green' alternatives to volatile organic compounds due to the favourable properties like low vapour pressure, wide liquid range, tunable properties, high radiolytic and chemical stability etc.[1,2] In most of the cases, imidazolium based ionic liquids has been exploited for the separation of actinides into ionic liquid. The present investigation delas with the tetraalkyl ammonium NTf_2 based ionic liquids: $Bu_3MeN.NTf_2$ (**IL1**) and $Me_3BuN.NTf_2$ (**IL2**) for the extraction of UO_2^{2+}, Pu^{4+} and Am^{3+} from aqueous nitric acid feed solution. The trend in D values followed the order: $D_{Pu} > D_U > D_{Am}$, which was attributed to the trend in their chemical potential. The D values for actinides were found to be more for $Me_3BuN.NTf_2$ as compared to those of $Bu_3MeN.NTf_2$. The steric hinderance around amounium N is more for $Bu_3MeN.NTf_2$ compared to that of $Me_3BuN.NTf_2$. The D values for UO_2^{2+} were found to increase with increase in nitric acid concentration upto 3-4 M, followed by reduction at further higher feed acidity.In case of Pu^{4+}, the D values were found to enhance continuously even beyond 3 M HCl, while for Am^{3+}, the D values were found to be almost insesitive to feed HNO_3 concentration with values ranging from 2-3. This fact indicates the possibility of exclusive separation of Pu^{4+} from UO_2^{2+} and Am^{3+} at higher feed acidity (beyond 6 M HCl). The D values for these actinides were found to be more for both the ionic liquid **IL1** and **IL2** diluted in $C_nmimNTf_2$ (where n = 4,6,8) (1:1 dilution) as compared to C_nmimPF_6 where n= 4,6,8). On the other hand, the D values for these actinides using both **IL1** and **IL2** foolowed the trend of $C_4mim^+ > C_6mim^+ > C_8mim^+$, might be associated with trend in the aqueous phase dissolution of these ionic liquid cations. The solvent systems were found to be radiolytically stable upto 500 kGy with a reduction in D values within the range of 10-15%.

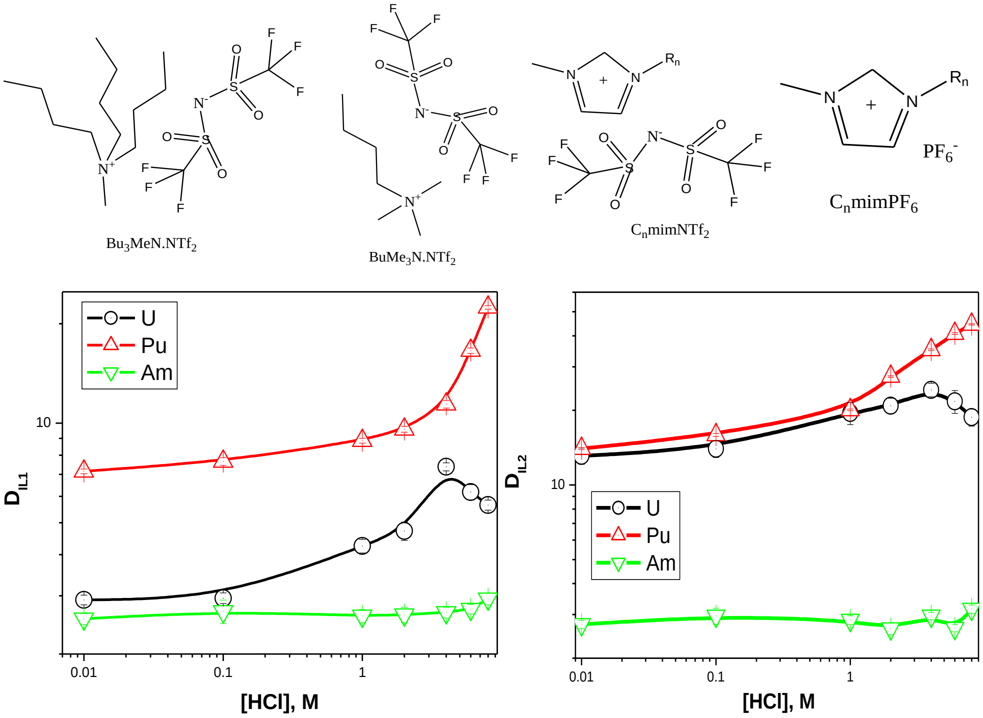

Fig. 1: (a) Structure of $Bu_3MeN.NTf_2$ (**IL1**), $BuMe_3N.NTf2$ (**IL2**), $C_nmimNTf_2$ and C_nmimPF_6; (b) Extraction profiles for U, Pu and Am using IL1 and IL2 in CnmimNTf2 (1:1)

Keywords: Ionic liquid, Actinides, Cation exchange mechanism, Radiolytic stability

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Extraction behavior of Sr from high-level liquid radioactive waste with Di-tert-butyl dicyclohexano-18-crown-6 (DtBDCH18C6)

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Abstract

The nuclear high-level liquid waste (HLLW) solution contains caesium and strontium as major fission products. ^{90}Sr ($t_{1/2}$=28.8a), contributes to a large part of the heat load and radioactivity. Removal of ^{90}Sr from the HLLW is beneficial, as the recovered ^{90}Sr can be used as heat source. The extraction of strontium was carried out using Di-tert-butyl dicyclohexano-18-crown-6 (DtBDCH18C6) in 100 % IDA (Iso-decyl alcohol) as diluent. Dicyclohexano-18-crown-6 (DCH18C6) is known for uptake of strontium [1]. Addition of di-tertiary butyl group enhances the selective separation of strontium in presence of other metal ions. For the purpose, DtBDCH18C6, whose chemical structural formula is shown in Fig.1 was prepared indigenously at ChED, BARC. Extraction behavior of strontium from radioactive Sr-bearing solution (cesium and uranium lean HLLW) with DtBDCH18C6 was studied in WIP (Lab), BARC, Trombay. A single contact was provided to Sr-rich HLLW having acidity 5M with 0.05M DtBDCH18C6 in 100% IDA solution. The organic to aqueous ratio was kept 1:1. After extraction the organic and raffinate streams were separated and analysed. The radio-chemical analysis of Sr-rich HLLW i.e. feed and the raffinate was carried out by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES). The D-extraction w.r.t strontium was 6.8 (87.18% extraction). The D values of other elements were very low in comparison to strontium, thereby indicating selectivity of the solvent. Analysis results are indicated in table-1. It is seen from the table that strontium can be selectively separated from actual high-level Sr-rich solution using DtBDCH18C6 quantitively. For stripping the loaded organic was given three contacts with 0.01M nitric acid and it was seen that more than 98% strontium was recovered in aqueous stream. The performance of indigenously prepared DtBDCH18C6 is deemed satisfactory for separation of strontium from HLW.

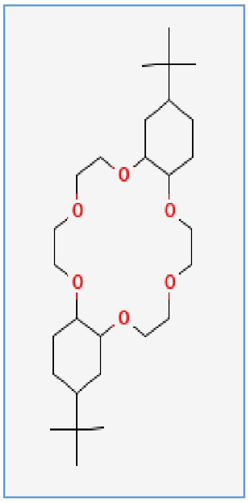

Fig.1: Structure of DtBDCH18C6

Table.1: D_{Cs} extraction values in 0.05M DTBDCH in 100% IDA

Element (mg/L)	Feed	Raffinate	D value
Sr-90 (Ci/L)	41.55	5.32	6.81
Sr	531.8	68.17	6.8
Ni	45	30.87	0.46
Fe	2762.5	2687	0.028
Mn	1160	1135	0.02
Cr	325	324	0.003
Ca	1737.5	1687	0.03
Ce	1025	1012	0.01
Ba	33	32.82	0.01
Na	530	521	0.02
Mg	85	72.45	0.17
La	465	452	0.03

Keywords: extraction, DtBDCH18C6, *HLLW, Stripping*

Reference

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Highly efficient method for separation and estimation of trace amount of thorium in bulk plutonium

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Thorium contamination <100 ppm in plutonium oxide matrix is desirous for its use as fuel in the fast reactors. Estimation of such a low concentration below 100 ppm in bulk quantity plutonium is required for the chemical quality control in any plutonium production facility. Conventional techniques like ICP-OES, TIMS, UV-VIS spectrophotometry or direct radiometry are not sufficient in quantifying Th due the major interference of bulk of plutonium when a solution PuO_2 containing Th impurity dissolved in nitric acid is used as it is for analysis. Thus a prior removal of bulk interference of Pu is required before analysis. Herein we developed a new process scheme to remove the bulk of plutonium contamination leaving behind Th in the raffinate using β-diketone, thenoyltrifluoroacetone (HTTA, **Figure 1(a)**) from PuO_2 dissolved in nitric solution. The extraction of Pu(IV) from 1-1.5 M HNO_3 is well known however the poor extraction of Th(IV) in that acidity is unusual [1] and that forms basis of our separation process of Pu and Th prior to analysis by spectrophotometry using arsenazo -III (**Fig 1(b)).** The entire process consists of six steps and details have been summarized as below:

1st Step: 1.0 mL sample taken to it 3 drops Fe(III)-nitrate, 2 drops hydroxyl ammonium nitrate, 10 drops $NaNO_2$ were added and final acidity adjusted in the range of 1-1.5 M; **2nd Step:** Extraction contact with 4.0 mL of 0.5M TTA/Xylene for 30 min; **3rd Step:** Removal of entire TTA as far as possible then to the aq. phase, 200 µl 10.0 M HNO_3, 3 drops Fe(III)-nitrate, 2 drops hydroxyl ammonium nitrate, 8 drops $NaNO_2$ were added and final acidity adjusted to : 1.12 M followed by 2nd extraction contact with 4 mL 0.5 TTA/Xylene for another 30 minutes: **4th Step:** Removal of the entire TTA phase and 0.5 mL of the aq. phase taken for spectrophotometric analysis: **5th Step:** To the 0.5 mL aq. phase, 5 mL 6.0 M HCl, 0.5 mL (0.2 wt% arsenazo-III) were taken and entire volume make up to 10.0 mL by 6.0 M HCl; **6th Step:** Measurement of absorbance at λ_{max}~665 nm against reagent blank consists of : 0.5 mL 1.0 M HNO_3, 5.0 mL 6.0 M HCl and 0.5 mL (0.2wt% aresanzo-III) volume make up to 10.0 mL by 6.0 M HCl.

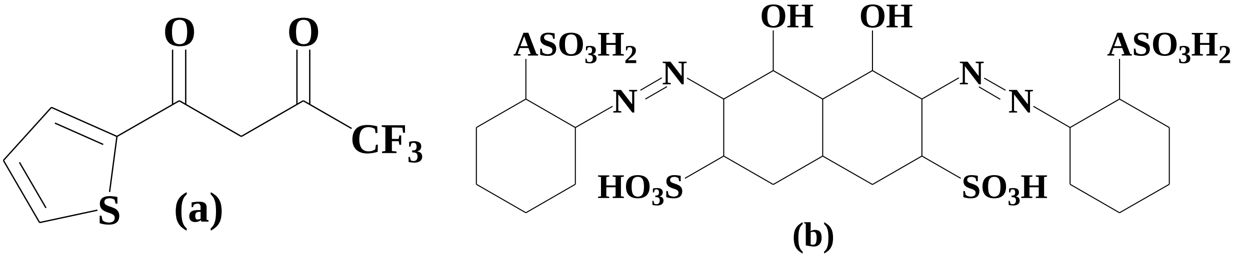

Fig. 1 Chemical structures of (a) thenoyltrifluoroacetone, (b) arsenazo III (1,8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis[(azo-2)-phenylarsonic acid])

Table 1: Validation of the analysis with known standard of Th

[Th] in standard solution of 1.2 M HNO_3, (mg/L)	**Absorbance**	**Slope of calibration plot of Th-Aresnazo III**	**[Th] determined, (mg/L)**
2.5	0.065	0.0265	2.45±0.12
5.12	0.137	0.0265	5.16±0.25
10.06	0.276	0.0265	10.41±0.56

Keywords: theonyltrifluoroacetone, thorium, plutonium, arsenazo III.

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Effect of Room Temperature Ionic Liquid on the extraction of Am(III) by a novel solvent, OBDA

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Room Temperature Ionic Liquids are known to have non-measurable vapor pressure, non-inflammability, high thermal stability and as a consequence are known to be ‘green’ alternatives to the presently used organic solvents. They are also ‘tunable’ with respect to the properties like polarity, viscosity, water-immiscibility by varying the cations and anions. The applicability of RTIL in Nuclear Fuel Cycle has been extensively reviewed in the literature [1]. We also have explored various extractants like TBP, BenzoDODA for their solvent extraction behavior of actinides in RTIL. In this connection, we hereby, report the solvent extraction behavior of Am(III) from nitric acid using a conformationally constrained, hydrolytically stable diamide, (N,N',-di-2-ethylhexyl)7-oxabicyclo[2.2.1]heptane-2,3-dicarboxamide (OBDA) containing conformationally constrained oxabicyclo[2.2.1]heptane skeleton [2]. The present study aims to understand the solvent extraction behavior of Am(III) in the presence of C_4mimTf_2N ionic liquid as diluent.

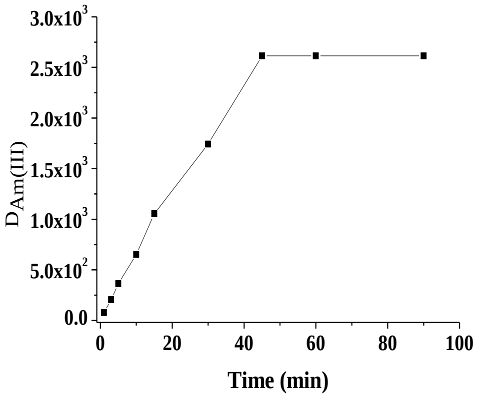

Fig. 1: Kinetics of Am(III) extraction using 0.01 M OBDA in C_4mimTf_2N from pH 2

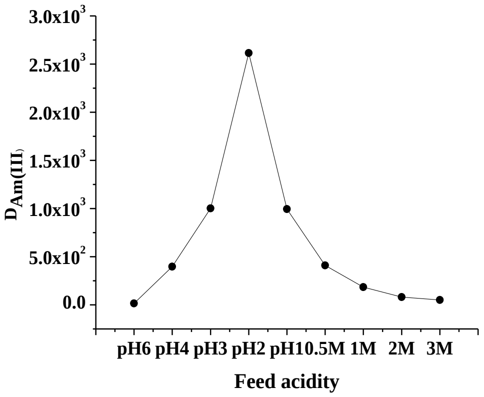

Fig. 2: Effect of feed acidity on $D_{Am(III)}$ using 0.01 M OBDA in C_4mimTf_2N

As can be seen from Fig.1, the kinetics of extraction was slower for C_4mimTf_2N with the equilibrium being reached in ~45 minutes. Feed acidity dependent variation of $D_{Am(III)}$ using 0.01 M OBDA in C_4mimTf_2N showed interesting observation with an increasing trend being observed from pH 6 to pH 2 which could be due to the solvation mechanism of extraction as observed for molecular diluents. Further increase in nitric acid concentration resulted in continuous decrease of $D_{Am(III)}$ which can be explained based on the cation-exchange mechanism. The cation exchange behavior can be written as:

$$Am(OBDA)_2{}^{3+} + 3C_n - mim^+Tf_2N_{(org)} \Leftrightarrow Am(OBDA)_2(Tf_2N)_{3(org)} + 3C_nmim^+ \quad \ldots\ldots\ldots\ldots\ldots (1)$$

Slope analysis was used to determine the number of OBDA molecules complexed with Am(III). The mechanism was further corroborated by carrying out experiments with varying carbon chain length of C_nmimTf_2N (n = 4, 6, 8). $D_{Am(III)}$ was found to be dependent on carbon chain length of the RTIL with higher carbon chain length resulting in decreasing value of distribution ratio. With increasing carbon chain length of the alkyl group, the solubility of the RTIL in the aqueous phase decreases due to increasing hydrophobicity of the RTIL. This fact makes exchange of the Am.OBDA complex with C_nmim^+ ion more difficult causing a decrease in $D_{Am(III)}$ values for OBDA with increasing carbon chain length

Keywords: RTIL, OBDA, Cation-exchange

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Extraction of trivalent and tetravalent radionuclides by conformationally constrained diamide, OBDA

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‘Actinide Partitioning’ has been proposed to be the way forward to deal with the radioactive liquid (High Level Liquid Waste, HLLW) produced during the management of spent nuclear fuel obtained after reactor operations. Various types of extractants have been developed for this purpose over the last 2-3 decades and been reviewed in detail [1]. Our group has also been involved in the search of ideal molecules for actinide partitioning specially in the investigation of DGA molecules on a rigid platform and understand the effect of rigidity on the physicochemical properties as well as extraction behavior for the radio-nuclides. We initially chose a conformationally constrained oxabicyclo[2.2.1]heptane skeleton with three embedded donor groups (one ether–oxygen and two amide groups) and expected that the rigid coordination sphere as well as proper orientation of the donor atoms would lead to a faster kinetics and also strong bonding with metal ions. Our first reported conformationally constrained diamide OBDA ligand **1a** (Figure 1) showed excellent extraction performance for trivalent Am(III) and Eu(III), fast kinetics of equilibration and significantly less extraction for the contaminant fission product Sr(II) [2].

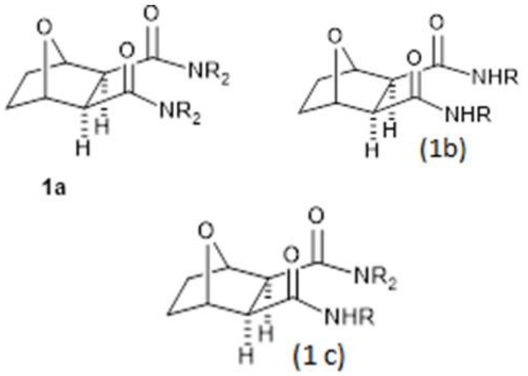

Fig. 1: Structure of OBDA (R= 2-ethyl hexyl)

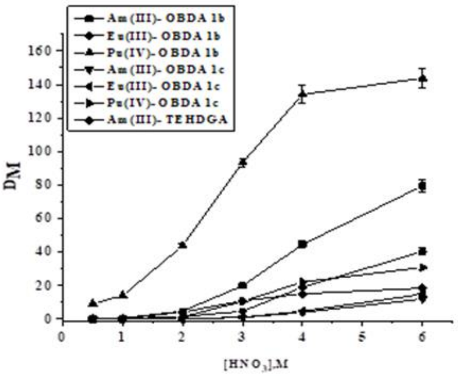

Fig. 2. Acidity dependent distribution ratio of Am(III), Eu(III) and Pu(IV) for 0.1 M OBDA

Unfortunately, OBDA **1a** was found to be unstable in higher concentration of HNO_3 putting up a limitation of its use as extractant. While investigating the hydrolytic stability of nanocantharadin derived dicarboxamides in acidic medium, we observed that tertiary amides are more prone to hydrolysis due to anchimeric assitance while other diamides were stable. Based on this observation, we modified the structure of OBDA by replacing the tertiary amide groups by secondary amides. This manuscript describes the extraction behavior of two structurally modified hydrolytically stable OBDA-type molecules OBDA(D2EH) **1b** with both secondary amides and OBDA(Te2EH) **1c** with one secondary and one tertiary amide groups (Fig. 1).

Kinetics studies of both the OBDA molecules showed fast kinetics of equilibration (~10 min). Acid dependent extraction of various trivalent and tetravalent radionucldies showed OBDA 1b to be more effective extractant compared to OBDA 1b. With increasing nitric acid concentration in the feed solution, distribution ratio of all the radionuclides increased significantly. Maximum distribution ratio was observed for Pu(IV)-OBDA 1b system, followed by Am(III)-OBDA 1b and Eu(III)-OBDA 1b system. Both the molecules were found to be hydrolytically stable (more than 60 days in the presence of 6 M HNO_3 solution)

Keywords: OBDA, Conformationally constrained, Trivalent,

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Unsteady state drag acting on a drop rising in a pulsatile flow field: An experimental study

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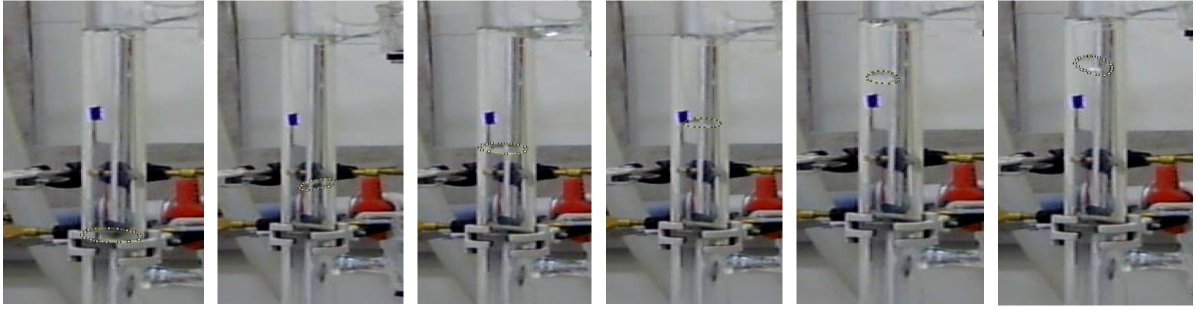
Air pulsed columns lie at the heart of nuclear (thermal) reprocessing plants. The hydrodynamics within these columns are highly intricate. Due to this complexity, there is scarce literature on the dynamics of an isolated liquid drop in a pulsating flow of the continuous phase. Although one recent paper addressed this phenomenon, it utilized a mechanical pulsator and focused on falling drop **[1]**. This study investigates the dynamics of a single liquid drop rising in an air-induced pulsatile flow for the first time. Pulsatile flow with amplitudes of 27.5 mm and 15 mm and a frequency of 1 Hz is created using a 3-way solenoid valve, a digital timer (30% duty cycle), and compressed air. The experimental setup includes a 1-inch diameter glass U-tube manometer filled with tap water. N-octane is introduced at 35 mL/min through a side port using a precise peristaltic pump. The movement of the drop is recorded using a CCD camera, and its vertical velocity is analyzed with ImageJ. Fig. 1 shows the snapshots of a typical drop rising in a pulsatile flow field (Axf=15 mm/s). Fig. 2a shows the Y-velocity under pulsatile and static flow filed. X-axis is the time of travel of the drop in non-dimensional form. Experiments are done in duplicate to ensure repeatability (average COV ~ 28 % for estimation of C_{DA}). It can be seen that the vertical movement of the drop is enhanced during the positive peak of the pulsing cycle while during negative peak its vertical movement is stalled. This effect tends to intensify as pulsing velocity is increased. As vertical movement of drop is dependent on the pulsing cycle it means that the drop is accelerating/decelerating. The acceleration is evaluated and used to determine unsteady state effective drag coefficient (C_{DA}) acting on the drop. Under accelerating conditions, buoyancy (driving force), drag, virtual mass and Basset (memory) (restraining) force acts on the rising drop. C_{DA} encompasses the effect of net restraining forces (drag, virtual mass and Basset force) [**2**]. Fig. 2b shows variation of C_{DA} as the drop rises in pulsatile vis-à-vis static continuous phase. Average (over entire pulsing cycle) C_{DA} under pulsing condition is seen to be similar to that under static/non pulsatile condition. This study proves that on an overall basis there is no significant effect of pulsing velocity on net drag coefficient (unsteady).



θ=0 *θ=0.2* *θ=0.4* *θ=0.6* *θ=0.8* *θ=1*

Figure 1: Snapshots of drop rising under pulsatile flow (Axf=15 mm/s, liquid flow rate = 35 mL/min)

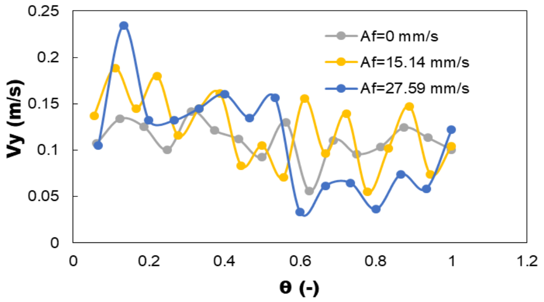


Figure 2a: Time v/s Y-velocity under pulsatile and static flow field.

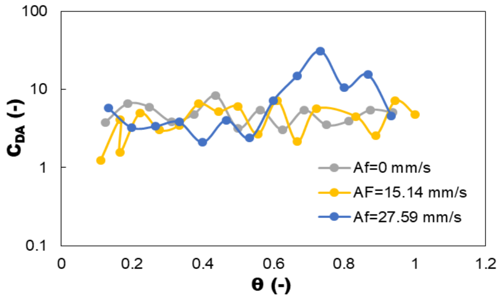


Figure 2b: Time v/s unsteady state drag coefficient (C_{DA}) under pulsatile and static flow field

Keywords: Air pulsed column, drop, drag coefficient, pulsatile flow, and unsteady state

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3. Zhang et al., *Chem. Engg. Sci.*, 63(8) (2008) 2099.

Studies on Distribution Ratio of Pu in TBP/n-DD System in Presence of Dibutyl Phosphate

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The effective utilization of nuclear fuel requires the reprocessing of spent fuel discharged from nuclear reactors. Generally, PUREX process is employed for the quantitative recovery of U and Pu leaving fission products in high level waste. In PUREX process, organic phase consisting of 30% tributyl phosphate (TBP) in n-dodecane (TBP/n-DD) is used as an extractant for U/Pu [1]. In the presence of a high radiation field and an aqueous phase acidity of 5-6 M, TBP undergoes radiolytic and chemical degradation, leading to the formation of dibutyl phosphate (HDBP) and mono-butyl phosphate (H_2MBP) [2]. The presence of these degradation products especially the complexation of Pu(IV) with DBP [3] affects quantitative stripping of nuclear materials from organic phase and it also results in formation of insoluble residue (crud) at low nitric acid concentrations. Hence, systematic studies were performed to find the distribution ratio of Pu (IV) nitrate in TBP/n-DD system in the presence of HDBP of envisaged concentration range as found in reprocessing of spent fuel with high burn-ups (155GWd/t). It is also aimed to assess the conditions with respect to aqueous phase acidity and HDBP concentration at which formation of crud is observed. And results thus obtained are used to set parameters for operating stripper in crud free zone. The organic phases of TBP/n-DD system in presence of HDBP of concentration range (100-1000 mg/L) were prepared. These organic phases consists various concentrations of HDBP were equilibrated with aqueous phases consisting Pu (50 mg/L) in dilute nitric acid of different concentrations. Then, equilibrated aqueous/organic phases were centrifuged, separated and analyzed for the concentration of Pu and acidity and distribution ratios were calculated. The experimental results shown in table 1 indicates that crud is formed when concentration of HDBP is in the range of 1 g/L and acidity is equal to 0.3 M. Formation crud under this condition is attributed to formation Pu-DBP in complex and its solubility is less at low nitric acid concentration. Results from Figure 1 indicate that Pu has a significant distribution ratio at lower aqueous phase acidity and increases with increasing HDBP concentration. Crud was observed at lower acidity and at higher HDBP concentration implies that at lower acidity HDBP is participating more towards extraction. The distribution ratio data thus generated is used as input data to optimize flow sheet conditions.

Sl.No	[HNO_3], M (Aq. Phase)	[HDBP], mg/L (Org. phase)	Remarks
1	0.301	300	No crud formation
2	0.301	500	
3	0.301	700	
4	0.301	1000	Crud formation
5	0.512	1000	No crud formation
6	1.021	1000	

Table 1: Effect of acidity and [HDBP] on formation of crud

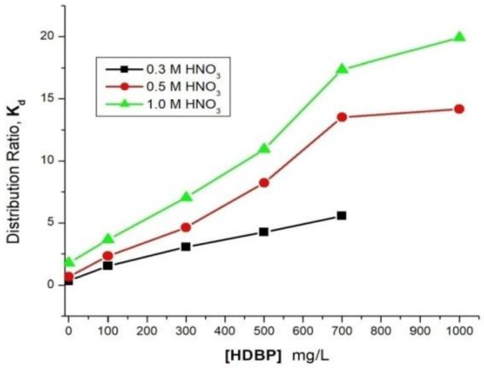

Figure 1: Effect of [HDBP] on distribution ratio of Pu TBP/n-DD system

Keywords: Plutonium, Distribution Ratio, Di-butyl Phosphate, Solvent Extraction, Crud

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Recovery of plutonium from oxalate bearing down streams generated during fast reactor fuel reprocessing

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Modified Purex process is adopted for the reprocessing of spent fuel discharged from FBTR with 1.1 M tributyl phosphate (TBP) in n-dodecane is used as the solvent (1). Subsequently the purified plutonium nitrate solution is precipitated as its oxalate. The filtrate contains Pu and oxalate ions of about 50 mg/L and 0.1 M respectively. The retained Pu from the spent solvent is removed by washing with sodium oxalate solution and the resulting aqueous solution also bears the comparable level of oxalate and Pu (2). This paper deals with the new approach for the treatment and recovery of plutonium from these streams in fast reactor fuel reprocessing (FRFR).

The corrosive nature and its strong complexing ability with actinides renders the presence of oxalate undesirable during the recovery of Pu in downstream by solvent extraction in FRFR. Hence oxalate destruction is essential. This is currently carried out by $KMnO_4$ oxidation in thermal reactor fuel reprocessing where about 1 kg of secondary solid waste per ton of spent fuel is generated. In FRFR it is more than 50 times. This plutonium bearing oxalate free stream is recycled in the former case. But in FRFR, it is not possible due to the typical flowsheet conditions. This necessitates a separate plutonium recovery cycle in FRFR which includes diluents wash, acid killing, evaporation followed by solvent extraction and eventually produces secondary liquid waste equal to the primary Purex cycle. Hence an alternate method was developed for the treatment and recovery of plutonium in FRFR based on precipitation and electrolysis.

Oxalate filtrate stream from plutonium reconversion laboratory and oxalate wash stream from spent solvent treatment generated at CORAL (Compact reprocessing of Advanced fuels in Lead shielded cell) facility were mixed and used as feed solution for the present study. Uranous nitrate solution (90g/L) was generated by electrolysis using Pt/Ti electrodes using hydrazine nitrate as the holding reductant with conversion efficiency greater than 90 percent. Experimental runs were performed in three steps as given below.

1. Uranous oxalate carrier precipitation

Simultaneous removal of residual Pu and oxalate ions is achieved by mixing the feed and uranous nitrate solution. Uranous is readily precipitated as its oxalate and carries Pu. U(IV) concentration of 12 g/L was optimized in the mixed solution by separate studies. The supernatant was decanted and filtered. The composition of feed and filtrate is given in **Table.1.**

2. Electrolytic dissolution of oxalate precipitate

The oxalate slurry resulted from step -1 is subjected to electrolysis in 4 M nitric acid medium under constant stirring. It was observed that the precipitate is completely dissolved within 2 h with greater than 95% of oxalate decomposition. The uranyl nitrate solution from step-2 is further subjected to electrolytic reduction to uranous nitrate in presence of hydrazine nitrate with acidity less than 2M. This solution is introduced into step-1 and recycled about 10 times before being transferred to Step-3.

3. Recovery of plutonium

Partitioning of plutonium from bulk of uranium was achieved by extraction of uranium into 30%TBP, leaving Pu^{3+} in the aqueous phase as in line with aqueous phase partitioning in primary Purex cycle.

Table.1

Components	Feed	Filtrate
Plutonium, (mg/L)	82.3	0.14
Uranium, (g/L)	0.110	1.1
$[H^+]$, M	2.15	1.8
$[C_2O_4^{2-}]$, M	0.09	0.003

Keywords: Uranous nitrate, plutonium, electrolytic reduction, reprocessing.

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Modeling the effect of HDBP influence on U(VI) distribution coefficient in 1.1M TBP

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The solvent extraction of U(VI) & Pu(IV) in TBP/n-DD leads to the degradation of the solvent. The dibutyl phosphate (HDBP) is one of the major degradation products of TBP. As compared to the thermal reactor fuel reprocessing, the quantity of DBP produced in fast reactor fuel reprocessing is high due to higher Pu and fission product content in the feed solution. The presence of HDBP in the solvent phase usually retains the metal ion in organic phase during stripping. The existing computer code does not take into account the effect of HDBP during the solvent extraction flow sheet simulation. Hence, for the realistic simulation of solvent extraction flow sheet, a model for the distribution coefficient of U(VI) and Pu(IV) in the presence of HDBP needs to be included. The present work focusses on the development of a model for the estimation of distribution coefficient of U(VI) in the presence of HDBP

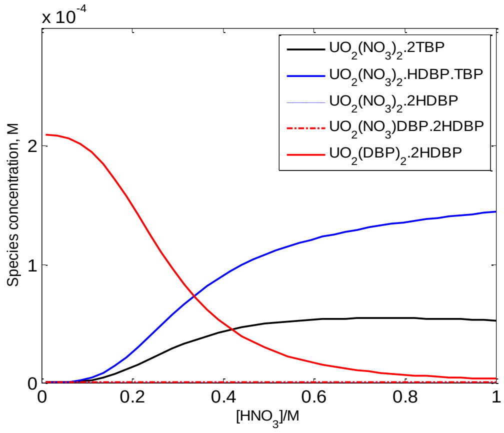

Fig 1: The concentration of various species in the organic phase as a function of nitric acid concentration for the initial U(VI) concentration of 50 ppm and HDBP concentration of 0.015M

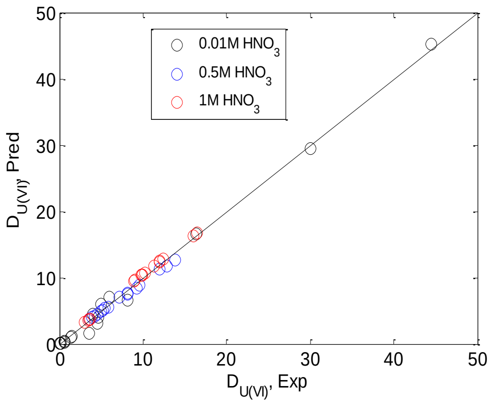

Fig 2: The comparison of experimental and estimated distribution coefficient of U(VI) in presence of HDBP for various nitric acid concentration

The distribution coefficient of U(VI) in the presence of DBP was modeled by considering the following species in the organic phase such as $UO_2(NO_3)_2$.2TBP, UO2$(NO_3)_2$.HDBP.TBP, $UO_2(NO_3)_2$.2HDBP, $UO_2(NO_3)_2$(DBP).2HDBP and $UO_2(DBP)_2$.2HDBP. The equilibrium constant for the formation of these species were estimated using the experimental distribution coefficient data measured for various nitric acid, DBP and U(VI) concentrations. The objective function i.e the relative squared error between the experimental and predicted concentration of U(VI) in the organic phase was minimized by optimization routine in python programming language. The concentration of various species in the organic phase is shown in fig 1 where $UO_2(DBP)_2$.2HDBP is the major species in the low nitric acid concentration and $UO_2(NO_3)_2$.HDBP.TBP is the most dominant species above 0.5M nitric acid concentration. Good match between the experimental and estimated distribution coefficient is obtained as shown in fig 2.

Keywords: Uranium, Distribution coefficient, modelling, TBP, HDBP

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Simultaneous Determination of Uranium and Free Acidity in Samples of Liquid-Liquid Extraction during Cold Run of DFRP by Chemometric based Spectrophotometry Method

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The Demonstration Fast Reactor Fuel Reprocessing plant (DFRP) is intended for reprocessing of spent fuel discharged from Fast Breeder Test Reactor (FBTR) in regular basis and reprocessing of spent fuel discharged from Prototype Fast Breeder Reactor (PFBR) in test basis. During cold commissioning activity, equipment such as extractor and stripper are validated by performing operation using feed solution consisting uranyl nitrate solution whose concentration could be equal to total extractable metal ion as per designed flow sheet condition. Therefore, samples are drawn and analyzed for the concentration of free acidity and uranium in view of monitoring whether, the performance of plant equipment as per design indent or not. Most of the conventional methods for U and free acidity determination have several disadvantages like high waste volume, difficult to recover active metal ions and addition of foreign metal ion in the waste solution. Hence, a chemometric method based on UV- visible spectrophotometry has been developed and implemented for the simultaneous analysis of U and free acidity in plant samples received during cold commissioning activities of DFRP using a single aliquot. The changes observed in UV-visible absorbance spectra as a function of free acidity and uranium concentration was utilized basis for this technique. The orthogonal signal correction assisted Principal Component Regression (PCR) method was employed for the determination of free acidity and U concentration in the sample from the pre-determined UV-Visible spectra of series of samples under simulated condition. The results in table 1 shows that concentration values obtained by this method are in good agreement with results of the conventional method. Totally, 27 samples were taken from different tank for validating this method for estimation of free acidity and uranium concentration. It was observed that method performed well for the uranium concentration more than 5 g L^{-1} and free acidity > 2 M. From the figures 1 it can be seen that % error in estimation of acidity is well within 5% if uranium concentration is 5-20 gpl. However, samples with higher concentration of Uranium can be analyzed using lower path length cuvette. As this is direct method hence it is fast and waste thus produced is devoid of corrosive chemicals. This method is amenable for online monitoring. Based on the concentration values obtained by developed and conventional method, performance of extractor and stripper systems were found to be satisfactory in aspects of design indent.

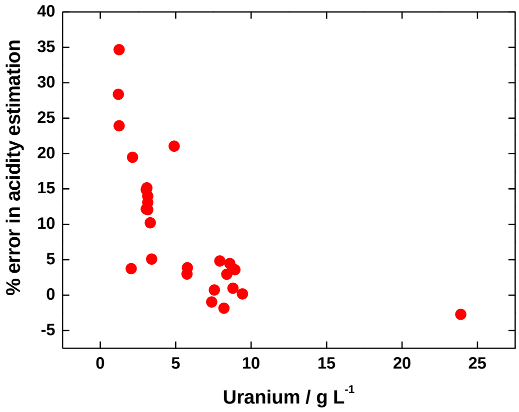

Figure 1: % error in estimation of acidity as a function of uranium concentration

Sl.No	Tank	Actual [U]	Actual acidity	Predicted [U]	Predicted acidity
4297	Dsoln	51.2	5.6	52.3	5.5
4299	DT2	40	4.95	42.1	4.7
4316	HACDT	23.9	4.28	20.1	4.4
4319	HCPT2	9.4	2.51	9.5	2.50
4336	2CPT2	8.58	2.54	8.98	2.43

Table 1: Actual vs predicted uranium and acidity content for different tank samples

Keywords: uranyl spectroscopy, PCR, chemometric, multivariate analysis

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Investigating the Extraction Behavior of Noble Metal Ions with Phosphonate and Phosphate Based Ligands

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The demand for noble metals is skyrocketing across various industries, yet their scarcity in the Earth's crust poses a significant challenge. However, a promising solution lies within spent nuclear fuel from power plants, offering a viable alternative source for these coveted elements. In our earlier study we found out phosphonate based solvents can be served as a very good extractants in the back end of the nuclear fuel cycle[1]. In this study, dibutylbutyl phosphonate (DBBP), diamylamyl phosphonate (DAAP), and tributyl phosphate (TBP) are harnessed as solvents to recover noble metals from high-level liquid waste (HLLW)[2]. Simulated solutions containing palladium, ruthenium, and rhodium of 500 ppm each were prepared in different nitric acid concentrations and extraction behaviour of these metal ions were examined with neat DBBP, DAAP, and TBP solvents. Interestingly, while palladium and ruthenium are efficiently extracted into the organic phase and the extraction of rhodium was found to be negligible at all acidities. The distribution ratios (*D*) of palladium decreases with increase in nitric acid concentration; whereas the *D* values for ruthenium initially increases up to 2M and decreases thereafter. Phosphonate based solvents outperform their phosphate based counter parts. This superiority is attributed to the direct C-P bond in phosphonate solvents, inducing a +I effect and enhancing electron density on the double-bonded oxygen atom. Due to the predominant extraction of palladium, a stripping study focused solely on this metal. Various concentrations (0.5-2M) of thiourea and ammonium thiocyante were examined for stripping of Pd from organic phase. The percentage stripping of Pd from organic phase increases with increases of strippnant concentration. The stripping of Pd from organic phase is found to be about 27-36% with the use of 0.5-2 M thiourea and it very marginal(0.5-2.5%) in the case of ammonium thiocyante. Thiourea emerges as a highly effective stripant compared to ammonium thiocyanate, offering promising potential for palladium recovery. In conclusion, phosphonate-based solvents, particularly DBBP and DAAP, showcase remarkable efficacy in extracting noble metals, notably palladium. Additionally, thiourea stands out as a superior choice for stripping palladium from the organic phase. These findings underscore the potential of alternative sources and innovative techniques to meet the growing demand for noble metals in various industries.

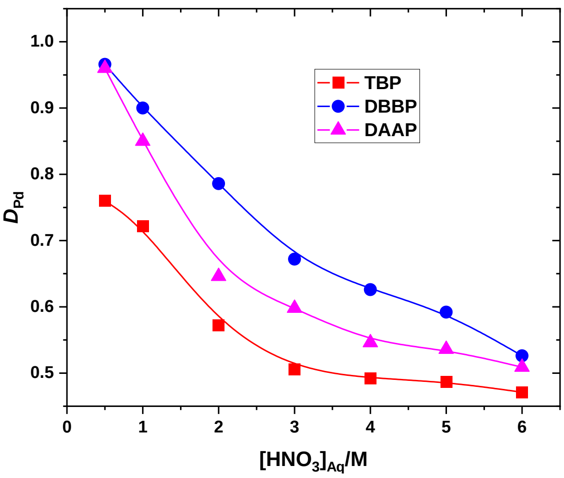

Fig 1: *D* values of Pd as a function of nitric acid for neat TBP, DBBP and DAAP

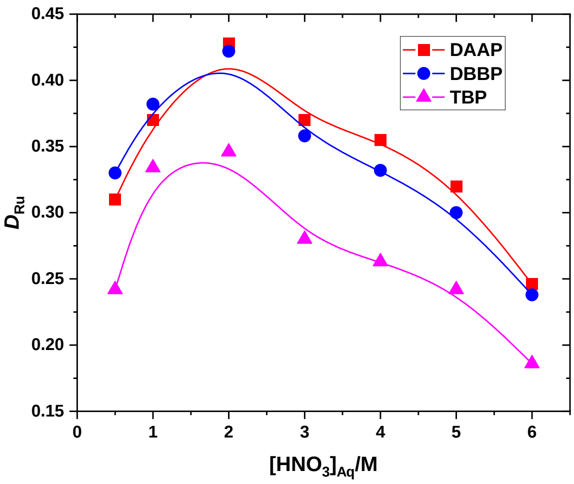

Fig 2: *D* values of Ru as a function of nitric for neat TBP, DBBP and DAAP

Keywords: Ruthenium, Rhodium, Palladium, TBP, DBBP, DAAP.

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Chemical quality control of refractory nuclear materials by CCD based DC-Arc-AES technique after physical separation of the major matrix: A 7-point standardization method

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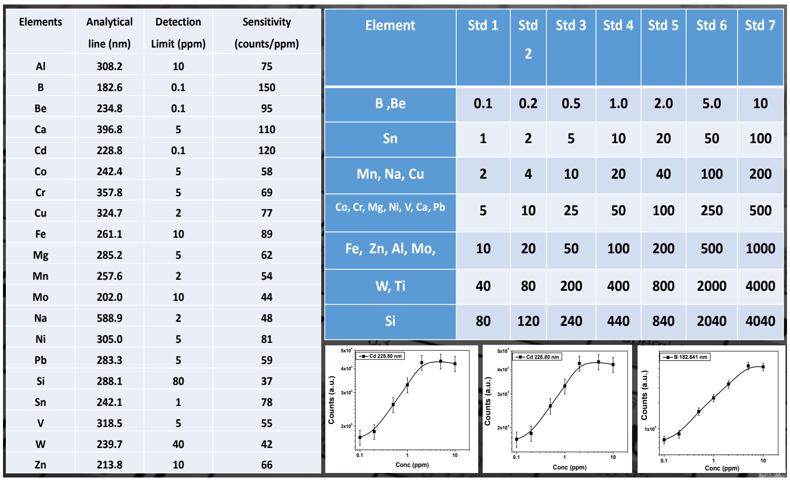
Trace metallic assay of nuclear fuel and related materials are a part of the broader chemical quality control (CQC). This is one of the pivotal steps to be followed at each step in the nuclear fuel cycle in order to ascertain that the materials meet the specification limits set by the fuel designers [1]. However, for such estimation, the major refractory matrix needs to be separated from the common metallic impurities present at trace and ultra-trace levels which is achieved either by chemical separation through solvent extraction or by physical separation.

The current paper deals with our study in developing an analytical methodology weherein, physical separation of the major matrix was achieved using a suitable carrier. This was followed by a 7 point standardization and estimation of common metallic impurities in various refractory nuclear materials. With this, we were able to extend the linear range and achieve more precise reporting. For this, a DC-Arc-AES (direct current arc atomic emission spectroscopy) unit was used equipped with array of CCD (charge coupled device) detectors. First, calibration graphs were established for 22 common metallic impurities in a number of refractory nuclear materials, namely, U_3O_8, PuO_2, $(U,Pu)O_2$and SS (stainless steel) using a set of 7 standards with varying impurity levels whose details are given in fig-1. The value of the standards was selected so that it can cater to multiple set of fuel and nuclear material samples having varying specification limits.



Elements	Analytical line (nm)	Detection Limit (ppm)	Sensitivity (counts/ppm)
Al	308.2	10	75
B	182.6	0.1	150
Be	234.8	0.1	95
Ca	396.8	5	110
Cd	228.8	0.1	120
Co	242.4	5	58
Cr	357.8	5	69
Cu	324.7	2	77
Fe	261.1	10	89
Mg	285.2	5	62
Mn	257.6	2	54
Mo	202.0	10	44
Na	588.9	2	48
Ni	305.0	5	81
Pb	283.3	5	59
Si	288.1	80	37
Sn	242.1	1	78
V	318.5	5	55
W	239.7	40	42
Zn	213.8	10	66

Element	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6	Std 7
B ,Be	0.1	0.2	0.5	1.0	2.0	5.0	10
Sn	1	2	5	10	20	50	100
Mn, Na, Cu	2	4	10	20	40	100	200
Co, Cr, Mg, Ni, V, Ca, Pb	5	10	25	50	100	250	500
Fe, Zn, Al, Mo,	10	20	50	100	200	500	1000
W, Ti	40	80	200	400	800	2000	4000
Si	80	120	240	440	840	2040	4040

Fig 1: Analytical lines, Standard values, and representative calibration graphs for elements in DC-Arc-AES

The analyses were carried out using AgCl as the carrier in the samples that sweeps the common impurities into the high temperature arc leaving behind the major matrix and thus achieving the physical separation. The concentration and corresponding intensity values were fed into an iterative equation of the type-

$$y = A_1 x + A_2\ x^2 + A_3 x^3 + \cdots$$

Here, A_1,A_2, A_3 are the scalar quantities and x is the concentration.

It can be seen from the calibration graphs that these are sigmoid in nature rather than linear for all the impurity elements. The graphs were having limited linearity range with saturations at both extremes. Based on the observations, a working range for each of the elements were calculated between Std-2 and Std-5. The analytical methods are being now regularly used for routine analysis of nuclear materials.

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Synthesis, Characterization and F-Block Metal ions Removal Efficiency of Engineered Super Paramagnetic Copper incorporated Cobalt Ferrite (Cu-CoFe$_2$O$_4$) Magnetic Particles

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Effective removal and remediation of radionuclides from radioactive waste water remains a serious issue despite its acute need, particularly for f block radiotoxic metals separation. Hence, decontamination of hazardous radionuclides from nuclear waste solution for safe and secure waste management still is a critical challenge, necessitates the development of a highly selective and high-capacity novel sequestering materials. Hence, we have attempted to address this issue. Here, in this work we have demonstrated the synthesis, characterization and application of copper incorporated cobalt ferrite (Cu-CoFe$_2$O$_4$) magnetic particles [1]. Subsequently, characterization of the newly synthesized Cu-CoFe$_2$O$_4$ materials was performed using the tools like powder X-Ray Diffraction (PXRD), Energy Dispersive Spectroscopy (EDS) and Scanning Electronic Microscopy (SEM) (Fig.1). The PXRD data (Fig.1) showed the characteristics peaks of cobalt ferrite (Cu-CoFe$_2$O$_4$) magnetic particles and thereby confirmed its formation. The Surface morphology of the particles as well as their size were also studied. The average particle size was found to be in the range of 50-60 nm (Fig 1). The incorporation of copper metal within the CoFe$_2$O$_4$ framework was established by X-ray elemental mapping. This material was employed for the removal of Pu(IV) and Am(III) metal ions from aqueous solution. The maximum K_d values achieved for Pu(IV) and Am(III) were 6900ml/g and 3600 ml/g respectively. We have also examined the effect of variation of acid strength of the aqueous acidic feed on the K_d value. We have studied the kinetics of sorption of Pu(IV) and Am(III) metal ions by the material (Fig 1). Optimum contact time was found for Pu(IV) and Am (III) were 60 min. and 45 min. respectively. In conclusion, Cu incorporated CoFe$_2$O$_4$ (Cu-CoFe$_2$O$_4$) magnetic particles has shown a great potential for Pu(IV) and Am(III) metal ions adsorption form aqueous acidic feed.

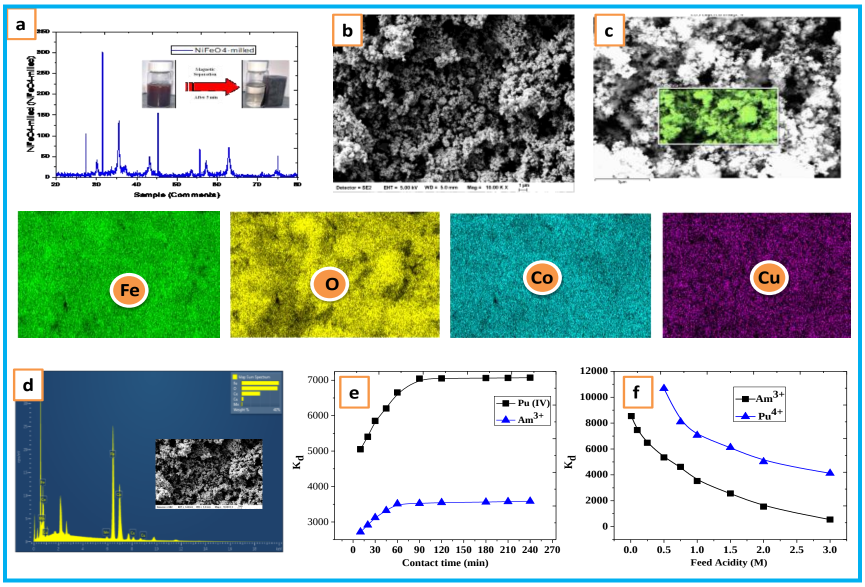

Figure 1: Characterization and applications of Cu-CoFe$_2$O$_4$ magnetic particles for Pu(IV) and Am(III) removal and remediation applications.

Keywords: *Cu incorporated CoFe$_2$O$_4$ (Cu-CoFe$_2$O$_4$), Tri (Am^{3+}) and Tetra (Pu^{4+}) valent actinides, Extraction*

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1. Synthesis and characterization of NiFe2O4 nanoparticles as reusable magnetic nanocatalyst for organic dyes catalytic reduction: Study of the counter anion effect, Materials Chemistry and Physics,2022, 292, 126793.

Task specific Thiol Functionalized Multi-Walled Carbon Nanotubes (SH-MWCNT) for the Sorption of Tri, Tetra and Hexa Valent Actinides from acidic feed

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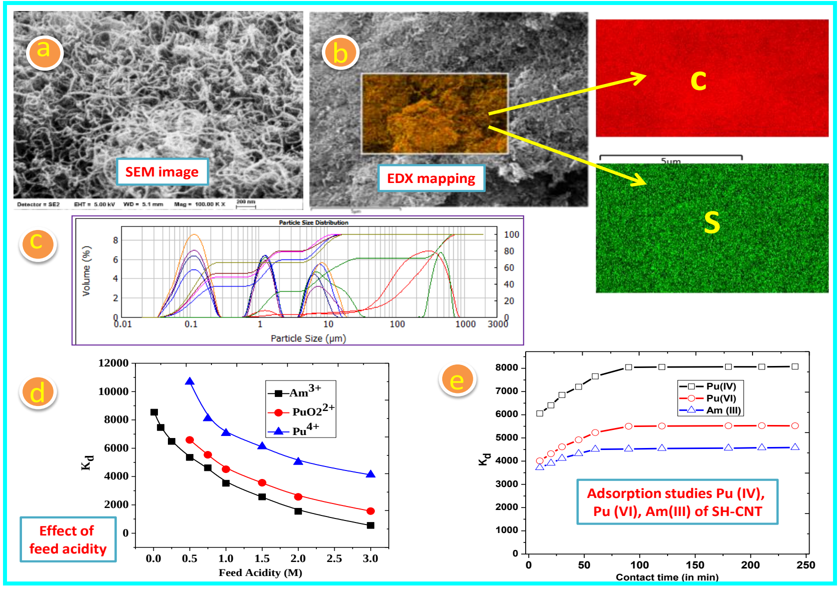
Multi-walled carbon nanotubes (MWCNT) have shown a significant potential for the removal and remediation of f-cations from aqueous medium [1]. First, Thiol-functionalized MWCNT (SH-MWCNT) were synthesized. Subsequently, they were characterized using Scanning Electronic Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). Then, they were employed for efficient and selective separation of plutonium (IV), plutonium (VI) and Americium (III) metal ions. The SEM image for surface morphology of the SH-MWCNT is shown in figure 1.a. From the EDX analysis it was confirmed that the sulfur (S) was incorporated in MWCNT (Fig 1.b). We have studied the particles size distribution also and it is depicted in figure 1.C. Distribution coefficient (K_d) of Pu (IV), Pu (VI) and Am (III) were evaluated under optimized condition. From the experiment, the measured K_d values for Pu (IV), Pu (VI) and Am (III) were 7055 µl/g (1M), 4512 µl/g (1M) and 3525 µl/g (1M) respectively. The effect of feed acidity (HNO_3) on K_d was studied in the range of 0.1 M to 3.0M and the experimental results are shown in Figure 1.d. It was observed that with the increase in the acidic strength the K_d value decreased, this may be due to the higher concentration of H^+ ions. The kinetics of any adsorbent is very important for adsorption of metals ions. The kinetics of adsorption of the Pu (IV), Pu (VI) and Am (III) metal ions were studied using SH-MWCNT under acidic condition. It was observed that 60 min. of contact time was sufficient to establish the equilibrium. Summarily, SH-MWCNT has shown a significant potential for the adsorption of Pu (IV), Pu(VI) and Am (III) metal ions under acidic condition.



Keywords: SH-MWCNT, Pu (IV), Pu (VI), Am(III), SEM, EDX, Adsorption

References:

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A process for reduction of NO_X during dissolution of Uranium metal chips in Nitric acid medium with Ammonium Nitrate

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Dissolution of uranium concentrates in nitric acid is one of the principal operations in the process flow sheets of uranium refining in the front end of fuel cycle. The nuclear pure metallic uranium is primary fuel for research reactors. However, significant quantity of scrap uranium metal in the form of chips and turnings is generated during fuel fabrication steps. These metal uranium scrap need to be recycled further for valuable uranium recovery. Further, dissolution of uranium metal chips & turnings in nitric acid is a critical process as the reaction is highly exothermic with intense generation of hazardous nitrogen oxide gases. The chemical reaction for U metal with nitric acid is given by following reaction 1 & 2 [1].

$U+4HNO_3 \rightarrow UO_2(NO_3)_2+2NO+2H_2O$ (<8 N HNO_3) (1)

$U+8HNO_3 \rightarrow UO2(NO_3)_2+6NO_2+4H_2O$ (>8 N HNO_3) (2)

It is essential to control the reaction rate as well as generation of NO_X to an appreciable level for combating uncontrollable reaction as the metal scrap has high specific surface area. It has been observed from literature that ammonium nitrate has the potential to react with nitrogen oxide gases converting it to nitrogen and regenerating nitric acid as per reaction 3 & 4 [2].

$2NO_2+NH_4NO_3 \rightarrow 2HNO_3 + N_2+H_2O$, (3)

$2NO+ 3NH_4NO_3 \rightarrow 2HNO_3 + 3N_2+ 5H_2O$, (4)

Hence, effort has been put to develop a new process of uranium dissolution with addition of ammonium nitrate. The objective of the process is to control the generation of NOx gases along with controlling the vigorous reaction rate. The advantages of addition of ammonium nitrate are: limitation of NOx generation to an appreciable level, reduction of nitric acid requirement/consumption and minimization of effluent /recycling of effluent. The resultant reaction of uranium in nitric acid with ammonium nitrate is given by eqn. 5.

$U + 2HNO_3 +3NH_4NO_3 \rightarrow UO_2(NO_3)_2 + 3N_2+ 7H_2O$, (5)

Lab scale experiments were performed to find the optimum dissolution condition in terms of conc. of ammonium nitrate, reaction rate and generation of NO_X. At the optimized condition, a substantial reduction in NOx generation (up to 40 %) and reduction in consumption of nitric acid (up to 25 %) is possible (At 100g/L NH_4NO_3, 5.3 N initial acid. [Table 1] acid compared to conventional dissolution process [Fig 1]. In this way, the process of dissolution of uranium metal scrap was successfully developed and recommended without any additional infrastructural facility, additional chemical consumption, additional energy requirement and additional effluent /waste generation in the process.

Table 1: Effect of ammonium nitrate conc. on NOx generation and acid consumption reduction

Conc. of NH_4NO_3(g/L)	Initial Acid (mole)	Acid left (Mole)	NOx generated (Mole)	% reduction in Acid consumption	% reduction in NOx
0	2.385	0.778	0.99	-	
50	2.385	0.995	0.75	13.93	24.2
100	2.385	1.193	0.59	25.31	40.4
150	2.385	1.284	0.50	31.9	49.5
200	2.385	1.369	0.37	37.1	62.6
400	2.385	1.66	0.20	55.1	79.8

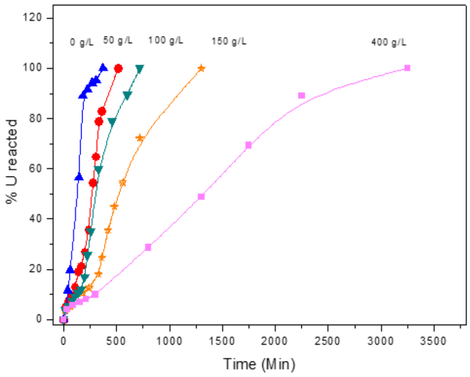

Fig 1: Uranium dissolution with time at different starting conc. of ammonium nitrate at a fixed initial conc. of nitric acid (5.3N)

Keywords: Uranium metal, Ammonium Nitrate, NOx, Dissolution, Nitric Acid

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Investigating Dibutyl Carbitol for Extraction of Uranium and Comparison with Tri-n-Butyl Phosphate: Experimental and Computational Studies

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Nuclear power is increasingly vital for low-carbon energy production, with uranium serving as a key element in various nuclear energy processes. With the escalating demand for energy and the constraints posed by diminishing fossil fuel reserves and greenhouse gas emissions, nuclear technology emerges as a viable alternative, assuming a progressively significant role globally. Uranium, primarily utilized as fuel in nuclear power plants, constitutes a pivotal element in the civilian nuclear energy sector. Among various extractants, dibutyl carbitol (DBC), utilized in Butex process, gained prominence as an extractant, owing to its favorable properties such as a high flash point, low solubility in water, and successful uranium extraction capabilities[1,2]. Despite its utility, limited literature exists elucidating the extraction mechanism of dibutyl carbitol with uranium. This work presents solvent extraction studies employing dibutyl carbitol for uranium extraction from nitric acid solutions. Also, the extraction ability of DBC(100%) towards uranium was compared with 30% tri-n-butyl phosphate(TBP) in n-dodecane(n-DD). It showed that the distribution coefficient of uranium in the case of TBP(30%) was much higher compared to that of neat DBC(100%). This also suggested the greater binding ability of P=O group towards U(VI) compared to ethereal oxygen donor atom present in DBC. In order to further validate the complexation behaviour of the ligands towards uranium, Density Functional Theory (DFT) computational studies were conducted insights into the bonding mechanism between the ligand and U(VI). The lowest energy structures of the ligands as well as uranium-ligand complexes were established using systematic geometry optimization procedure at BP86/def2-TZVP level followed by harmonic frequency calculation to confirm that these structures are minima in the potential energy hyperspace. Complexation energies were evaluated for both TBP and DBC according to the following scheme:

$UO_2(NO_3)_2{\cdot}2H_2O + 2L = UO_2(NO_3)_2{\cdot}2L + 2H_2O$, where L denotes the ligands. Upon comparing the values of the complexation energies, it was found that the complexation energy in the case of TBP is much higher than DBC, as was found in experimental studies.

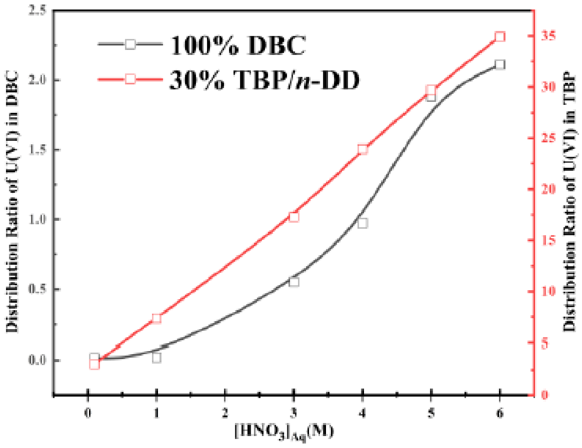

Fig. 1: Variation of *D* for U with aqueous feed acidity for 100% DBC and 30% TBP/n-DD

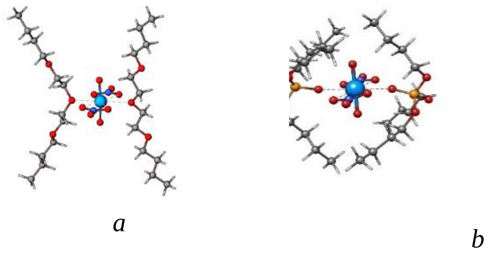

Fig. 2: Lowest energy structure for
(a)$UO_2(NO_3)_2{\cdot}2DBC$ complex
(b) $UO_2(NO_3)_2{\cdot}2TBP$ complex

Keywords: Uranium, solvent extraction, carbitol, BUTEX

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Study on particle size distribution during partial decommissioning of vitrification cell

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Objective of the current study is to measure the activity distribution of the aerosols generated during partial decommissioning of vitrification cell. The Advanced Vitrification System (AVS) is used for the vitrification of High Level Waste (HLW) using Joule Heating Ceramic Melter (JHCM). The vitrification cell is partially decommissioned and around 5E7 TBq of gross βγ activity was removed from the cell. Due to the residual activity inside the melter cell air activity keeps on generating which further leads to exhaustion of the exhaust filter banks especially Pre-filters. Air samples were taken utilising a Particle Aerodynamic Size Separator (PASS) cascade impactor to characterize the aerosol activity generated inside the cell. Samples were characterized to correlate the particles size captured by exhaust filter banks specially the pre-filters. The experimentally determined particle distribution was also compared with the default activity median aerodynamic diameter (AMAD) value for occupational workers to see the inhalation risk in case of any accidental releases. A study was also performed to determine the isotopic composition of the aerosols generated inside the vitrification cell.

Radiologically contaminated aerosols produced by vitrification cell equipment present a number of challenges for health physics professionals. The primary concern is the potential for internal deposition of radioactive particulate through inhalation by workers. The secondary concern is the potential of radioactive dust and aerosols from uncontrolled release to the general public and environment. The objective of this study was to calculate AMAD and geometric standard deviation (GSD) of aerosols generated inside vitrification cell. Assuming log-normal particle distribution, the following equation is used to calculate particle size geometric standard deviation (σg):

$$\sigma_g = \frac{84th\ percentile\ value}{50th\ percentile\ value}$$

Aerosols were sampled using the 7 stage PASS cascade impactor designed by EAD, BARC. The impactor operates at 45 lpm and separates particles in size range 0.53 to 8.95 µm in 7 class intervals. Glass fiber filter papers are used in this work as it has a higher pressure drop compared to cellulose filter papers and provides good filtration efficiency (> 99%). Samples for homogenization were to be repeated in the morning, afternoon, and evening to observe the difference between particle sizes generated. The average sample collection time was 1-2 hours. Three sets of samples were collected each time. The sample was also analyzed for isotopic composition using High Purity Germania (HPGe).

The activity data sets were developed collectively by combining the three sets. The results were used to develop aerodynamic diameter distribution table (Table 1) and AMAD and GSD were then determined by plotting data on a log-probability plot (Fig.1). The AMAD was determined to be 5.8 µm with its GSD equal to 1.8. The ^{137}Cs distribution obtained in HPGe confirms predominant radionuclide in the facility. Obtained AMAD is consistent with the default AMAD value for occupational workers i.e. 5 µm as referenced in ICRP 66.

Stage	Activity (Bq)	Cumulative Activity fraction	Effective Cut-off diameter ECD (µm)	Collection size range (µm)
1	6.2	1	8.95	>8.95
2	2.47	0.62	7.91	8.95-7.91
3	2.64	0.47	6.09	7.91-6.09
4	1.52	0.31	4.15	6.09-4.15
5	1.48	0.21	2.94	4.15-2.94
6	0.95	0.12	1.03	2.94-1.03
7	0.41	0.07	0.53	1.03-0.53
Backup	0.66	0.04	-	<0.53

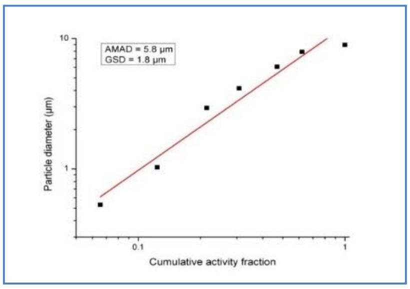

Table 1: Stage-wise activity distribution
Fig. 1: Log probability plot for AMAD estimation

Keywords: Particle Size, Dismantling, Vitrification

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Comparative Studies on the Surface Activities of Structurally Related Glycolamide Extractants

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Separation methods involving liquid-liquid extraction of metal ions from aqueous spent fuel solutions have been effectively employed for reprocessing and waste management applications in nuclear fuel cycle. The choice of extractants to be employed for such liquid-liquid extraction processes greatly depend on their physico chemical properties under extraction conditions. The ease of mixing of phases and separation of phases after mixing are important factors determining the kinetics and effectiveness of extraction processes. The surface activity of extractants is one of the key parameters controlling the above factors, and the measurement of interfacial tension (IFT) in extraction systems for assessment of surface activity is essential for engineering calculations in extraction systems [1]. We have explored the use of a Drop Shape Analyzer System (Theta Flex Optical Tensiometer, M/s Biolin Scientific) for the measurement and comparison of IFT in some of the glycolamide based solvents after equilibrating with different nitric acid solutions.

N,N,N',N'-tetraoctyldiglycolamide (TODGA) is one of the extractants widely studied for treatment processes of high-level nuclear waste solutions (HLW) all over the world. The use of this extractant without a phase modifier usually results in separation of a third phase during extraction of metal ions from nitric acid solutions. However, the monoglycolamide derivative of TODGA, N,N-di-octyl-2-hydroxyacetamide (DOHyA) has been identified as a better extractant showing minimal phase separation problems under similar extraction conditions. Figure 1 compares the IFT values measured for TODGA and DOHyA solvents in *n*-dodecane diluent, against 4 M nitric acid as the aqueous phase. The IFT values decreased significantly with increase in concentration of both TODGA and DOHyA in the beginning, and thereafter, the values were independent of extractant concentration. The minimum concentration of the extractant necessary to start a significant adsorption of the extractant at the interphase was calculated from these data plots. This concentration is referred to as the 'Critical Micellar Concentration' (CMC) which also corresponds to the minimum extractant concentration for formation of reverse micellar aggregates in the organic phase [2]. The CMC for TODGA was nearly 20 times lower than that of DOHyA, indicating high surface activity of TODGA. These observations were in line with the high aggregation tendency of TODGA in comparison to DOHyA. The equilibrium IFT values of TODGA solvent system were always higher than that of DOHyA under similar concentrations. The differences between the properties of these structurally related solvents indicated that the surface activities of extractants can be effectively tuned by suitable structural modifications.

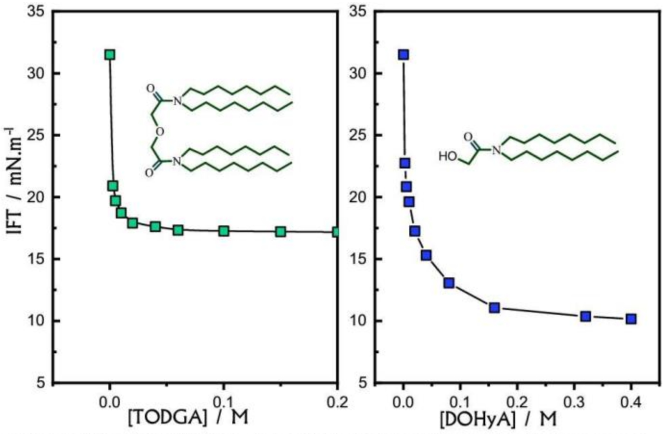

Fig. 1: Variation in the IFT of two different glycolamide solvents with extractant concentration. Aq. phase: 4 M nitric acid, Organic Phase: TODGA or DOHyA in n-dodecane.

In the current study, the IFT measurements were also carried out with different aqueous phase nitric acid concentrations for both TODGA and DOHyA solvent phases. When the diluent *n*-dodecane was modified with 5 vol.% of 1-octanol, the IFT values of TODGA followed a reverse trend, indicating significant effect of polarity of diluent on surface activity of extractants. In all the cases, data was fitted with Szyszkowski's adsorption isotherm equation [1] and the Szyszkowski co-efficients were derived to calculate the free energy of adsorption (ΔG_{ads}) and the minimum interfacial area occupied by a statistical molecule (A_{min}) in the adsorbed layer.

Keywords: Diglycolamide, Interfacial Tension, Drop Shape Analyzer, Critical Micellar Concentration

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Evaluation of the Efficiency of the Irradiated Extraction Chromatographic Resin Containing TAM-3-DGAfor Actinide uptake from Acidic Feeds

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In the nuclear reprocessing facility, one of the most challenging tasks is radioactive waste management, particularly the management of high level waste (HLW). One of the proposed strategies for HLW is to recover entire actinides from it followed by its disposal in deep geological repositories after immobilising into suitable solid matrix. The earlier attempts to recover actinides from HLW suggested one of the diglycolamide (DGA), well known as TODGA, as the most promising ligands [1]. In the recent year, different multiple DGA ligands, with 3 – 4 DGA units on a suitable scaffold have shown much better extraction efficiency for the trivalent actinides as compared to TODGA [2].

Recently, unique tripodal DGA ligand was synthesized where three DGA moieties were chemically grafted on a triaza-9-crown-3 scaffold (termed as TAM-3-DGA). Solvent extraction and complexation studies with the ligand gave encouraging results for actinide partitioning over other DGA-functionalized extractants reported so far [3]. It was of interest, therefore, to prepare an extraction chromatographic resin (ECR) containing TAM-3-DGA ligand for the separation of actinides from radioactive waste.

Our results with TAM-3-DGA based ECR showed promising extraction effciency for the trivalent and tetravalent actinides above 2 M HNO_3. Therefore, this ECR material has limitation for separation of actinides from low level laboratory waste having acidity < 1 M HNO_3. It was planned, therefore, to employ a room temperature ionic liquid (RTIL) for preparation of the ECR, which is known to give better extraction efficiences at lower acidities [2]. For real application, it is an important aspect to understand the radiation stability of the ECRs materials when proposed for radioactive metal ion separation. Therefore, the TAM-3-DGA-ECR material studied in this work was irradiated in a gamma chamber upt0 1000 kGy absorb dose for evaluating its radiation tsability.

Batch uptake studies were carried out with Am^{3+} and Pu^{4+} ions with the irradiated resin containing molecular diluent, showed good uptake and the distribution coefficient values increased with the increase in the feed acidity and good reusability. The kinetic study also followed the similar pattern with that of the pristine. The resin exposed to 100 Mrad was employed for column studies which showed 86.7% of the resin capacity with respect to the batch study and the formation of 1:2 (metal/ligand) complex was ascertained.

Irradiated RTIL based ECR was utilized for both Am(III) and Pu(IV) yielded with promising uptake efficiency in the lower range of acidity. These ECRs showed good reusability like pristine one. In order to evaluate the performance of the irradiated resins in the column operations, two independent columns were prepared with the TAM-3-DGA-IL irradiated resins (50 Mrad and 100 Mrad) having identical column parameters each. The column performance was not affected after irradiation of the resins upto 100 Mrad absorb dose.

It can be concluded that the ECRs have showed no such degradation effect upon irradiation upto 100 Mrad absorb dose. Hence these ECRs can be employed in the high dose field with confidence.

Keywords: *Actinides, Diglycolamide, Extraction chromatography, HLW*

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Demonstration of strontium removal from fast reactor simulated high-level waste using crown ether impregnated resin

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Radioembolization, which involves selective trans-catheter and intra-arterial injection of micrometer sized particles loaded with ^{90}Y, is a proposed therapy approach for hepatocellular carcinoma (HCC), a chronic liver cancer condition [1]. The radioisotope ^{90}Y is a pure beta emitter with a half-life of 64.2 hours, usually produced through neutron bombardment of ^{89}Y in a reactor. ^{90}Y can also be produced as a daughter product of ^{90}Sr ($t_{1/2}$: 29 years), which is produced by uranium (plutonium) fission. The recommended procedure is to isolate ^{90}Sr from PUREX raffinate, an aqueous solution formed after removing uranium and plutonium from spent fuel dissolver solutions [2]. The ^{90}Y necessary for the treatment can be extracted from ^{90}Sr using an appropriate separation procedure. On the context of the above, separation of Sr from a fast reactor simulated high-level liquid waste (FR-SHLLW) was studied. 4′,4″(5″)-Di-tert-butyldicyclohexano-18-crown-6 (*tert*-DCH18C6) impregnated Amberlite ™ XAD-7 resin (40 % (w/w)) was employed for the selective separation of Sr. The impregnated resin was characterized by FT-IR and CHNS analyzes. Batch experiments were conducted for studying the effect of nitric acid concentration (Fig. 1) and effect of Sr concentration in aqueous phase (Fig. 2). The studies divulged the possibility of Sr separation from nitric acid concentration above 2 M and a maximum Sr loading of around 22 mg/g. The results of studies on extraction kinetics of the impregnated resin showed the feasibility of separation of Sr using normal flow rates (3 ml/minute) during column experiments. Based on the results, a column experiment was performed with FR-SHLLW corresponding to a burn up of 80,000 MWd/Te. 200 mL of the feed solution was passed through the resin (2 g) packed in a glass column (8 mm diameter) and the effluent samples (10 mL each) were analyzed by ICP-OES. Nearly 100 mL of the effluent samples collected from the column did not show the presence of Sr, indicating its quantitative loading in the column. The Sr content of successive effluent fractions showed a gradual increase. Adsorption of all the trivalent elements in FR-SHLLW to the column was insignificant, whereas small amounts of Ba and Ag were loaded to the column. Further studies on scrubbing the column using 4 M nitric acid and stripping of Sr using 0.1 M nitric acid were also carried out. The results indicated the feasibility of employing *tert*-DCH18C6 impregnated resin for the bulk removal of Sr from HLLW.

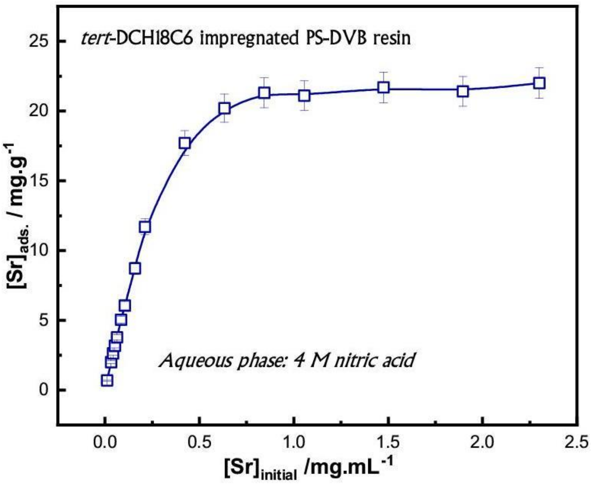

Fig. 1 Adsorption of Sr(II) on the crown ether resin while using different concentrations of Sr(II) in 4 M nitric acid.

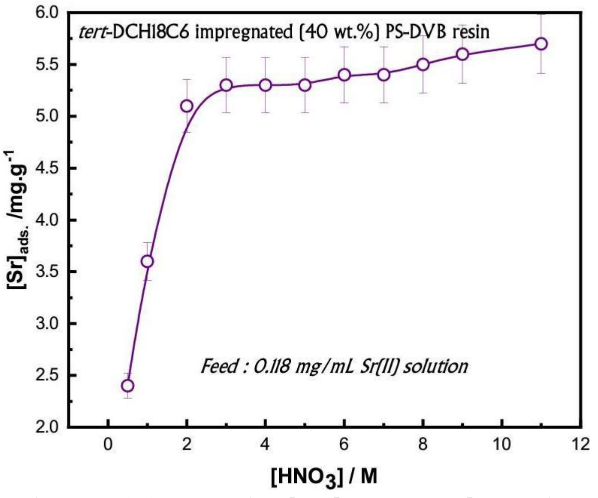

Fig. 2 Sr(II) extraction by the crown ether resin at different acidities of aqueous phase.

Keywords: ^{90}Y, ^{90}Sr, tert-DCH18C6, impregnation, Amberlite XAD-7, FR-SHLLW

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Highly Selective Phenanthroline Diamides For Separation of Am(III) And Lanthanides(III)

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Nuclear power is an essential source of energy with minimal carbon dioxide emissions, which is of great importance in connection with climate change issues. However, its main disadvantage is the formation of high-level waste (HLW). One approach is the concept of “partitioning and transmutation.” It consists of separating radionuclides into groups (partitioning) and further converting them into radionuclides with shorter half-lives (transmutation) using fast neutron reactors. However, for this, it is necessary to separate Am(III) and lanthanides(III) (Ln(III)), which is a difficult task since the physicochemical properties of these elements are very similar. Solvent extraction is one of the most suitable methods for this on an industrial scale. Phenanthroline diamide ligands (DAPhen) are a promising class of compounds to implement this. The hard amide oxygen atoms provide affinity for trivalent f-elements, while the soft phenanthroline nitrogen atoms provide selectivity for Am(III) in the presence of Ln(III). The extraction properties of DAPhen can be influenced by varying both the substituents on the amide nitrogen atoms and on the phenanthroline ring.

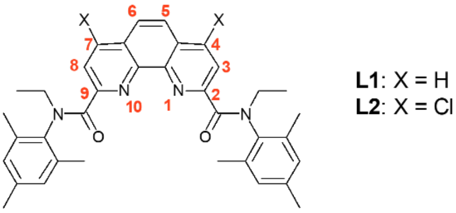

Fig. 1. Structural formula of diamides **L1-L4.**

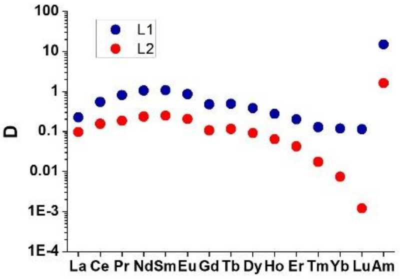

Fig. 2. Distribution ratios of Ln(III) and Am(III) for extraction by 0.01 M **L1** and **L2** from 3 M HNO_3.

In this work, the extraction and coordination properties of two alkyl-aryl DAPhen ligands (L1 and L2, Fig. 1), differing in the presence of atoms in the 4,7-positions of the phenanthroline core, were studied. F-3 (3-Nitrobenzotrifluoride) was used as a solvent. The introduction of methyl groups into the ortho positions of the aryl fragment at the amide nitrogen atoms leads to a drastic change in the extraction of lanthanides(III) (Fig. 2). As a result, record values for the separation factors of Am(III) and light lanthanides(III) at 3 mol/L HNO_3 were obtained: $SF_{Am/La}$ = 66 for L1 and 16 for L2, $SF_{Am/Ce}$ = 27 for L1 and 10 for L2. Extraction systems based on these highly selective ligands make it possible to separate Am(III) from an HLW imitator solution containing a significant amount of light lanthanides(III) (10.7 g/L) and 3 mol/L HNO_3. Preliminary assessment of radiolysis also showed that extraction systems based on diamides L1 and L2 continue to bind Am(III) at an absorbed dose of up to 1000 kGy.

The study of the compositions of complexes with $Eu(NO_3)_3$ using UV-vis titration showed that in acetonitrile, the formation of two types of the complex is observed: $EuL(NO_3)_3$ and $EuL_2(NO_3)_3$. To elucidate the coordination chemistry in the solid state, we obtained single crystals of complex compounds with nitrates of almost the entire series of lanthanides for L1 and L2 (25 single crystals). Their structural features were studied using X-ray diffraction. All obtained complexes in the solid state have the composition $LnL(NO_3)_3$. The coordination number of lanthanide(III) in all complexes is 10 (Fig. 3). As the ionic radius of the lanthanide decreases, the lengths of the Ln-O_{amide}, Ln-Nphen and Ln-ONO_2 bonds decrease.

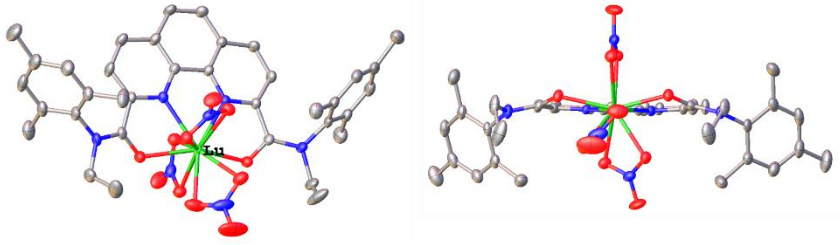

Fig. 3. Molecular structure of L1•$Lu(NO_3)_3$.

The work was carried out with the financial support of the Russian Science Foundation, project 20-73-10076.

Keywords: Solvent extraction, Americium, Lanthanides, Phenanthroline diamides

Desorption and Recyclability Evaluation of Cationic Membranes for Selective Separation of Cobalt from Zirconium Alloys

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Separations at major, minor and trace levels are needed for pre-concentration / recovery of valuables as well as purification of effluents / water bodies. Ion exchange membranes are widely used for separation having advantages of low consumption of sample, fast equilibration and excellent efficiency over other separation technique [**1**]. However, for enhancing selectivity towards specific analyte, modification of ion exchange membranes is necessary.

The selective separation of Co from Zr and Nb is important for the decontamination of pressure tubes from pressurized heavy water reactors [**2**]. Initial experiments were carried out using the respective radiotracers. These laboratory scale studies explore the feasibility of using oxalic acid, a benign complexing medium, for the Zr–Nb matrix, with targeted sorption of trace levels of ^{60}Co on cation exchange membranes.

Characterization and stability evaluation of the cation exchange membranes were carried out using SEM-EDS, FT-IR, moisture retention capacity, at various experimental stages of the Co-separation studies. EDXRF was used for the quantification of sorbed Co on the membranes. The detection limits of EDXRF for Co on the membrane was found to be ~ 1.3 µg.

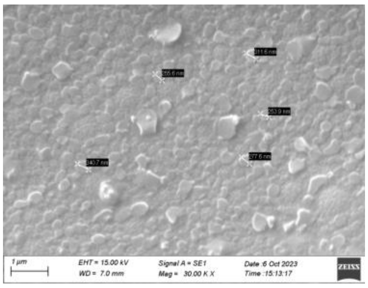

Fig.1: SEM image of wet cation exchange membrane

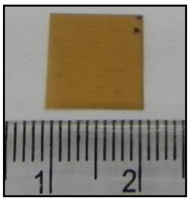

Fig.2: Cation exchange membrane (BDH) Chemicals polystyrene / DVB with SO_3H
Thickness: 0.15-0.17 mm
Water uptake: 1.13 %

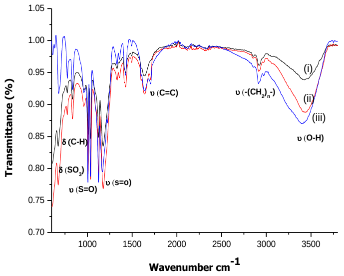

Fig.3: FTIR spectrum of membrane

The sorption of Co(II) was quantitative at 0.001 M oxalic acid. As the sample amounts were increased from 0.03 g to 1 g, 0.1 M oxalic acid was required to form anionic complexes with Zr and Nb, though there was a reduction in the uptake of Co (~ from 99% to 66%). Quantitative sorption of Co was attained within 60 min of equilibration, which followed pseudo second order kinetic model. Batch equilibrium studies revealed that the saturation capacity is 1.89 meq of Co (II) per g of the membrane [**2**]. EDXRF was used for the quantification of sorbed Co on the membranes.

Further, the desorption and recyclability of the membranes were evaluated, with different concentrations of HCl. The desorption kinetics was found to be fast, leading to quantitative removal in ~ 60 minutes. Recyclability was obtained up to ten cycles with quantitative uptake and 98% desorption, using 3 M HCl.

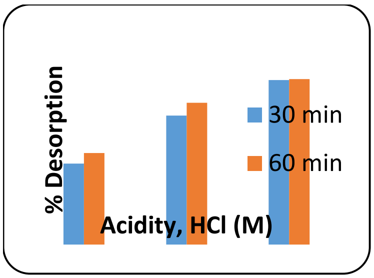

Fig.4: Regeneration - acidity variation

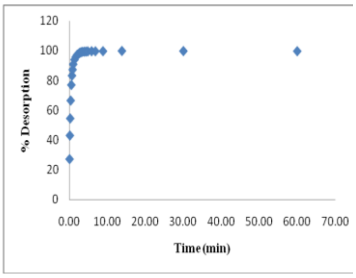

Fig.5: Regeneration kinetics

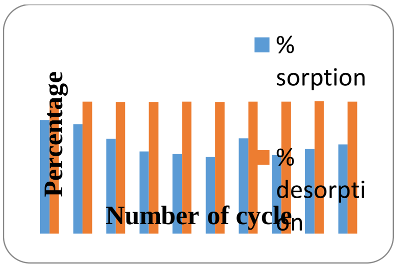

Fig.6: Recycling of membrane

Keywords: Desorption, Cobalt, Cation Exchange membrane, Recyclability, EDXRF

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Synthesis, Characterization and Evaluation of Polyethersulfone – Tri-isoamyl Phosphate Composite Beads for Recovery of Pu from Aqueous Acidic Feed

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In Nuclear field, it is prime requirement to manage the wastes generated from different cycles. It is necessary in radiological point of view and for ecology. Tri-butyl phosphate (TBP) is known worldwide as the workhorse of the PUREX process in the reprocessing of the PHWR spent fuel for several decades. Although it has many merits like excellent selectivity in extracting U and Pu over other fission products, good phase separation, ease of stripping the loaded U and Pu, good hydrodynamic properties but it possess demerits too like third phase formation and degradation when subject to extraction under high radiolytic and hydrolytic environment **[1].** The degradation products decrease the decontamination factor of the products and also due to crud formation the hydrodynamic properties changes.

Hence, to overcome these shortcomings separation scientists have recently developed tri-iso-amyl phosphate (TAP), higher homologue of TBP as the most competent one. It retains the benefits of TBP but mitigates the demerits **[2].** It is much economic rather than TBP and its efficacy for the extraction of U and Pu has already been established by different research groups. In this direction we have tried to encapsulate this promising extractant (TAP) within polyethersulfone (PES) in composite bead form to further enhance its radiolytic and hydrolytic stability and extends its applicability. The tri-iso-amyl phosphate encapsulated polyether composite beads of varying concentration were synthesised, characterised and evaluated for recovery of Pu(IV) from aqueous acidic feed.

At first, the polyethersulfone was dissolved in NMP solvent to make a 10-15% (w/w) solution of the polymer. This polymer solution was added into the desired organic extractant, tri-iso-amyl phosphate (TAP) in a definite polymer to extractant ratio (5:1) under continuous stirring condition. The solution looked like an emulsion. This mixed solution was filled in a syringe having a suitable diameter and then the solution was cast into the water (anti-solvent) taken in water bath from an appropriate height in drop wise manner. This instantly formed the white spherical beads encapsulating the desired extractants. The freshly prepared composite beads were kept incubated in deionized water for 24 hours in stirring condition. Then the beads can be used for extraction purpose.

The TAP encapsulated beads were characterised using SEM, TGA and FTIR to check any morphological changes and proper ligand intrusion within the matrix. These beads showed promising extraction efficiency for Pu(IV) in a wide range of acidity. The attainment of the equilibrium was within 15 minutes. The kinetic data showed linearity in pseudo second order kinetics, indicating monolayer chemisorption. Nonlinearity in Elovich model proved the absence of multiplayer sorption. Oxalic acid was selected as the best stripping agent in the view of stripping efficacy. To check the reusability of the composite beads, successive loading and stripping studies were carried out in 1M nitric acid medium in batch process. The procedure was continued for 10 cycles, indicating reasonably good stability of the beads for reusability purpose. These composite beads were employed for the highest metal loading capacity and the data were fitted in to various isotherm models, which also validated the presence of monolayer chemisorption phenomena. Due to its high extraction efficiency, these beads can be used promisingly for the acidic feed in the place of TBP encapsulated one to recover Pu.

Keywords: *Isoamyl phosphate, Polyethersulfone, composite beads, extraction, Pu(IV)*

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Chemical treatment and characterization of Solid Muck removed from ILRE uptake line in reprocessing plant by ICP-AES

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The PUREX process is used for recovery of U and Pu from spent nuclear fuel using tri-n-butyl phosphate (TBP) diluted with *n*-dodecane, which gets degraded mainly due to high radiation and acid-catalysed de-alkylation [1]. The degraded solvent has adverse effects on the process performance in the form of reduction in the decontamination factors against fission products, loss of U& Pu to the waste streams, formation of interfacial cruds and precipitates [2]. These precipitates along with silica, corrosion product and other fines escaped from feed clarification forms solid (muck) which get deposited at specific locations in process lines. Muck creates operational flow problem by chocking transfer line and making hindrance in solution transfer from one process tank to another. Recently, this problem was encountered in ILRE (intermediate level raffinate evaporator) uptake line of PREFRE plant. A small amount of muck sample was removed from the line with the help of string rounded at head. The chemical composition of these solid is required to be known for its remedial action of removal. Present work describes the method standardised for chemical treatment and characterization of muck by ICP-AES method.

The muck was treated by various chemicals for its dissolution prior to its analysis by ICP-AES and is described here elaborately. First of all the recovered muck was dried under IR lamp and after cooling an accurate weight of muck was transferred in a quartz beaker. Few mL of concentrated perchloric acid added to dried muck and was evaporated to dryness for the decomposition of the organic chemicals. The residue was then treated with another few mL of concentrated HCl for transition metals dissolution and was evaporated to dryness. Afterward, the residue was treated with concentrated HNO_3 and dried. Finally, the residue was dissolved in 10 ml of 3 M HNO_3 and suitable dilution of this solution was taken for analysis by ICP-AES. Similarly, sample blank was prepared without actual muck in it. Total 24 elements were determined by ULTIMA-2 ICP-AES instrument. Optimized instrumental working parameters are summarised in Table 1 [3]. The intensity measurements were made without background correction. The calibration curve of all the analyte elements were linear with correlation coefficient approaching unity. The measurement precision calculated on the basis of 10 replicates at 1ppm level was found to be better than 5% (RSD). The analytical result of muck sample is presented in Table 2. As can be seen from the table major elemental content of muck comprises Fe, Cr, Ni, Si, Na, Zn and P. These elements are coming mainly due to corrosion of process vessels/lines along with impurities of raw materials used in the process. The P (2.122%) content was assumed to be present mainly due to the degradation of TBP. The present method makes analysis of process solids by chemical treatment and characterisation using ICP-AES, which helps the process operation for taking corrective measures for removal of muck from different locations of process lines.

Table 1: Instrumental parameter

Plasma power	1100 (W)
Plasma Gas	12.0 L/min
Auxiliary Gas	Nil
Nebulizer gas	1.25 L/min
Nebulizer pressure	2.25 bar
Nebulizer type	Meinhard
Pump speed	15(rpm)
Sample uptake	1.0 ml/min

Table 2: Analytical Results

Element	% Content	Element	% Content
Al	0.0350	Mg	0.0285
B	0.0025	Mn	0.0383
Ca	0.0256	Mo	0.0035
Co	0.0005	Na	11.940
Cr	0.268	V	0.0013
Cu	0.0028	Zn	0.279
Fe	3.961	P	2.122
Ni	0.246	Zr	0.022
Pb	0.0035	Nb	0.0035
Si	0.137	Sm	0.135
Ti	0.010	Sn	0.017
U	2.105	Pu	0.001

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Signature of Regime Transition in Measurement of Axial Dispersion in Pulsed-Sieve Plate Extraction Columns

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Residence time distribution for the continuous and the dispersed phase in countercurrent flow in a pulsed sieve-plate extraction column is measured using the step-tracer technique using 1M KCl tracer. The aqueous phase is water and organic phase is n-dodecane. Axial dispersion coefficient is then calculated using the axial dispersion model. For the measurement of continuous phase (resp. dispersed phase) axial dispersion, water is used as the continuous phase (resp. dispersed phase). The sieve-plate column has diameter 5 cm and has 11 plates with 5 cm inter-plate spacing. The sieve hole diameter is either 3 mm or 4 mm. The fraction free area is either 12% or 20%. The axial dispersion coefficients are calculated for the pulse velocity in the range 4-12 mm/s and superficial velocities in the range 2.6-10.4 mm/s.

While the continuous phase axial dispersion coefficient E_c increases monotonically with the pulse velocity Af, though the variation is muted at lower values of dispersed phase superficial velocity V_d, the dispersed phase axial dispersion coefficient E_d has either an inflection point (at lower V_d) or a local maximum (at higher V_d). at pulse velocity 8 mm/s (for plates with sieve hole size 3 mm, Fig 1). For the plates with sieve hole diameter 4 mm, a local maximum is obtained for all V_d studied. (fFig 2). The non-monotonic dependence of dispersed phase axial dispersion on pulse velocity has been previously reported [1] for water/toulene and water/butyl acetate systems. The critical pulse velocity ~8 mm/s corresponds to the regime transition from the mixer-settler to dispersion by visual inspection. Hence, the study shows that a signature of regime transition can be observed in the measurements of axial dispersion in pulsed-sieve plate extraction column in a water/n-dodecane system. The measured axial dispersion coefficients are compared with the published correlations [2].

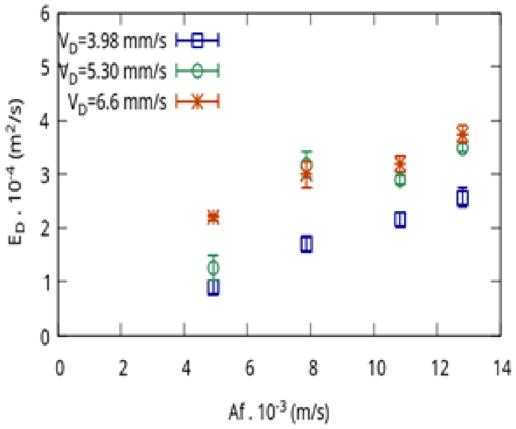

Fig.1 Af vs Ed for three different values of Vc for plates with 3 mm hole diameter. Vd is fixed at 2.65 mm/*s*

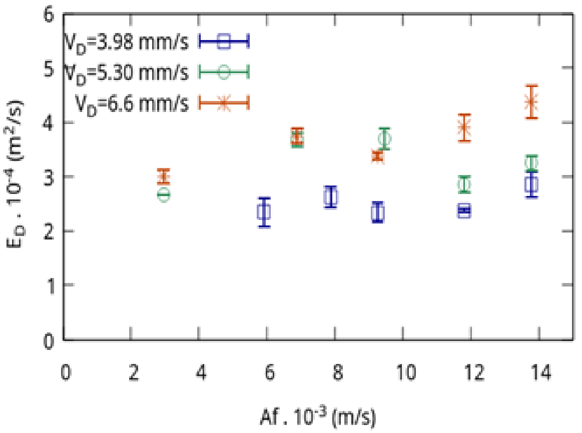

Fig 2: Af vs Ed for three different values of Vc for 4 mm hole diameter. Vd is fixed at 2.65 mm/s.

Keywords: Pulsed sieve-plate column, axial dispersion, residence time distribution

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Effect of Unequal Plate Spacing on Hydrodynamic Characteristics of Pulsed-Sieve Plate Extraction Columns

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Flooding capacity limits the maximum throughput of a pulsed sieve-plate column (PSPC) that are employed for extractive purposes. Normally the plates are vertically placed in an equispaced manner but it was suggested that the flooding capacity of a given PSPC may be enhanced by optimized placement of unequally spaced plates [1]. In particular, the plate spacing may be increased in the region of the column where the flooding is suspected to have been initiated. It is then interesting to consider hydrodynamic characteristics of a PSPC with unequally spaced plates. Here, we report on experiments on a small experimental PSPC with unequally spaced plates.
Initially a PSPC with 11 equally spaced plates (the "*Geo1*" internals) was run in a single-phase mode and its axial dispersion coefficient calculated. Column with diameter was 40 mm was filled with water and fraction of free area kept at 0.22. Plate spacing was 50 mm. The column was operated at superficial velocity of 5.3 mm/s to 9.3 mm/s. Tracer (1M KCl) was injected from over the topmost plate and tracer conductivity was continuously monitored below the lowest plate. The pulse velocity (*Af)* was varied between 5.5 mm/s and 12 mm/s. Following these measurements, the plates were moved such that the third and the fourth stage from the top had spacing of 75 mm. This required a loss of one stage since the column length was unchanged (the "*Geo2*" internals). Following the rearrangement of the column internals, the axial dispersion coefficient was measured again.

The axial dispersion coefficient *E* was not found to change significantly by placement of enlarged stages. Only for *Vc*=5.3 mm/s and *Af*=12.0 mm/s, there is a shift in *E* values that exceeds the error bars (Fig 1). For *Vc*=9.3 mm/s, the axial dispersion coefficient *E* for unequally spaced plates slightly exceeds *E* for equally spaced plates for all values of pulse velocity *Af* considered.

Thus, we conclude that while PSPC internals with unequally spaced plates may enhance the flooding capacity, the axial dispersion coefficient is unaffected.

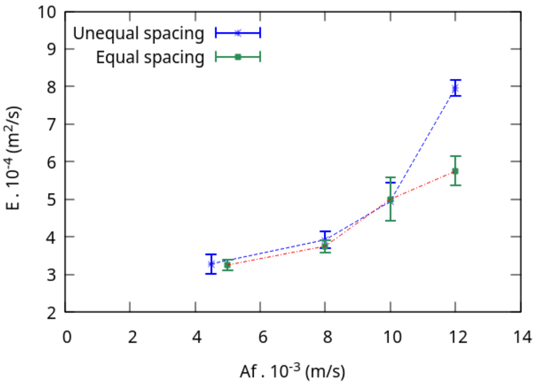

Fig.1 Axial dispersion *E* vs pulse velocity *Af* for V_C=5.3 mm/s for equal and unequal plate spacing

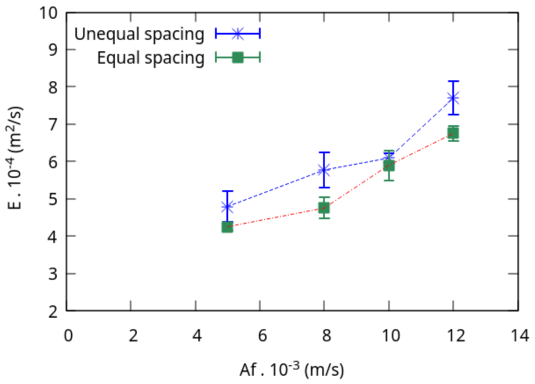

Fig.2 Axial dispersion *E* vs pulse velocity *Af* for V_C=9.3 mm/s for equal and unequal plate spacing

Keywords: extraction columns, axial dispersion, residence time distribution.

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Study of Recovery of Actinides from Aqueous Acidic Feed Employing Irradiated and Non-irradiated Polyethersulfone-TBP and DEHPA Composite Beads

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In the reprocessing facility handling and the management of the high active liquid waste (HLLW) are key challenges to the separation chemists. The heat generating and the long lived actinides (U, Pu and Am) need to be addressed wisely to ease the management of the HLW in the deep geological repository. Recoveries of these radiotoxic elements are highly essential to restrict their movement into the nature and thereby increasing the public acceptance of the nuclear energy. Several attempts were made to develop different extractants and methodologies in the view of separation of the actinides and the lanthanides from the wastes [**1**].

Hence, to get an appropriate method to overcome these drawbacks, we have attempted to develop novel polymeric composite beads encapsulating different extractants e.g TBP, DEHPA and a combination of them. According to the literature survey, these types of solvent encapsulated beads have high porosity with excellent thermal, hydrolytic and radiolytic stability. These beads can be loaded with target specific extractant for their applications in the extraction of the metal ions over multiple cycles. In the present scenario, we have chosen the polyethersulfone as the polymer backbone as it has promising thermal, radiolytic and hydrolytic stability and well compatibility with the loaded extractant [**2**].

These composite beads were studied thoroughly in irradiated and non-irradiated conditions. For all these beads morphological behaviour and the encapsulation of the ligand were assured with the help of the tools, viz., FTIR, TGA and SEM. For non-irradiated beads, in the batch study, mixed type beads showed promising extraction efficiency for U(VI) and Pu(VI) than the other beads. The attainment of the equilibrium was within 15 minutes. The kinetic data were tried to fit in various models and showed linearity in pseudo second order kinetics. Nonlinearity in Elovich model proved the absence of multiplayer sorption, which was also supported by pore diffusion model. The stripping study was performed using different complexing agents for U and Pu, respectively, and the best stripping agent was selected in the view of stripping capacity. To check the reusability of the composite beads, successive loading and stripping studies were carried out in 1M nitric acid medium in batch process. The procedure was continued for 10 cycles, indicating reasonably good stability of the beads for reusability purpose. The effect of the temperature on the distribution coefficient of the actinides was also evaluated for the mixed extractant encapsulated beads. These composite beads were employed for the highest metal loading capacity using Pu and the data were fitted into different isotherm models, viz., Langmuir, Freundlich, Temkin and D-R plots. These data also validated the presence of monolayer chemisorption phenomena.

The irradiated beads also showed promising extraction efficiency for the above mentioned actinides with the insignificant changes with that of the pristine beads. The equilibrium was reached within 15 min like the non-irradiated one. These beads showed good radiological stability and easy to strip with the complexing agents used for the non-irradiated beads. Highest metal loading capacity for these beads were performed using Pu and showed comparable results with that of the un-irradiated condition. Hence, these beads can be utilized for the extraction of the actinides from the high active liquid samples with the wide range of acidity of the feed solution with confidence.

Keywords: *Polyethersulfone, composite beads, extraction, actinides, mixture of TBP and DEHPA*

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Efficient recovery of plutonium from lab waste by TODGA-IL based extraction chromatography resin

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Extraction chromatography (EC) has been widely used as a versatile analytical separation method, showing the advantages of both the solvent extraction and the ion exchange methods [1]. In our previous study, diglycolamide (DGA) extractants along with ionic liquid [C_4mim.NTf_2] as diluent and Chromosorb-W as a solid support have been employed in EC resins for efficient uptake of tetravalent *f*-cations from acidic feeds [2]. Same resins needs to be evaluated for actual applications to nuclear waste processing such as lean effluents emanating from laboratory waste. In our laboratory, the plutonium product (PuO_2) samples were dissolved in nitric acid before those were analyzed for elemental impurities. For analyte preparation from this sample, major plutonium matrix was separated from the rest of the sample solution and the separated plutonium solutions were sent back to the process stream. The final analyte solution was analyzed by ICP-AES method for the determination of elemental impurities. As only 3–5% of the analyte solution was used into the plasma after aspiration, the balance (97–95%) goes into the drain. This drain solution contained small amount of plutonium which needed to be recovered before its final discharge into the waste. For the recovery of Pu, 100 mL of the above drain solution was taken in a clean 250 mL quartz beaker and was evaporated to dryness. 5 ml of concentrated HNO_3 was added to the dried mass along with a few drops of concentrated perchloric acid and the sample was evaporated to dryness for the decomposition of the organic chemicals. The residue was then treated with another lot of 5 ml of concentrated HNO_3 and 2–3 drops of concentrated $HClO_4$ and was again evaporated to dryness. The residue was dissolved using 15 ml of 3 M HNO_3 and few milligrams of $NaNO_2$ was added to it after which the solution was left for 20 min for the conversion of plutonium to its +4 state. This solution was passed through a preconditioned column containing the TODGA-IL impregnated EC resin to enable the Pu loading onto the column. For quantitative elution of Pu from the column, a solution containing 0.5 M oxalic acid in 0.5 M HNO_3 was used as reported in an earlier publication [2].

The procedure for the separation of Pu from lab waste solutions using the EC method is given above and summarized in Fig. 1. The solution obtained after pre-treatment of the lean solution (acidity: 3 M HNO_3) was fed to TODGA-IL resin column for the separation of plutonium. The feed solution was passed slowly (4–5 drops per minute) through the column, so that Pu got loaded onto the column quantitatively. Subsequently, the column was washed with the required amount (3–4 bed volumes) of 3 M HNO_3. For quantitative elution of plutonium from the column, a solution containing 0.5 M oxalic acid in 0.5 M HNO_3 was passed which efficiently eluted the loaded Pu from the column in a minimum volume with a sharp elution peak. Fig.1 shows the loading, washing and elution zones (marked with dotted vertical lines) for Pu^{4+} using the TODGA-IL resin column which were obtained by analyzing every mL of the eluted volume by alpha counting. It was found that more than 99% plutonium was recovered from the lab waste solution following this method before its final discharge.

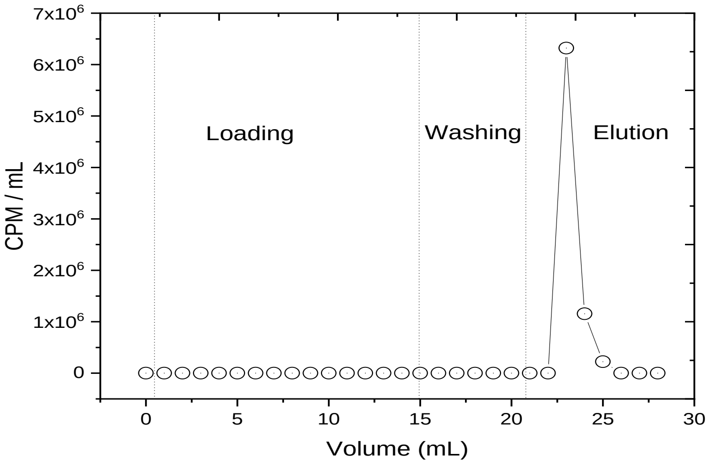

Fig.1. Recovery of Pu from lab waste using the TODGA- IL EC resin based column.

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Solvent extraction systems for separation of An(III) and Ln(III) based on N,O-donor ligands with hydrophobic anions

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The management of high-level waste generated during the reprocessing of spent nuclear fuel using the PUREX process (Plutonium Uranium Reduction EXtraction) is one of the key challenges in modern radiochemistry. The fractionation concept developed to reduce the total radioactivity of disposed waste involves the separation of Am(III), Cm(III), and lanthanides(III), which is difficult due to their similar physicochemical properties [**1**]

The most suitable method for addressing this issue in chemical technology is solvent extraction. Currently, one of the main research directions in this field is the development of highly selective ligands. Extraction systems based on N,O-donor ligands in combination with polar fluorinated organic solvents show promise [**2,3**]. For example, metanitrobenzotrifluoride **F-3** (Fig. 1.d) exhibits high solubilizing capacity for highly polar compounds, as well as chemical, radiation, fire, and explosion resistance. Additionally, enhancing the extraction parameters of the system by introducing anionic synergistic additives is of interest.

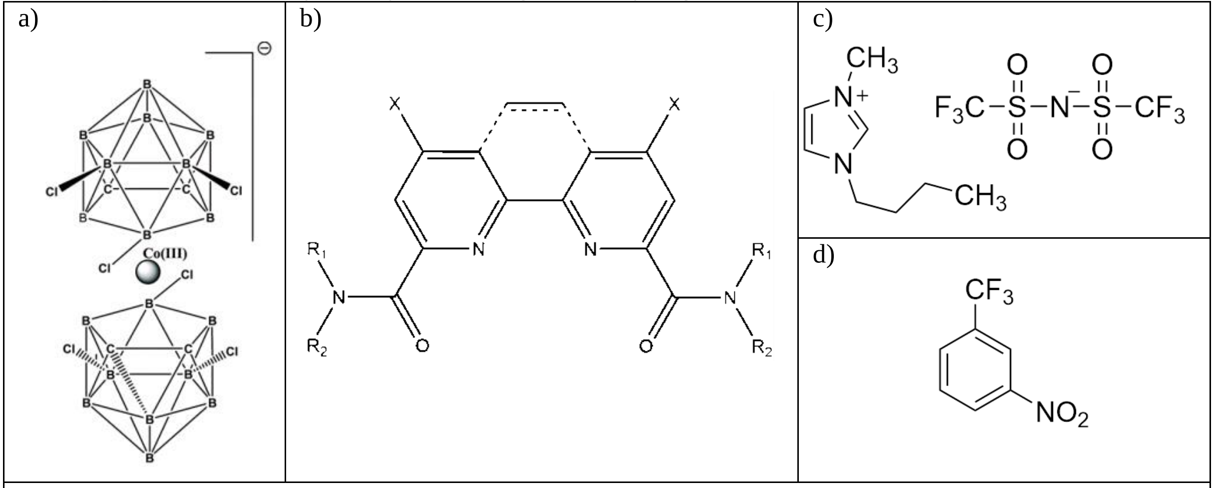

Fig. 1. Structures of chlorinated cobalt dicarbollide **CCD$^-$ (a)**, N,O-donor ligands **(b)**, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide **C$_4$mimNTf$_2$ (c)**: metanitrobenzotrifluoride **F-3** (d)

We hypothesize that by adding hydrophobic anions to the extraction system, it may be possible to increase the selectivity of extractants for actinides in the presence of lanthanides [**4,5**]. Consequently, in this study, we explored the possibilities of modifying extraction systems for the separation of *f*-elements based on diamides of 1,10-phenanthroline-2,9-dicarboxylic acid and diamides of 2,2'-dipyridyl-6,6'-dicarboxylic acid (Fig. 1. b) by introducing hydrophobic anions into the organic phase: chlorinated cobalt dicarbollide (**CCD$^-$**) (Fig.1. a) and bis(trifluoromethanesulfonyl)imide (**NTf$_2^-$**) using the ionic liquid C$_4$mimNTf$_2$ serving as the anion source (Fig.1. c). Special attention was devoted to establishing the mechanism of complexation and the forms of minor actinides and lanthanides in the studied systems. For this UV-visible titration, XRD-study, radiometric methods and DFT-calculations were used.

The work was supported by the Ministry of Science and Higher Education of Russia (Grant 23-73-30006).

Keywords: f-elements, solvent extraction. N,O-donor ligands, synergetic effect, hydrophobic anions

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Understanding the Extraction Behavior of Zr in Nitric acid Medium with TiAP and Comparison with TBP

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In the realm of solvent extraction processes, the formation of a third phase presents a significant challenge when extracting tetravalent metal ions like Zr(IV), Th(IV), and Pu(IV) using tri n-butyl phosphate (TBP). Previous investigations on alternative reagents revealed that tri iso-amyl phosphate (TiAP) exhibits a lesser tendency for third phase formation when interacting with these metal ions[1, 2]. Zr is being used in various stages of the nuclear fuel cycle, and it is separated from other metal ions using a TBP based solvent extraction process. It is essential to explore the extraction behavior of this element with TiAP-based solvent. In the present study, distribution ratios for the extraction of Zr were measured with various solutions of TBP and TiAP in n-DD from nitric acid (0.5–6 M) media. Results indicate that the $D_{Zr(IV)}$ increases with an increase in nitric acid concentration, as shown in Fig.1. Extraction data also indicate that the D values for the extraction of Zr(IV) with TBP is slightly higher than that of TiAP. Cross-current experiments using 1.1 M and 1.5 M solutions of both TBP and TiAP in n-dodecane(n-DD) with an aqueous phase containing about 15 g/L of Zr in nitric acid concentrations of 4 M and 6 M were also carried out. Interestingly, third phase formation was observed with Zr in the case of 1.1 M and 1.5 M TBP/n-DD during the extraction of Zr from 6M nitric acid feed solution, whereas no signs of third phase were detected with TiAP-based solvents. The stage profiles for the extraction of Zr from the aqueous feed solution in 4M nitric acid with 1.1M solution of TBP and TiAP in n-DD are depicted in Fig. 2. The concentration of Zr in the aqueous phase decreases with stage number, indicating that percentage extraction of Zr increases with stage number. As they both belong to the phosphate-based solvent family, the extraction efficiency of both TBP and TiAP is nearly similar. Dynamic Light Scattering (DLS) emerged as a crucial technique to study the aggregation behavior in solvent extraction systems. In this context, we examined the aggregation behavior of TBP and TiAP loaded with Zr(IV) using DLS. Results from the DLS experiments revealed that the aggregate size of the Zr-ligand complex was larger for TBP compared to TiAP. This discrepancy explains why TBP exhibits third phase formation with Zr during the extraction from 6M HNO_3 while TiAP does not form third phase. Moreover, the study indicated that the aggregate size of the Zr-TBP complex was more widely distributed, suggesting the formation of a less stable complex. In conclusion, TiAP, with its smaller aggregate size compared to TBP, proves to be a more suitable option for extracting tetravalent metal ions, thereby avoiding the formation of a third phase during solvent extraction.

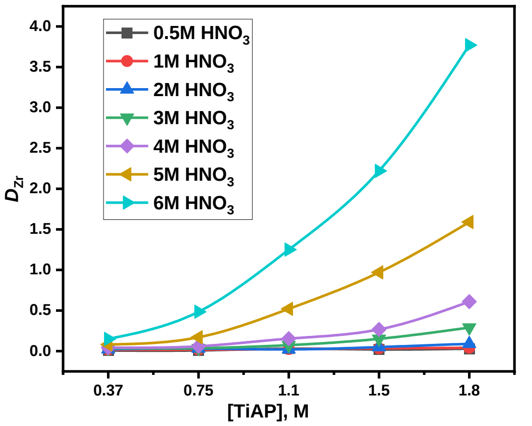

Fig.1: Variation of $D_{Zr(IV)}$ as a function of concentration of nitric acid and extractant

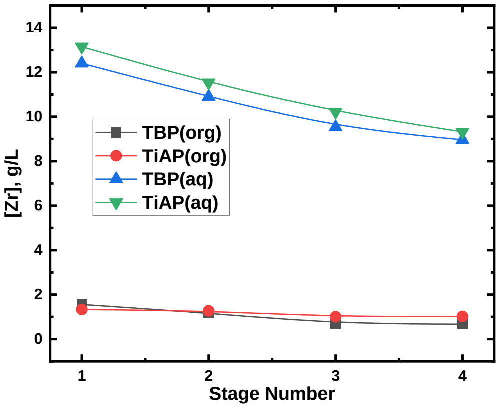

Fig.2: Stage profiles for the extraction of Zr by 1.1M solutions of TBP and TiAP in n-DD from 4M HNO_3

Keywords: Zirconium, TBP, TiAP, Solvent extraction

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Performance evaluation of a continuous precipitator with multiple impellers for the continuous precipitation of plutonium oxalate

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The reconversion process is an essential step in spent nuclear fuel reprocessing which involves the conversion of decontaminated uranium and plutonium nitrate solutions back into solid forms suitable for fuel fabrication. Current practice in nuclear-spent fuel reprocessing plants involves precipitation of plutonium as plutonium (IV) oxalate from the nitrate solution using oxalic acid in a batch or semi-continuous precipitator, followed by filtration and washing of the oxalate precipitate, which is then calcined to yield plutonium dioxide. A glove box adaptable continuous precipitator with mixed suspension overflow was developed for the precipitation of plutonium oxalate. Due to radioactivity of plutonium, a preliminary performance testing of the precipitator was carried out using cerium, a non-radioactive surrogate of Pu which is commonly used for the testing and development of Pu oxalate precipitators. Height equal to double the diameter was used for designing precipitator to increase the operating volume without affecting criticality safety. The operating volume of precipitator is about 1.76 L. Experiments were carried out using cerium nitrate and oxalic acid to identify the range of operating conditions required to yield mixed suspension overflow from the precipitator without any product classification. Solid concentration in the outlet stream as function of time during the experiment and the concentration of cerium oxalate inside the precipitator at the end of the experimental run and the corresponding particle size distributions were used as criteria for analyzing the performance of the precipitator. Residence time was varied from 2.5 min to 20 min and the impeller speed was varied from 250 to 1150 rpm. Cerium nitrate solution containing 7 g Ce / L was used for carrying out the experiments. Impeller speed up to 750 rpm at 20 min residence time, the cerium oxalate concentration in the outlet stream was inconsistent and substantial accumulation of cerium oxalate was observed inside the precipitator, and it was found that a minimum 1000 rpm was required at 20 min residence time to yield mixed suspension overflow. While varying the residence time from 2.5 min to 20 minutes at 750 rpm, it was found that the residence time must be less than 10 min to yield mixed suspension overflow without any product classification. Comparison of solid concentration and particle size in the overflow and the precipitator holdup had shown that minimum 5 residence times were required for the precipitator to reach steady state under the conditions identified for yielding mixed suspension overflow.

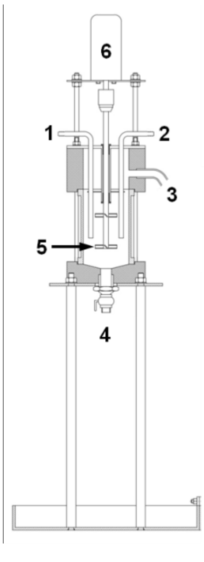

Fig 1: Schematic of continuous precipitator: 1 - feed; 2 - precipitant; 3 - overflow; 4 - drain; 5 - impeller

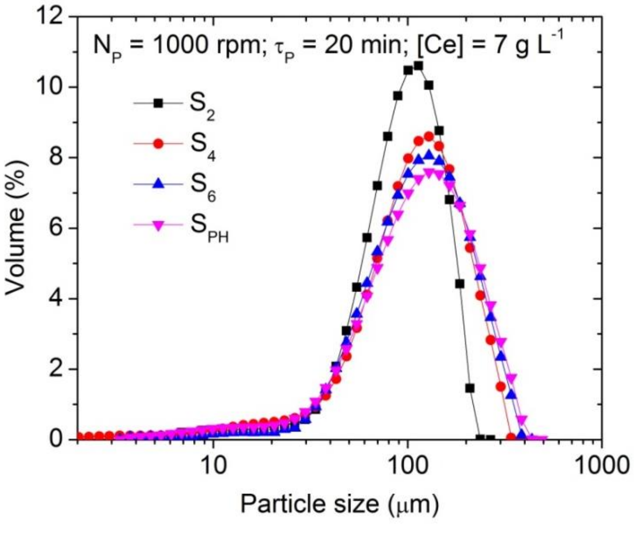

Fig 2. Particle size distribution of cerium oxalate in the overflow of the precipitator (S_2, S_4, S_6) as a function of time and the cerium oxalate present in the precipitator (S_{PH}) at the end of the run

Keywords: PUREX, spent fuel reprocessing, plutonium oxalate, reconversion, cerium

Mass transfer performance of Annular Centrifugal Extractor in presence of HDBP in 1.1 M TBP/n-DD solvent

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The Annular Centrifugal Extractor is a candid candidate for the Fast Breeder Nuclear Fuel reprocessing application. In CORAL facility ACE was successfully operated for more than two decades to extract U & Pu from the FBTR spent fuel. One of the major challenges in the FBR's Fuel reprocessing is solvent degradation. Dibutyl Phosphate (HDBP) is one of the major degraded solvent products and interferes during stripping operation. To understand the effect of HDBP, the Extraction and stripping experiments are conducted in 16 stages of ACE setup. In the present study, the extraction behavior of Uranium (1 g/L) in 1.1 M TBP (with 3 g/L HDBP)/n-DD was studied with dual acid scrubbing. Similarly, the stripping behavior of U (VI) from the loaded organic phase (1.1 M TBP with 3gpl HDBP/ n-DD, product from extraction experiment) was studied with single and dual feed strip acid flow conditions. The extraction experiment was conducted for about 2.5 hrs and results show that the ACE setup has reached the steady state condition within 20 mins. Later, the single strip acid flow experiment was conducted for 2 hrs and results show that given ACE reached steady state condition within 15 minutes. Similarly, the dual feed strip acid flow experiment was conducted for 6.5 hrs and results show that given ACE has reached the steady state condition within 15 minutes. The stage samples (both aqueous and organic phases) from all the above three experiments are collected and results are shown in below Fig 1 to 3.

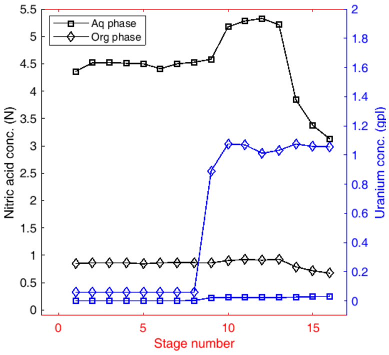

Fig. 1: U and acid conc. in the aq. and org. phases w.r.t stage numbers in the extraction experiment

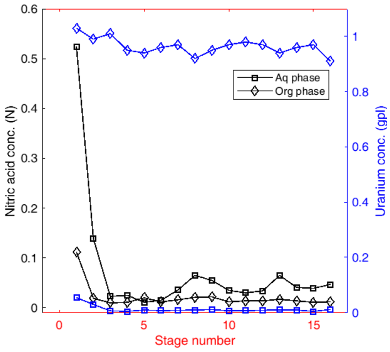

Fig. 2: U and acid conc. in the aq. and org. phases w.r.t stage numbers in the single strip acid flow stripping experiment

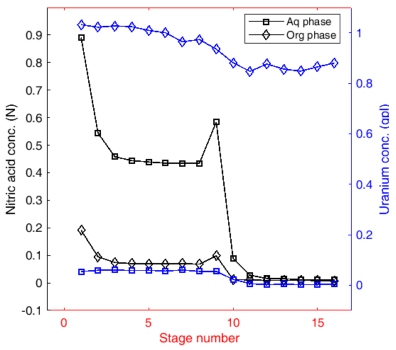

Fig. 3: U and acid conc. in the aq. and org. phases w.r.t stage numbers in the dual feed strip acid flow stripping experiment

From Fig. 1 it has been found that three counter-current stages are enough to complete the uranium extraction. In single strip acid stripping experiment result (Fig. 2) shows that U concentration in the organic phase is almost constant irrespective of stage number and not stripping out from the organic phase. Similarly, the dual strip acid stripping experiment result (Fig. 3) shows that U is not stripping out from the organic phase in the presence of HDBP. Uranium concentrations in the dual strip acid stripping experiment from 9th stage to 16th stage is slightly lower than that of 1st stage to the 8th stage. It is due to the introduction of 4N nitric acid in the 9th stage as per the Pu stripping flow sheet condition. It is concluded that the U is not stripping out from the organic phase in the presence of HDBP.

Keywords: Annular Centrifugal Extractor, Di-Butyl Phosphate, PUREX process, Extraction, Stripping

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In-situ stripping/partitioning of Plutonium in Annular Centrifugal Contactor in presence of HDBP in 1.1 M TBP/n-DD

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In FBR's fuel reprocessing by PUREX process, U and Pu are co-extracted in 1.1 M TBP/n-DD to effect decontamination from fission products and other trivalent minor actinides. In a subsequent partitioning step, U and Pu are separated by selective reducing of Pu(IV) to Pu(III). The uranous nitrate is one of the reducing agents that converts Pu(IV) to Pu(III). The Annular Centrifugal Contactor is used in the Fast Breeder Nuclear Fuel reprocessing application. One of the main advantages of ACC is less contact time and low solvent degradation. To understand the effect of HDBP and the performance of ACC, the Pu stripping/partitioning experiments are conducted in 16 stages of ACE setup. In this work, stripping/partitioning of 0.8 g/L Pu from 1.1 M TBP with 8 g/L HDBP/n-DD by uranous solution is studied in the ACC. Based on previous experiments from mixer settler, two experiments are conducted in the 16 stages ACE. Photographic view of 16 stages of ACE setup, experiment condition one flow sheet, and experiment condition two flow sheet are shown in Fig. 1 to 3 respectively.

Fig. 1: Photographic view of 16 stages belt driven ACC system

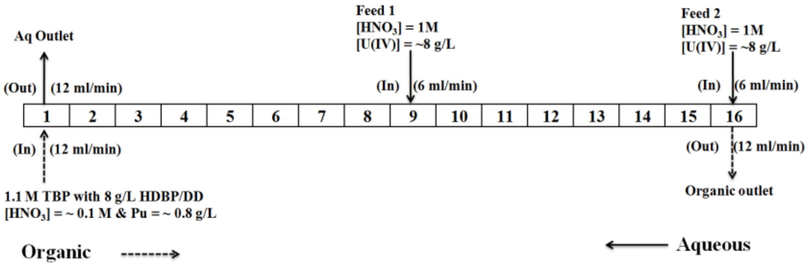

Fig. 2: Experiment one flow sheet condition

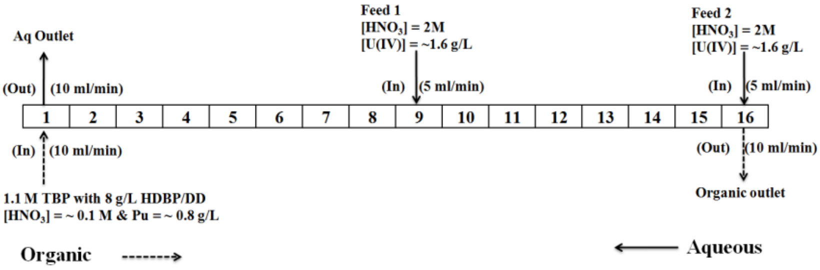

Fig. 3: Experiment two flow sheet condition

The Pu concentration in the organic outlet is < 8.0 mg/L for the first flow sheet condition and around 300 ppm for the second flow sheet condition. Further experiments are planned to optimize the flow sheet and also evaluate the mass transfer performance of ACC.

Keywords: Annular Centrifugal Extractor, Pu Partitioning, Uranous nitrate, Di-Butyl Phosphate, PUREX process, Pu Stripping

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Study on Cesium Tetraphenyl Boron in Geopolymer by FTIR spectroscopy

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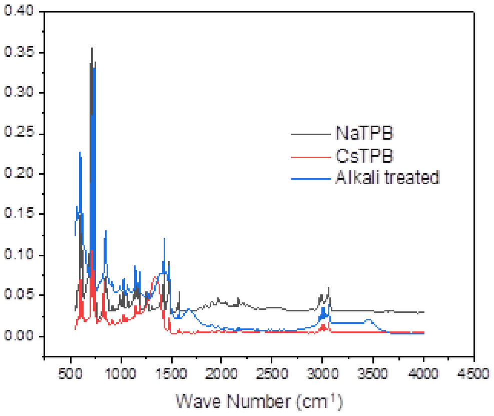
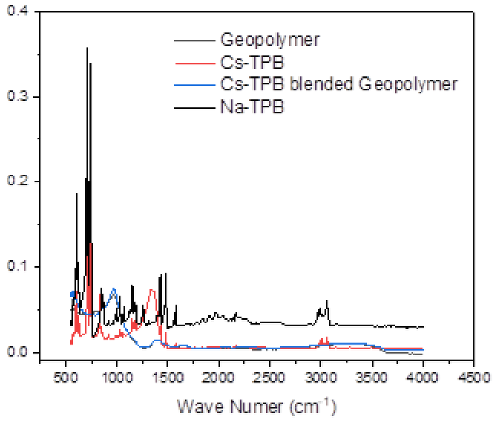
High active alkaline waste with high concentration of Cs^{137} and Cs^{134} is generated during the operation of reprocessing plant. Sodium tetraphenyl boron (Na-TPB) is found as a promising reagent to treat that waste by in tank precipitation of Cesium as Cesium tetraphenyl Boron (CsTPB)[1]. 0.005M sodium tetraphenyl boron was added to 5mL of waste at pH 9-10 with 1 Ci/L ^{137}Cs in 30% V/V. After overnight settling decontamination factor (DF) of 55 was obtained, suggesting good uptake for cesium. Management of the precipitate can be by incorporating in Geopolymer[2]. The present study intends to give light on the Cesium Tetraphenyl boron in precipitated and geopolymerised form.

0.005 (M) Sodium tetraphenyl boron (Na-TPB) solution was prepared in aqueous media. The solution was added to the inactive cesium nitrate solution in 30% V/V and kept for overnight settling. White precipitate of CsTPB was separated by filtration. 10% CsTPB precipitate was geo-polymerized in flyash-slag mixture.

Sodium tetraphenyl boron showed characteristic bands at 536, 604, 709.8, 740.9, 1425.8 and 1476.7 cm^{-1} by Fourier Transformation Infrared Spectroscopy (FTIR). The Cesium tetraphenyl boron showed a broad absorption band at 1369 cm^{-1} which was absent in NaTPB. This broad band may be due to hydrated cesium borate formation. Addition characteristics studied are required to differentiate between NaTPB and Cs-TPB. 12 N NaOH treated sample showed slight breakdown in structure with reduction in band around 1300 cm^{-1} and additional band after 1500cm^{-1}.

About 10% Cesium tetraphenyl boron was added to geopolymer formulation and product was analysed by FTIR. Characteristic gel feature observed in geopolymer between 3000-3500 cm^{-1}. Si-O-Al bond characteristic band of geopolymer observed at ~1000 cm^{-1}. No separate characteristic spectrum of cesium tetraphenyl borate was observed in the geo-polymerized product, which suggested that the gel has assimilated cesium into its structure. Borate degraded in the matrix has also entered into the aluminoslicate gel structure.





Keywords: High Active Waste, Cesium, FTIR

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Atomistic Understanding of Microstructure of Multi-component Glasses using Molecular Dynamics Simulations

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Immobilization of High Level Waste (HLW) in sodium borosilicate (NBS) matrix and further disposal into geological repository has been regarded as one of the best ways for long-term isolation of HLW from the biosphere. Blending of bivalents oxides in NBS glass produces a unique balance of improved glass properties. For example, addition of Barium oxide (BaO) extends the solubility of thorium and uranium in NBS glass matrix. Similarly, studies have reported that addition of only a very small number of ZnO might lead to a significant enhancement of various properties including chemical durability and mechanical strength. Addition of TiO_2 leads to decrease in viscosity of glass melts and improved mechanical strength of vitrified glasses. However, the origin of such an alteration is still unclear. The lack of understanding about the microscopic structure of these glasses and the local environment around doped ions is the center of the problem while dealing with the optimization glass composition for numerous applications. Considering that, extensive MD simulations have performed used to understand the role of composition for various structural and physical aspects. Significant amendment in short- and intermediate-range orders of glasses was captured with various short and medium range order parameters. Successively, the effect of microscopic structural modification on the macroscopic properties was analyzed in terms of mechanical strength, thermal stability and chemical durability has been evaluated. Order of connectivity illustrated that hydrolysis of glass will slow down with addition of either of $ZnO/BaO/TiO_2$ in the NBS glass matrix. Low R (Na_2O/B_2O_3) and high K (SiO_2/B_2O_3) of doped sodium borosilicate glass surface compared to bare NBS represents the more stable structure of glass surface will be produced for doped-NBS than NBS. During contact with water, Na^+ ions were less likely to leach out from glass to aqueous solution for doped NBS glasses. The enhanced chemical resistivity of doped NBS was also established from the increasing activation energy for diffusion of Na ions. The systematic study of linkage between network formers, ring statistics, diffusion dynamics and ion/water migration provides significant understanding of glass dissolution mechanism. The studies have been furthermore extended to explore the systematic study of structural disorder and depolymerization of NBS glass matrix under radiation. The analysis results show how amorphous structure of NBS glass matrix continues to evolve as a results of repeated radiation damage until the saturation threshold is achieved. Thus, the overall studies disclose many interesting microstructure, dynamics and thermodynamics of pristine NBS glass as well as doped-NBS glasses.

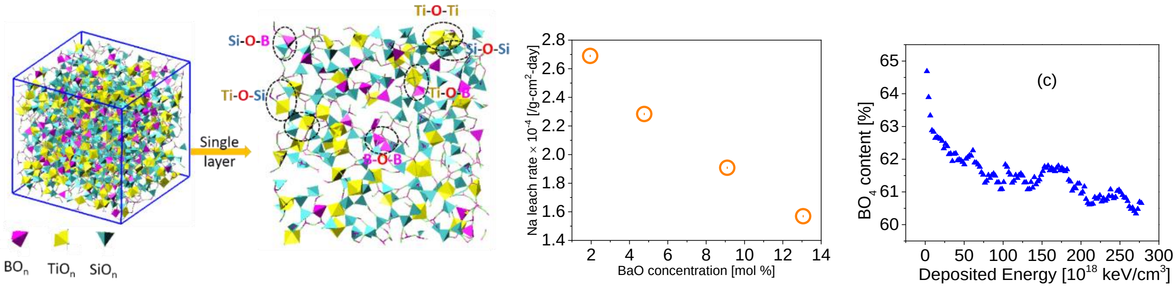

Fig. (a) Snapshot representing microscopic view and connectivity of glass atoms, (b) Leaching of sodium ions from glass to aqueous solution as function of BaO concentration in the glass matrix, (c) Reducing BO4 fraction due to BO4→BO3 conversion as function deposited energy during radiation exposure of glass.

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Development of electrochemical power source for routine recovery of actinide from solution phase

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In nuclear industry, the recovery of actinides from several aqueous and non-aqueous solution phases is essential for the advancement of non-aqueous processing, closed nuclear fuel cycle, to create samples for alpha spectrometry, and to produce irradiation low enriched uranium targets to fabricate radiopharmaceuticals as ^{99}Mo [1-2]. In this regard, the electrochemical method is a better option than the conventional method which uses chemical reagents for recovery. the electrochemical method has inherent advantages such as reduced criticality concern, minimization of liquid waste, ability to handle fuels after shorter cooling times, and avoid the use of chemical reagents and no generation of secondary wastes. Electro-deposition is an important electrochemical technique for depositing solid compounds on the surface of conductive substrates in a variety of industrial applications, including electroextraction, refining, and electroplating of metals and alloys. Although there is an electrochemical workstation for electrodeposition of actinides however it is costly, maintenance is also not possible in house due to SMD and programmed chips, and it is not easy to leave switched ON for overnight or when the electrolysis need several days for routine recover of actinides. Therfore, a simple electrochemical power source instrument is required for routine electrdeposition of actinides. As per requirement, we have developed an in-house equipment viz., programmable electrolysis instrument for both constant current and constant potential electrolysis. The specificity of this equipment is that it can works for several days without any interruptions. Each and every parts of the equipment are designed and fabricated in house such as constant current and voltage power supply, amplifier circuit, microcontroller based data acquisition and user interface software.

To check its feasibility for routine deposition, we have employed our developed instrument initially for recovery of uranium (50 mM at pH 2.5) from aqueous phase. The electrolysis of uranium containg sample was carried out in constant current mode at 15 mA for 24 hours using two electrode system with Cu plate as working electrode (1×1 cm) and Pt-gauge electrode as counter electrode. The black particle deposition on the Cu-plate surface was perceived, which was characterized by powder XRD. The results indicates the black deposited particles as UO_2. Therefore, the UO_2^{2+} through discharge process at Cu-plate deposited in the form of UO_2. Following the similar process, the uranium was recoverd from the aqueous medium and its recovery was found to be ~ 90%.

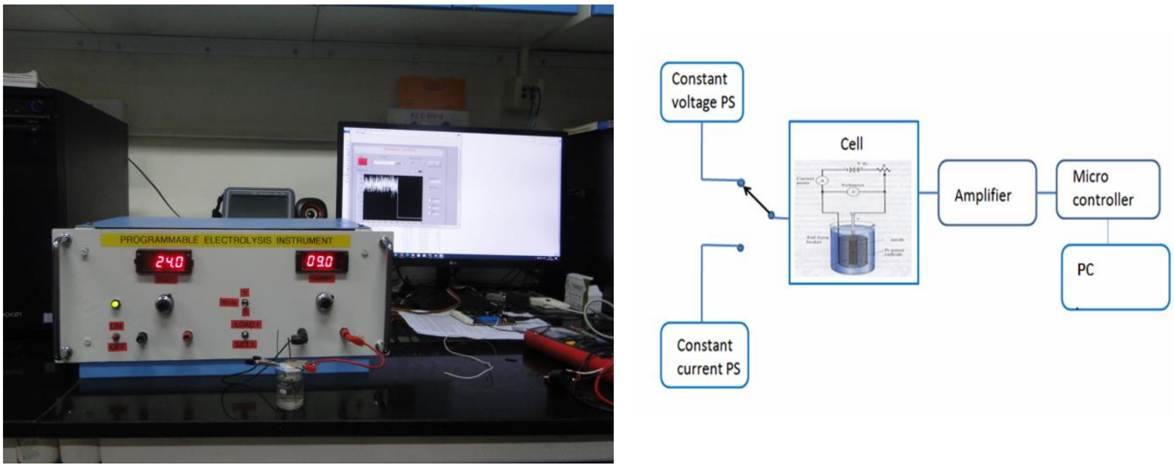

Fig. 1: (a) The Progammable electrolysis instrument for constant current and constant potential recovery of actinides (b) Circuit diagram for electrolysis

Keywords: *Electrodeposition, solution phase, constant current/potential source, actinides*

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Mechanisms of actinide and lanthanide extraction by polydentate N,O-donor ligands

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The isolation of actinide elements from spent nuclear fuel represents the most significant step in closing the nuclear fuel cycle. Developing new extraction systems to accomplish this is a challenging interdisciplinary task that draws on the expertise of radiochemistry, organic chemistry, physical chemistry, and coordination chemistry. One promising class of ligands for selective isolation of americium is N,O-donors, which exhibit a high rate of equilibrium establishment and the potential for a wide range of synthetic modifications. One important feature of this class of ligands is the use of highly polar aromatic solvents such as meta-nitrobenzotrifluoride (F-3), which significantly affects the form of complex compounds that pass into the organic phase as well as the likelihood of ion pair formation therein.

This report will focus on the possible extraction mechanisms of various subclasses of N,O-donor ligands, such as tri-dentate ligands using the example of pyridine diphosphonates as well as various tetradentate diamides of 2,2'-bipyridyl-6,6'-dicarboxylic acid, 1,10-phenanthroline-2,9-dicarboxylic acid and phenanthroline diphosphonates. As an integral part of the extraction system, we will discuss the extraction of nitric acid and its effect on the kinetics of extraction. We will also discuss the forms of the ligands in the organic phase and of nitric acid competition with *f*-element cations during extraction. At the beginning, we will present the forms of complex compounds, including $Am(NO_3)_3$, $Ln(NO_3)_3$, $UO_2(NO_3)_2$, and Np, in various oxidation states, obtained both in the solid state using SC-XRD and spectroscopic methods such as UV-Vis, XANES, EXAFS and NMR applied directly to the organic phases. Based on these data, we will discuss how the composition of the complex compounds influences trends in extraction selectivity. Additionally, organosoluble additives, such as ionic liquids and chlorinated cobalt dicarbollid, and their effects on the main extraction parameters and the forms of complex compounds, will be discussed.

It has been summarized that polydentate extractants, which are believed to have solution extraction mechanisms, can extract 5f- and 4f-elements by various mechanisms depending on the conditions (nitric acid concentration, initial form of element, type of substituent) in polar solvents. These elements can be extracted through various mechanisms, such as hydrate/solvate extraction, cation exchange, and anion exchange.

Acknowledgments: This work was supported by Russian Scientific Foundation (grant № 20-73-10076.)

Keywords: Actinides, lanthanides, solvent extraction

Investigation of Insoluble Precipitate in product Streams of PUREX Process: A Case Study

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In Purex process, the final purification and concentration of plutonium is accomplished either by solvent extraction or by ion exchange method. In research reactor fuel reprocessing, ion exchange method is employed. Prior to ion exchange, Plutonium nitrate solution obtained after partitioning step is conditioned for Pu concentration, valency adjustment and acidity in the conditioner tank and transferred to ion exchange feed tank. Quantitative conversion of Pu to its tetravalent state is a prerequisite before loading of Pu into anion exchange resin [1]. Conditioning of Pu valency to its tetra valent state is carried out with NO_2 gas and uranus nitrate. During plant operation some white-greyish precipitate was observed in few samples in conditioner tank and ion exchange feed tank indicating the precipitate might have formed during evaporation in the conditioner tank. In order to study the nature of precipitate and to assess the condition of its occurrence, sample is filtered, dried and a known quantity of precipitate is taken for investigation. Initially, 4M &10M HNO_3 was taken for dissolution of precipitate. Due to insoluble nature of precipitate in acidic conditions, 2% Na_2CO_3 was used for the dissolution of precipitate and leaching of Pu. The precipitate was not soluble completely in any of these reagents. However, three contacts of 2% Na_2CO_3 (4mL each) has resulted in three distinct solutions. Partial dissolution of precipitate was observed in first contact while solution became greenish in second contact indicating the presence of uranous nitrate. A clear solution was observed in third contact. Samples were analysed for Pu and dissolved organic present (dissolved TBP and DBP). Pu is assessed by radiometry in clear leach solution. Dissolved organic analysis is carried out by Gas Chromatography with standardized procedure [2].

Table:1 Experimental condition and findings of leaching and dissolution of precipitate

Sample No:	Reagents used	Pu in Leach Solution (mg/g)	Diss. DBP (ppm)	Diss. TBP (ppm)	Presence of Uranous nitrate
A & B	4M HNO_3	0.22	<10	<10	NO
	2% Na_2CO_3 -1st contact	2.0	<10	<10	NO
	2nd contact		**3000**	<10	**Yes**
	3rd contact		<10	<10	NO
C	2% Na_2CO_3 -1st contact	0.6	**793**	<10	**Yes**
	2nd contact		**466**	<10	NO

Thermal degradation of entrained purex solvent in the conditioner tank leads to the formation of DBP and the presence of dissolved DBP can be attributed to the formation of precipitate with uranus nitrate solution used for quantitative conversion of Pu into tetra valence state. Pu in acid leached solution was less whereas in carbonate leached solution, Pu might have leached along with uranous and dissolved DBP.

Keywords: Insoluble precipitate, dissolved organic, TBP, DBP, uranous nitrate

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Double U(VI) uptake by tetradentate ligands via solvation-anionic mechanism

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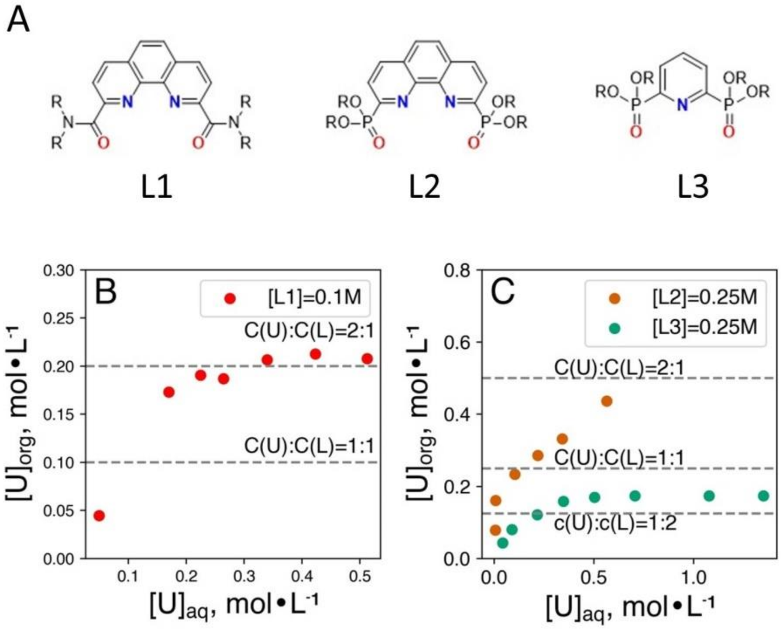
The process of complexation of organic ligands with actinides is the basis of nuclear technologies used for spent nuclear fuel processing. Phenanthroline- and pyridine-based ligands (Figure 1a) are promising for group separation of actinides. Previously it has been shown that such N,O-donor ligands efficiently extract U(VI) and Th(IV) at concentrations 10^{-7} – 10^{-3} mol•L^{-1} of metal in ligand excess to form 1:1 complexes $\{[UO_2\mathbf{L}(NO_3)]^+(NO_3)^-\}$. However, the composition and structure of complexes during extraction from highly concentrated industrial solutions (>0.1 mol•L^{-1}) in metal excess over ligand have not been determined. In an effort to fill this gap, we investigated the extraction of macroquantities of uranium by tri- and tetra-dentate ligands in F3 solvent.



First of all an isotherm for the extraction of uranyl nitrates were constructed (Figure 1b,c). Phenanthroline- based ligands demonstrated a high U(VI) capacity providing an U:**L1** and U**:L2** concentration ratio in the organic phase up to 2:1. A combination of spectroscopic methods (UV-vis, EXAFS, XRD) and DFT was used to demonstrate formation of $\{[UO2\mathbf{L}NO_3]^+[UO_2(NO_3)_3]^-\}$ complexes both in organic and solid phases. Moreover, it was shown that large-volume tetradentate ligands extract actinyl-cations via solvation-anionic exchange mechanism which is a combination of two already well-known mechanisms: solvation and ion-pair anion exchange mechanisms. Whereas, tridentate pyridine-based ligands extract U(VI) via solvation mechanism with formation of diverse complexes resulting in concentration ratio in the organic phase up to 1:1.5.

Keywords: Uranium, Extraction, Spectrophotometry, X-ray absorption

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-73-30006.

A Methodology for Recovery of Uranium from Graphite Mould Employed for Melting

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The reprocessing of spent metallic fuel from future FBRs is proposed to be carried out by the pyroprocessing method [1, 2]. In electrorefining of U, the dendritic cathode deposit was scrapped remotely and placed in a graphite crucible. A graphite crucible is employed for melting and consolidation of uranium in electrorefining process. After few cycles of operation, graphite mould develops cracks and hence needs to be disposed as solid waste. However before disposal, any remains of uranium present in graphite mould need to be recovered. The recovery of residual uranium from graphite mould was investigated by leaching in nitric acid medium. Graphite mould (2 kg) was characterized by gamma spectrometry and it reveals the presence of significant quantities of uranium in graphite mould. Graphite mould was also characterized by XRD, TGA and SEM-EDX analysis. SED-EDX also reveals the presence of significant quantities of uranium in graphite mould samples. It is important to recover such significant quantities of uranium from graphite mould. In this context initially recovery of uranium from graphite mould was investigated in different nitric acid medium such as 4 M and 8 M HNO_3 in small scale(10 g). Graphite mould was placed in nitric acid medium at 80°C for 8 h. Recovery of uranium from 4 M and 8 M HNO_3 was found to be in the range of 40% and 10-30%, respectively, indicating that the presence of uranium in graphite mould is not uniform at all the locations. Small quantities of yittrium and zirconium was leached from graphite mould in to nitric acid medium. Second dissolution was also performed to for complete recovery of uranium; and only <0.5% of uranium was recovered in second dissolution indicating that most of the uranium was leached into nitric acid medium in the first dissolution itself. In the later studies, bulk dissolution of graphite mould about 400-500 g in 4 batches was dissolved in 8 M HNO_3. The recovery of uranium in each batch is in the range of 5-17% (Table 1). The residual graphite from all the four batches was combinedly dissolved in 8 M HNO_3 in subsequent batches and the cumulative recovery of uranium increases from 1st batch to 6th batch (Fig.1) and the recovery of U in 6th batch is only about 0.04%. Fig.1 also reveal that about 86% of U was recovered in 1st batch itself and it decreases and flattens with batch number. The gross recovery of uranium was found to be around 13% from 2 kg of graphite mould. These studies indicate that uranium can be quantitatively recovered from graphite mould by successive leaching in nitric acid medium. The methodology demonstrated in the present study can be employed for recovery of uranium from graphite mould/crucibles in various stages of nuclear fuel cycle.

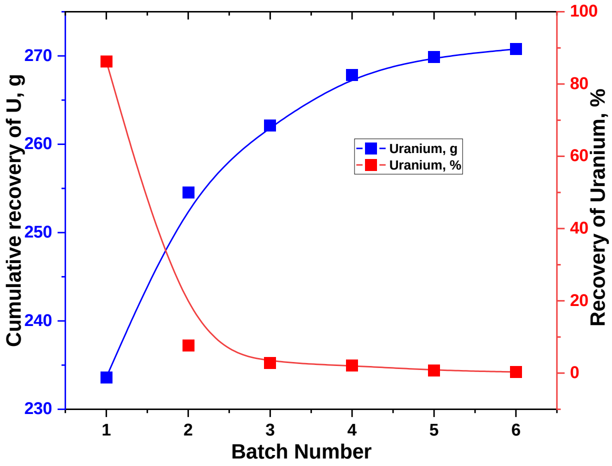

Fig.1: Cumulative and percentage recovery of U in different batches from graphite mould by leaching in 8M HNO_3 at 80°C for 8 h.

Wt. of Graphite mould, g	[U], mg/mL	Volume, mL	Total U, (g)	Uranium in graphite, (%)
467	260	100	26	6
479	131	250	33	7
577	308	250	77	13
560	391	250	98	17

Table 1: Batch wise recovery of U from graphite mould by leaching in 8M HNO_3 at 80°C for 8 h.

Keywords: Graphite mould, Characterization, Recovery, Uranium, Nitric acid

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Highly efficient Bimetallic Zn-Cd Metal Organic Frameworks for the Extraction of Uranium from Aqueous Solutions

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Nuclear power is increasingly vital for low-carbon energy production, with uranium serving as a key element in various nuclear energy processes. This underscores the growing demand for uranium(VI) in the long term. Despite the availability of multiple energy sources, nuclear energy stands out for its cleanliness and high power density. However, the disposal of radioactive elements like uranium presents environmental and health hazards. Efficient recovery of uranium(VI) from radioactive waste is crucial to mitigate these risks. While various adsorbents have been utilized for uranium(VI) extraction, the need for materials with high sorption capacity, regeneration ability, and surface area remains important. Metal-organic frameworks (MOFs) have emerged as promising solid-phase extractants due to their large surface area, tunable porosity, and high extraction efficiency[1,2]. This study focuses on the synthesis and characterization of bimetallic MOFs incorporating zinc (Zn) and cadmium (Cd) in different molar ratios, using 2-amino benzene dicarboxylic as a linker, namely Zn-Cd-MOF-1, Zn-Cd-MOF-1, and Zn-Cd-MOF-3, with Zn:Cd molar ratios 1:3, 1:1 and 3:1, respectively. Characterization techniques such as FTIR, Powder XRD, and TGA were employed to assess the synthesized MOFs' properties and thermal stability. The synthesized bimetallic MOFs were then utilized as adsorbents for U(VI) extraction across a pH range of 2-9. It was observed that the bimetallic MOF having Cd and Zn in the molar ratio of 1:3 exhibited excellent sorption ability of 99.6 % at pH 4, which is higher than other bimetallic MOFs as well as parent MOF, Cd-BDC-NH_2. Further, kinetics studies were performed with the MOFs which showed all the MOFs follows pseudo-second order kinetics where the MOFs attained saturation sorption capacity within 15 minutes showing rapid kinetics of U(VI) sorption on MOFs. Additionally, the effect of variation of concentration of U(VI) on the sorption capacity was studied, where the data revealed that the adsorption followed Langmuir adsorption model suggesting that U(VI) adsorption was essentially monolayer.

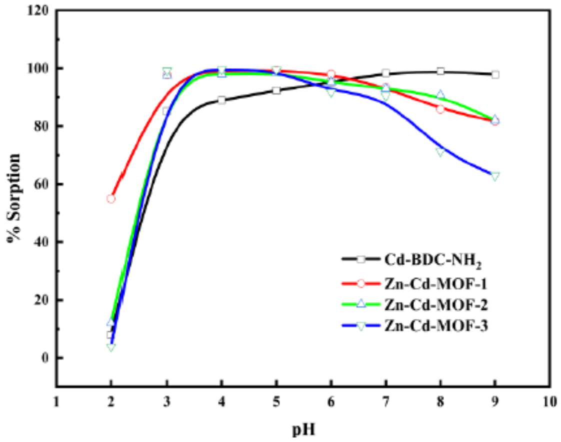

Fig.1: Variation of % sorption of U as a function of pH with parent and bimetallic MOFs and

MOF	Maximum Sorption Capacity(mg/g)
Cd-BDC-NH_2	185.9
Zn-Cd-MOF-1	214.1
Zn-Cd-MOF-2	212.3
Zn-Cd-MOF-3	214.4

Table 1. Maximum sorption capacity of parent and bimetallic MOFs at pH 5

Keywords: Bimetalllic MOFs, Synthesis, Characterization, Uranium, Sorption

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Multilayer-Graphene/ZIF-90 Composites for Efficient Extraction of U(VI) and Th(IV) from Nitric Acid Medium

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Metal Organic Frameworks (MOFs) are crystalline nanoporous materials consist of metal nodes connected with organic ligands. Zeolitic Imidazolate Frameworks (ZIFs) are a subclass of MOFs having high chemical and thermal stability, high surface area, easy pore architecture tunability, and facile synthesis [**1**]. ZIFs have various applications in gas storage, gas separation, catalysis, sensing, heavy metal removal, etc. Recently ZIFs have been employed in removal of rare earth elements [**2**]. In the present study, ZIF-90 (metal: Zn; Ligand: 2-Imidazolecarboxaldehyde) and its composite with multilayer-Graphene (ZIF-90G) having high surface area and interconnected pore network are synthesized, and used for extraction of Th^{4+} and UO_2^{2+} f-block elements in aqueous medium. The K_d values for Th^{4+} extraction were observed to be higher than UO_2^{2+}, which can be attributed to difference in their ionic potentials i.e. charge/size ratio of the actinides. The K_d values were found to continuously enhance with enhancement in pH value, reaching maxima at pH ~ 3–4 followed by a reduction at higher pH values [Fig. 1(a,b)]. The sorption was found to follow the Langmuir isotherm model involving monolayer coverage without any participation from neighboring groups. Pseudo 2nd order reaction kinetics was found to be predominantly followed, as seen from the linear regression analysis of the kinetics model [Fig. 1(c,d)]. The conditional extraction constants were found to reduce with the reduction in temperature confirming that the sorption processes were endothermic in nature. The changes in the Gibb's energy for these extractions were found to be negative indicating spontaneity of the biphasic separation. Using Positron Annihilation Lifetime Spectroscopy, it was confirmed that U(VI) is adsorbed throughout the pore network of ZIF-90 and ZIF-90G viz. aperture, central cavity, and inter-crystalline voids.

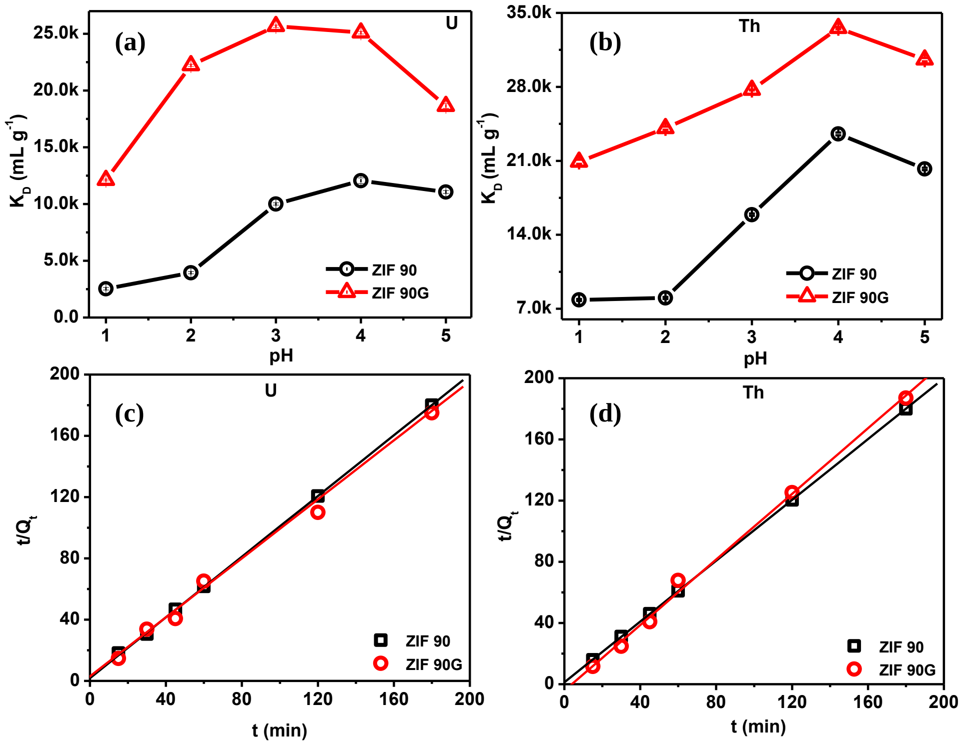

Fig.1: (a,b) effect of pH on K_d of U(VI) and Th(IV) extraction (c,d) regression analysis considering the pseudosecond-order kinetics.

Keywords: Zeolitic Imidazolate Frameworks, Isotherm, Kinetics, Soprtion

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Removal of ^{125}Sb by amino modified metal organic framework

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The high level liquid waste (HLLW) generated during reprocessing contains fission products along with traces of unextracted uranium, plutonium and minor actinides. Desired fission products and actinides are separated by solvent extraction process using TBP, 1,3-dicotyloxycalix-[4]-arenecrown-6 and T2EHDGA respectively at WIP, Trombay. After the removal of U, Cs, Sr, lanthanides and actinides from HLLW the raffinate solution mainly contains fission products such as ^{125}Sb and ^{106} Ru and some amount of unextracted Cs. Sequestration of radioactive antimony from nuclear waste is essential for the efficient and safe management of nuclear waste in the back-end fuel cycle operation. Among different remediation technologies such as adsorption, coagulation, co-precipitation and electro-deposition, adsorption process has emerged as a promising and viable approach due to its high efficiency, simplicity, economical nature and technical flexibility. In this study, we report the removal of Sb(V) by solid phase adsorption technique from nuclear waste solution given in **Table 1** with functionalized Zr-based metal-organic framework: UiO-66-NH_2. Amine functionalized MOF (UiO-66-NH_2) is synthesized and characterized by XRD spectra given in **Fig.1** and **Fig.2** respectively.It is used for sorption of ^{125}Sb from above said waste solution. UiO-66-NH_2 is made up of zirconium (IV) clusters interconnected by 2-amino terephthalic acid, resulting in a highly porous three-dimensional structure that is used for the extraction of ^{125}Sb from above said nuclear waste solution. Kinetics study **(Fig.3)** shows that ~20 min is required for attainment of sorption equilibrium signifies fast extraction kinetics. A batch scale study shows (**Fig.4**) that more than 85% of the ^{125}Sb along with ~20 % ^{106}Ru can be removed from the waste solution in a single extraction process.

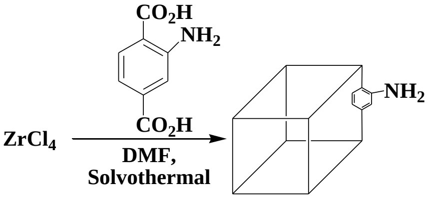


Fig.: 1. Synthetic scheme of UiO-66(NH_2)

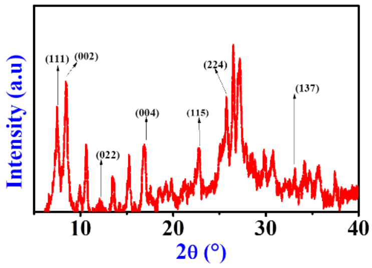


Fig.: 2. XRD spectrum of UiO-66-NH_2

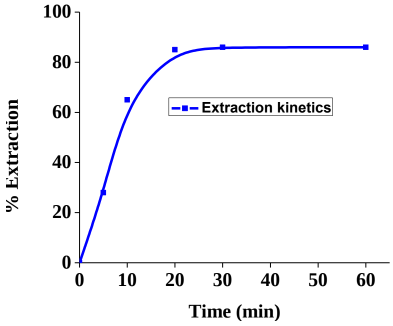


Fig.: 3. Extraction kinetics of ^{125}Sb

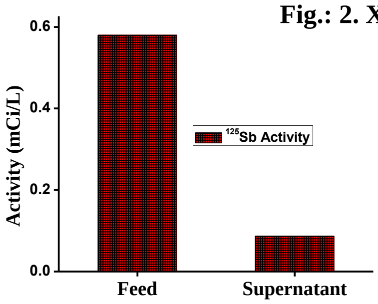
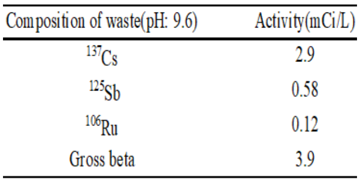


Fig. 4: ^{125} Sb activity in feed and supernatant



Composition of waste(pH: 9.6)	Activity(mCi/L)
^{137}Cs	2.9
^{125}Sb	0.58
^{106}Ru	0.12
Gross beta	3.9

Table:1. Waste constituents after actinide partitioning

Keywords: Reprocessing, Actinide, Lanthanide, MOF, Sorption,

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Solvent extraction studies with simulated U-Zr dissolver solutions using tri-iso-amyl phosphate and tri-n-butyl phosphate

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The present study is to explore the possible use of aqueous reprocessing method as an alternate to pyro-processing of metallic fuels [1]. In this context solvent extraction studies in the batch mode were carried out with simulated U-Zr feed solutions. Studies carried out in our laboratory have established that TiAP is a promising extractant for the processing of spent nuclear fuels [2]. The objective of the study is to understand the extraction and stripping behavior of U, Zr and various fission products such as alkali, alkaline earth metal ions, noble metals, molybdenum and lanthanides. Batch solvent extraction experiments (extraction and stripping) for the separation of U(VI) from Zr(IV) and fission products were carried out in cross-current mode. The concentrations of U and Zr along with other fission products in the feed solution were found to be 103.4 and 5.3 g/L in 4.2 M HNO_3. The concentrations of U and Zr in the 1st loaded organic phase (LO1) of 1.1M TiAP/n-DD were ~87.7 and 0.14 g/L, respectively, and the percentage extraction of U and Zr increases from 1st stage to 4th stage (Fig.1). The concentration of U in the raffinate was found to be about 0.05 g/L after four successive contacts. The quantitative extraction of U (99.9%) was observed within 4 stages. The extraction of Zr was about 25.5% and that of raffinate concentration was about 4.75 g/L. The concentration of some of the fission products (Zr, Ru and Lns) in the raffinate (obtained after 4 successive contacts) was found to be lower compared to that of aqueous feed indicating that these fission products are extracted into the organic phase in the 3rd and 4th stages of extraction. The concentrations of U and Zr in the loaded organic phase (mixture of LO1 and LO2) were found to be around 56.5 and 0.38 g/L, respectively in 0.63 M HNO_3. The concentration of Zr in the aqueous phase was below detection limit (<0.2 µg/mL) from stage 2 onwards, indicating the possibility of complete stripping of Zr in the first stage. The concentration of U decreases from 1st stage to 4th stage and the concentration of U in the lean organic was found to be 0.47 g/L after four successive stripping contacts and the stripping of U was >99%. These studies indicated that loss of U into the aqueous phase during extraction and lean organic streams during stripping is negligible. These studies may pave way for the development of alternate route of metal fuel reprocessing using PUREX process.

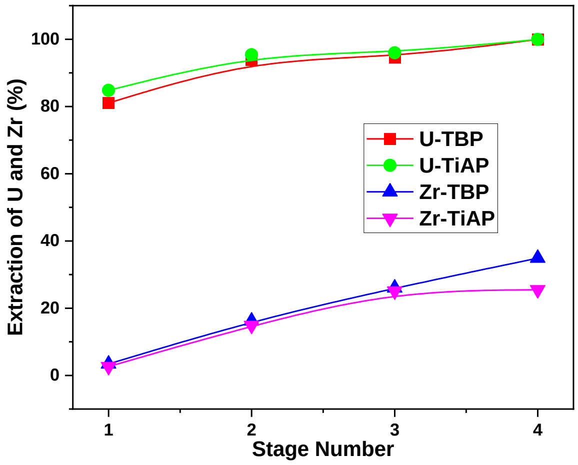

Fig.1 Percentage Extraction of U and Zr using 1.1M TalPs in n-DD from simulated U-Zr solution in cross-current mode

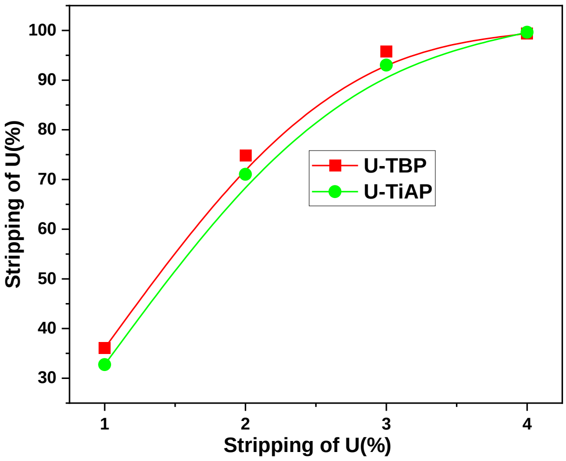

Fig.2 Percentage stripping of U from loaded 1.1M TalPs using 0.01M HNO_3 in cross-current mode

Keywords: Simulated U-Zr, TBP, TiAP, Cross-current, Extraction, Stripping

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Selective Recovery of U(VI) over Am(III) Employing Polyethersulfone-Tri-isoamyl Phosphate Composite Beads from Aqueous Acidic Feed

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In our progressing world human development is indexed by energy consumption. For the sustainable development of our society energy security is the most important factor. As of now although fossil fuel based energy is the prime source of energy, it is depleting in nature and also endangering our Earth. Here, nuclear energy is considered as the carbon free cleanest form of energy, which generates minimum amount of waste and therefore nature benign. Most of the nuclear reactors used worldwide for commercial power production is of PHWR type and the technology for the reprocessing of its spent fuel by PUREX process is also well established. Reprocessing of spent fuel is very important for closing of nuclear fuel cycle, maximization of utilization of fissile uranium and plutonium and minimization of discharge of nuclear waste in to the Nature.

In PUREX process, tri-butyl phosphate (TBP) is the key solvent used which possesses many benefits as well as few drawbacks too. The major challenges associated with the TBP are its third phase formation and degradation under a strong radiolytic and hydrolytic condition. Due to these many physico-chemical and hydrodynamic properties of the solvent alter which result in poor decontamination of the products and difficulty in the PUREX process. Hence, in search of a potential alternative for TBP, separation scientists have developed tri-iso-amyl phosphate (TiAP) [1, 2] a higher homologue of TBP. Tri-iso-amyl phosphate holds many benefits of TBP and also mitigates/eliminates the drawbacks of TBP [1, 2]. In this aspect we have attempted to develop polyethersulfone based composite beads encapsulating TiAP with a purpose to fortify its stability and extraction capability. We have demonstrated its preparation method in our earlier paper. Also we have utilized it for the recovery of Pu(IV), which showed promising extraction efficiency. Hence, it was planned to deploy the ligand encapsulated bead for the extraction of U(VI) and Am(III) from the acidic feeds.

The TiAP encapsulated beads were characterised using the tools, viz., SEM, TGA and FTIR to check any morphological changes within the matrix. These beads showed promising extraction efficiency for U(VI) over Am(III) in a wide range of acidity. The equilibrium condition reached within 15 minutes. The kinetic data were fitted into pseudo second order kinetics, implying monolayer chemisorption phenomena. The monolayer sorption was verified by employing Elovich model and pore diffusion model. The beads showed good stability towards reusability over 10 cycles of absorption-desorption. The highest metal loading was evaluated using both U(VI) and Eu(III), a surrogate of Am(III). The data was fitted into different isotherm model, viz., Langmuir, Freundlich, Temkin and D-R plot for the confirmation of the sorption phenomena. The beads were irradiated to check any radiological derogation. After irradiation also, those beads were morphologically characterized by different tools and by means of distribution coefficient, kinetics and sorption. After irradiation, not so significant changes were observed for the distribution coefficient value in comparison to that of the pristine one. These beads can be employed to the selective recovery of U(VI) from a mixture of U(VI) and Am(III), waste streams over a wide range of acidity.

Keywords: *Isoamyl phosphate, Polyethersulfone, composite beads, extraction, U(VI) and Am(III)*

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Separation of Neptunium (Np) from High-level Liquid Waste Using TBP and Aliquat-336 Systems

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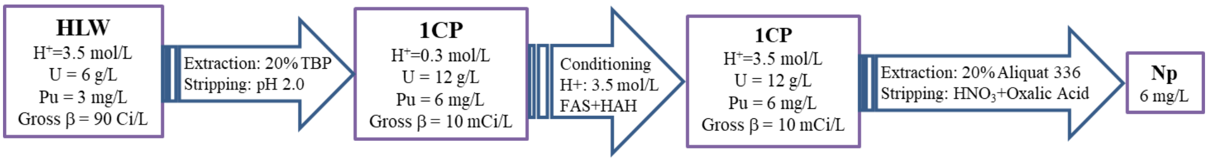
Separation and determination of neptunium isotopes (^{237}Np and ^{239}Np) present in the high-level liquid waste (HLW) are essential for accountability and understanding their behavior in vitrified waste products. In addition, ^{237}Np finds application in producing ^{238}Pu (used as a heat source in RTGs) by neutron activation. Though the content of Np is lesser than ^{241}Am [1] in high-level liquid waste (HLW), the long half-life of ^{237}Np ($t_{1/2}$: 2×10^6 y, α emitter) and short half-life of ^{239}Np ($t_{1/2}$: 2.3 days, β-γ emitter) constitute a significant concern due to its daughter products. Hence, the study was initiated to quantify the Np in the HLW solution by extracting heavy metals using TBP-dodecane and separating Np using aliquat-336 systems. The composition of the solvent systems used in the present study for heavy metal and Np separation is 20%TBP and 20% aliquat-336, respectively. The demonstrated scheme with the characterization and conditions are shown in Scheme 1.



Scheme 1. Np separation from HLW

The resultant product solution was analyzed using an HP-Ge gamma-ray spectrometer, alpha spectrometer, and thermal ionization mass spectrometer. The alpha and mass spectra results are shown in Fig. 1. Alpha and mass spectral analysis confirms the separation of ^{237}Np from HLW. The recovered Np-237 from HLW is 6 mg/L. HP-Ge gamma-ray analysis (not shown here) revealed the extraction ^{239}Np and was further confirmed based on decay.

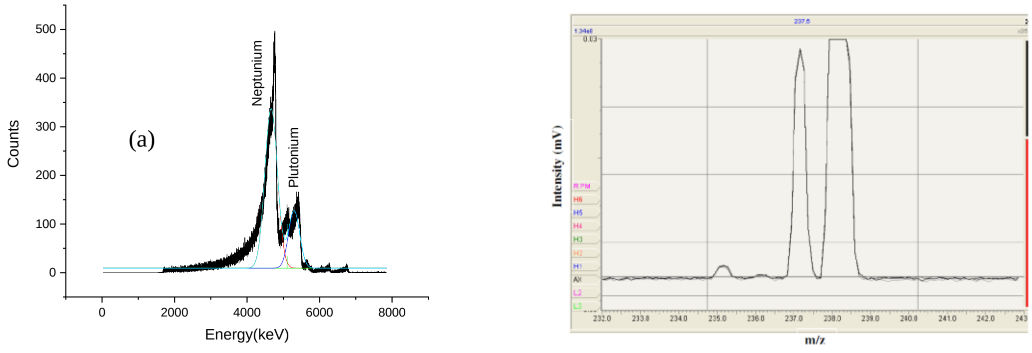


Figure 1. (a) Alpha and (b) Mass spectrum of the Np-product solution

Keywords: Neptunium, HLW, Aliquat 336, TIMS, ^{239}Np

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Desorption of ^{210}Po from Uranium Mill tailings

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Uranium mill tailings containing traces of radioactivity is customarily stored in engineered impoundments for its long-term storage and safety. The migration behaviour of radionuclides and metals in the tailings is controlled by a complex set of chemical process and biophysical processes occurring within the soil such as chemical speciation, ion exchange and adsorption phenomena, complexation and redox reactions etc. Leaching study of ^{210}Po was carried out in the uranium mill tailings to ascertain the desorption characteristic of polonium from the waste depository to adjacent environment. Standard sampling protocols were followed to make sample representative. Different leaching media were selected for this study. Rain water, 0.5N HCl and 1N Ammonium Acetate were used with contact time of 30, 60, 120 and 240 and 360 min. 10 g of tailings < 1mm size fraction with leachant was taken in a reaction vessel with a ratio of 1:10. The reaction vessel was constantly agitated during the leaching period. After the required reaction time the leachant liquor was filtered with 0.45 µm filter paper and evaporated to dryness. The evaporated sample was converted to HCl medium by repeated addition and evaporation with 0.5 M HCl. Auto deposition of ^{210}Po was carried out in the leached liquor as described in earlier sections. Uranium mill tailings containing 2.8 Bqg^{-1} of ^{210}Po was used for the desorption study. Ultrapure water prepared by Millipore water purification system was used for the experiment.

Desorption study with ultrapure water did not provide encouraging results as the medium was de-ionized and ionic strength plays a vital role for desorption. Nearly 1% desorption of polonium occurs during the study. When the leaching media was changed to ammonium acetate the amount of ^{210}Po removed was increasing with increase in reaction time. A maximum 6% activity found to be leached when reaction time was 360 min. This also helps in finding the exchangeable fraction of polonium present in uranium tailings. For lab scale studies the leaching time is kept in minutes. On the basis of ammonium acetate medium, the exchangeable fraction of ^{210}Po was varied from 0.6 to 6.5 % (Fig. 1). The change of extraction media to 1N. HCL results in maximum 31.8% (Fig. 2) leaching as it forms soluble chloride complex in hydrochloric acid solutions, probably as $PoCl_6^{2-}$ or $PoCl_4^{2-}$. The presence of other ionic species such as Fe and Mn in tailings may influence the desorption mechanism is to be studied further.

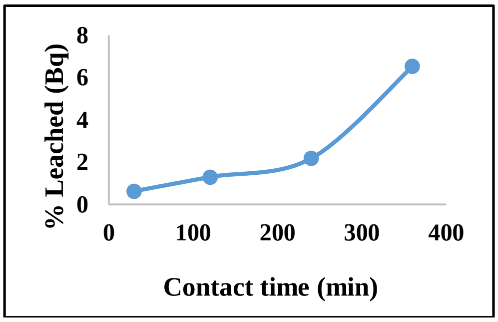

Fig 1: Desorption of ^{210}Po using 1N Ammonium Acetate

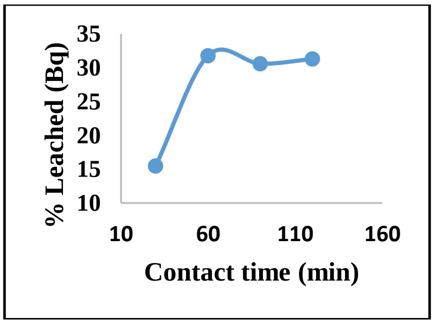

Fig 2: Desorption of ^{210}Po using 0.5 N HCl

Keywords: Mill tailings, Polonium, desorption

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Development of a novel High Efficiency Structured Packing Catalyst for hydrogen isotope separation by hydrogen-water exchange process

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Hydrogen-water chemical exchange is a solid catalyzed heterogeneous reaction involving the exchange of hydrogen isotopes between gas and liquid phases intimately contacted in multifunctional packed bed reactors for carrying out Liquid Phase Catalytic Exchange (LPCE) and Combined Electrolysis and Catalytic Exchange (CECE) processes. These processes are adopted for hydrogen isotope separation in different nuclear fuel cycle applications like the production of heavy water and deuterium depleted water and for the decontamination of heavy water effluents from nuclear reactors [1]. The separation efficiency and overall process economics is functionally depended upon the availability of a high performance hydrophobic supported platinum catalyst tailor-made for offering high catalytic activity and long term stability in varying process conditions. This paper describes the indigenous efforts for the development of a novel structured packing module made of SS 304 stacked with corrugated wire mesh strips of varying heights and lengths with the alternate wire mesh strips coated with high activity hydrophobic catalyst (Pt on carbon aerogel with PTFE/PFA as hydrophobic agent and binder) developed in-house [2]. The novelty in the structured packing modules thus assembled is attributed to the densely packed hydrophobic catalyst and hydrophilic bare SS wire mesh strips alternately arranged as typically required for gas-vapour reaction and gas-liquid scrubbing taking place simultaneously in LPCE reactors. Standard wire mesh of suitable size with desired Pt on Carbon Aerogel loading was selected from kinetics experiments carried out using spinning catalyst basket batch reactor for screening and selection. The synthesis of catalyst particles yielded a mean cluster size of 2-3 nm of active metal platinum. The control on size of Pt cluster is essential to improve the fractional availability of free active metal for a given loading in the catalyst mix. This improvement in platinum dispersion implies more availability of catalyst surface per unit reactor volume resulting in the reduction of overall separation plant reactor volume for a desired degree of isotope exchange and thus improving the process separation efficiency. The wire mesh hence selected exhibited an intrinsic reaction rate of 3.8 mol/kg(cat)/min at 333 K, relatively superior to similar supported catalysts reported in literature for hydrogen-water isotope exchange reaction. Structured packing modules of 3” diameter and different heights are fabricated for process optimization studies. It is estimated relative to 20% Pt on Carbon Aerogel (CA) loaded on Dixon ring mixed packed bed reactor, the catalyst loaded structured packing modules contains 3 times more active metal Pt per volume of packed bed reactor, due to the high specific surface area of structured packing. This resulted in the reduction of overall height of the exchange columns designed for decontamination of radioactive heavy water effluents for the desired separation load. Owing to the modularity, high porosity and low pressure drop characteristics, these packing modules can be deployed for easy scale-up with high liquid processing capabilities.

Deuterium Isotope Exchange Reaction between Water Vapour and Hydrogen Gas

$HDO_{(v)} + H_{2\,(g)} \leftrightarrow H_2O\,(v) + HD\,(g)$ (on supported Pt catalyst)

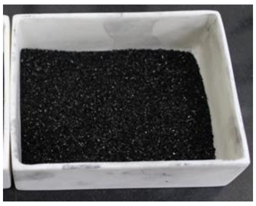
Fig. 1.
Carbon Aerogel support synthesized for making Pt-CA powder

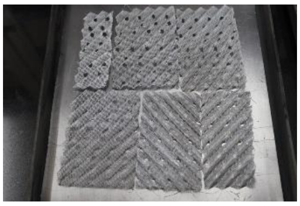
Fig. 2.
Uncoated SS Wire Mesh Strips after corrugation and punching

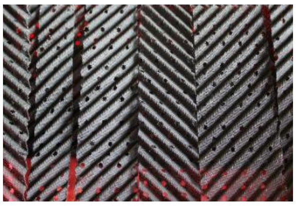
Fig. 3.
SS wire mesh strips after catalyst coating and reduction

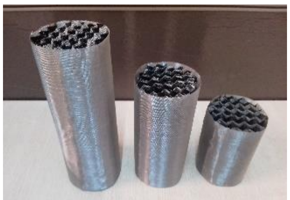
Fig. 4.
3” OD structured packing modules after assembly with heights

Keywords: Hydrophobic catalyst, Structured packing, LPCE, CECE

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Theoretical Study of Heavy Water Production by CECE process

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Heavy Water is one of the most essential components of the nuclear power programme in India. Due to the rapid deployment of reactors taking place in India of PHWR type, production of heavy water needs also to increase to cater the growing demand of heavy water by the reactors. There are many processes available worldwide for the production of this valuable product. One of these processes which has been studied widely for the production of heavy water is the Combined Electrolysis and Chemical Exchange (CECE) process. Although this process has the advantage of a very high separation factor and mild operating conditions, the process did not gain much application because of the slow kinetics of the chemical exchange reaction. Due to this reason, other processes gained popularity over the course of time namely Hydrogen sulfide-Water exchange or Ammonia-Hydrogen exchange process, etc. Now due to the development of an efficient wet proof catalyst for the hydrogen-water exchange process and the recent advancements in the field of electrolysers, interest has been renewed to explore the possibility of production of heavy water by this method. In this process, a huge amount of hydrogen is also released in the tails with a much lower deuterium content. This hydrogen can be also sold as product along with heavy water. *Due to the growing hydrogen market (global hydrogen demand is expected to grow to 129 million tonnes by the year 2024 (Osman et al., 2022), this process can become an economical one if this process gets coupled to hydrogen generation (Hammerli, 1980).* In this study, feasibility of this CECE process for the production of heavy water has been studied. For studying the feasibility of this process, a model for an ideal cascade for the production of heavy water has been developed which is to deliver a capacity of 250 tons of heavy water per annum of 10% isotopic purity. This 10% isotopically pure heavy water is to be further enriched to reactor grade purity using conventional means which contributes to a very small percentage to the overall cost of heavy water. Using the model, diameter and height of the columns, volume of the catalyst required for this exchange, capacity of the electrolysers and recombiners required, and amount of feed required for achieving the desired production have been evaluated. It has been seen for each kg of D_2O produced of reactor grade quality, the amount of energy required in the CECE process is equal to 66GJ per kg of heavy water considering the hydrogen produced. Here the energy required is to be supplied in the form of electrical energy instead of heat energy as required by the other process used worldwide. These results are used to calculate the operating and capital cost of the plant which are finally used to determine the cost of heavy water produced by the above process.

Keywords: Combined Electrolysis and Catalytic Exchange (CECE), Heavy Water, Chemical Exchange, Wet proof Catalyst, Elecrolyser

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Liquid-liquid extraction of oxalic acid by alkyl phosphine oxide ligand

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Zirconium is an important structural and cladding material in nuclear industry. Zr metal should contain less than 100 ppm hafnium for use in nuclear reactor due to opposite nuclear properties. Zr and Hf coexist in nature so their separation is important for use in nuclear reactor. Numerous techniques that are effective in separation of Zr and Hf are multiple crystallization, solvent extraction and extractive distillation. In India TBP based solvent extraction method is used to produce nuclear grade Zr [1]. However, an in-house synthesized Alkyl Phosphine oxide (APO) ligand has been identified which provides better separation factor and extraction compared to TBP at less feed acidity [2]. Zr is transferred from aqueous phase to organic phase as zirconium nitrate during extraction. Zr loaded in organic is stripped using oxalic acid in APO based process [3]. It is observed that during stripping free oxalic acid gets transferred from strip solution to organic phase. Thus, lean organic obtained after stripping cannot be recycled to extraction. It is important to understand the liquid-liquid extraction of oxalic acid by APO to understand the chemical interactions during stripping.

In the present study, liquid-liquid extraction batch studies are conducted to establish effect of concentration of oxalic acid and concentration of APO on distribution coefficient of oxalic acid, as shown in figure 1. The stoichiometry of oxalic acid extraction by APO was determined via slope method. It was found that 2 moles of APO are required for extraction of a mole of oxalic acid. Investigations are done to calculate equilibrium constant for APO-oxalic acid system. Loading of 1M APO is found experimentally by providing cross-current stage-wise contact with 0.5 M oxalic acid. The loading capacity of 1 M APO for oxalic acid is found to be 0.53 M oxalic acid and is shown in figure 2. The oxalic acid loaded in APO is stripped with water and effect of concentration of oxalic acid and APO are investigated.

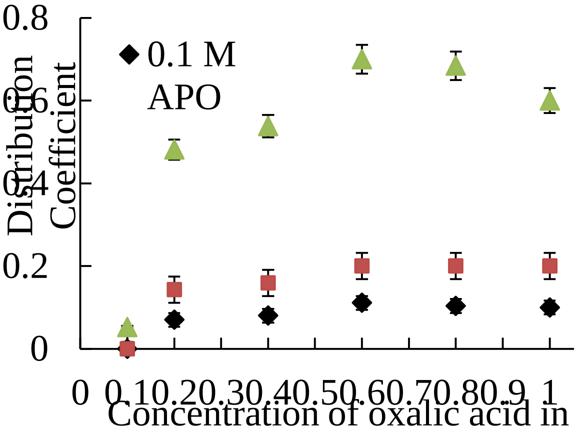

Figure 1: Effect of oxalic acid concentration in feed on distribution Coefficient; O:A 1:1, Equilibration time : 15 mins

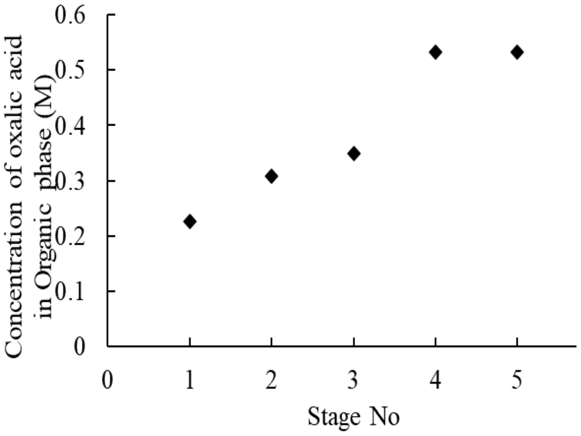

Figure 2: Loading capacity of alkyl phosphine oxide; Organic phase: 1 M APO in 50:50 DD:ID; Aqueous phase: 0.5 M oxalic acid; equilibration time in each stage: 15 mins

Keywords: Alkyl phosphine oxide ligand, Oxalic acid, Solvent extraction

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Investigation on Aqueous Partitioning of Tri-n-Butyl Phosphate in Solvent Extraction of Radionuclides

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Tri-n-butyl phosphate (TBP) is one of the major extractant used in spent fuel reprocessing in nuclear industry to extract uranium and plutonium from the fission products using PUREX process. TBP is also employed in TRUEX and THOREX processes for extraction of actinides from spent fuel solution [**1**]. TBP diluted in n-dodecane or other hydrocarbon diluent (3-40%) is used as organic phase in these processes. Due to its water solubility, TBP also extracted into the aqueous phase along with actinide ions. The presence of TBP in aqueous stream is undesirable due to its violent reaction during evaporation [**2**]. Therefore, study of aqueous partitioning of TBP during above solvent extraction processes is of sufficient importance to minimize the loss of TBP from organic phase. Although several literature reports are available on the solubility of TBP in aqueous solution in various extraction condition, there is lot of ambiguity in the solubility data which ranges from 6.0 to 0.3 g/L [**3**].

In the present study, aqueous partitioning of TBP in pure and diluted form were studied as a function of concentration of TBP, acidity, presence of salts and temperature. The variation of solubility of TBP during extraction of actinides and lanthanide ions are also studied. The concentration of TBP in aqueous phase were measured indirectly from the amount of phosphorus in the aqueous phase using ICP-OES spectrometer. Fig. 1 showed that aqueous partitioning of TBP increases with increase in TBP concentration. The solubility of TBP was 0.8 g/L at 30% TBP in n-dodecane and 2.3g/L at pure TBP. The solubility of TBP increased during extraction of actinide and lanthanide ions up to 200 mg/l and then decreased (Fig. 2).

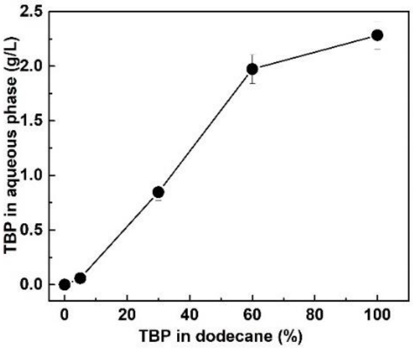

Fig. 1: Effect of TBP concentration in aqueous partitioning of TBP

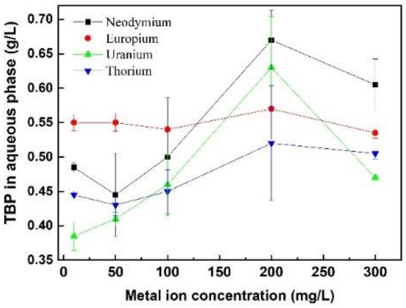

Fig. 2: Effect of metal ion extraction in aqueous partitioning of TBP

Keywords: Tri-n-butyl phosphate, Aqueous partitioning, Actinide-lanthanide extraction, Solubility of TBP

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3. A. Wright, P. Paviet-Hartmann, Sep. Sci. Technol., 45 (2010) 1753.

Separation, Adsorption and Recovery of Ytterbium(III) with Crown Ether Grafted Resin

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Rare earth elements (REEs) are being widely used as important strategic materials in various high-tech fields, such as modern communication, aerospace developments, petrochemicals, energy, etc., and as essential components in lasers, lenses, electronics, phosphors, fiber optics, superconductors, high-intensity lightning, coloured glasses, refining industry, nuclear technology, etc. [**1**]. Ytterbium, a heavy rare earth element, has another application apart from above common uses of REEs in the field of nuclear medicine. Carrier-free ^{177}Lu radioisotopes which is emerging as an important candidate for broad therapeutic use, such as treating prostate, breast, colon, and brain cancer, is obtained from ^{177}Yb produced by neutron capture on ^{176}Yb stable isotope with natural abundance of 12.9% [**2**]. Due to the shortages of supply of REEs, it is necessary to recover Yb(III) ions from secondary sources like rare earth waste water. Among various methods of recovery, adsorption based processes are found to be more effective because of the low operational cost, high efficiency for removal of metals present in diluted effluents, ease of operation, and generation less secondary wastes. In view of this, in this work polymethylacrylate (PMA) resin were grafted with benzo-15-crown-5 (B15C5) and the functionalized resin, PMA-B15C5 was evaluated for the separation of Yb(III) ions from aqueous solution. Adsorption of Yb(III) were studied with varying pH, contact time, feed metal ion concentration and temperature. The selectivity of Yb(III) separation in presence of other light and heavy REE metal ions was studied. The recovery of Yb(III) ions from simulated waste water solution was also investigated.

4-Amino-benzo-15-crown-5, synthesized from B15C5, was coupled with carboxylic acid group of PMA resin to prepare PMA-15C5 which was then characterized using FTIR and TGA analyisis. The pH dependent Yb(III) adsorption om PMA and PMA-B15C5 data showed that adsorption increases with increase in pH from 1 to 3 and then decreases showing maximum adsorption at pH 3 (Fig. 1). The speciation of the Yb(III) due to hydrolysis at higher pH may be responsible for the weaker interaction of the trivalent lanthanide ion with the surfacr of the PMA and PMA-B15C5. Fig. 2 depicts the variation of adsorption capacity of the adsorbents with equilibrium metal ion concentration in solution. PMA-B15C5 showed doubled adsorption capacity compared to PMA indicating the role of crown ether group for the complexation of Yb(III) ions. The equilibrium data were fitted with Langmuir and Freundlich isotherm model and found to be fitted better with Langmuir model indicating surface complexation mechanism for the adsorption process.

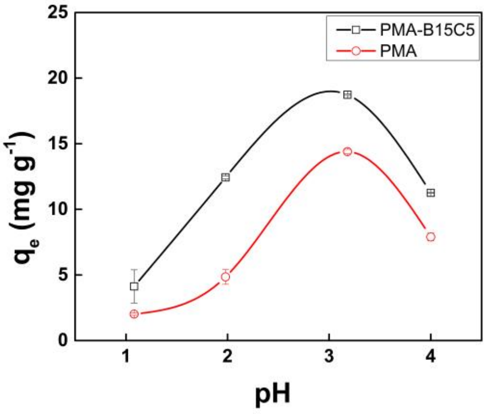

Fig. 1: Effect of pH on the adsorption of Yb(III) by PMA and PMA-B15C5

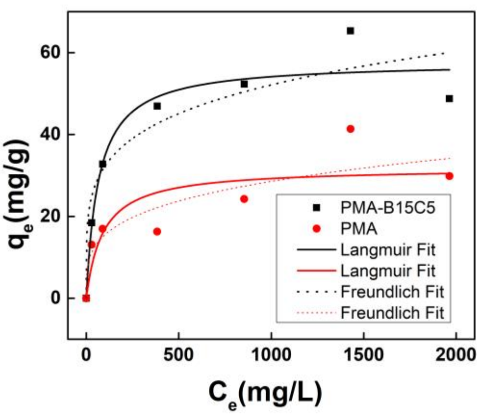

Fig. 2: Adsorption isotherm plots for the uptake of Yb(III) by PMA and PMA-B15C5

Keywords: Ytterbium adsorption, Crown ether grafted PMA resin, Adsorption isotherm, Adsorption selectivity

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Liquid-Liquid Extraction (LLE) of Uranium using n-n-Dihexyl OctaneAmide (DHOA) Solvent: Prospects and Challenges

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Refining of Sodium Di-Uranate (SDU) concentrate from Tummalapalle (T) Mill through TBP based LLE or solvent extraction (SX) process is little challenging[1] due to (i) third layer formation in liquid interphase, (ii) loss of solvent with raffinate, (iii) froth formation during ADU precipitation, (iv) low density of product UO_3 etc. Here, as an alternative to TBP, DHOA has been studied to assess the extraction behavior specifically with Tummalapalle source SDU slurry feed materials. Here, we have compared its performance w.r.t. TBP for processing of slurry from SDU(T) and purity of the product UNPS. Effects of solvent degradation due to radiolysis/ hydrolysis on process were also studied. Also, the mass transfer rates and the settling rates have been studied under identical process conditions and compared with the behavior with TBP. Mass transfer experiments were carried out in separating funnels of 125 mm size using 1M DHOA and 30% TBP (both supplied by HWB) in n-dodecane as solvent. Mass transfer rates and settling rates were measured in 100 ml glass beakers with magnetic stirrers. Gamma irradiation of solvent was given for 40 Gy. For effect of alpha irradiation, the solvent was kept saturated with natural uranium for 6 months (120 gpl U, 0.15 N HNO_3). It has been found that (i) UNPS obtained using DHOA is as pure as the UNPS produced through TBP extraction. (ii) Also, there is no third layer formation in any stage and there is no appreciable loss of solvent through the raffinate stream. (iii) There is no observable effect of solvent degradation on process due to hydro/ radiolysis. (iv) The density of product UO_3 is in the acceptable range. However, (i) There is a tendency to form a second organic layer in high U saturation in DHOA. (ii) The overall mass transfer rate is slower for DHOA than TBP. (iii) The settling rate for DHOA is slower than the TBP, especially for higher saturation levels of U.

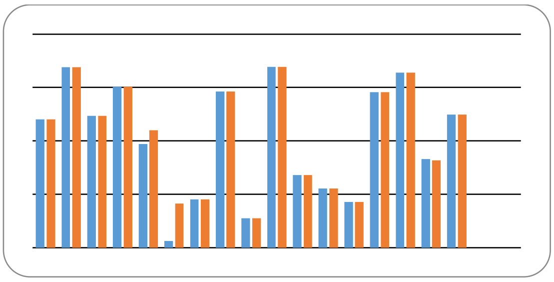

Fig. 1: Comparison of Selectivity of DHOA and TBP extraction process while processing SDU (T)

Fig. 2. Settling behavior of TBP (top) and DHOA (bottom) solvents while processing SDU (T)

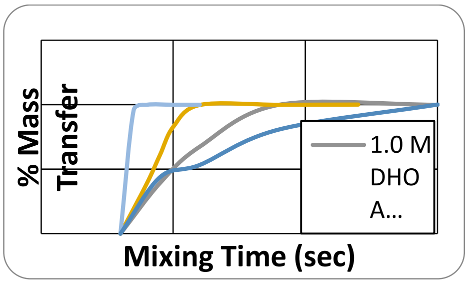

Fig. 2: Mass transfer rates comparison for TBP and DHOA

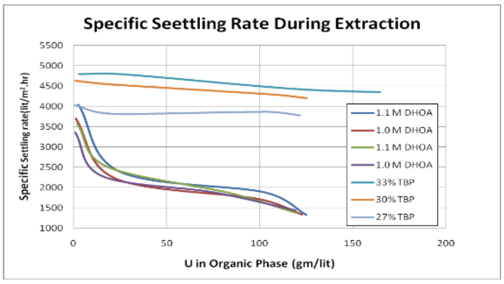

Fig. 3. Settling rates comparison for TBP and DHOA

Based on above it is found that DHOA is a very promising candidate for refining of uranium, especially for SDU (T) material. However, owing to its slower mass transfer rates and settling rates, a new set of mass transfer equipment (such as pulsed column where only one settler is required per operation) need to be deployed.

Keywords: DHOA, TBP, Uranium, Solvent, Liquid liquid extraction.

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Kinetics of solvent extraction of Am(III)/Eu(III) pair by N,O-donor phenanthroline ligands

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One of the most studied and effective methods of separation of multicomponent systems such as high-level waste is solvent extraction. To date, two main types of extractors are used in industry: centrifugal extractors and sump mixers. Small contact time of phases in centrifugal extractors allows to reduce radiolysis of components of extraction systems, however, it increases the requirements to the extraction rate.

It is necessary to develop laboratory methods to compare and quantify extraction rates and mass transfer rates. This approach will help to select the extractants that provide rapid extraction of the target component and the establishment of structure-property relationships for ligands. Microfluidics has been used to quantitatively describe the kinetics of solvent extraction (see Figure 1).

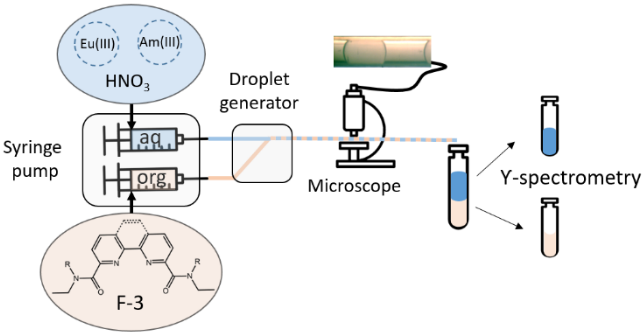
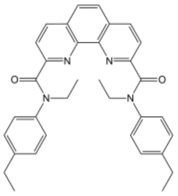
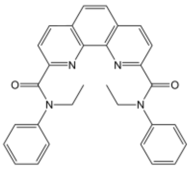
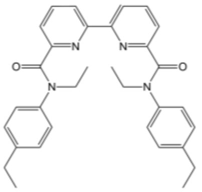


Fig 1 Microfluidic solvent extraction system

One of the most promising extractants for the separation of f-elements is N-, O-donor ligands. Due to the combination of soft nitrogen atoms and hard oxygen atoms separation of cations with similar chemical properties such as An(III)/Ln(III) is possible.

The ligand BiPy-PhEt were chosen as an extractant. Structural modifications of the ligands included replacement of the bipyridyl fragment with a phenanthroline fragment, which can affect the mobility of the backbone and increase the number of conformations. The substituent at the amide group (PhenEt/Phen) was also varied (**Error! Reference source not found.**).

Structure			
Abbreviation	Phen-PhEt	Phen-Ph	BiPy-PhEt

In this work, we quantitatively investigated the kinetics of extraction of Am(III)/Eu(III) pair for a selected series of extractants and determined the rate constants of the process. The structure-kinetic properties relationship (interfacial transfer rate constant for Am(III) and Eu(III)) for this series was established and the influence of structural modifications on the extraction rate was shown. Also, we measured interfacial tension to characterize the interface in the studied systems.

Also we have shown how protonation affects the kinetics of extraction and ligand pre-organization. For this purpose, we determined Am(III)/Eu(III) mass transfer constants in different media in a system with BiPy-PhEt using a microfluidic setup. To explain the differences in the extraction kinetics and the relation of kinetic parameters to the pre-organization of the ligand, we obtained single crystals of protonated and de-protonated forms of the ligand, used NMR spectroscopy to describe conformational transformations

The complexation study of this work were supported by Russian Science Foundation (Grant 23-73-30006)
Keywords: microfluidic extraction, extraction kinetics, Am(III)/Eu(III)

Extraction of uranium (VI) employing TBP and room temperature ionic liquid as diluent

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Room temperature ionic liquids (RTILs) have potential applications in nuclear fuel cycle [1] as a replacement for volatile organic compounds (VOCs) used as solvents in the reprocessing process. RTIL possess attractive properties, [2] such as thermal stability, solubility for organic and inorganic materials and insignificant vapor pressure. This paper outlines the results towards applications with respect to recovery of uranium from feed nitric acid solution by tri-n-butyl phosphate (TBP) in RTIL. To recover valuable U from waste like rejected fuel pins, they are dissolved in nitric acid and the resultant feed solution is processed for extraction with typical TBP/dodecane organic phase. In this study we aim to utilize IL as a diluent and assess the performance of TBP in ionic liquid. Here, the extraction behaviour of U (VI) by TBP dissolved in the ionic liquid, namely 1-butyl-3-methylimidazolium hexafluorophosphate ($BMImPF_6$) and 1-octyl methylimidazolium hexafluorophosphate ($OMImPF_6$) is carried out. The effect of important parameters such as the concentrations of nitric acid and TBP, on the distribution ratio of U (VI) is reported.

The extraction studies were carried out at ambient temperature in 1:1 organic to aqueous phase ratio. First, the extraction of U(VI) as a function of TBP concentration in the ionic liquid phase was studied by equilibrating 0.5 ml of 0.2 M TBP/ $BMImPF_6$ and 0.2 M TBP/ $OMImPF_6$ with 0.5 ml of sample UNS for three hours. The feed UNS has nitric acid conc. around 3-3.5 M. Same experiments were carried out in IL with variation of TBP concentration from 0.4M to 1.1M. Fig. 1 shows that in both the medium extraction of U increase steadily with increase in TBP conc. Next, extraction of U (VI) was studied as a function of nitric acid concentration by equilibrating (for three hours) 0.5 ml of 1.1 M TBP/$OMImPF_6$ organic phase with 0.5 ml of nitric acid solution. The concentration of nitric acid in the test solution was varied from 0.1 M to 8M. Fig. 2 shows the distribution ratios as well as percentage extraction of U (VI) in 1.1M TBP/ $OMImPF_6$ phase as a function of nitric acid conc. So the extraction of U(VI) by TBP/$OMImPF_6$ and TBP/$BMImPF_6$ is similar to the traditional behavior exhibited by TBP/DD ,thereby finds its usefulness in U recovery from valuable nitric acid based waste solutions.

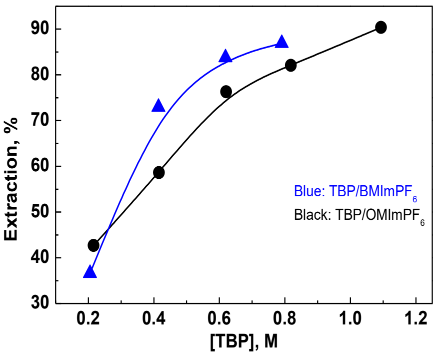

Fig.1: Variation of TBP concentration for the extraction of U(VI) in various TBP/diluent

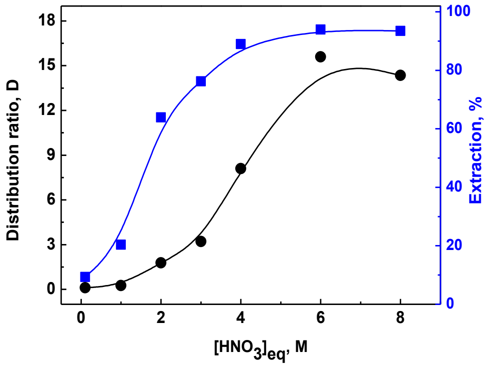

Fig.2: Distribution ratio with equilibrium concentration of nitric acid for the extraction of U(VI) in 1.1M TBP/OMIm

Keywords: Room temperature ionic liquids, uranium recovery, solvent extraction

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DAE-BRNS SESTEC-2024
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Comparison of diameters of bubbles formed for different orientations of a nozzle immersed in a quiescent liquid phase

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Mechanical agitation for gas-liquid mixing is commonly used in chemical processes. However, in radiochemical processes, it is always preferred to use passive mixing devices instead of mechanical agitation to avoid maintenance. Bubble size, rise velocity of bubbles and gas holdup depend on the design of mixing device. These variables affect mixing, degree of turbulence and hence mass transfer or heat transfer, as applicable. One such mixing device consists of a diffuser having multiple holes in different orientations through which gas is pushed into the liquid medium. Hole size, pitch, orientation of the holes affects the size of bubbles produced. To fundamentally understand bubble formation phenomenon in such devices, experiments have been carried out with a top-submerged nozzle having side hole immersed in a quiescent liquid. Data reported in literature on bubble formation at the tip of bottom-submerged nozzles and in our previous study on bubble formation at the tip of top-submerged nozzles are also used [1,2]. The generated and reported data are used to compare diameter of the bubbles produced for different orientations of nozzle. Eq (1) gives the correlation to estimate bubble diameter for top-submerged nozzles [2]. Eq (2), which is based on force balance, is reported to estimate bubble diameter for bottom-submerged nozzle [1]. Eq (3) gives the correlation obtained from regression of the data obtained for bubble formation for top-submerged nozzle with a side hole. These equations have been used to compare bubble diameter for top-submerged, bottom-submerged and top-submerged nozzle with side hole. The comparison is done for different flow rates of air, nozzle diameters and liquids. Figure 1 shows one such comparison. For bubble formation at a nozzle submerged in a liquid, buoyancy force and gas momentum force expedite bubble formation. In case of top-submerged nozzle, these forces act in opposite directions. As a result, for a given nozzle size (hole size), gas flow rate and liquid, largest bubbles are produced at top-submerged nozzle. For bubble formation at bottom-submerged nozzle, these two forces act in unison in the same direction leading to faster bubble formation, which leads to smaller bubbles. Diameter of the bubbles formed at top-submerged nozzle having side hole is in between the diameter of the bubbles formed at top- and bottom-submerged nozzles, gas momentum force and buoyancy force are perpendicular to each other. Figure 1 also shows that diameter of bubbles formed at top- and bottom-submerged nozzles increases significantly with increase in air flow rate. With increase in flow rate inertial force (a restraining force) increases leading to increase in bubble diameter. For top- and bottom-submerged nozzles, inertial force acts vertically, countering the buoyancy force. In case of top-submerged nozzle with side hole, inertial force acts horizontally and is not as effective in countering buoyancy force as in case of top- or bottom-submerged nozzle. Thus, in case of top-submerged nozzle with side hole, the effect of gas flow rate on bubble diameter is insignificant.

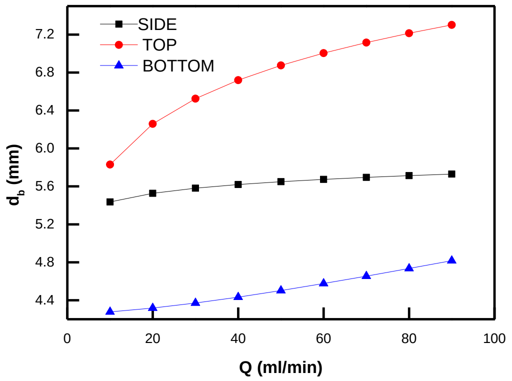

Figure 1: Comparison of bubble diameter obtained for top and bottom submerged nozzles and nozzle having side hole submerged in 4N nitric acid. Hole diameter is 3 mm in all cases.

$$d_b/d_h = 3.34 Fr^{0.0512} Bo^{-0.174} Ga^{-0.0163} \quad (1)$$

$$d_b = \left[\left(\frac{6 d_h \sigma}{\rho g}\right)^{4/3} + \left(\frac{81 \mu Q}{\pi g \rho}\right) + \left(\frac{135 Q^2}{4\pi^2 g}\right)^{4/5}\right]^{0.25} \quad (2)$$

$$d_b/d_h = 55.199 Fr^{-0.131} Bo^{-0.255} Ga^{-0.01197} \quad (3)$$

(Fr: Froude number; Bo: Bond number; Ga: Galileo number; d_b: bubble diameter, d_h: nozzle diameter; Q: air flow rate; μ: liquid viscosity; ρ: liquid density; g: gravity; σ: surface tension)

Keywords: Bubble diameter, Buoyancy force, Gas momentum force, Mixing device, Submerged nozzle

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Recovery of High Purity Vanadium from Bayer's Sludge

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Vanadium has its own importance in nuclear energy program due to its high melting point with a low neutron capture cross section. Additionally it alloy namly V-15Cr-5Ti and V-3Ti-1Si are the principle candidates for fusion reactor structural materials with notable advantages like high thermal conductivity, low thermal expansion coefficient, high temperature strength and good corrosion resistance in liquid lithium and Pb-17Li eutectic alloy. Considering its importance and less availability of primary sources, a program was taken up to recover vanadium from secondary sources and waste materials. Bayer`s sludge is one such waste generated during aluminum production contains high concentration of vanadium. Bayer`s sludge analysing V_2O_5: 23.5%, Na_2O: 29.5%, Al_2O_3: 5.1%, As_2O_3: 3.7%, P_2O_5: 5.7%, SiO_2: 0.62% etc was taken up for the development of hydrometallurgy scheme for efficient recovery of vanadium. Leaching of sludge with hot water at 60-80ºC under optimized conditions of S/L ratio, digestion time, pH etc preferentially dissolved vanadium along with considerable value of arsenic. The leach liquor having 40 g/L V_2O_5, 4 g/L As_2O_3, 6 g/L P_2O_5, 1 g/L SiO_2 and 3g/L F^- was taken for the recovery of vanadium by solvent extraction. Alamine 336 is selected for SX studies and process development. Since both arsenic and vanadium, present in Bayer sludge leach liquor (BSLL) form anionic complexes, their separation using an amine would be expected to be difficult. However, speciation data for vanadium (V) and arsenic (VI) indicates that the separation could be made possible by varying the pH, since different ionic species would have different extractabilities. As expected, it was found that at a pH of 5, the extractability of arsenic from BSLL (whose feed composition has been adjusted to 25 g/L V_2O_5) is almost negligible while the extractability of vanadium falls only a slightly (by < 10%). Effect of feed acidity, O/A ratio, Alamine 336 concentration, number of stages in extraction, scrubbing, stripping cascades, scrub and strip reagents were optimized to >98% vanadium of high purity. Subsequently under optimized process variables (feed: 25g/L at pH 2.5 with water as scrubbing agent and 4M ammonia solution as stripping agent) counter current mixer settler unit comprising 6 stages for extraction, 2 stages for scrubbing, 4 stages for stripping and 2 stages for regeneration of the organic phase was carried out, which resulted in dischargeable raffinate (< 5 mg/L V_2O_5) with improved stripping characteristics. The pH of the product stripped solution was adjusted to 8.0 to precipitate vanadium as ammonium metavanadate (AMV). AMV was calcined at 550^0 C to produce pure V_2O_5.

Fig. 1: Mini mixer settler setup

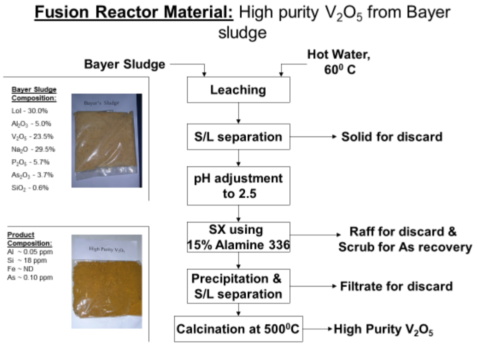

Fig. 2: Vanadium recovery flowsheet

Studies on a Causticisation process for recovery of uranium from Tummalapalle leach liquor

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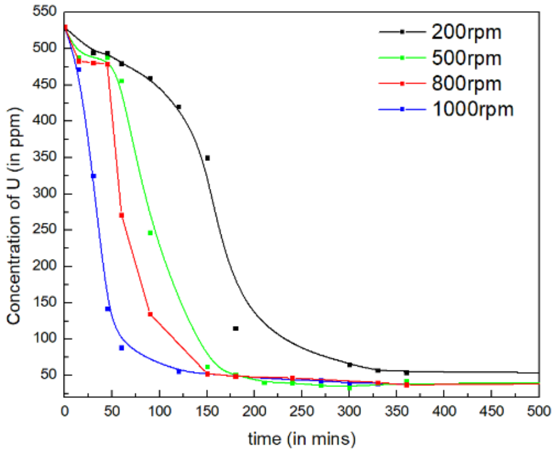
Leach liquor produced at Tummalapalle mill is very lean in uranium (typically <400ppm U). For further processing, its concentration is increased by using two recycle streams [1]. Recycle streams also increase the concentration of impurities. These affect the process efficiency as well as the purity of the product Sodium Di-Uranate (SDU) cake. To circumvent these problems, a novel process has been proposed by A.K.Singh et.al. [2]. This involves the precipitation of uranium using causticisation of leach liquor by $Ca(OH)_2$ and leaching of uranium from the causticised cake using carbonation (CO_2 purging) process.

In this present work, causticisation process for uranium precipitation from Tummalapalle leach liquor containing ~500ppm U has been studied in a 2-litre batch reactor with pitched blade turbine as an impeller. It was observed that if the stirring speed of the impeller was increased from 200 to 1000rpm then the time required for precipitation of 90% uranium decreased from 5hours to 2hours indicating diffusion control. Similarly, when the reagent stoichiometric excess was increased from 10% to 15% then there was a marginal change in kinetics. But only 30% of uranium was precipitated in 6hours when exact stoichiometry was used. Also, the kinetic studies with varying temperature indicates that if the temperature is increased then the rate of precipitation of uranium decreased. The resultant cake after causticisation process was analysed using XRD and observed that it contains mostly $CaCO_3$ and unreacted $Ca(OH)_2$ and no $CaSO_4$ was found. Mother liquor was contained 30ppm of uranium as indicated by ICP-OES analysis. Thus around 94% of uranium was recovered from the leach liquor by the causticisation process.



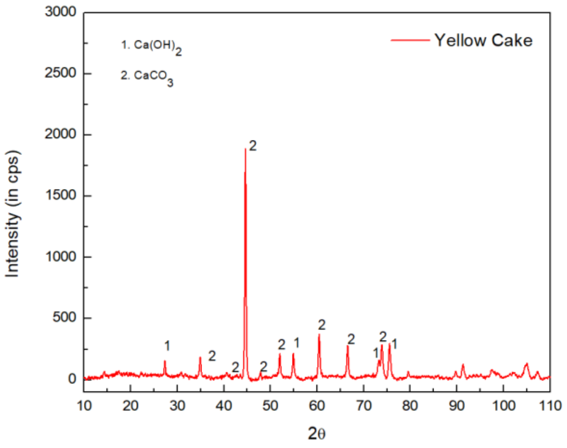


Figure 2: Effect of stirring speed on causticisation process *Figure 3: XRD of causticisied cake*

Keywords: Tummalapalle Uranium mill, SDU, Causticisation, Batch reactor, kinetics

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Comprehensive Process for the Recovery of Valuable Radionuclides and Partitioning of Active and Inactive Constituents of High-level Radioactive Liquid Waste

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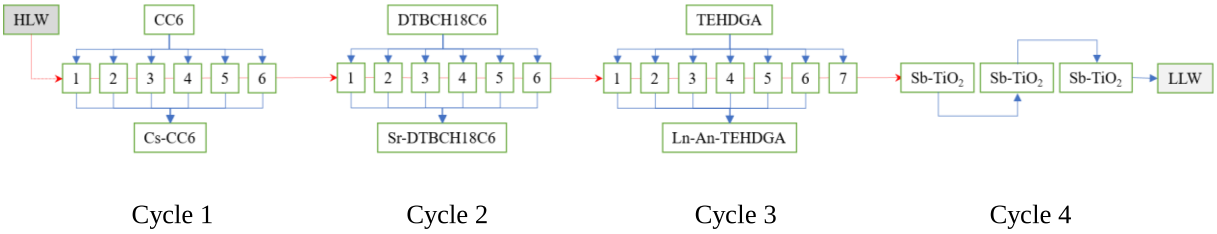
Selective separation of radionuclides of high-level liquid waste (HLW) stream reduces the long-time radiotoxicity associated with HLW-vitrified products. Furthermore, it minimizes the size and the design requirements of (or even averts the need for) a deep geological repository (DGR). Also, a few of them have the potential to be used in various energy, industrial, and societal applications [1]. Hence, a comprehensive flowsheet was designed and developed to selectively separate valuable radionuclides and active/inactive constituents of HLW to fulfill the above projections.

The demonstrated comprehensive flowsheet is shown in Scheme 1. The selective extractant systems used in the study were 0.03 mol/L CC6 in iso-decyl alcohol/n-dodecane, 0.1mol/L DTBCH18C6 in iso-decyl alcohol/n-dodecane, 0.2 mol/L TEHDGA in iso-decyl alcohol/n-dodecane, and Sb-spec resin (TiO_2-chitosan composite). Sb-spec resin's preparation, characterization, and adsorption mechanism were reported elsewhere [2]. The separation efficiency was calculated, by equilibrating equal volumes of aqueous (simulated acidic HLW, H^+ 3.5 mol/L) with the above extractant systems (5 mL each) in a glass vial and mixing at 1150 rpm using a vertex mixer, as the ratio of concentration (or radioactivity) of metal ions in the extractant phase to the aqueous phase. A 0.01 mol/L HNO_3 was used as a back-extractant for the first 3-cycles, where an alkaline (NaOH) solution was used for the 4th-cycle. Geiger-Muller and scintillation detectors, HPGe-gamma ray, alpha, and optical emission spectrometers were used to characterize the feed, raffinate, and product streams of the flowsheet. In addition, the selectivity of targeted radionuclides to other active and inactive contents was determined based on gamma and optical spectrometers.



Scheme 1. Flowsheet demonstrated the selective extraction of radionuclides

The phase separation was instant and transparent. The achieved separation of selected radionuclides, in percentage, by each stage, was 99.98 (^{137}Cs by 6 contacts), 99.89 (^{90}Sr by 6 contacts), 99.99 (^{154}Eu-^{241}Am by 7 contacts), and 98.9 (^{125}Sb by 3 contacts). The decontamination factor (DF) achieved by the developed and tested flowsheet for gross alpha, beta, and gamma was 7290, 875, and 1300, respectively. The gross alpha, beta, and gamma of the raffinate of the flowsheet (at the end of the fourth stage) was 1.4×10^{-4} mCi/L, 0.14 mCi/L, and 0.03 mCi/L. The exotic solvents were recovered with permissible radioactivity (<3.7Bq/mL) after the same number of contacts as the extraction cycle with the strip acid. Hence, the above results demonstrate that the developed flowsheet is comprehensive and suitable for industrial use.

Keywords: High-level Liquid Waste, Solvent Extraction, Calix-crown, Diglycolamide, Minor Actinides

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Separation of Krypton from Air using Activated Charcoal

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During any severe accident in a nuclear reactor, there's a risk of air borne activity release through the fission products. Noble gases such as Krypton-85 and Xenon-133 form as fission products in the nuclear reactor that cannot be trapped with the typical filtration system. These radioactive gases can lead to significant dosage to the operating personnel working in the reactor containment building or control room due to the leakages through ventilation system. Activated Charcoal has been identified as one of the promising adsorbents [1] for the separation of Krypton from Air background. The isotherm data available in the literature considers single component adsorption on the Activated Charcoal, whereas the equilibrium adsorption capacity of Krypton in presence of air is observed to be very low. For designing a filtration system that can trap Krypton from the air that enters the Control Room, adsorption studies have been carried out with Activated charcoal of different sizes and makes such as 4-8mesh, 1.2mm pellets, 3.2mm pellets etc. Breakthrough studies have been carried out at room temperature with 1% Krypton in air mixture and screening of the adsorbent material has been carried out based on the adsorption capacities obtained. 4-8mesh Activated charcoal of Sigma Aldrich make got the highest adsorption capacity of ~0.2 cc/g. Analytical model has also been developed and validated with the experimental data.

Table 1: Property of Adsorbent material

Parameter	Sigma Aldrich AC
Specific surface area (m^2/g)	600 - 675
Form	Granular
Size	4-8 mesh

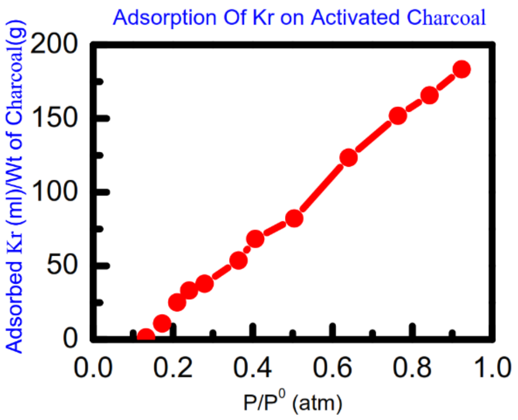

Fig 1. Adsorption Isotherm of Kr on 4-8mesh Activated Charcoal at Room temperature

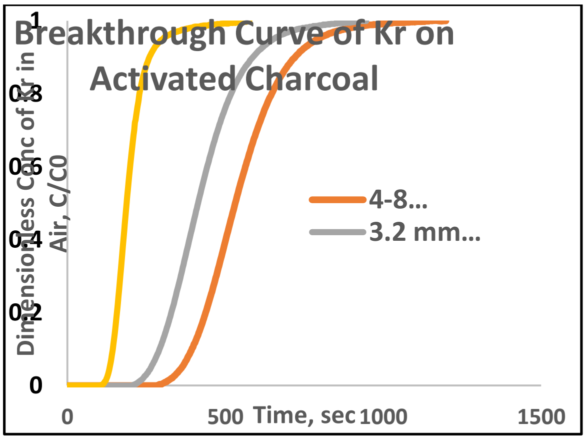

Fig 2. Breakthrough curve of Krypton in Air on different Activated Charcoal adsorbents at room temperature

Keywords: Krypton, Adsorption, Breakthrough, Ventilation

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Hydrometallurgical Process Development to Recycle Cobalt and Nickel from Maraging Steel Scrap

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Maraging steel, a high-strength steel widely used in aerospace, defense, and high-performance equipment, contains critical metals such as Co, Ni, and Mo. Given the limited availability of these metals and their high demand, recycling maraging steel (65% Fe, 8-12 % Co, 18% Ni, 3-5% Mo etc) becomes crucial. This study aimed to develop of a hydrometallurgical process for the efficient recovery of Co, Ni, and Mo from maraging steel scrap. Solvent extraction (SX) is one of the most important separation processes to recover Co and Ni from aqueous media at industrial scale by hydrometallurgy[1].

The development process involved evaluation of different leaching agent i.e. sulphuric acid, nitric acid, hydrochloric acid and mixed acid to attain complete leaching of maraging steel scrap. Results indicated total dissolution is possible in optimized mixture of 25 % V/V H_2SO_4 and HNO_3. However selection of leaching agent is also dependent upon complete conversion of iron to Fe(III), which is a crucial condition for precipitative removal of iron from leach solution. Various oxidizing agents like H2O2, MnO2, NaOCl and HNO3 was explored. Nitrating mixture i.e. mixture of HNO3 and H2SO4 was found to fulfill both (complete leaching and Fe oxidation) the requirements. The next step of the process was precipitative removal of impurities such as iron (Fe), titanium (Ti), and aluminum (Al), which involved optimization of precipitating agents (NaOH, $Ca(OH)_2$, KOH, Na2CO3 etc) and pH adjustment (2-4.5), which effectively removed impurities. The resultant liquor obtained after the precipitation step contains Co, Ni along with minor quantities of Ca and Fe (Ca- 0.65g/L, Co – 3.35g/L, Ni – 4.82g/L, Fe – 0.15g/L).

To remove the calcium impurity, a solvent extraction (SX) process is developed and referred as first cycle. In this step, a 2-stage extraction and 2-stage stripping using 10% D2EHPA in HNP as an extractant is employed. The pH of the feed solution is kept at 2.9, and 2.5M HCl is used as the strip reagent. The strip liquor with Ca – 0.420g/L is generated, and the raffinate stream (Ca – 0.098g/L, Co – 3.2g/L, Ni – 4.65g/L) forms the actual feed solution for the Co-Ni separation in the second cycle. The developed scheme shown in Fig. 1 successfully recover Co-Ni mixed solution free from other elements, which can be fed in Co Ni purification by Solvent extraction process.

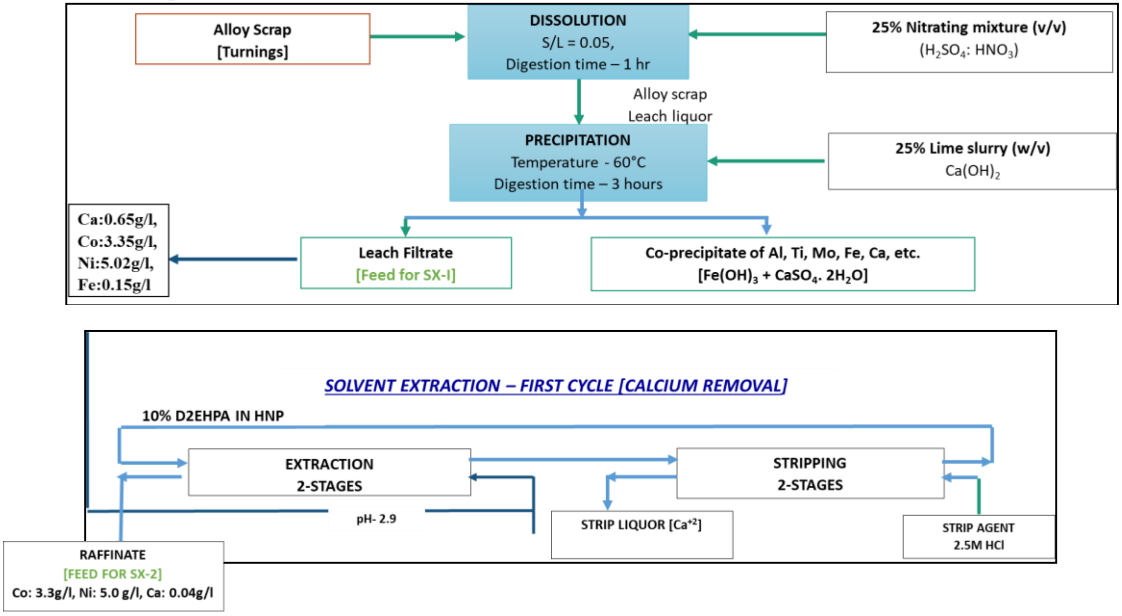

Fig. 1 Process flow sheet for Co-Ni recovery from Maraging Steel scrap

Keywords: Cobalt, Nickel, Recycling, Hydrometallurgy, Maraging Steel, Solvent extraction

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Assessment of Rare Earth Element Content in Phosphogypsum from Indian Fertilizer Plants: Experimental Insights and Analytical Results

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The utilization of rock phosphate, in the magnitude of millions of tons, is integral to Indian fertilizer plants for the production of phosphatic fertilizers. Rock phosphates apart from P_2O_5 contain a variety of other elements, including Si, Fe, and small quantities of uranium (U), rare earth elements (REEs). These raw materials undergo processing such as the dihydrate process for phosphoric acid production. This process yields wet phosphoric acid (WPA) and dihydrate phosphogypsum ($CaSO_4{\cdot}2H_2O$). Notably, within the dihydrate process, a significant portion of REEs, roughly 15-30%, enters the phosphoric acid product, while the remainder is transferred to the phosphogypsum.

The primary objective of the present study was to assess the rare earth element (REE) content within phosphogypsum (PG) samples sourced from various Indian fertilizer plants. Samples were collected from prominent facilities and coded as PG 1 to 7. Processing steps are designed to leach all the REE content from phosphogypsum phase to liquid phase for analysis and separation. The collected PG samples were subjected to calcination at 150°C for 2 hours to determine moisture content which was found to be in the range of 14% to 28% across all seven samples. Particle size distribution analysis of the PG samples was conducted utilizing the CILAS Laser Particle Size Analyzer 1090, revealing mean diameters within the spectrum of 35µm to 90µm. Elemental analysis of the PG samples was performed using the Rigaku Supermini 200 Wavelength Dispersive X-ray Fluorescence (WDXRF) analyzer. The analysis unveiled major constituents listed in Figure 1.

Further leaching studies were carried out to selectively transfer REEs into aqueous phase through sample leaching with hydrochloric acid (HCl) and sulfuric acid (H2SO4). Leaching parameters including acid concentration, solid-to-liquid ratio, and digestion time were varied within ranges of 10-50% HCl, 5-25% H2SO4, 1:1 to 1:50 S/L ratio, and 1- 4 hours digestion time, with temperature variation from RT to 70°C. Under optimal leaching conditions with employing 50% HCl yielded a 75% REE leaching, while H2SO4 leaching runs resulted in only 5 to 25% extraction due to the low solubility of REEs in sulfate medium.

Total REE concentrations in the PG samples were also determined by complete dissolution of PG samples and are as follows: PG-1: 104ppm, PG-2: 148ppm, PG-3: 228ppm, PG-4: 533ppm, PG-5: 389ppm, PG-6: 495ppm, and PG-7: 3160ppm. Notably, PG-7 exhibited the highest total REE content among the samples analyzed. Individual fractions of total REEs are detailed in Table 2.

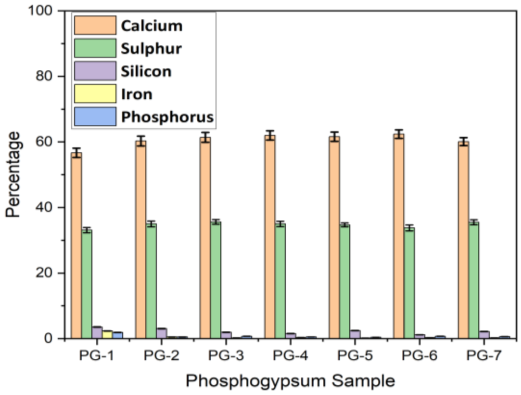

Fig. 1: WDXRF analysis of PG sample

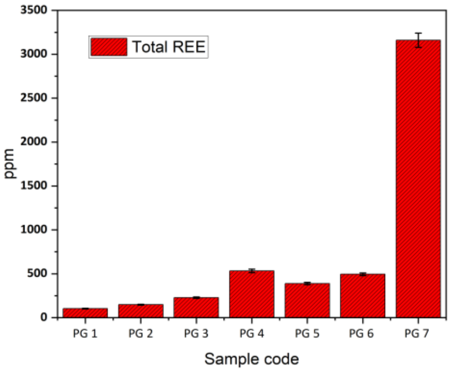

Fig. 2: REE in different PG Sample

Keywords: Rare Earth Elements, Phosphogypsum, Leaching, Analysis

References:

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Synthesis of platinum based catalyst for U(IV) generation for the partitioning of U(VI) and Pu(IV)

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In PUREX process, the uranous nitrate has been employed for partitioning of U(VI) and Pu(IV) present in the organic phase[1]. At present, the U(IV) is being generated by an electrochemical method, which has the limitations of poor kinetics, lower efficiency (50-60%) and frequent maintenance of the electrodes. In fast reactor fuel reprocessing plants the amount U(IV) required for Pu(IV) reduction is much higher than thermal reactor fuel reprocessing plants, due to the presence of higher amount of plutonium in fast reactor fuel. Therefore, there is a need to develop an alternative method for the preparation of uranous nitrate. In our laboratory we are working on the development of advanced materials and methods for the production of uranous nitrate. In this content, a number of platinum-based catalyst materials have been synthesized in-house and evaluated for the reduction of U(VI) by employing H_2 and N_2H_4 as reducing agents.

The platinum catalyst material was synthesized by impregnating H_2PtCl_6 on various solid materials such as SiO_2, Al_2O_3, CeO_2, C (activated carbon), ZrO_2, SBA-15, TiO_2. After impregnation, the catalyst was calcined at 823 K in air followed by reduction in flowing 8% H_2/Ar gas mixture at 573 K. The amount of platinum loaded in the catalyst was estimated to be ~ 1%. The catalyst further characterized and evaluated for the reduction of U(VI) in nitric acid solution. The experiments were carried out in a stainless-steel autoclave. The experimental condition employed for U(VI) reduction is shown in Table 1. The results on the effect of support material on the reduction of U(VI) is shown in Figure 1. It could be seen from Figure 1 that among all the catalysts, Pt/C gave near 100% conversion using H_2 and N_2H_4 as reducing agents in 6 minutes and 15 minutes respectively. It could be because of higher surface area of activated carbon which resulted in higher platinum dispersion leading to smaller crystallite size and higher surface area. Therefore Pt/C with larger platinum surface area showed the better catalytic activity compare to other materials employed in this work. To substantiate this observation, further investigations to determine the particle size of Pt is in progress.

Table 1. Experimental conditions employed

for U(VI) reduction

	Reducing agent	
	H_2	**N_2H_4**
Agitation speed	**1200 rpm**	**1000 rpm**
$[U(VI)]$ / M	**0.25 M**	**0.25**
$[HNO_3]$ / M	**1.0**	**1.0**
$[N_2H_4]$ / M	**0.1**	**1.1**
Catalyst loading per g of U/ mg	**1.5 mg (or) (C:U=1:4000)**	**31.5 mg (C:U=1:200)**
H_2 pressure	**3 bar**	**---**
Temperature	**303 K**	**353 K**
Volume of the solution	**100 mL**	**100 mL**

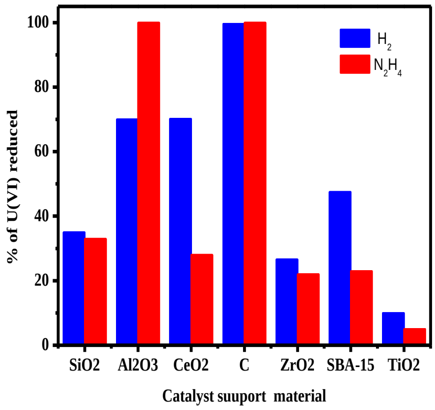

Figure 1 Catalytic reduction of U(VI) over Platinum impregnated support [The percentage of U(VI) reduced was calculated at 6 minutes in H_2 method and 15 minutes in N_2H_4 method]

Keywords: PUREX process, catalytic reduction, Uranium, Hydrogen, hydrazine

Reference:

Sood D.D., Patil S.K., Chemistry of nuclear fuel reprocessing: Current status, *J. Radioanal. Nucl. Chem.*, (1996), 203, 547–573

Effect of HDBP on the extraction and stripping behavior of uranium in PUREX process conditions

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In nuclear fuel reprocessing plants, PUREX process is widely employed solvent extraction based process for the recovery of uranium and plutonium present in the spent fuel. In this process 1.1 M TBP/*n*-DD is used for the extraction of uranium and plutonium from the feed aqueous solution. In fast reactor spent fuel reprocessing plants, the solvent 1.1 M TBP/n-DD will be in contact with high acidic and active feed solution in the extraction stage. Because of this high acidity and activity of aqueous feed solvent undergoes severe degradation and forms various degradation products like HDBP, H_2MBP, H_3PO_4 etc. Among these degradation products HDBP will be formed in more quantity and it behaves like an acidic extractant and may interfere in the process. Therefore, the effect of HDBP on the extraction and stripping behavior of U(VI) and Pu(IV) need to be understood in detail under various experimental conditions for the optimization of process flow sheet conditions for the quantitative extraction and recovery of uranium and plutonium. In view of this, batch experiments were conducted to determine the distribution behavior of U(VI) with 1.1M TBP/n-DD and 1.1M TBP+0.015M HDBP)/n-DD as a function of various U(VI) and nitric acid concentration conditions. Cross current studies were also carried out to find out the number of contacts required for quantitative extraction and stripping of U(VI) by maintaining 4 M acidity during extraction and 0.01M HNO_3 during stripping.

The distribution behavior of 1 gpl U(VI) as a function of acidity is shown in Figure 1. It can be seen from the Figure 1. that in the higher acid region (> 0.5 M) both the extractants extracts U(VI) in the similar manner, but in the lower acid region (<0.5 M) the K_d of U(VI) is higher for (1.1M TBP+0.015M HDBP)/n-DD and it increases with decrease in the acidity. In lower acid region HDBP acts as acidic extractant and it into H^+ and DBP^- and this dissociation increases further with decrease in the acidity. Therefore the increased DBP^- ion concentration with decrease in acidity is responsible for the observed higher K_d in the lower acid region. The cross current studies carried in batch mode to determine the number of contacts required for the quantitative extraction and the experimental results indicated in both the cases three stage are sufficient for quantitative extraction of U(VI). The stripping behavior of U(VI) from the loaded organic phases containing 1 gpl U(VI) using 0.01 M HNO_3 as stripping agent is shown in Figure 2. It can be observed from the Figure 2 that, in the case of 1.1M TBP/n-DD, quantitative stripping of U(VI) was observed in three stages however in the case of 1.1M TBP+0.015M HDBP/n-DD less than 50% of U(VI) only stripped even after 11 stage of contacts. The above results clearly indicates the HDBP the degradation product of TBP will have strong influence in the stripping conditions of U(VI) in PUREX process.

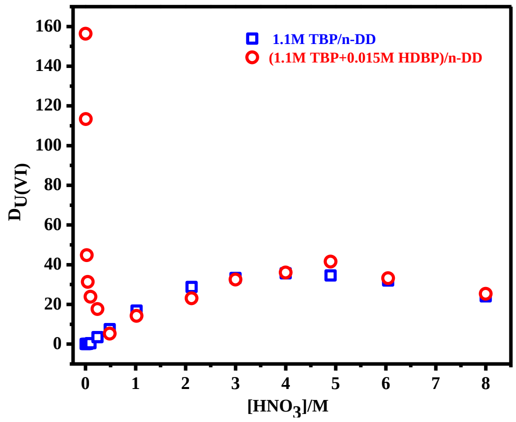

Figure 1. Distribution behavior of 1 gpl of U(VI) as function of HNO_3

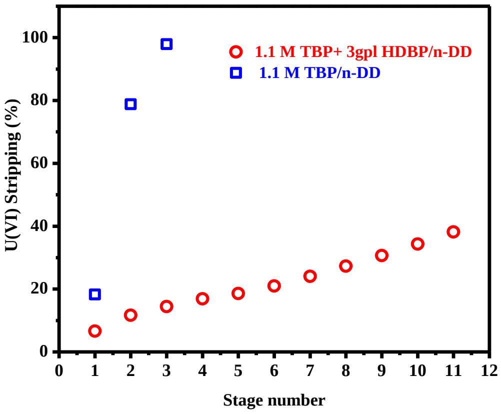

Figure 2. Stripping behavior of 1 gpl U(VI) loaded in organic phase with 0.01M HNO_3

Keywords: *PUREX process, Tri n-butyl phosphate, Di-n- butyl phosphate, Uranium, Nitric acid*

Mixer-Settler runs for the Evaluation of Diamylamyl Phosphonate for Extraction and Stripping of Uranium

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The phosphonates are found to be superior extractants as compared to phosphates, as they extract uranium and thorium better than the corresponding phosphates. Phosphonates do not have very high D values with metal ions as in the case of phosphinates and phosphine oxides; hence the recovery of the metal ion from the loaded organic phase is easier in the stripping stage. Diamylamyl phosphonate (DAAP) was synthesized in our laboratory as reported elsewhere[1] and liquid-liquid solvent extraction runs were performed with uranium 1.1M DAAP/n-Dodecane(n-DD) using ejector mixer-settler facility. The details and working principle of the mixer-settler is described in our earlier paper[2]. A feed solution containing uranium about 101.54 g/L in 3.99 M HNO_3 was prepared. Mixer-settler runs were carried out with U(VI) solution to understand the extraction and stripping behavior of DAAP with U(VI) in nitric acid media for a continuous solvent extraction process under high solvent loading conditions. Counter-current extraction of U(VI) was carried out by passing the uranyl nitrate solution as the aqueous feed from 1st stage and 1.1 M DAAP/n-DD solution as the solvent from 16th stage Extraction profiles for HNO_3 and uranium are shown in Fig.1. Results indicate that the concentration of uranium in the organic phase is found to be about 85-100 g/L from stage 1 to 10; it decreases from thereafter and it was found to be below detection limit (0.2 mg/L) in 16th stage indicating the quantitative extraction(>99.9%) of uranium was achieved with 1.1 M DAAP/n-DD in mixer-settler runs. The extraction of nitric acid into the organic phase was found to be about 0.2-0.4 M in the stages 1 to 10 and it was about 0.5 M from stages 10 to 16. Subsequent stripping of U(VI) from the loaded organic phase was carried out by passing loaded organic from 16th to 1st stage and 0.01 M HNO_3 from 1st stage to 16th stage in a counter-current manner. The profiles for HNO_3 and U(VI) in the strip run are shown in Fig.2. Results indicate that both the concentrations of HNO_3 and uranium decrease towards the 1st stage, where the strippant enters the mixer-settler bank. The decreasing trend of HNO_3 and uranium concentrations towards 1st stage is an indication that both are stripped from the loaded organic phase. However, uranium concentration in the lean organic is found to be significant and is around 13.6 g/L. This indicates that more number of stages(>16) required for the quantitative stripping of uranium from loaded 1.1 M DAAP/n-DD. The present study demonstrates the feasibility of using DAAP as the extractant for reprocessing applications.

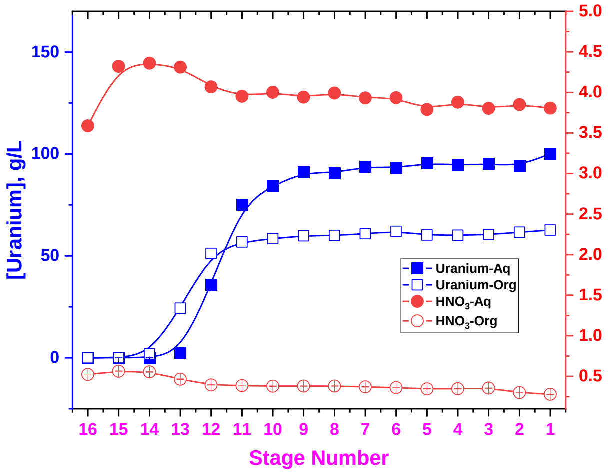

Fig.1 Organic and aqueous stage profiles for Uranium and HNO_3 in the extraction run-U(VI)-4M HNO_3-1.1M DAAP/n-DD system.

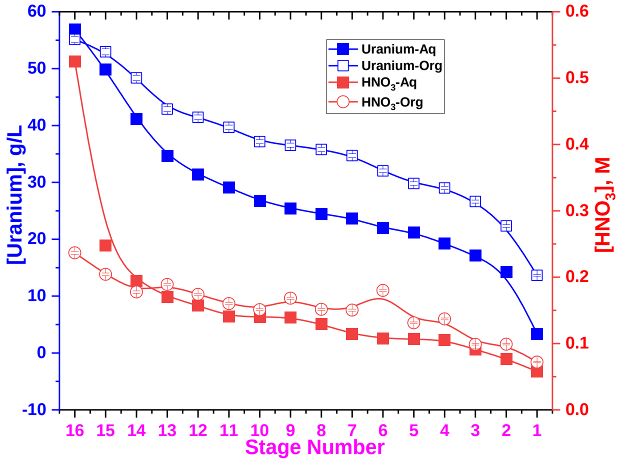

Fig.2 Organic and aqueous stage profiles for Uranium and HNO_3 in the strip run-U(VI)-0.01M HNO_3-1.1M DAAP/n-DD system.

Keywords: Uranium, DAAP, HNO_3, Extraction, Stripping, Mixer-settler

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Extraction of Uranium from Various Media using Dialkylhydrogen Phosphonates and Tri-n-Butyl Phosphate

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Hydrogen phosphonates belongs to the family of organophosphorous compounds which contains P=O groups which binds with various metal ions. H-phosphonates behave like bi-functional extractants due to the different mechanisms of extraction, namely cation exchange at low acidity and solvation mechanism at higher acidity. H-phosphonates were investigated for various studies in our laboratory [1, 2]. Phosphonates possess higher distribution ratios than phosphates making them suitable for recovery of various metal ions different media. In the present study H-phosphonates such as Diheptylhydrogen phosphonate(DHHP) and Diamylhydrogen phaosphonate(DAHP) were investigated for recovery of uranium from various media such as HCl, HNO_3 and pH medium. In this context feed solution of U about 1-2 g/L in HCl, HNO_3 and pH medium was prepared; the extraction of behavior of U was examined with 0.5 M solutions of DHHP and DAHP in n-Dodecane(DD) and results were compared with 0.5 M TBP/n-DD under identical conditions. The extraction of uranium from chloride medium was found be negligible with H-phosphonates whereas it increases from 3 to 77% from 0.1 to 6 M HCl using 0.5 M TBP/n-DD. In contrast, the extraction of U was found to be negligible from pH medium using 0.5M TBP/n-DD and it was found to be about 94-99% from pH medium(1-6) by 0.5M DHHP/n-DD. This is due to H-phosphonates extracts uranium through P-OH group by cation exchange mechanism. The extraction of behavior of uranium was also examined with various concentrations of DHHP, DAHP and TBP(0.1-0.5) from nitric acid media(0.1-6 M). The distribution ratios of uranium by H-phosphonates is maximum at lower acidities and it decreases with increase in nitric acid concentration(Fig.1). The higher extraction of uranium by H-phosphonates at lower acid is due to cation exchange mechanism through P-OH group. *D* values for U by H-phosphonates also increases with increase in extractant concentration. This is due to the availability of free extractant molecules for complexation with U at higher extractant concentrations. Similarly the extraction behavior of U was also investigated using different concentrations of TBP in n-DD from nitric acid medium. In contrast to H-phosphonates, the *D* values for U by TBP/n-DD increases with increase in nitric acid concentration as well as extractant concentration. The extraction of U by TBP is through solvation mechanism with P=O group. The percentage extraction of uranium from nitric acid was also examined by H-phosphoantes and TBP. Quantitative extraction(>99%) of uranium is possible only with 0.5 M DHHP/n-DD at lower acidities (<2 M HNO_3). The present study reveal that H-phosphonates efficiently extracts U from pH and nitric acid medium.

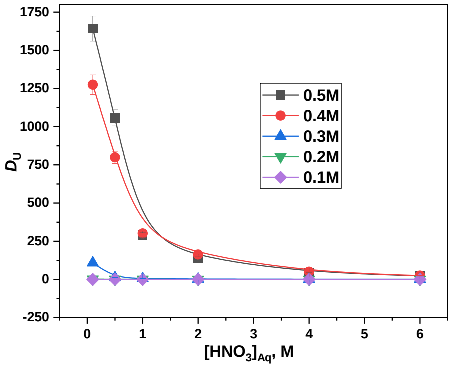

Fig.1. Variation of distribution ratios for uranium as a function of aqueous phase nitric acid concentration at different concentrations of DHHP in n-DD

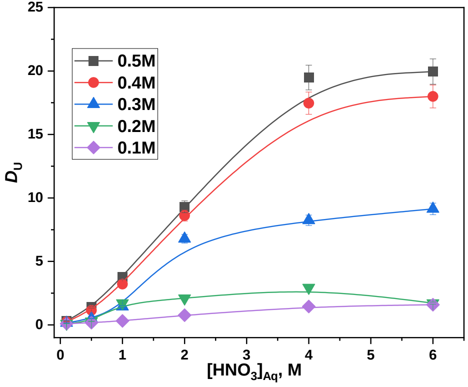

Fig.2. Variation of distribution ratios for uranium as a function of aqueous phase nitric acid concentration at different concentrations of TBP in n-DD

Keywords: H-phosphonates, TBP, Uranium, pH, HCl, HNO_3

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Optimisation study of Cement waste product preparation for conditioning of radioactive chemical sludge

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Chemical treatment is being done for the management of Low level radioactive liquid waste (LLW). Radioactive Sludge gets generated during this chemical treatment. Multiple batch chemical treatment is being carried out in the settler to get maximum sludge volume reduction. When the sludge level in the tank reaches threshold level, it is transferred to Solid waste management facility (SWMF) for fixation in cement matrix. Chemical treatment process carried out in two different plants (LWTP & TRAP) at Tarapur, are generating radioactive sludge having different characteristics. Specified ratio of sludge, cement and vermiculite are taken for cement fixation of sludge and the cement waste product (CWP) is prepared in situ in the RCC trench. The present study has been initiated to optimize a range of sludge, cement and vermiculite ratio so as to get optimum quality CWP.

The actual radioactive sludge was collected from both plants and brought to laboratory taking all safety measures. Detailed characterisation of both sludge samples was carried out. Both sludges have around 17% total solid content. The alpha and beta activity of LWTP sludge is high (0.004mCi/L & 1.0mCi/L respectively) compared to TRAP sludge (MBL & 0.08mCi/L respectively). Also, the LWTP sludge has high Na content (~6.5 g/L) than that of TRAP sludge (0.4 g/L)
Active cement waste products of both sludges were prepared having different ratio of sludge, cement and vermiculite (Table-1). Inactive products of same compositions were also prepared for compressive strength study. Curing time of 28 days was given to each CWP. Chemical durability study of the active products was done and is continued.

The compressive strength of CWP prepared with ratios **1: 0.9: 0.1 to 1:1.2:0.1** are having compressive strength better than acceptable limit. The leach rate study is going on and initial results are within the limit.

Table – 1: Composition of inactive CWP and their properties

Sr. no.	Ratio	Sludge	Cement	Vermiculite	Compressive strength (Kg/cm^2)
1	1:0.7:0.1	1	0.7	0.1	17.0
2	1:0.8:0.1	1	0.8	0.1	29.4
3	1:0.9:0.1	1	0.9	0.1	39.6
4	1:1:0.1	1	1	0.1	49.9
5	1:1.2:0.1	1	1.2	0.1	52.2

Keywords: Cement waste product (CWP), Compressive strength, leaching, Low level radioactive liquid waste (LLW), sludge fixation.

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Effect of alkyl chain branching of some diglycolamide ligands on the extraction of tetravalent ions from acidic feeds

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The diglycolamide (DGA) ligands are reported to be one of the most efficient extractants for 'Actinide Partitioning' which is considered relevant at the back end of nuclear fuel cycle for the management of high level liquid waste (HLLW). [1] *N,N,N',N'*-tetra-alkyl diglycolamide (alkyl group: octyl namely TODGA), one of the most studied DGA ligands extracts trivalent actinide ions such as Am^{3+} from moderate concentrations of nitric acid (3 – 4 M) to a much greater extent than the UO_2^{2+} ion underlining its utility in HLLW management as compared to previously known and well studied ligands such as CMPO (carbamoylmethyl phosphine oxide),[2] DIDPA (di-iso-decylphosphoric acid),[3] TRPO (tri-alkylphospine oxide), malonamides [4], etc.which extract UO_2^{2+} ion to a much larger extent than the Am^{3+} ion. [1]

In the present study, extraction of Np(IV), Th(IV) and Pu(IV) was performed using different branched DGA ligands with branching at α, β, and γ positions with respect to the amidic nitrogen atom. The extraction of all these metal ions was found to be increasing with increasing feed acidity for all the studied ligands. This suggests solvation mechanism of extraction by all the ligands in the molecular diluent (30 % *n*-octanol + *n*-dodecane and octanol) used in present study. The amyl, iso-amyl and iso-butyl derivatives show similar extraction efficiency for Np(IV), whereas the *n*-butyl derivative shows higher extraction in both *n*-octanol and its mixture with 70% *n*-dodecane. In general, the branching of the alkyl chain reduces the extraction of the tetravalent ions for both the *n*-amyl and *n*-butyl ligands. The distribution of Np(IV) decrease with the addition of *n*-dodecane for all the ligands (Fig. 1(a)).The slope analysis suggested formation of 1:2 complexes with all the ligands in 30% *n*-octanol + *n*-dodecane at 3 M HNO_3 (Fig. 1(b)).

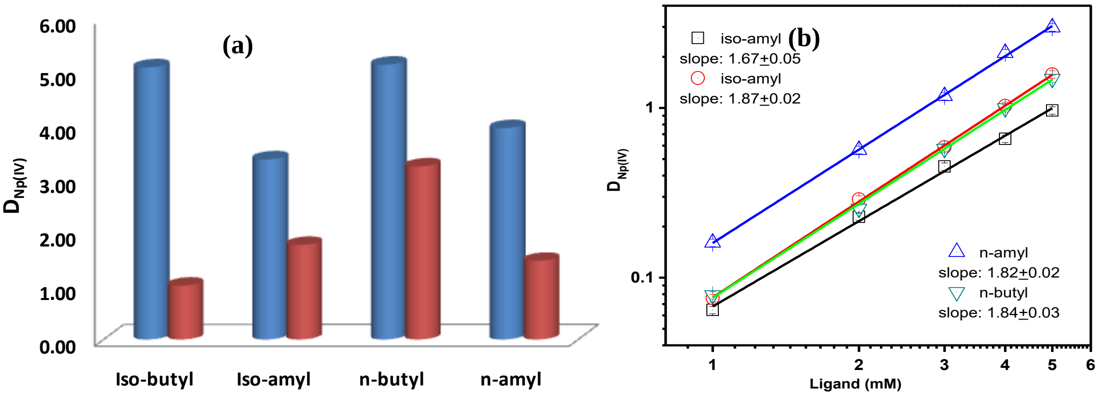

Fig. 1. The distribution ratio of Np(IV) in pure (blue bar) and 30% octanol + n-dodecane mixture (red bar), and (b)slope analysis of Np(IV) extraction with different DGA ligands at 3M HNO_3.

Keywords: Tetravalent actinides, diglycolamides, *High level liquid waste, liquid-liquid extraction*

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Studies on separation of nitrate and uranium from ammonical sol-gel waste using anion exchange resin

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Internal gelation process, one of the sol–gel processes originally developed at the KEMA Lab[1], has been widely studies worldwide and also modified at the FCD, BARC, Mumbai[2] for the nuclear fuel fabrication. This process offers several advantages over conventional powder pellet route. However, one of the limitations of the process is generation of large volume of alkaline liquid waste containing hexamethylenetetramine (HMTA), urea, ammonium nitrate, ammonium hydroxide and traces of uranium. For the preparation of 1 kg of urania microspheres by sol-gel process approx. 15 litres of alkaline waste generates containing HMTA (0.2M), urea (0.2M), NH_4NO_3 (0.3M), NH_4OH (3M) and few mg/L of U. It has been reported[3] that uranium species present in the waste are $((UO_2)_3(OH)_7^-$, $(UO_2)_3(OH)_8^-$, $(UO_2)_3(OH)_{10}^-$ etc. For effective recycle of excess gelation agents in the waste it is required to remove uranium from the waste so that secondary waste produced is inactive and suitable for disposal. The present work investigates feasibility to remove uranium anionic species from the waste in presence of relatively large amount of competing nitrate ion by Dowex 1x4 anion resin in OH_ form of mesh size 50-100 micron. The separation of nitrate is also crucial as it forms explosive mixture in presence of HMTA.

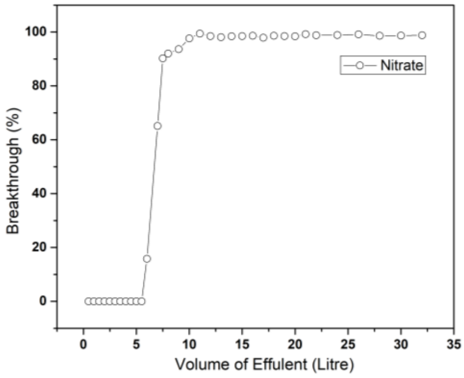

Fig. 1: Break through curve of nitrate

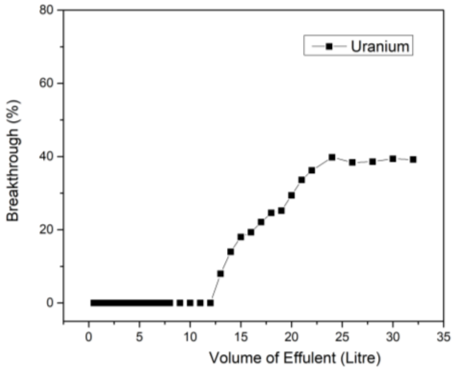

Fig. 2: Break through curve of Uranium

In the column experiment, Dowex 1x4 resin (650 g) in OH form was taken in a glass column (7.5 cm dia and 75 cm height) and with bed volume (bv) =1.7 litre. The waste solution was passed through the column at the flow rate 1 bv/hr and the effluent fractions were assayed for both nitrate ion as well as for uranium. The determination of nitrate was carried out spectrophotometrically using Cary-500-SCAN-UV-VIS-NIR spectrophotometer. Absorbance at 302nm for nitrate was recorded. Uranium was determined using Arsenazo (III) as colouring agent. Content of nitrate and uranium in the waste solution were determined to be 0.25M and 0.7 ppm, respectively. Fig.1 and Fig.2 give breakthrough curves for nitrate and uranium, respectively, where it can be seen that in the former case more than 95% breakthrough occurs after passing 8 litres of waste but in later case about 40% breakthrough occurs even after passing 32 litres of waste through the column. This shows that uranium species are absorbed by the resin in preference to nitrate ion but due to slower kinetics of the bulky uranium anionic species, uranium breakthrough initiates much earlier than it should be in view of very low concentration of uranium compared to nitrate concentration. It can be estimated through Fig. 2 that uranium breakthrough starts after passage of about 12 litres of waste, i.e. absorption of about 8 microgram of uranium. Sluggishness of uranium uptake is indicated by flattening of breakthrough curve at 40% after passage of 32 litres of waste. On the other hand, nitrate breakthrough occurs sharply once the resin is saturated with nitrate, about 3 meq /gram. From the result it can be concluded that ammonical waste can be made uranium free by ion exchange using Dowex 1x4 resin.

Keywords: Sol-gel, Uranium, HMTA, Spectrophotometer, Doex 1x4resin

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Performance Evaluation of Indigenously Developed TIMS Using NBS Certified Standard Reference Material

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Abstract

Determination of isotopic composition of Uranium and Plutonium is one of the prime requirements in the field of nuclear technology. Thermal Ionization Mass Spectrometry (TIMS) is widely used and internationally accepted technique for precise and accurate atom ratio measurements of various elements [**1**]. Electromagnetic Application & Instrumentation Division (EmA&ID), at BARC has been developing TIMS for specific usages [**2**]. A 20 cm radius, stigmatic geometry and air cooled magnetic sector based indigenously developed TIMS (Fig-1) is recently installed in Fuel Reprocessing Division (FRD), BARC. The initial performance of this TIMS is evaluated by analyzing uranium samples of NBS certified standard reference material. High purity zone refined rhenium was used as filament material. About 1 µL of sample solution, having uranium concentration around 1000ppm, was loaded on both the sample filaments of triple filament assembly. Twelve such assemblies mounted in a separate turret were employed for analysis of isotopic standards. After optimizing the $^{187}Re^+$ beam focusing parameters to get the signal about 150 mV at centre Faraday cup, the sample filament was then heated slowly and parameters were adjusted to obtain a signal of 30 mV for $^{235}U^+$ at the same cup and 4-5 V for $^{238}U^+$ at different cup. The measurement of $^{234}U/^{238}U$,$^{235}U/^{238}U$ and $^{236}U/^{238}U$ atom ratio was carried in 30 scans/cycle in triplicate. The calculated atom percentage of three sets of isotopic standards (U-005, U-015 & U-200) are presented in table-1 along with NBS certified values. The K-factor, i.e. ratio of obtained to the certified atom % is closed to 1 which indicates satisfactory performance of the indigenous TIMS instrument. However, detail studies have to be carried out with regards to sensitivity and precision.

Table.1 Results of obtained atom % of uranium along with NBS certified values.

SRM	NBS certified Atom % (A)				Indigenous TIMS obtained Atom % (B)			
	^{234}U	^{235}U	^{236}U	^{238}U	^{234}U	^{235}U	^{236}U	^{238}U
U-005	0.00218	0.4895	0.00466	99.504	0.00219	0.4977	0.00398	99.496
U-015	0.00850	1.5323	0.0164	98.443	0.00896	1.5458	0.0139	98.431
U-200	0.1246	20.013	0.2116	79.651	0.1359	20.103	0.2188	79.541

K-factor = (obtained/ certified) Atom percentage (B/A)

	^{234}U	^{235}U	^{236}U	^{238}U
U-005	1.0041	1.0169	0.8540	0.9999
U-015	1.0538	1.0089	0.8523	0.9999
U-200	1.0910	1.0045	1.0341	0.9986

Specification of the Instrument

- Resolution: 300
- Mass range: up to 400 amu (@ 5kV acceleration)
- Precision: 0.1% for natural Uranium
- Sensitivity: One ion for 580 atoms of Uranium
- Analyzer: Magnetic sector (Air cooled, solid core, stigmatic geometry, 20 cm radius, 90° deflection angle, maximum field 1.0 Tesla@ 20A/28V)
- Accelerating Potential: up to 10 kV
- Sample Changer: Turret with 12 Filament Assemblies (with auto positioning and pre-heating facility)
- Filament Assembly: Ceramic base Triple Filament Assembly
- Collector: Seven Faraday collectors with Zoom Optics
- Windows based software for control & data acquisition

Fig.1 TIMS (Model: 2090-7F-FRD-2023) developed by EmA&ID, BARC

Keywords: Isotopic ratio, TIMS, Uranium isotopic standard

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Studies on the extraction of tetra and hexavalent actinides in room temperature ionic liquids using monoamide extractants.

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Tri-*n*-butyl phosphate (TBP) is known as workhorse for the reprocessing of spent nuclear fuel. However, it has some disadvantages such as secondary waste generation, production of deleterious degradation products and high aqueous solubility. Therefore, attempts have been made for alternate extractant such as amide-based CHON ligands which generates innocuous secondary wastes. Also, considering various advantages of room temperature ionic liquids (RTIL) over molecular diluents viz., low vapor pressure, high electrochemical window, ability to dissolve wide range of organic solvents and tunable physico-chemical properties [1], extraction of actinides in the former has been studied widely. Though the extraction behavior of actinides using monoamides such as dihexyaloctanamide (DHOA) is widely studied [2], studies involving its lower homolog, i.e., dihexylhexanamide (DHHA) are scarce in literature. Considering the above facts, an evaluation of DHHA for the extraction of U (VI), Np(VI), Pu(IV) and Np(IV) in RTIL C_8mim•NTf$_2$was carried out. Comparison of the results was made with the results observed with DHOA in the same ionic liquid medium.

Batch extraction studies indicated fast extraction kinetics for both the extractants. It was seen that the equilibrium was reached within 15 minutes. Extraction of the tetravalent ions (Pu^{4+} and Np^{4+}) were exceptionally higher as compared to that of the hexavalent ions (UO_2^{2+}, NpO_2^{2+}) for both the extractants. The higher extraction of tetravalent ions compared to actinyl ion is attributed to higher ionic potential of the former ion compared to the later ion. Further, the distribution ratios of the metal ions were comparable for both the extractants. Acid variation study indicated increasing D values as a function of acid concentration for UO_2^{2+}, and NpO_2^{2+} while for Pu^{4+} and Np^{4+}, D value increases up to 3M HNO_3 beyond which a plateau like behavior was observed indicating extraction of metal ions by a solvation mechanism for both the extractants. To investigate the nature of the extracted species, nitrate ion variation and ligand variation studies were carried out. For both the extractants, the slope values from ligand variation study were close to 2 for the actinyl ions while for Pu (IV), the slope value was found to be close to 1.5 and for Np (IV) the slope value was close to 1. This indicated the presence of ML_2 type of species for the actinyl ions. Similar results were reported when n-dodecane was used as diluent [3]. The extraction of mixed species (ML and ML_2) was seen in the case of tetravalent Pu^{4+} and ML type species for Np^{4+} ions. Results were compared to the previously reported study involving n-dodecane as medium [3]. Although the concentration of DHOA used was half (0.5 M) in the present study compared to the previous one, it was seen that the extraction of tetravalent ions in C_8mim•NTf$_2$ was significantly higher compared to n-dodecane. However, for hexavalent cations, the extraction was found to be comparatively lower in RTIL than that in n-dodecane.

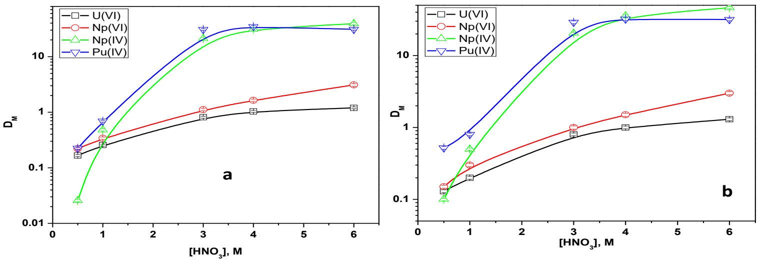

Fig. 1. Variation of distribution ratio as a function of nitric acid concentration a) DHHA as extractant and b) DHOA as extractant (0.5 M in C_8mimNTf$_2$).

Keywords: Solvent extraction, Ionic liquid, actinides

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Separation of Am^{3+} and Cm^{3+} using branched DGA and hydrophilic ‘N’ donor ligands

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Mutual separation of Am^{3+} and Cm^{3+} is highly challenging as soft donor ligands show poor selectivity between these two adjacent actinide ions in their trivalent state.[1] The separation of Am^{3+} and Cm^{3+} can be done by exploiting the cooperative effect of two ligands of opposite selectivity taken in two different phases to improve the overall selectivity.[2**]** Wagner et al, proposed to use TODGA in combination with the hydrophilic ligand, 3,3’,3’’,3’’’-([2,2’-bipyridine]-6,6’-diylbis(1,2,4- triazine-3,5,6-triyl))tetrabenzene sulfonic acid (SO_3PhBTBP) in the Americium Selective extraction (AmSel process) from a PUREX raffinate where a S.F. of 2.5 was achieved for Cm^{3+} over Am^{3+}.[3] It will be, therefore of interest to compare different lipohilic DGA derivatives along with the hydrophilic aqueous complexants, viz. SO_3PhBTP, SO_3PhBTBP or SO_3PhBTPhen for the separation studies of Am^{3+} and Cm^{3+}. Seven different DGA derivatives, viz. *N,N,N*’,*N*’-tetra n-butyl diglycolamide (TBDGA), *N,N,N*’,*N*’-tetra *iso*-butyl diglycolamide (TiBDGA), *N,N,N*’,*N*’-tetra *sec*-butyl iglycolamide (TsBDGA), *N,N,N*’,*N*’-tetra *n*-pentyl diglycolamide (TPDGA), *N,N,N*’,*N*’-tetra *iso*-pentyl diglycolamide (TiPDGA), TODGA and T2EHDGA are compared to their separation efficiency towards Am^{3+} and Cm^{3+} when used in combination with SO_3PhBTP, SO_3PhBTBP or SO_3PhBTPhen.

The extraction efficiency increased for both the metal ions with increasing the aqueous phase acidity. The S.F. values, however, decreased with increasing acidity in case of both the DGA derivatives and highest selectivity was observed at 0.2 M HNO_3. Lowering the HNO_3 concentration further, resulted into the extraction efficiency too low to measure and therefore in the subsequent studies, where we aimed for maximizing the S.F. values, the aqueous phase HNO_3 concentration was fixed at 0.2 M. The BTPhen derivative is reported to show selectivity for Am^{3+} over Cm^{3+}.[4] In the present work, these DGA derivatives, when used along with SO_3PhBTPhen as the aqueous complexant, no improvement in selectivity is noticed in case of TsBDGA. TBDGA, however, showed a significant improvement in the selectivity towards Cm^{3+} with a S.F. value of 4.1 for Cm^{3+} over Am^{3+}. TiBDGA shows most promising result where the S.F. values are observed to be 5.3. The selectivity for Cm^{3+} over Am^{3+} was found to be further enhanced at lower concentration of TiBDGA and a S.F. value of ~10 is observed at 20 mM TiBDGA.

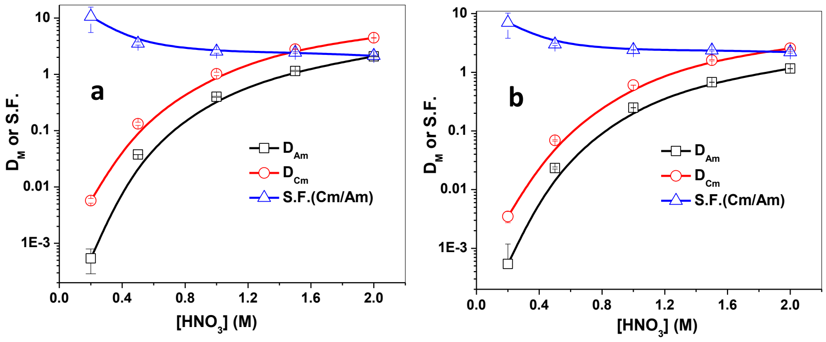

Figure 1: Effect of HNO_3 concentration on the extraction of Am^{3+} and Cm^{3+} by TiBDGA (a) and TiPDGA (b); Org. Phase: 20mM DGA derivatives in n-octanol; Aq. Phase: 1 mM SO_3PhBTPhen in varying concentration of HNO_3

Keywords: Americium, Curium, BTPhen

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DAE-BRNS SESTEC-2024
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Mass transfer performance of Annular Centrifugal Extractor in presence of HDBP in 1.1 M TBP/n-DD solvent

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The Annular Centrifugal Extractor is a candid candidate for the Fast Breeder Nuclear Fuel reprocessing application. In CORAL facility ACE was successfully operated for more than two decades to extract U & Pu from the FBTR spent fuel. One of the major challenges in the FBR's Fuel reprocessing is solvent degradation. Dibutyl Phosphate (HDBP) is one of the major degraded solvent products and interferes during stripping operation. In fast breeder fuel reprocessing campaigns at CORAL facility observed as high as 8 g/L HDBP in the lean organic stream and average HDBP content was around 3 g/L [3]. To understand the effect of HDBP, the Extraction and stripping experiments are conducted in 16 stages of ACE setup. In the present study, the extraction behavior of Uranium (1 g/L) in 1.1 M TBP (with 3 g/L HDBP)/n-DD was studied with dual acid scrubbing. In fast breeder At CORAL facility as high The HDBP concentration was selected based on our CORAL Similarly, the stripping behavior of U (VI) from the loaded organic phase (1.1 M TBP with 3gpl HDBP/ n-DD, product from extraction experiment) was studied with single and dual feed strip acid flow conditions. The extraction experiment was conducted for about 2.5 hrs and results show that the ACE setup has reached the steady state condition within 20 mins. Later, the single strip acid flow experiment was conducted for 2 hrs and results show that given ACE reached steady state condition within 15 minutes. Similarly, the dual feed strip acid flow experiment was conducted for 6.5 hrs and results show that given ACE has reached the steady state condition within 15 minutes. The stage samples (both aqueous and organic phases) from all the above three experiments are collected and results are shown in below Fig 1 to 3.

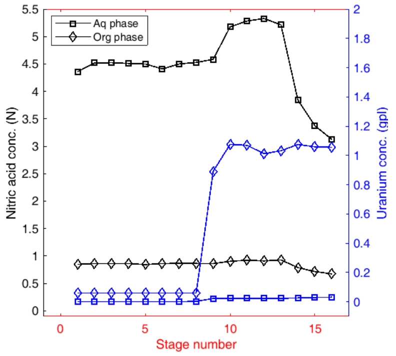

Fig. 1: U and acid conc. in the aq. and org. phases w.r.t stage numbers in the extraction experiment

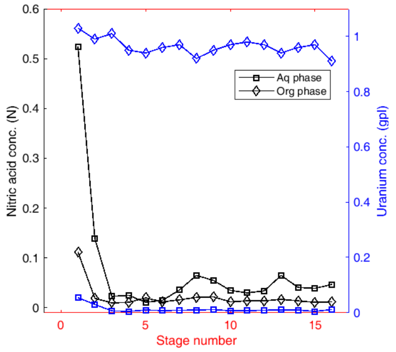

Fig. 2: U and acid conc. in the aq. and org. phases w.r.t stage numbers in the single strip acid flow stripping experiment

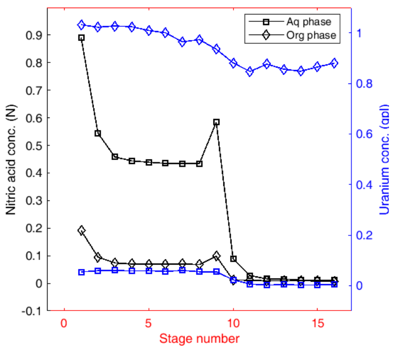

Fig. 3: U and acid conc. in the aq. and org. phases w.r.t stage numbers in the dual feed strip acid flow stripping experiment

From Fig. 1 it has been found that three counter-current stages are enough to complete the uranium extraction. In single strip acid stripping experiment result (Fig. 2) shows that U concentration in the organic phase is almost constant irrespective of stage number and not stripping out from the organic phase. Similarly, the dual strip acid stripping experiment result (Fig. 3) shows that U is not stripping out from the organic phase in the presence of HDBP. Uranium concentrations in the dual strip acid stripping experiment from 9th stage to 16th stage is slightly lower than that of 1st stage to the 8th stage. It is due to the introduction of 4N nitric acid in the 9th stage as per the Pu stripping flow sheet condition. It is concluded that the U is not stripping out from the organic phase in the presence of HDBP.

Keywords: Annular Centrifugal Extractor, Di-Butyl Phosphate, PUREX process, Extraction, Stripping

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Unsteady drag coefficient acting on a drop forming at tip of a top-submerged nozzle

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Air pulsed columns with nozzle plates are the workhorse solvent extraction equipment in reprocessing industry. Nozzle direction is oriented downwards which ensures formation of aqueous drops in an organic continuous phase. There is a scarcity of literature on drop formation in top submerged nozzle. As drops form they transition from a growth to necking phase. Thus center-of-mass of evolving drop is accelerating or decelerating. As of now a steady state drag coefficient is considered in all mathematical models that describe drop formation. But in reality due to acceleration/deceleration drag coefficient is variable and not constant. There is a recent study that estimates drag experienced by a falling drop in a pulsatile flow **[1]**. Here we report for the first time how drag experienced by an aqueous droplet evolves as the drop forms at the tip of a top submerged nozzle and undergoes transition from growth to necking phase. Under accelerating conditions, inertial, buoyancy (driving force), drag, virtual mass and Basset (memory) (restraining) forces act on the evolving drop **[2]**. C_{DA} encompasses the effect of net restraining forces (drag, virtual mass and Basset force) [**2**]. The experimental setup comprises of a beaker containing 30% TBP in dodecane (saturated with uranium). 109 g/L uranyl nitrate solution (aqueous dispersed phase) is injected at desired flow rate using a precise syringe pump. Nozzle inner diameter is 1.91 mm. Fig. 1a and b shows the snapshots of a drop forming at the tip of the submerged nozzle (3 ml/min), along with the complete experimental setup. A high speed camera is used to capture the process (125 f/s). Image analysis is used to determine X-Y locations of center of mass of the evolving drop. Backward differencing is used to determine velocity and acceleration terms. Fig. 2 a shows temporal variation of C_{DA} **[2]** for three aqueous phase flow rates. Initially there is an increase in drag as the evolving drop becomes flat (oval shaped) during growth phase. Thereafter during necking phase the drop becomes pear shaped and this results in a lower drag. However this effect tends to die down at higher flow rates. Also absolute values of drag coefficient reduces at higher flow rates. The inverse relationship between C_{DA} and Re is also established (Fig. 2 b).

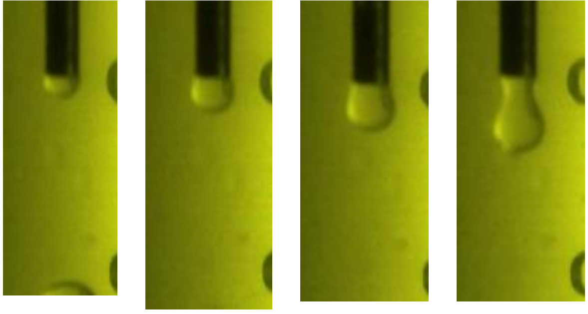
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Figure 1a: *Snapshots of drop formation (3 ml/min)*


Figure 1b: *Experimental setup*

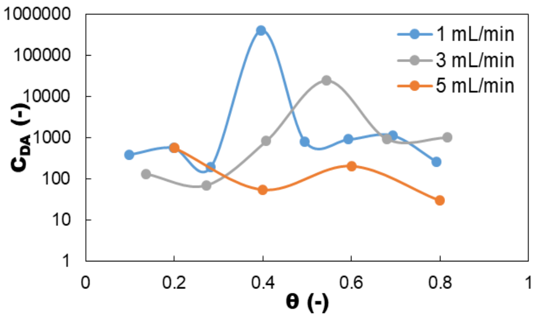

Figure 2a: *C_D v/s time for varying flow rates*

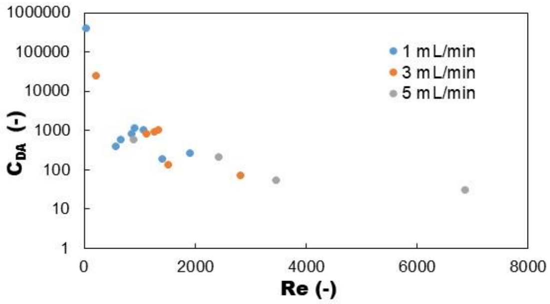

Figure 2b: *C_D v/s Re for varying flow rates*

Keywords: *drop formation, drag coefficient, top-submerged nozzle, uranyl nitrate, unsteady state*

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Solid phase extraction of trivalent actinides using Chromosorb resin impregnated with TREN-DGA in RTIL and molecular diluent

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Separation of the minor actinides such as Am, Np and Cm from the acidic effluents generated in reprocessing of nuclear waste is important for recycling and effective management of nuclear waste. [1] Extraction chromatography found to be advantageous than that of other methods such as solvent extraction, precipitation etc., for separation of actinides from effluents due to its lower solvent inventory, lower secondary waste generation and ease of operation [2]. We have synthesized several tripodal DGA ligands where the DGA arms are appended to either a central 'N' atom [3] or a planar benzene moiety [4] and reported the extraction of trivalent actinide/lanthanide ions such as Am^{3+}/Eu^{3+} from nitric acid feeds. In the present work, two extraction chromatographic resins were prepared by impregnating TREN-DGA ligand (tripodal DGA ligand) on Chromosorb in RTIL medium i.e. 1-butyl-3-methylimidazolium bis(trifluoromethanesulphonyl) imide (C_4mim NTf_2) (R-I) and other in 5% *Iso*-decanol dodecane medium (R-II) for separation of trivalent actinides from acidic feed. Extraction chromatography studies have been carried out using these resins and the resins were characterized by FTIR, TGA and SEM techniques.

Kinetic study suggests attainment of equilibrium in 60 min. for both resin R-I and R-II. Acid variation studies were carried out using both the resins by measuring K_d-Am and K_d-Eu as shown in Fig 1. Acid variation studies suggest that K_d values of Am and Eu decreases with increase in acidity indicating cation exchange type of mechanism for R-I resin whereas K_d values of Am and Eu increases with increase in acidity indicating solvation type of mechanism for R-II resin. Sorption isotherm studies were carried out using both the resin and data were fitted to different isotherm such as Langmuir, Freundlich and DR isotherm. The best fitting was observed for Langmuir adsorption isotherm with a sorption capacity 11.5(±0.23) and 10.24(±0.25) mg/g for R-I and R-II respectively. Column studies were carried out at 3M HNO_3 and break through were obtained at 10 ml for R-I and 9 ml for R-II as shown in Fig 2 and both the column were successfully eluted using 1M guanidine carbonate + 0.05M EDTA in distilled water. Reusability studies were carried out using both the resins for five stages and it was found that both the resins were found to be good up-to three stages of extraction.

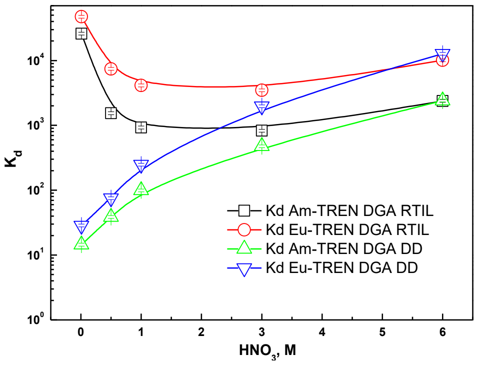

Fig 1: Uptake of Am(III) and Eu(III) as a function of feed nitric acid concentration.

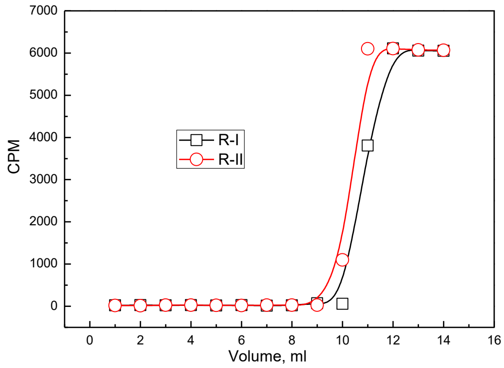

Fig. 2. Breakthrough profiles obtained with R-I and R-II resins. Feed: 0.4 g/L Eu- nitrate solution in 3 M nitric acid.

Keywords: Extraction chromatography, actinides, ionic liquid,

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Demonstration of Tri-iso-amyl phosphate (TiAP) as an alternate extractant to tri-n-butyl phosphate (TBP) for separation of Zr(IV) and Hf(IV)

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At present, Tri-n-butyl phosphate(TBP) is being used as a solvent for separation of Zr(IV) and Hf(IV). However the experience gained in the last six to seven decades revealed that TBP has some limitations such as higher aqueous solubility(0.4 g/L), chemical and radiation degradation, and third phase formation[1]. Third phase formation is an important phenomenon during the processing of tetravalent metal ions such as Pu(IV), Th(IV), Zr(IV) etc. Third phase formation with Zr(IV) using TBP based solvent is possible when the zirconium concentration in the organic phase surpass definite concentration limit called limiting organic concentration (LOC). Tri-iso-amyl phosphate (TiAP) is considered as an alternate solvent to TBP especially for processing tetravalent metal ions due to higher third phase limits[2]. LOC values for Zr(IV) with 1.1 M TiAP/n-DD and 1.1 M TBP/n-DD at 6 M HNO_3 are 20 g/L and 8 g/L, respectively at 303 K. In the present study solvent extraction studies were carried out with solutions containing Zr(IV), Hf(IV) and Ti(IV) with TBP and TiAP based solvents. A feed slurry containing Zr, Hf and Ti about 82, 2.4 and 0.21 g/L, respectively in 4.5 M HNO_3 was employed. The third phase formation behavior with Zr was examined using 1.1M and 1.47M TiAP and TBP solutions in n-Dodecane (n-DD) with different A/O ratios. Third phase was observed with 1.1M TBP/n-DD even in the case of 1:6; and third phase was not observed from 1:7 onwards. Similarly third phase was not observed with 1.47M TBP/n-DD from 1:4 onwards; whereas third phase was not observed both in the case of 1.1M and 1.47M TiAP/n-DD from 1:3 onwards indicating that the third phase limits are higher in the case of TiAP system. Cross-current experiments were carried with zirconium feed slurry using 1.47M TiAP/n-DD with 1:3 A/O ratio. The extraction of Zr(IV), Hf(IV) and Ti(IV) was found to be about 89.8%, 23.8% and 21.5%, respectively in the case of 1.1M TiAP/n-DD after four successive contacts. Similarly cross-current experiments were also carried out with both fresh and used TiAPs with 1:3 A/O ratio for extraction and stripping studies. Old stock of TiAP(from ZC) was washed with 1:1 ratio of 5M NaOH followed by water wash(5 times) to remove any impurities. The concentration Zr decreases from stage 1 to 5 during the scrubbing(4 M) and stripping(0.01M) of Zr from loaded TiAP (Fresh and Used)(Fig.1 and 2). No emulsions were observed either during extraction, scrubbing and stripping with TiAP based solvents or phase separation was clear. Small fraction of Hf and Ti is extracted into organic phase and the extracted Hf and Ti is quantitatively stripped in the first stage itself. These studies may pave way for the development of flow sheets for separation of Zr from Hf and Ti using TiAP based solvent with high throughputs.

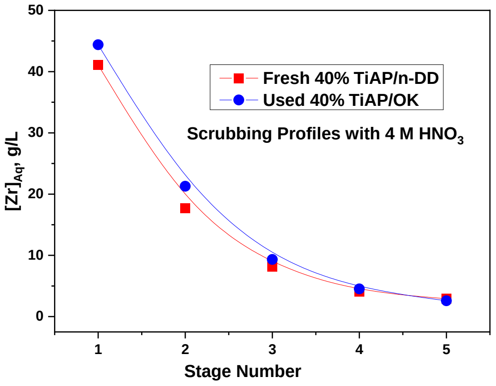

Fig.1 Scrubbing profiles for Zr with 1.47M TiAP in n-DD and kerosene with fresh and used solvents

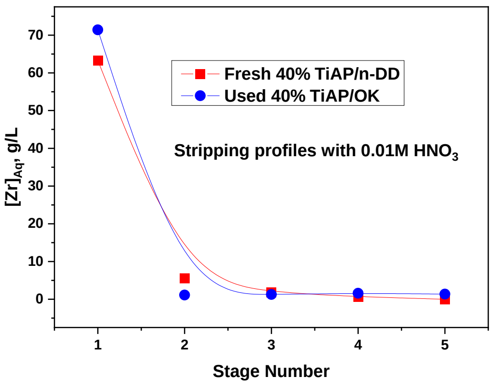

Fig.2 Stripping profiles for Zr with 1.47M TiAP in n-DD and kerosene with fresh and used solvents

Keywords: Simulated U-Zr, TBP, TiAP, Cross-current, Extraction, Stripping

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Separation of ^{229}Th from ^{233}U using Solvent Extraction for application in TIMS

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Isotope dilution-thermal ionization mass spectrometry (ID-TIMS) is a benchmark method for the high-precision determination of different elements and one of the pre-requests of this method is the availability of spikes with an isotopic composition entirely different from that of the sample. Isotopically enriched ^{229}Th is employed as a spike for the ID-TIMS determination of thorium in different matrices. Trace quantities of ^{229}Th produced from the α-decay of ^{233}U can be isolated after careful separation procedures. Different separation methods such as solvent extraction, ion exchange, extraction chromatography, etc. are reported for separating thorium and uranium based on their charge and chemical properties [1].In the present work,solvent extraction studies were carried outusing Aliquot 336 (tricaprylmethylammonium chloride, a quaternary ammonium salt) as an extractant for the separation of thorium and uranium in^{233}Uslag samples.

The experiments were carried out by dissolving aliquot 336 in xylene to yield a solution with a concentration of 5%.This solution was equilibrated multiple times with 4M nitric acid (HNO_3) to convert the quaternary ammonium salt (Aliquot 336) to its nitrate form.The concentration of nitric acid in the slag sample (200 mL) was adjusted to 4M and the solvent extraction was performed three times with the conditioned extractant. Following the extraction, thorium was stripped into the aqueous phase by contacting with 5M of HCl. In 4M of nitric acid, thorium forms anionic thorium-nitrate complex which gets extracted into the organic phase by Aliquot 336. When the medium is changed from HNO_3 to HCl, thorium forms cationic species and is transported into the aqueous phase.

The extent of separation of ^{229Th} from ^{233}U and other decay products was monitored by HPGe analyses of purified and un-purified samples of slags. As can be seen in Fig.1, the signature peaks of ^{229}Thcorresponding to the gamma energies at 85.4 keV and 88.4 keV are present but the peak corresponding to ^{233}U at 71.82 keV is absent in the purified sample. Figure 2 shows the mass spectrum obtained by the TIMS analysis of the purified thorium fraction which indicates the presence of both ^{229}Th and ^{232}Th isotopes. The peaks corresponding to ^{233}U could not be seen in the mass spectrum and this implies that the extraction process employed for the separation of Th and U is quite efficient.

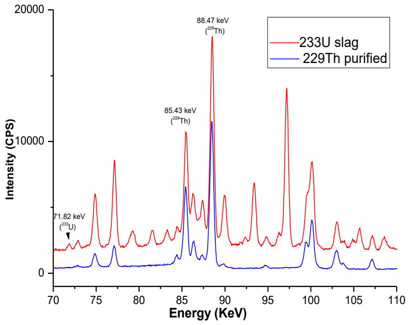

Fig. 1: Gamma spectrum of the slag sample before and after the separation

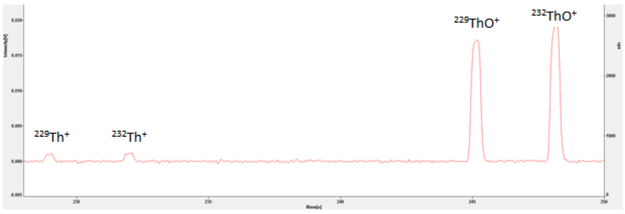

Fig 2. Mass spectrum of Purified thorium fraction

Keywords: Thorium, Uranium, Solvent extraction

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A Novel Method for Plutonium Extraction and Quantification Using Supported Liquid Membrane for Alpha Spectrometry

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Quantification of actinides in the complex environmental, biological, process and waste streams requires multiple steps like selective pre-concentration and matrix elimination, solid source preparations generally by evaporation or electrodeposition, and finally alpha spectrometry [1,2]. A novel method has been developed in the present work for extraction of plutonium from acidic samples using an amide functionalized supported liquid membrane (SLM), followed by preparation of alpha source by direct decomposition of the SLM for the quantification of Pu by alpha spectrometry. The DOHA@PP SLM was prepared by physical immobilization of a solution of the extractant N,N'-dioctyl,α-hydroxyacetamide (DOHA) in dodecane, within the pores of commercially available polypropylene (PP) membrane.

Figure 1 represents the effect of DOHA concentration in the SLM on the extraction of Pu from 3 M HNO_3. It can be seen from Figure 1 that, if DOHA concentration in the membrane is increased from 0.05 M to 2 M, sorption efficiency for Pu(IV) increased from 14±1% to 96±2%. Figure 2 shows the extraction of Pu from aqueous samples having Pu concentration in the range 1–10 ppb. It can be seen from Figure 2 that Pu extraction efficiency of DOHA@PP SLM constantly decreases from 87±2% to 63±1% when Pu concentration in the aqueous medium reduces from 10 ppb to 1 ppb. After extraction, the membrane pieces were placed at the center of electro-polished stainless steel planchet and slowly ignited in flame to red-hot to prepare an alpha source. During such heating, the membrane was completely decomposed and the Pu pre-concentrated in the membrane was deposited at the center of the plachette. The alpha spectra of Pu from these planchettes were recorded using PIPS detectors and various parameters affecting the quality of alpha spectrometry e.g. FWHM, percentage tail contribution, peak-to-valley ratio etc. were found to be comparable with those obtained from a conventional drop-evaporated alpha sources. Determination of ($^{238}Pu/^{239}Pu+^{240}Pu$) alpha activity ratio in (U,Pu)C fuel sample was carried out using membrane deposited source and the results were found to agree within 1% to the results obtained using drop-evaporated alpha sources. Further studies are in progress for the quantification of ppb level of plutonium in aqueous samples using the developed method.

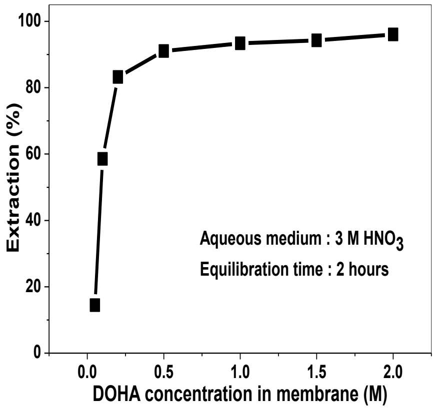


Fig. 1. Effect of DOHA concentration on Pu extraction

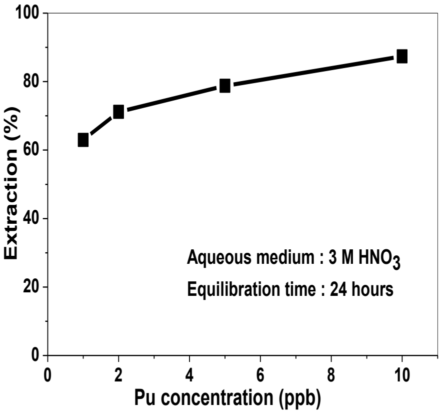
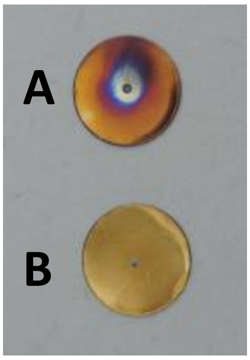


Fig. 2. Extraction of ppb level of Pu from aqueous medium.



A: Drop evaporated source
B: Membrane deposited source

Keywords: Plutonium, supported liquid membrane, trace analysis, alpha spectrometry

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Partitioning of Thorium from Uranium in Nitric Acid Medium using Amide modified Supported Liquid Membrane

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In recent times, nuclear power based on the concept of fast reactors, advanced heavy water reactor (AHWR) and accelerator driven sub-critical system (ADSs) have gained significant attention [1]. In AHWR, ^{232}Th-^{233}U is used as the primary fuel for power generation. The ADSs based on the ^{232}Th-^{233}U fuel cycle is important as it can produce nuclear power with the use of thorium as main fuel. Extraction and partitioning of various actinides in the complex process and waste streams is very crucial at various stages of operation of any nuclear reactor – also in each chemical purification stage, it is always necessary to estimate the amount of U and Th. The present work involves selective extraction of thorium in presence of uranium in acidic samples using an amide functionalized supported liquid membrane (SLM). The DOHA@PP SLM was prepared by physical immobilization of a solution of the extractant N,N'-dioctyl,α-hydroxyacetamide (DOHA) in dodecane, within the pores of commercially available polypropylene (PP) membrane. Figure 1 represents the extraction profiles of DOHA@PP SLM for U(VI) and Th(IV) as a function HNO_3 concentration in the aqueous medium. It can be seen from Figure 1 that, at any given nitric acid concentration, the extraction efficiency of DOHA@PP SLM for Th(IV) is significantly higher than the extraction efficiency for U(VI) – this could be attributed to the higher ionic potential of Th(IV) compared to U(VI). At 4 M HNO_3 medium, the extraction efficiency for Th(IV) and U(VI) was found to be 72±1% and 8±2%, respectively – this indicates that DOHA@PP SLM may preferentially extract Th(IV) in presence of U(VI). To check the selectivity of DOHA@PP SLM towards Th(IV), extraction studies were carried out from an equimolar mixture of (U+Th). Figure 2 shows the variation of separation factor S.F. = D_{Th}/D_U as a function of HNO_3 concentration in the aqueous medium. It can be seen from Figure 2 that, the optimum S.F. is achieved in 4M HNO_3 medium. Further studies are in progress for the quantification of thorium in aqueous samples using the developed membrane.

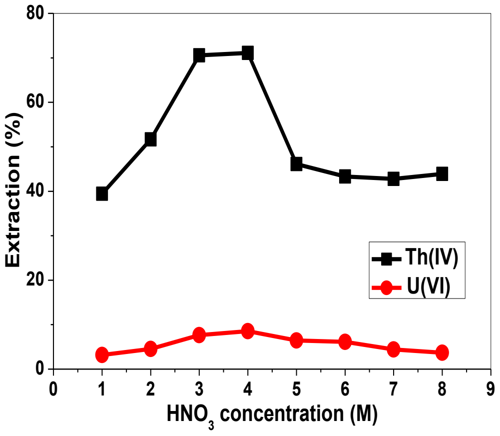

Fig. 1. Extraction of Th(IV) and U(VI) by DOHA@PP SLM from nitric acid medium.

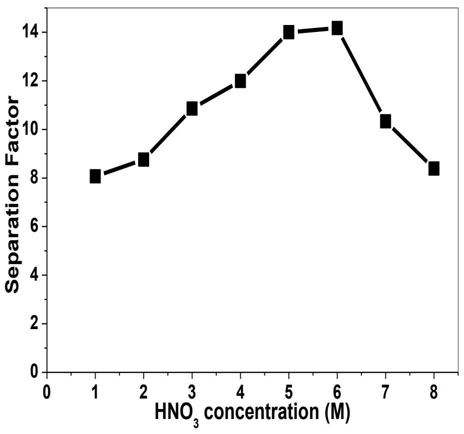

Fig. 2. Separation factor as a function of nitric acid concentration.

Keywords: Thorium, Uranium, supported liquid membrane, actinide partitioning

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Understanding the Extraction behavior of Hafnium and Titanium in Presence of Zirconium with Tri-n-Butyl Phosphate

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Titanium (Ti) is one of the critical impurities apart from hafnium in nuclear grade Zirconium oxide. The extraction behavior of Ti was investigated by several authors [1, 2]. The concentration of Ti varies in washed dry frit (WDF) based on the source of sand. Zircon sand is available at three locations in India namely Manavalakurichi-Tamilnadu (MK grade), Chavara-Kerala (Q grade) and Chatrapur- Odisha (OR grade) with varying TiO_2 concentration of 0.25, 0.3 and 0.8% respectively. As per the current trends of zircon sand reserves, the MK grade sand and Q grade sand (containing low TiO_2 values) are depleting and sand having higher TiO_2 concentration (OR grade – OSCOM) has to be utilized in future for producing nuclear grade ZrO_2. Titanium exhibits similar extraction behavior as Zr and Hf. However, in order to use zircon sand with higher levels of Ti, exclusive study of solvent extraction of Ti from nitric acid media with TBP solvent is required. In this context, extraction behavior of Ti in the presence of Zr and Hf using 33% TBP/kerosene from nitric acid medium under ZOP operating conditions was examined. Separation factors for Zr against Ti and Hf at various free acidities with TBP was investigated. Initial trials with MK Sand WDF and OSCOM Sand WDF extracted using 33% TBP/Kerosene at 4.8 M HNO_3. The extraction of TiO_2 was found to be 88.6% and 38.4% in the case of OSCOM and MK Sand WDF respectively with the extraction of ZrO_2 about 96.1% and 91.9%. The percentage extraction and distribution ratios (*D*) of ZrO_2, HfO_2, and TiO_2 were investigated with 33% TBP/Kerosene as a function of aqueous phase nitric acid concentration at A/O ratio of 1:5 with MK sand WDF. The *D* values for Zr, Hf and Ti also follows similar trend. Generally *D* values of Zr increases with increase in acid concentration if the metal ion concentration in the feed is maintained uniformly. The trend in the present study is due to non-uniform concentration of ZrO_2 in feed slurry. The separation factors for Zr against Hf and Ti was also evaluated for 33% TBP/Kerosene as a function of HNO_3 concentration. The percentage extraction Ti shows a minima at about 2 M HNO_3 and the extraction of Ti is lower at higher acidities(>4M) resulting in higher separation factor. Solvent extraction experiments were also carried out different A/O ratios such as 1:6, 1:7, and 1:10 with OSCOM and MK Sand WDF feed slurry using 33% TBP/Kerosene. The effect of phase ratios was also investigated on the percentage extraction of metal ions and separation factors.

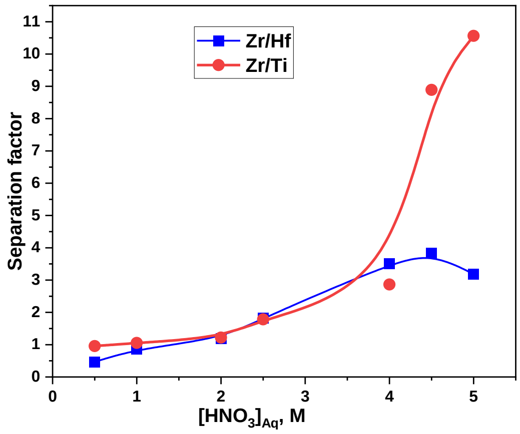

Fig.1: Separation factors for Hf and Ti over Zr by 33% TBP/Kerosene as a function of nitric acid concentration

Keywords: Zirconium, Hafnium, Titanium, TBP, Separation factor

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Extraction of Nd(III) in Room Temperature Ionic Liquid using Benzyl chloroacetamide ligand

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Lanthanides are becoming increasingly important as they serve critical roles in numerous sophisticated modern technologies. Therefore, the development of optimal process for their recovery, whether from primary or secondary sources, has become very important to meet the growing global demand [1]. Traditionally, liquid-liquid extraction is the most commonly employed method for the extraction and recovery of lanthanides from various sources. However, conventional liquid-liquid extraction technologies pose environmental risks due to the use of organic solvents which are volatile, combustible and harmful. Room temperature ionic liquids (RTILs) have emerged as a new class of tunable solvents which are considered to be more environment friendly and can be an alternative for traditional volatile organic solvents in Liquid-Liquid extraction. RTILs have low volatility and combustibility, high thermal stability, wide liquidus range and offer great efficiency, making them a suitable candidate to replace conventional volatile solvents [2]. Here, we report a highly efficient extraction of Nd(III) metal ions from 1.0 M nitric acid media employing a benzyl chloroacetamide ligand and [C_4mim][SbF_6] ionic liquid as solvent for liquid-liquid extraction process. Benzyl Chloroacetamide was synthesized by reaction of chloroacetyl chloride with benzyl amine and was characterized using FT-IR and NMR spectroscopy. The influence of various factors, such as contact time, acid concentration, cation concentration, nitrate ion concentration, and ligand concentration on the extraction efficiency was examined, the aqueous phase before and after extraction was analyzed for quantification of Nd(III) using ICP-AES and UV-Vis spectroscopy. It was observed that almost quantitative extraction of Nd(III) from the aqueous to the IL phase was achieved within 10 minutes of equilibration time with this solvent system.

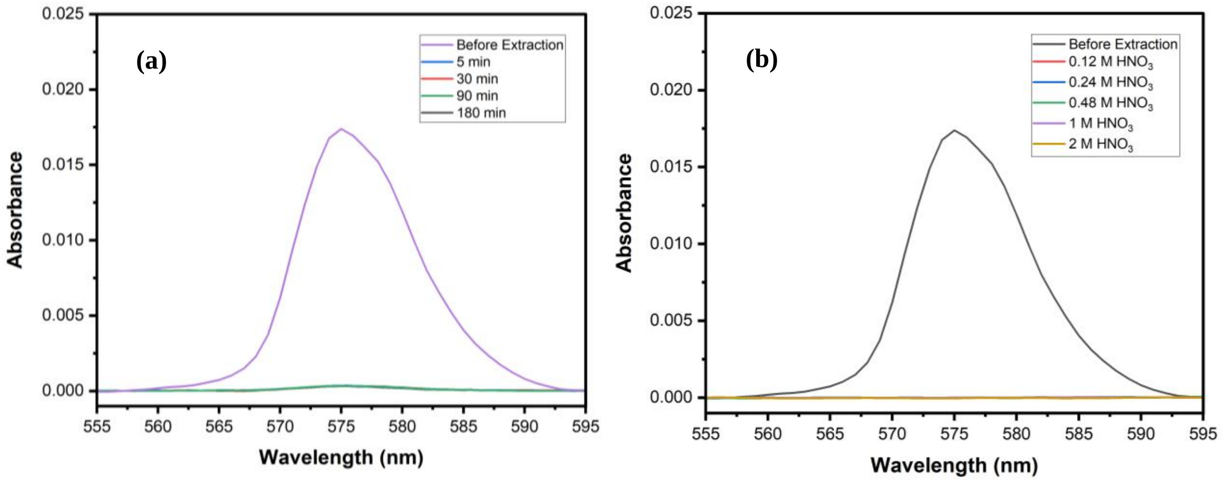

Figure. UV-Visible spectra of Nd (III) metal ion in aqueous phase, before and after extraction at (a) different equilibration time and (b) various acid concentrations

Keywords: Lanthanides, Ionic Liquids, Solvent Extraction, UV-Vis Spectroscopy, ICP-AES

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Separation of REEs from Phosphogypsum

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Rare earth elements (REEs) are found in notable amounts in Rock Phosphate(RP) deposits around the world [1]. REEs have unique magnetic, optical, and electrical properties that make them indispensable elements in many high-tech processes [2]. RP is processed for production of PA, which in turn used for fertilizer manufacturing. The processing of RP forms large amounts of waste by-product Phosphogypsum (PG). PG displays varying concentrations of REEs depending on the source. Around 70% to 85% of REEs present in RP ends up in PG [3]. Extracting REEs from PG presents formidable challenges due to their trace concentrations (usually < 0.1% wt.) and their intricate entrapment within mineral phases. As a result, experiments that effectively work with PG from one site might yield different outcomes when applied to another PG stack. These distinctions stem from differences in the phosphate ore (origin) processed, processing conditions, and the quality of sulfuric acid utilized in wet-phosphoric acid processing. To surmount this, a range of physicochemical pre-treatment methodologies have been explored. This research aims to devise a process for extracting REEs from PG obtained by processing of Egyptian Rock Phosphate. The utilization of adequate pre-treatment, followed by nitric acid leaching were optimized. Extraction efficiencies for Rare Earths have been determined across different experimental conditions. Optimization of variables such as nitric acid concentration, liquid to solid ratio (ml: g), temperature, and contact time has been conducted. EPG derived from sulphuric acid digestion of Egyptian Rock Phosphate (ERP) is prepared. For elemental analysis of ERP and EPG were multi-acid microwave assisted digestion followed by subsequent ICP-MS analysis. ∑REE in ERP and EPG were ~1470 ppm and ~930 ppm respectively. Nitric acid leaching of PG showed that an increase in acid concentration from 2 M to 8 M a drop in %L was observed.
The process yields REEs leachate alongside purer PG.

Table 1 Studies for optimization of HNO_3 concentration

REEs	EPG	at Equilibrium			
	Initial	2 M	4 M	6 M	8 M
	mg.kg^{-1}	mg.kg^{-1}	mg.kg^{-1}	mg.kg^{-1}	mg.kg^{-1}
Y	222.34	92.64	55.09	44.06	28.02
La	143.19	63.85	41.80	34.86	23.35
Ce	248.96	114.84	74.02	60.67	39.56
Pr	32.11	15.05	9.85	8.04	5.20
Nd	135.68	65.45	42.81	34.60	22.23
Sm	27.96	12.38	7.56	6.87	4.13
Eu	8.39	3.42	2.07	1.89	1.13
Gd	32.29	14.50	8.58	7.78	4.66
Tb	5.15	2.20	1.29	1.18	0.71
Dy	28.95	12.78	7.34	6.89	4.07
Ho	6.67	2.72	1.54	1.46	0.87
Er	18.60	8.07	4.70	4.28	2.54
Tm	2.66	1.05	0.59	0.57	0.34
Yb	15.64	6.47	3.66	3.54	2.08
Lu	2.59	1.00	0.57	0.54	0.33
∑REE	931.16	416.40	261.46	217.23	139.19

ICP-MS analysis was carried out at 0.6g.L^{-1} sol.

$$\%L = \left(\frac{REEconcentration \in Leachate}{REEconcentration \in PG}\right) X100$$

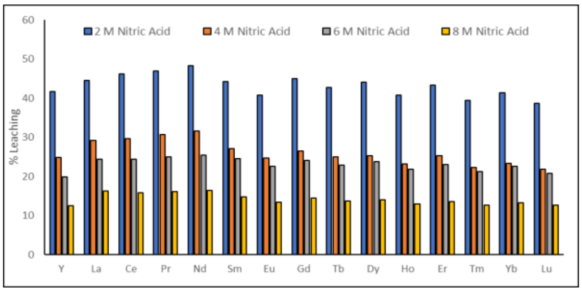

Figure 1. % Leaching of REEs in different nitric acid

Keywords: Rare Earth Elements, Rock Phosphate, Phosphogypsum, Acid Leaching.

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A Green Approach for Recovery of Lanthanides from Coal Fly Ash using Supercritical Fluid Extraction

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Rare earth elements (REE) (lanthanides, yttrium and scandium) play an important role in variety of technologies, ranging from consumer products to defense applications. These materials are crucial in the production of computer memory chips, rechargeable batteries, cell phones, and fluorescent lights. However, due to growing demand and supply constraints, these materials have been classified as critical materials [1]. In the recent past, coal fly ash (CFA) has been emerged as a potential source for the REEs. Acid leaching, solvent extraction and ion-exchange based methods are widely employed for recovery REEs from different sources. In the present study, a green approach, based on the supercritical fluid extraction was examined for recovery of lanthanides (Lns) from CFA.

The fly ash samples are obtained from Indian Thermal Power Plants. These samples are characterized and amount of Lns present in the CFA are determined using neutron activation analysis, reported in **Table 1**. TBP-HNO_3 acid adduct was prepared by equilibrating equal volumes of neat TBP and 70 % nitric acid and employed for recovery studies. Supercritical carbon dioxide ($SCCO_2$) containing the acid adduct was utilized for extraction studies. 5 g of CFA and 3 mL of acid adduct were loaded into a high pressure equilibrium cell and the vessel was filled with $SCCO_2$ till it reaches to desired pressure of 15 MPa at 323 K. The contents were kept for static equilibration at 15 MPa and 323 K for period of 2 h. Subsequently, a dynamic extraction with neat $SCCO_2$ is carried out for a period of 3 h. During the static equilibration, the lanthanides present in the CFA converted the respective nitrates. Subsequent reaction between Ln nitrates and TBP leads for the formation of a CO_2 soluble Ln-TBP complexes. These Ln-TBP complexes are carried over to collection vessel with dynamic mode of extraction. Ln species present in the complex were back striped with 0.01 M HNO_3. The quantification of Lns is carried out using Reversed Phase High Performance Liquid Chromatography with a monolith column. A combination of 0.05 M α-hydroxy-*iso*-butyric acid and 0.01 M camphor-10-sulfonic acid with a pH of 3.8 was employed as mobile phase. Ln complexes were monitored at 655 nm with UV-Visible detector using arsenazo (III) as a post column reagent. Extraction and recovery of Lns from CFA is provided in **Table 1**. The extraction efficiency was found to about 75% to 80%. Complete extraction of Lns can be achieved by optimizing the experimental parameters such as temperature, pressure, nitric acid concentration and extraction time. These preliminary studies have demonstrated the recovery of lanthanides from CFA with minimum generation of liquid waste.

Table 1. Supercritical fluid extraction efficiency of lanthanides from coal fly ash

S.No.,	Lanthanide	Concentration of lanthanides in fly ash (ppm)	Extraction efficiency (%)
1	Lanthanum	340	83
2	Cerium	812	84
3	Neodymium	69	77
4	Samarium	118	82
5	Europium	30	78
6	Gadolinium	14	75
7	Terbium	15	74
8	Holmium	13	72
9	Ytterbium	38	77

Keywords: Coal Fly Ash, Green Chemistry, Lanthanides, Supercritical Fluid Extraction, Tributyl Phosphate,

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Dissolution of UO_2 in a ionic liquid with subsequent electro-deposition: Sustainable strategy for non-aqueous reprocessing

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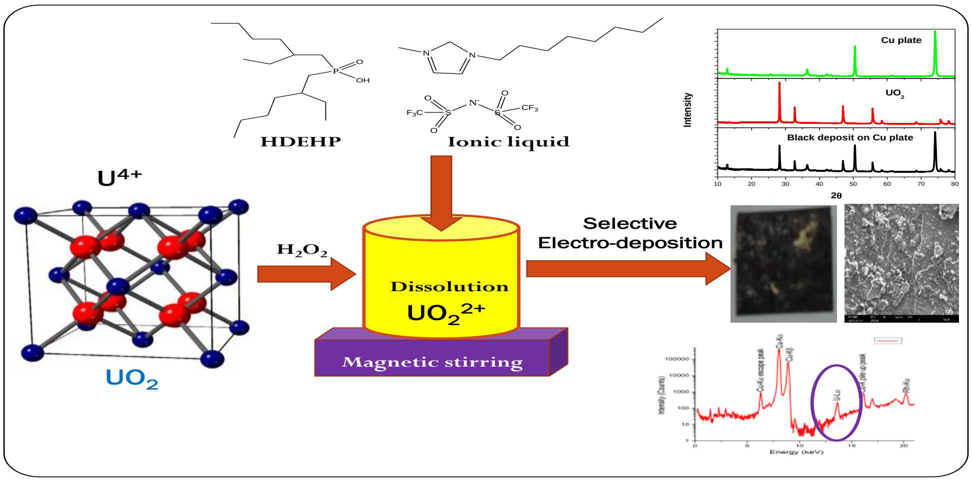
Molten salt based pyroprocessing is reported to have a good potential for short cooled spent fuel reprocessing[1]. However, the major limitations of this have been the requirement of high temperature and high pressure and highly corrosive chemical environment due to the chloride salts. Application of ionic liquid has been proposed as potential alternatives to non-aqueous reprocessing, wherein fuel material oxides are dissolved in the first step; while in the second step, selective electro-deposition to be performed[2]. The deposited solid can directly be used for fuel fabrication as selective electro deposition would eliminate the need of muti-step purification. The high solubilizing ability of ionic liquid, good radiation stability and large electrochemical window would be the primary properties to be exploited in this attempt.

The quantitative oxidative dissolution of UO_2 into C_8mim.NTf_2 ionic liquid was successfully performed using H_2O_2 as the oxidizing agent and 0.4 M HDEHP as the complexing agent with four hours of equilibration with an oxide to ionic liquid ratio of 10 mg mL^{-1} which increased to 8 h for 50 mg mL^{-1} as the ratio. The dissolution trend observed was $UO_3 > UO_2 > U_3O_8$ which was in accordance to their lattice energy. Out of several oxidants tested (H_2O_2, $NaClO_4$, HNO_3, RCO_3H etc.), H_2O_2 was found to be the most effective (10µL for 10 mg of UO_2 dissolution in 1 mL of C_8mim.NTf_2); while the optimized HEDEHP concentration was 0.4 M. At higher temperature, the dissolution was found to be faster indicating the endothermic nature of the dissolution, which was further confirmed by calorimetric determination. The dissolution was found to follow the pseudo 2nd order kinetic model predominantly with $UO_2(HDEHP)^+$ species having D_3 symmetry. Based on the electrochemical behavior of UO_2^{2+} in C_8mim.NTf_2, a selective electro-deposition of uranium from loaded ionic liquid phase has been optimized. Appearance of black deposit on Cu electrode with enhanced surface roughness has been observed. The presence of U in the deposit was confirmed by EDXRF, while the XRD pattern indicated the deposition of UO_2, which was further corroborated by the FTIR spectra obtained for the black deposit in comparison with UO_3, UO_2 and U_3O_8. **Fig.1** gives a sechamtic presentation of the non-aqueous ionic liquid based dissolution and subsequent electro-deposition for UO_2



Keywords: DFT, Uranium, Complexation, Coordination modes, ADA

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Utilizing a controlled H^+ ion removal strategy of a highly fluorinated β diketone for the selective leaching of Nd_2O_3 from its mixture with Pr_6O_{11}

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The Nd based magnet is one of the strongest known magnets, while Nd-YAG is the four state laser popularly used for opto-electronic applications. The Ta based machinary and the low density alloy fomation are some of the important applications. The specific applications needs the high purity materials. However, due to the similar chemical nature and existance of +3 oxidation state, their mutual separation is extremely difficult. The higher lattice energy of Pr_6O_{11} (-76 eV) compared to that of Nd_2O_3 (-36 eV), led to the preferential dissolution of Nd_2O_3 into ionic liquid in the presence of a suitable β diketone with seven fluorine atoms, i.e., 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione (HFOD). The controlled release of H^+ from the enolate form is reponssible for the selective leaching of Nd^{3+} from the Nd_2O_3 crystal. The presence of water in the ionic liquid phase facilitated the dissolution process. Sintering of both the oxides at 700°C was required for conversion of the most refractory Nd_2O_3 and Pr_6O_{11} in subsequent dissolution. Literature reports suggested separation factors (S.F.) in the range of 1.5-2.1 which are not adequate for spectroscopic grade separations in a single step. However, in the present case, very impressive S.F. values of 490, 732 and 900 were achieved for 1:1, 2:1 and 4:1 mixtures of Nd_2O_3:Pr_6O_{11}, respectively. The HFOD concentration was found to vary from 0.01 M to 0.5 M, the optimum concentration was found to be 0.1 M with the S.F. ~920 [**Fig.1**].

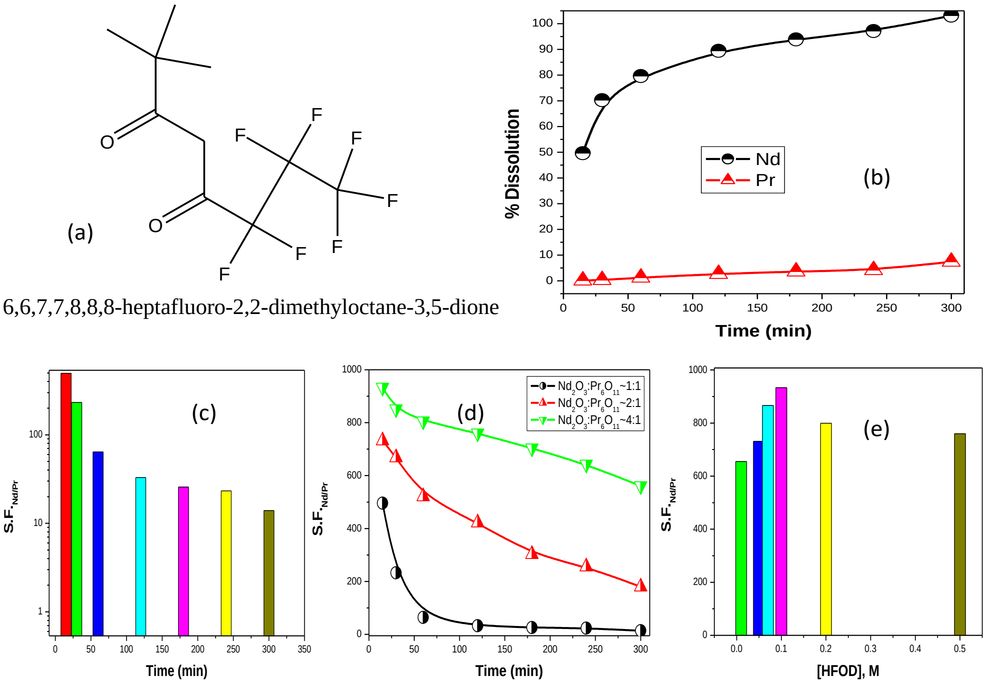

Fig.1 (a). Chemical structure of HFOD; (b) % Dissolution of Nd and Pr into C4mimNTf2 containing 0.1 M HFOD; (c) Separation factor of Nd over Pr into C4mimNTf2 containing 0.1 M HFOD (d) Separation factor of Nd over Pr into C4mimNTf2 containing 0.1 M HFOD at various compositions of Nd2O3 and Pr6O11; (e) Separation factor of Nd over Pr into C4mimNTf2 at various HFOD concentrations

Keywords: Ionic liquid, Actinides, Polymeric beads, DGA, Radiolytic stability

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Effect of powder and granulated form of zirconium phosphate on metal removal efficiency

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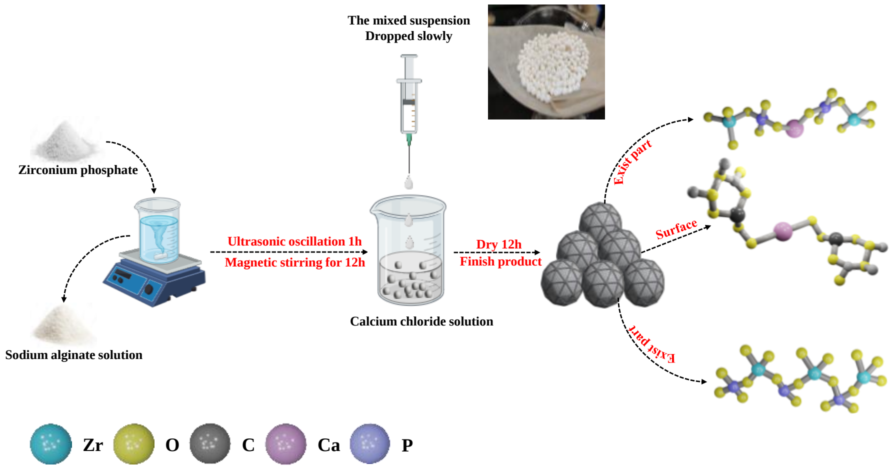
Water pollution is one of the most pervasive problems affecting people worldwide. Ion-exchange method for the removal of contaminants from water is one of the most widely used methods, especially at lower concentrations. For the past few decades, the researcher's interest in insoluble tetravalent metal acid (TMA) salts has increased due to their superior ion exchange capacity and high stability towards ionizing radiation, temperature, and oxidizing solutions [**1**]. In this work, the powder and granulated form of zirconium phosphate have been prepared, of the class of TMA salts, have been prepared using sodium alginate as per reported method [**2**]. The morphology and phase structure of material were analyzed using SEM and XRD analysis. The presence of functional groups in the materials are confirmed by FT-IR analysis. The amount of Zr, C, N, O, and P were calculated by XPS analysis. Thermal stability of ZrP and CA@ZrP is assessed by thermo gravimetric analysis. Further, the metal sorption potential of synthesized ZrP and CA@ZrP has been demonstrated for the removal of toxic metal ions, namely Pb^{+2}, Cd^{+2}, and Hg^{+2} from aqueous solution, and their sorption properties have been compared as well. This study includes a systematic investigation of the effect of *p*H, contact time, and initial metal ion concentrations on metal removal efficiency of ZrP and CA@ZrP. Further, the Langmuir isotherm and pseudo-second-order kinetic models have been investigated in order to understand the metal sorption mechanism. The synthesized composite bead form of material (CA@ZrP) with a calcium-containing phase has been found to possess higher selectivity for heavy metal ions than powder form of ZrP material. The highly selective composite bead material can be prepared in batches and easily recycled, providing a promising opportunities for practical engineering applications. In summary, this strategic modification represents a significant advancement in tailoring zirconium phosphate for efficient and sustainable heavy metal remediation.



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Scheme 1. Synthetic route of ZrP / CA@ZrP

Keywords: Tetravalent Metal Acid, Metal Phosphate, Zirconium Phosphonate, Hybrid Cation Exchanger, Organic Granules

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Direct Supercritical Fluid Extraction of Molybdenum from solid matrices

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The transition metal molybdenum has crucial industrial applications viz. alloy production, catalyst for hydrogenation in petroleum industries as well as production of ^{99}Mo, the parent of the radio diagnostic workhorse ^{99m}Tc. However, it has limited natural resources emphasising the requirement for recycling. It has been enlisted as "critical minerals" by Ministry of Mining, Government of India (June 2023 report). Hence, it is imperative to develop selective molybdenum recovery scheme employing sustainable routes. In the present study, properties of SC CO_2 [1] viz. low viscosity and high diffusivity so as to penetrate into solid matrices, has been exploited to carry out direct, acid-free extraction of Mo from solid matrices (molybdenum trioxide and ammonium molybdate). The selection of complexing agents for the present study (Fig.1) were based on well explored Mo complexation behaviour for ABO and highly CO_2-philic-metal complex formation reported for HPFOA, thus driving the direct dissolution-SC CO_2 extraction of Mo. Conditions for extraction are: 200 atm, 50 ºC, 60 min. static (matrix ~10 mg + 0.1 mL water) + 60 min. dynamic (0.2 mL/min complexing agent); 0.05 M of complexing agent in methanol; results are mean of triplicate extractions (Table 1). Mo has a complex redox speciation with pH conditions and the extractable species, Mo_2^{2+} exists at pH ~2 [2]. Also, the pH of water in contact with SC CO_2 is ~2.8. Mo content in the SC CO_2 extract was determined by Energy Dispersive X-ray Fluorescence technique. Mo extraction efficiency of >70 % and >80 % were obtained for complexing agents, ABO and HPFOA, respectively for both the matrices. Further enhancement in Mo extraction and selective extraction of Mo from solid matrices is being investigated.

Keywords: Molybdenum oxide, Ammonium molybdate, Supercritical carbon dioxide, Extraction Efficiency

Table 1. SC CO_2 extraction efficiency of Mo

MATRIX	COMPLEXING AGENT	EXTRACTION EFFICIENCY (%)
MoO_3+H_2O	--	1.4±0.4
MoO_3+H_2O	ABO	70.1±0.5
MoO_3+H_2O	HPFOA	82.6±0.8
$(NH_4)_6(Mo_7O_{24})$+H_2O	--	1.6±0.3
$(NH_4)_6(Mo_7O_{24})$+H_2O	ABO	72.3±0.4
$(NH_4)_6(Mo_7O_{24})$+H_2O	HPFOA	84.6±0.2

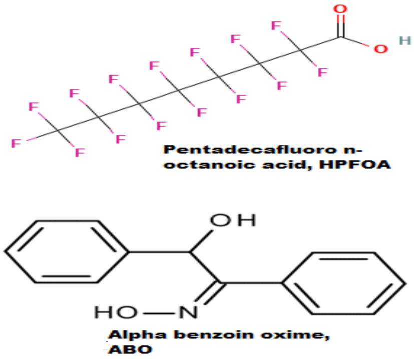

Fig. 1. Complexing agents used in the study

Acknowledgements: Persistent support from Dr. P. K. Mohapatra, AD, RC&IG, Dr. A. Bhattacharya and Dr. N. Rawat is acknowledged.

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Investigating Dissolution of different Fuel matrices in Non-aqueous Biodegradable Methane sulphonic acid medium

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Development of environmentally friendly, non-aqueous alternatives to hydrometallurgical processes that find application in various stages of fuel cycle augment the green quotient of the nuclear industry. Biodegradable, organic acid, methane sulphonic acid (MSA) is a novel candidate that provides reduced environmental impact compared to mineral acid-based methods [1], offers selectivity and single oxidation state stabilisation as reported by our group for dissolution of Pu-based matrices [2].The present study delves into exploring fluoride-free, non-aqueous dissolution behavior of refractory U-Th oxide based nuclear fuel matrices. Electrochemical insight was obtained in terms of cyclic voltammogram, CV (Fig.1) as well as differential pulse voltammetry (DPV), where signature of U(VI) system was universally revealed. A single irreversible reduction peak was perceived at -0.43±0.03 V in CV plots corresponding to all U-compounds. From scan rate variation (SRV) study, the diffusion co-efficient of U for UO_3, UO_2, UO_2 +ThO_2 (Blend) and (U, Th)O_2 were determined to be 1.23×10^{-9}, 2.33×10^{-8}, 3.53×10^{-7} and 9.24×10^{-7} cm^2 s^{-1}, respectively. The kinetics of dissolution of UO_2 (Fig.2) and UO_3 at various temperatures (maintained by sand bath) were monitored by online peak current quantification, I_p using DPV plots. Experimental investigations were conducted over a temperature range of 40°C, 50°C, and 60°C for both UO_2 and UO_3 matrices, revealing exponential enhancement followed by saturation. Solubility quantification of uranium through Ti(III) reduction based biamperometric method exhibited UO_3 concentrations at 40°C, 50°C and 60°C to be 2.9, 3.785 and 5.073 mg ml^{-1}, respectively. Similarly, for UO_2 concentrations of 3.312 and 6.06 mg ml^{-1} at 40°C and at 50°C, respectively were obtained.

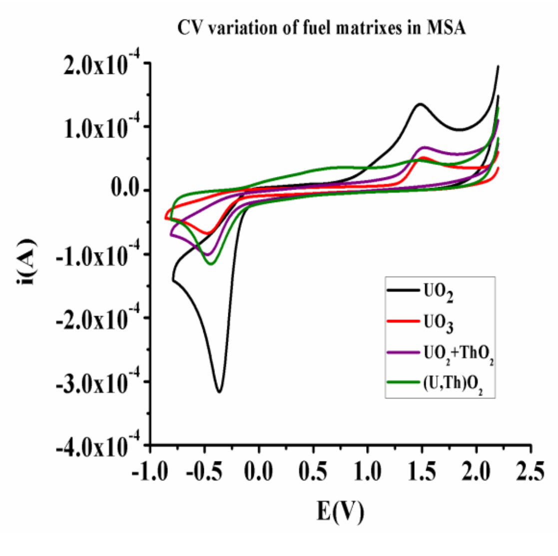

Fig. 1. CV of matrices dissolved in MSA

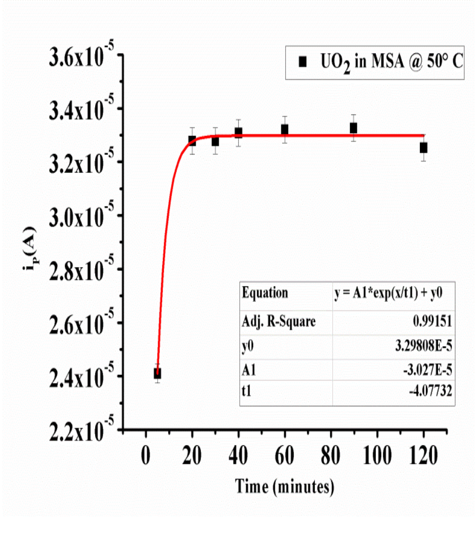

Fig.2. Kinetics of UO_2 dissolution in MSA

Keywords: Uranium oxide, Thorium oxide, Methane sulphonic acid, Kinetics, Voltammogram, Dissolution

Acknowledgements: Dr. P.K. Mohapatra, AD, RC&IG, Dr. N. Rawat, RCD and Dr. A. Goel, AINST and Ms. A. Yadav, AINST are acknowledged for their support and encouragement.

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Effect of structural modification in β-diketones in the mutual separation of Nd and Pr by preferential dissolution into an ionic liquid

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Neodymium is one of the prominent rare-earth elements for myriad industrial applications viz. in cryo-coolers,permanent magnets, and inoptical industry as Nd-glasses as well as Nd-based lasers. On the other hand, Pr exhibits several applications in photonics, optics, glass materials, fiber laser, optical amplifier, up-conversion nonmaterial, phosphors, etc. In view of such wide spread applications, there is a thrust for having Nd in the required purity, i.e., sans Pr contaminations. However, Pr and Nd, with atomic number 59 and 60 having very similar chemical potential, are difficult to separate. In the present investigation, a highly efficient ionic liquid based mutual separation strategy has been developed utillizing the controlled release of H^+ from the β diketones for the selective dissolution of Nd from Pr in their oxide mixture i.e., Nd_2O_3 and Pr_6O_{11}. The acetyl trifluoromethyl acetone (ATA) and benzoyl trifluroacetyl acetone (BTA) have been chosen as the β diketones. In $C_4mimNTf_2$ containing 0.1 M BTA, ~80% Nd was found to get dissolved in 6 h in continuous stirring conditions, while ~9.7 % Pr was co-dissolved resulting in a separation factor (S.F.) of ~10 [**Fig.1**]. Though the separation factor was found to be almost 5 times more than the conventional hydrometallurgical methods of separation, further improvement was desired for which ATA was used with an improved S.F. vaoue of ~ 544 within initial 15 minutes of equilibration. The S.F. value subsequently reduced with time and after 6 hours became ~200. The present report recorded ~360 times higher value than that reported in the earlier literature.[1-3] The Nd_2O_3 dissolution was found to be exothermic. The higher sintering temperature, the water content of ionic liquid, the relative compositions of the oxide mixtures (Nd_2O_3 and Pr_6O_{11}) significantly influenced the dissolution characteristics and in turn, the separation factor.

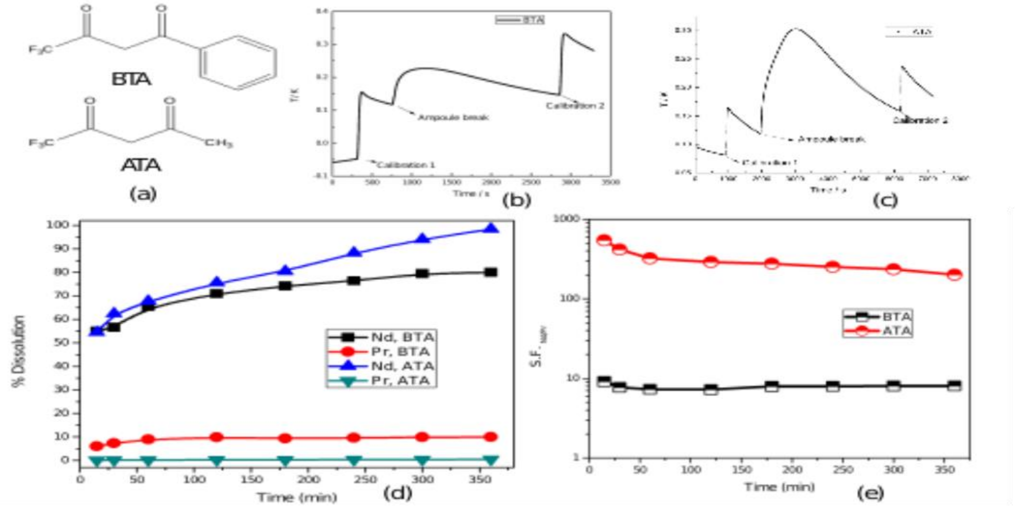

Fig. 1: (a) Structures of BTA and ATA; (b) Calorimetric studies of Nd_2O_3 dissolution in $C_4mim.NTf_2$ containing 0.1 M (b) BTA and (c) ATA; (d) % Dissolution of Nd and Pr and (e) into $C_4mim.NTf_2$ containing 0.1 M ATA and BTA

Keywords: Ionic liquid, Mutual separation, Exothermic, Separation factor

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DGA functionalized MWCNT incorporated polymer beads for effective separation of trivalent lanthanides and actinides

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Diglycolamide (DGA) ligands are known to extract trivalent f-cations from nitric acid feeds. DGA-functionalized carbon nanotubes (DGA-CNT) showed high affinity towards the trivalent f-cations[1], however, processibility of these tiny functionalized CNT is quite challenging. In view of this, DGA-CNT has been chemically augmented onto polysulphone (PS-DGA-CNT) and its efficacy towards the extraction of Am^{3+} and Eu^{3+} have been investigated. The FTIR Spectrum of the pristine and PS-DGA-CNT beads is presented in **Fig. 1(a)**. which shows a characteristic peak for carbonyl group (>C=O), observed at 1665 cm^{-1} whose intensity increased with increasing DGA-CNT in the polysulfone matrix. Further, -OH bending peak for carboxylic acid was also observed at 1405 cm^{-1}. The observations confirm incorporation of DGA-CNT into the polysulfone polymeric beads. The TG analysis of the PS-CNT beads (**Fig. 1(b)**) indicates two regions with distinct mass losses. The first region between 100-160°C belongs to loss of moisture trapped in the PS-CNT beads. The other sharp decrees in mass can be attributed to decomposition of polysulfone. Further, a highly porous nature of PS beads is confirmed by SEM image of pristine beads (**Fig. 1c**). However, the porosity is observed to be significantly reduced after incorporation of DGA-CNT into the polysulfone beads (**Fig. 1d**) suggesting successful incorporation of DGA-CNT into the PS beads. The BET surface area analysis indicates the average surface area of PS-DGA-CNT beads is 200 $m^2\ g^{-1}$. The effect of aqueous phase pH on removal of Am^{3+} and Eu^{3+} was studied **(Fig.1 (e)**). The K_d values increase with increasing pH upto a pH value of 4 beyond which there was a sharp fall. The poor sorption at lower pH can be attributed to low dissociation of diglycolamic acid reducing the uptake of metal ion. The plot of t/q_t v/s t gives a straight line with linear regression coefficient 0.9930 and 0.9970 for Am^{3+} and Eu^{3+} respectively, indicating the predominance of pseudo-2nd-order kinetics. On exposure to 300 kGy, the uptake by PS-DGA-CNT beads was found to be slightly lower (91 % and 77% for Am^{3+} and Eu^{3+}, respectively) than that of the unirradiated beads. Upon irradiation to 500 kGy, further reduction in uptake capacity of beads was observed (76 % and 74% for Am^{3+} and Eu^{3+}, respectively) **[Fig.1 (f)**].

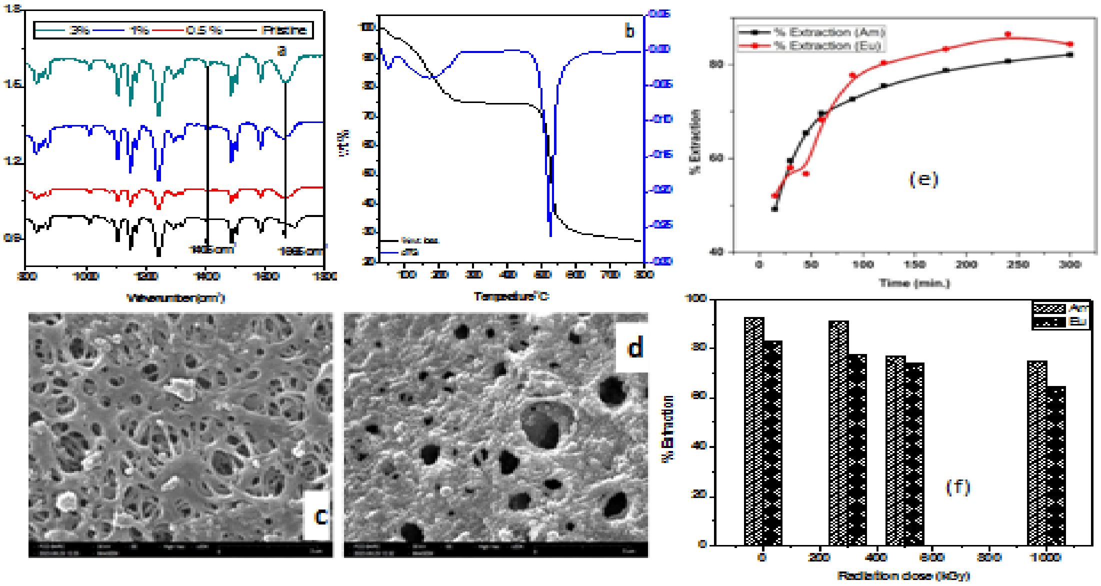

Fig.1 (a). FTIR spectrum of Pristine and DGA-CNT loaded polysulfone beads; (b) TG curve of DGA-CNT loaded polysulfone beads; (c) SEM image of pristine polysulfone beads (d) SEM image of loaded polysulfone beads; (e) The K_d values for Am^{3+} and Eu^{3+} at different pH; (f) Radiolytic stability of polymeric bids

Keywords: Ionic liquid, Actinides, Polymeric beads, DGA, Radiolytic stability

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Highly efficient separation of Pu^{4+} from UO_2^{2+} and Am^{3+} from aqueous nitric acid stream using a task specific ionic liquid

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Ionic liquids have been considered as a class of ‘green’ diluents alternative to the volatile organic diluents and have extensively been exploited for the separation of actinides[1]. In functionalized ionic liquids (FILs), the desired functional groups have been covalently attached to the ionic liquid to be exploited for task specific applications to improve the efficiency as well as selectivity. Phosphine oxides, phosphate functionalities covalently attached to the imidazolium cations were utilized for an efficient separation of uranyl ions from aqueous acidic streams[2]. Diglycolamide (DGA) and carbamoyl methyl phosphine oxide (CMPO) based FILs exhibited drastic improvements in the extraction efficiency towards trivalent actinides viz. Am^{3+}, Cm^{3+},etc. compared to the combination of a conventional ionic liquid with a ligand with an analogous functional group[3]. An ammonium based task specific ionic liquid, *N*,*N*-dioctyl-(4-trihexylammonium)butyramide bis(trifluoromethanesulfonyl)imide has also been used for the efficient extraction of the Am^{3+} ion [4]. In the present study, trihexyl tetradecyl phosphonium bis 2,4,4 trimethyl pentyl phosphinate exhibited efficient extraction of UO_2^{2+}, Pu^{4+} and Am^{3+} with the trend: $D_{Pu} > D_U > D_{Am}$ [**Fig 1**]. The D values for U, and Am were found to decrease with increase in aqueous phase acidity, indicating the predominance of a cation exchange mechanism, which was also supprted by the speciation studies. For Pu^{4+}, though there was an initial reduction in the D_{Pu} values as a function of the aqueous phase acidity upto 3 M HNO_3, there was an upward trend at higher acid concentrations. The extraction profiles suggested the possibility of separation of Pu^{4+} from UO_2^{2+} and Am^{3+} with a separation factor of 100 and 500, respectively from 6-7 M HNO_3. Formation of hexanitrito anionic Pu^{4+} complex is responssible for the observed extraction profile for Pu^{4+}. In 1 M as well as 7 M HNO_3, the formation of 1:2, 1:2 and 1:3 complexes were evidenced for Pu, U and Am, respectively. In 1 M HNO_3, the extraction was faster compared to that of 7 M HNO_3. The solvent system showed good radiolytic stability upto 500 kGy.

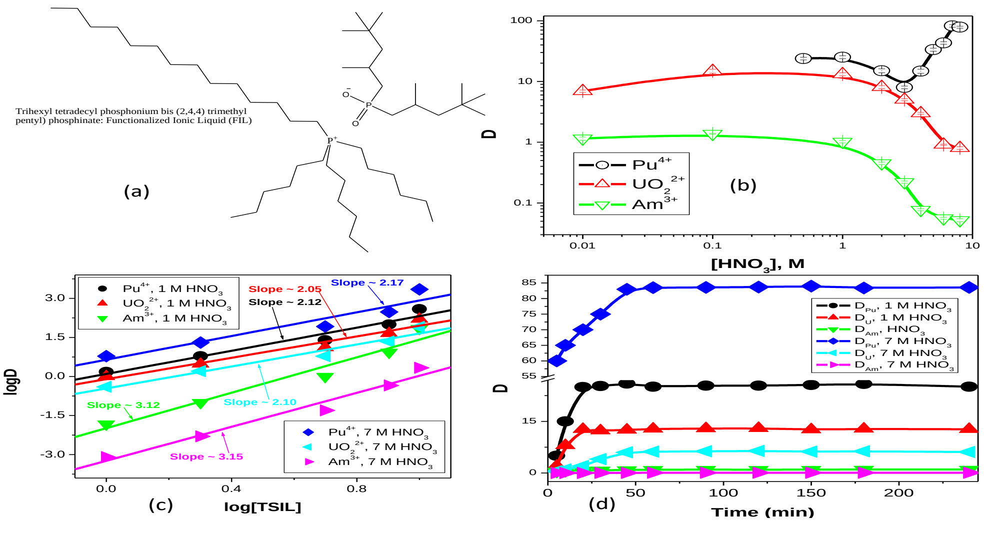

Fig. 1: (a) Structure of TSIL; (b) Extraction profiles for U, Pu and Am; (c) Variation in D values as a function of TSIL concentration; (d) The variation in D as a function of time of equilibration

Keywords: Ionic liquid, Actinides, Cation exchange mechanism, Radiolytic stability

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Development of code for prediction of yield of crystallization product from varying composition of electrolyzer effluent for thermochemical Cu-Cl cycle for hydrogen production

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Thermochemical Cu-Cl cycle is a promising process for H_2 generation without emission of greenhouse gases. It involves four steps viz. electrolysis, crystallization, hydrolysis and thermolysis to achieve closed loop splitting of water into H_2 and O_2. In the electrolysis step, electrolyzer produces H_2 gas and spent electrolyzer solution (electrolyzer effluent) consists of quaternary solution having $CuCl_2$, CuCl, HCl and water. The composition of the electrolyzer effluent may vary based on electrolyzer operating conditions. This effluent is fed to crystallizer for separation of $CuCl_2$ crystals which are utilized in hydrolysis step, while the remaining solution is recycled back as part of the feed to the electrolyzer. Thus, crystallization step is essential for sustaining the cyclic operation. Due to narrow range of conditions under which this crystallization occurs, every electrolyzer effluent may not yield crystals on cooling. This makes predictions on the extent of crystallization and its limiting conditions for processing electrolyzer effluent of varying composition important before any physical trials.

In the present work, a code has been written in python 3.0 interpreter to predict yield of $CuCl_2$ crystallization for varying composition of electrolyzer effluent through mass balances of CuCl and $CuCl_2$ around crystallizer using reported solubility [1,2]. Input parameters for the code are acid concentration, crystallization temperature, initial concentration of CuCl in electrolyzer feed and electrolytic conversion. After successful execution, the code provides the yield of CuCl and $CuCl_2$ crystals. This code is beneficial in terms of prediction of feasibility of $CuCl_2$ crystallization for a given electrolyzer effluent prior to physical run. Figure 1 and 2 show the output of the code in terms of yield of crystals for given input parameters. Operating conditions considered for prediction are 2M CuCl as electrolyzer feed, crystallization temperature 10°C, batch time 2 hours. In Figure 1, HCl concentration is taken as 9 N with varying electrolytic conversion and in Figure 2, conversion is taken as 75 % with varying HCl concentration.

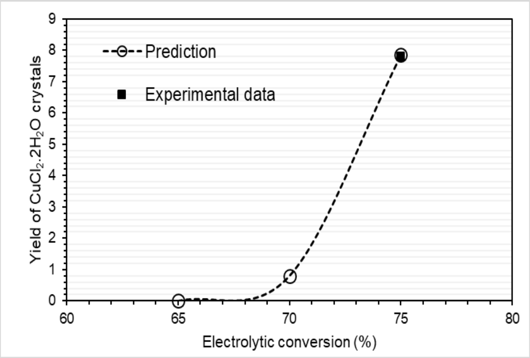

Fig. 1: Comparison of predicted and experimentally observed crystallization yield of $CuCl_2$ for varying electrolytic conversion using simulated electrolyzer effluent (electrolyzer feed: 2M CuCl, 9N HCl); crystallization temperature 10°C, batch time 2 hours.

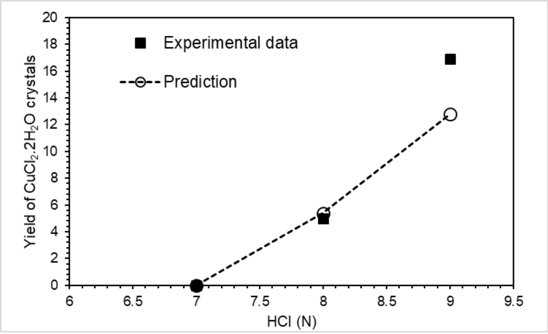

Fig. 2: Comparison of predicted and experimentally observed crystallization yield of $CuCl_2$ for varying HCl(N) concentration using simulated electrolyzer effluent (75% converted electrolyzer feed of 2M CuCl); crystallization temperature 10°C, batch time 2 hours.

Keywords: Cu-Cl cycle, solubility, yield of crystals

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An eco-friendly way of designing 2D nanosheets integrated TFN nanofiltration membranes for heavy metal ions removal

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The work involves the synthesis of eco-friendly 2D nanosheets suitable for integration into thin-film nanocomposite (TFN) nanofiltration membranes. These membranes are engineered to remove heavy metal ions from water sources selectively. Methodologies encompass green chemistry principles to ensure environmentally sustainable production processes. The research explores innovative approaches to enhance membrane performance and metal ion removal efficiency. Ultimately, it contributes to the development of eco-conscious water purification technologies. Nanofiltration (NF) membranes are a type of advanced membrane technology that provides flexibility in control, selective separation, and energy efficiency. These membranes can be specifically designed for their intended application [1-3]. To develop an eco-friendly NF membrane, we replaced the conventional dip coating interfacial polymerization (IP) method with modern vapor phase interfacial polymerization (VP-IP). This method facilitates organic solvent-free fabrication and involves fewer reagents than traditional IP [1] (Fig. 1). We prepared TFN membranes with varying concentrations of the GO-NH-NH_2 nanosheets using diethylenetriamine (DETA) and trimesoyl chloride (TMC) vapors for amine and acyl chloride monomers, respectively. The potential of resulting membranes was studied in terms of water permeability and rejection of heavy metal ions. In our experiment, we obtained ~96%, ~95%, ~94% and ~92% rejection of Na_2SO_4, $Pb(NO_3)_2$, $CuSO_4$ and $CdSO_4$ salts, respectively, with a maximum of 46.57 LMH pure water permeability at 10 bar. Various characterization techniques (XPS, FT-IR, FE-SEM, HR-TEM, AFM, contact angle, Zeta potential, etc.) were employed to analyze prepared membranes' surface morphology and elemental behaviour. The antifouling characteristics and antibacterial activity of the membrane were also assessed, revealing that the inclusion of nanosheets has elevated these properties of TFN membranes. The newly developed method has the potential to fulfil the goals of SDG 6 and has scopes in the water treatment, energy production, clean water production, and medical and pharmaceutical industries.

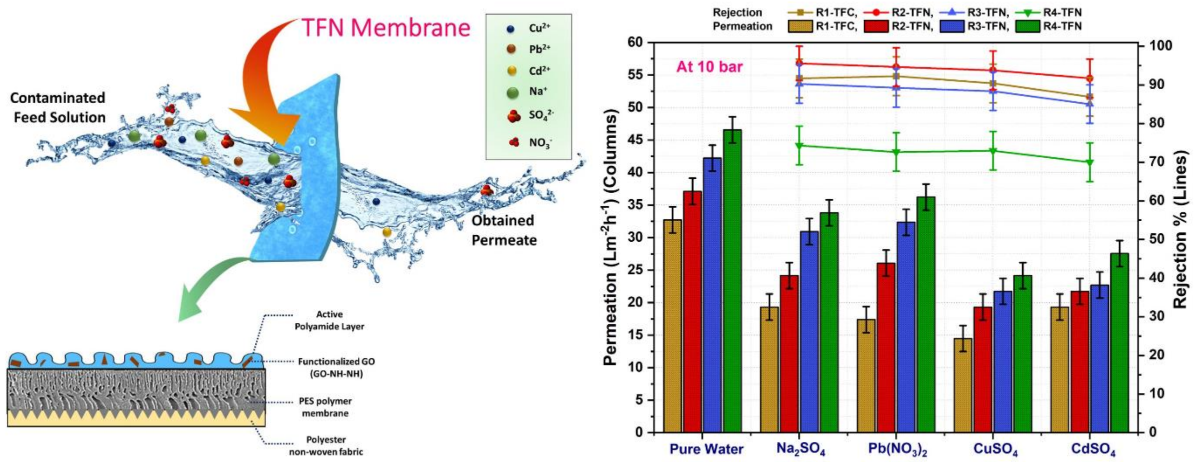

Fig. 1: TFN membrane preparation using spray coating followed by VP-IP method and obtained performance graph at 10 bar against metal and heavy metal salts.

Keywords: TFN membranes; Spray coating; Vapor phase Interfacial polymerization; Nanofiltration; Antifouling membrane; Heavy metal ions removal.

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Utilizing Deep Eutectic Solvents for Electrochemical Dissolution and Characterization of Metallic Uranium

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Uranium separation and purification holds significant importance in the nuclear industry, playing a crucial role in energy generation, as well as the decommissioning and disposal of spent fuel. Effective waste management necessitates reprocessing and recycling; however, current methods are intricate and pose hazards. Over the past decade, deep eutectic solvents (DES) have found applications in various fields, such as analytical methodologies, electrochemistry, metal/metal oxide dissolution, catalysis, carbon dioxide absorption, separation science, and synthetic chemistry, owing to their ionic nature and adjustable solvation potential [1]. This study delves into the speciation and electrochemical behavior of uranium ions in DES based on heptyltriphenylphosphoniumbromide and Decanoic acid [2]. The investigation involves a direct anodic dissolution of metallic uranium, conducted through Chronoamperometry with a constant potential of 0.1V applied for 7 hours. During the process, the DES changed color to a dark yellow, accompanied by the formation of a black precipitate in the solution. The uranium, solution, and precipitate were subsequently separated and individually characterized. UV-Vis spectral analysis of the uranium solution revealed a broad band peaking at 470nm, indicative of the presence of uranium complexed as U(VI). Voltammetry investigations in the DES exhibited an irreversible reduction peak at -1.2V, corresponding to the U(VI)-U(IV) reduction. Characterization of the precipitated uranium species identified it as being in the +4 oxidation state based on XRD patterns. Additionally, FTIR spectra indicated U-O stretching with a peak at 920 cm^{-1}, confirming the presence of the UO$_2$ phase. Morphological insights were obtained through Scanning Electron Microscopy (SEM) and EDX analysis. Comprehending the basic forms of uranium within DES systems and its electrochemical behavior has the potential to advance the development of an environmentally sustainable nuclear fuel cycle and the recycling of uranium through the utilization of DESs.

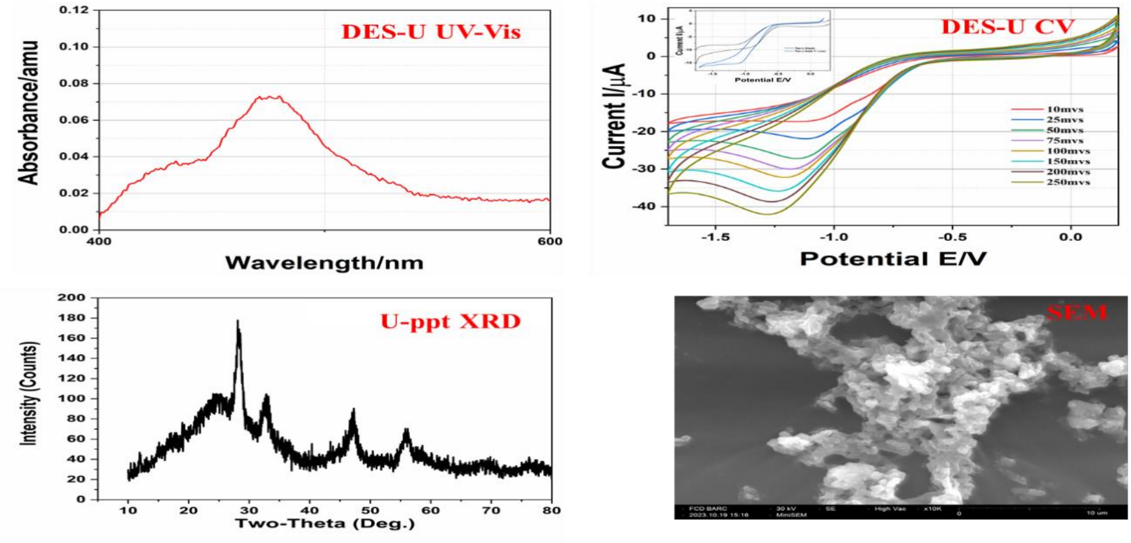

Figure 1. *Uranium speciation via UV visible spectrometry, cyclic voltammetry, XRD and SEM.*

Keywords: DES, Electrochemical dissolution, metallic uranium, SEM

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Ultrasonic-Assisted Deep Eutectic Solvent Extraction for Phenolic Compounds from Finger Millet Husk: Optimization, Comparison, and Bioactivity Evaluation

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A novel extraction protocol was developed to leverage the synergistic effects of natural deep eutectic solvent and ultrasound assisted extraction (NADESs-UAE) as a green alternative extraction solution of phenolic compounds from finger millet husk. Five Natural Deep Eutectic Solvents (NADES) systems based on choline chloride as a hydrogen bond acceptor (HBA) and citric acid, urea, glucose, glycerol and proline as hydrogen bond donors (HBD) were investigated . Furthermore, synthesized NADES was characterized using FTIR with the appearance of a widening hydroxyl peak, indicating the presence of hydrogen bond interactions. The final selection of the NADES composition was based on maximizing the total phenolic content (TPC) extraction yield. Total phenolic content result showed that the best composition of NADES solvent was choline chloride and proline in a ratio of 1:1, providing an polyphenol concentration of 5.34 mg FAE g^{-1}. Polyphenols are recovered by precipitation method using water as an antisolvent system.

The optimal extraction parameters were determined using response surface methodology (RSM) with a Central Composite Design (CCD). The optimized process parameters were identified as follows: DESs with a water content of 20 mL/100 mL, solid-liquid ratio of 1:20, amplitude set at 80 %, extraction temperature maintained at 50°C, and an extraction duration of 30 minutes. Under these optimized conditions, the TPC of the extract was measured at 32 ± 1.37 mg ferulic acid equivalent (FAE)/g, aligning closely with the model predictions. Moreover, the extraction mechanism of NADESs-UAE was explored through kinetic modeling. It was found that NADES-based UAE outperformed conventional solvent extraction methods, yielding higher total phenolics, total flavonoids, and in vitro antioxidant activity. Analysis of the phenolic extract revealed the presence of fifteen phenolic compounds in finger millet husk, with p-coumaric acid, ferulic acid, apigenin-C dihexoside, and N',N"-di-p-coumaroylspermidine being the predominant constituents. Additionally, scanning electron microscopy (SEM) confirmed microstructural differences in finger millet husk samples justifying the mutual effect of NADES and ultrasound assisted extraction, further validating the efficacy of the DES-based UAE method.

Keywords: green extraction, optimization, waste to wealth, agro-residue utilization, bioactive compound.

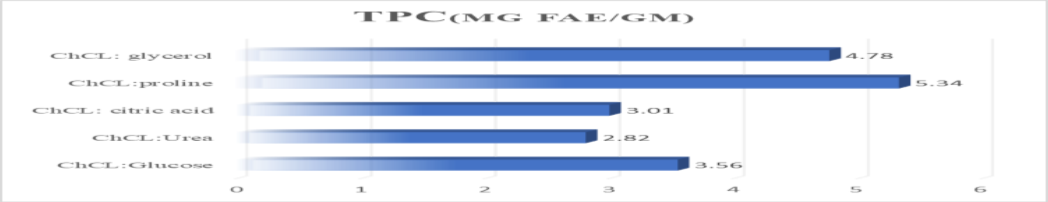

Figure 1: Total polyphenol concentration after ultrasound-assisted extraction using NADEs

Table 1: TPC concentration at different experimental conditions

Solvent	*Process Condition*	*TPC(mg FAE/gm)*
NADESs ChCL:Proline+20% water	Ultrasonicated(80% amplitude,30 min time,50˚C temperature,1:20 S/L ratio)	32mg FAE/gm of biomass
NADESs ChCL:Proline+20% water	-	25mgFAE/gm of biomass
70% acetone	Ultrasonicated(80% amplitude,30 min time,50˚C temperature,1:20 S/L ratio)	19mgFAE/gm of biomass
70% acetone	Conventional maceration method	4mgFAE/gm of biomass

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Simultaneous Removal of Mercury, Lead, Manganese, and Iron from Groundwater by oxidation- coagulation-adsorption at optimized pH

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Rapid population growth and global industrialization are linked to water scarcity creating hurdles in access to safe drinking water and necessitate research into operational and economic water treatment methods. Oxidation-coagulation-adsorption at optimized pH (OCOP) based method, using $NaHCO_3$, $KMnO_4$, and $FeCl_3$ as pH conditioner, oxidant, and coagulant, respectively, in the same way as the nature does in aquifers, is an efficient and cost-effective method for arsenic and iron removal from groundwater, which is gaining popularity in India, especially in Assam. Here we present a piloting of the OCOP for the simultaneous removal of neurotoxic mercury, lead, manganese, and iron ions from groundwater. For this, laboratory batch experiments were performed to optimize the doses of $NaHCO_3$, $KMnO_4$ and $FeCl_3$ using response surface methodology (RSM). Two small community filters, each with a capacity of 1000 liters, were installed at a children's rehabilitation center located in Duliajan town. Additionally, 15 household filters, with a capacity of 30 liters each, were installed in a nearby village in the Dibrugarh district of Assam. Mercury, lead, manganese, and iron ions were successfully removed to levels well below the WHO guideline values of 1 µg/L, 10 µg/L, 0.1 mg/L, and 0.3 mg/L, respectively. The initial concentrations of these ions were 10 µg/L, 100 µg/L, 0.5-5 mg/L, and 1-8 mg/L. The OCOP method was slightly adjusted to achieve these results, and the recurring cost was only Rs. 0.01 per liter. The OCOP method employs simple, cost-effective chemicals. It's efficient, safe, eco-friendly, doesn't require power and is an affordable option for the simultaneous removal of heavy metal contaminants from drinking water, making it a sustainable green separation technology.

***Keywords**: mercury removal, lead removal, manganese removal, OCOP*

A study on implementation and performance of Fluoride Nilogon in some fluoride affected states of India

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As many as 19 states of India alone are reported to have groundwater with fluoride concentration beyond the acceptable limit of 1 mg/L putting millions of Indians at risk of skeletal and dental fluorosis. This paper provides an overview of the performances of Fluoride Nilogon filters implemented in the Indian states of Assam, Chhattisgarh, Karnataka and Rajasthan along with the war torn middle eastern country of Yemen. Fluoride Nilogon. is an efficient cost effective and environmentally friendly patented hybrid technology based on precipitation and adsorption.

Since 2018, over a thousand of Fluoride Nilogon filters ranging from household to community level have been installed across Karbi Anglong), and Kamrup districts in Assam. In Chhattisgarh, 208 Fluoride Nilogon filters including 204 household (HH), 2 institutional and 2 small community units were installed during the last five years covering seven Gaon Panchayats across the district of Kanker for removal of fluoride from groundwater. In Karnataka, 35 household filters of 21litre capacity were installed in Outer Bangaluru district. A few Fluoride Nilogon filters were installed at some villages in Dausa, Nagaur and Churu districts in Rajasthan. The Fluoride Nilogon filters have also been installed in Lahj Governorate in Yemen where 300 household units were installed in its first phase. The installation of Fluoride Nilogon have been facilitated by the support of various organizations such as WaterAid, ZOA, Samarthan, Art of Living, Swami Vivekananda Youth Movement (SVYM), various Gaon Panchayats as well as the enthusiastic involvement of numerous individuals with the technical guidance provided by our research group in the Department of Chemical Sciences, Tezpur University.

Limestones necessary for the process were obtained from various mines situated at different regions across the country and its suitability were tested at our laboratory as not all limestone has the same efficiency. The fluoride concentration and the pH of treated water have been found within the permissible limit of BIS and WHO. Higher user satisfaction and continuous usage over the years reflect its sustainability and consistent performance. A high capacity of limestone, no residual contamination, non-requirement of power supply with little solid non leaching sludge, simplicity and ease of operation makes Fluoride Nilogon a green method of purification suitable for rural application. Now ongoing, a 3rd and an expanded 2nd phase of implementations of Fluoride Nilogon respectively by WaterAid in Gaya in Bihar and by ZOA in Al Dhaleʼe Governorate in Yemen also indicate the acceptance of the Fluoride Nilogon method in international level.

Keywords: Fluoride Nilogon, rural technology, precipitation, adsorption, purification, Sustainable technology

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Adsorptive micellar flocculation and cloud point extraction procedures for extraction of Rhoduline Violet dye and determination of thermodynamic parameters

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Adsorptive micelle flocculation (AMF) and cloud point extraction (CPE) techniques were used to extract the Rhoduline Violet (3-Amino-7-N, N- Dimethylamino - 2-methyl-5-Phenyl phenazinium chloride) (RV) dye. In the AMF study, the RV dye was extracted using a 1:2 ratio of aluminium sulphate (flocculant) and sodium dodecyl sulphate (SDS). Concentration of SDS, concentration of aluminium sulphate, the pH, the temperature, and the contact time were all optimized. The calibration range and detection limit were found to be 0.0-2.95 μg/mL and 1.902 ng/mL, respectively. The RV dye was extracted using Triton X-114 (TX-114) and DOSS mixed micelles in the case of CPE. The pH, concentration of both surfactants (TX-114 and DOSS), concentration of Na_2SO_4, temperature, and time parameters impacting dye extraction were optimized. The calibration range and detection limit were found to be 0.0-2.58 μg/mL and 0.356 ng/mL, respectively. Thermodynamic parameters were determined in both AMF and CPE studies. The proposed methods were applied for extracting RV dye from sea and tap water samples and more than 97% extraction was obtained in both AMF and CPE.

Sustainable & Green Separation of Copper from Waste Printed Circuit Boards

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With the increasing quantities of electronic waste (e-waste) globally, it has become a challenge to recycle e-waste mainly printed circuit boards (PCBs) efficiently. PCBs usually contain copper, nickel, iron, aluminum, tungsten and a certain amount of precious metals such as gold, silver, palladium and platinum. Out of these metals copper is mainly attached to the board by a solder containing lead and tin. The concentrations of copper (60-270)kg/ton found in waste PCBs is higher than its natural ore[1], therefore PCBs can be a rich secondary source of copper that makes its recycling important from both economic and environmental perspectives. Several methods have been adopted by various research groups to recover metal from PCBs including pyrolysis, electrostatic separation, magnetic separation, hydrometallurgical separation and bio-metallurgical separation [2]. However, environmental consequences and high energy requirement are the major limitations of the available technologies which inhibit their use at large scale. Hence, there is a strong need of an effective solution which addresses limitations of conventional approaches and provides an eco-friendly alternative for extraction of copper from PCBs. Present research work focuses on the recovery of copper from waste PCBs using gamma radiation technology. Waste PCBs samples were irradiated using gamma rays in the range of 10 kGy to 100 kGy to degrade the thermoset resin. Irradiated samples of PCBs were treated with dimethyl sulfoxide (DMSO) from room temperature to 100 °C for different intervals of time, 1 - 4 hrs. The solvent can be distilled and reused again for recovery process. Results have shown that copper can be easily recovered from the PCBs by gamma radiation. The copper foil from PCBs can be separated without any loss in quality and quantity during the process. The developed process for copper recovery is green and sustainable that can be used efficiently for large scale recycling of PCBs without affecting the ecosystem.

Figure: Recovery of Copper from Waste PCBs using Gamma Radiation

Keywords: Waste printed circuit boards, copper, recovery, gamma radiation,

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Microwave digestion assisted direct determination of trace rare earth impurities in dysprosium titanate

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The most widely used control rod materials like boron carbide (B_4C) and cadmium have disadvantages like radiation induced damages caused by (n,α)-reactions on ^{10}B isotopes, helium formation, swelling, toxicity of cadmium during the fabrication stages, low availability and high cost of cadmium etc. Consequently ceramic absorber materials based on Dy, Eu, Sm, Gd and Ho are being investigated worldwide [1]. The post-irradiation investigations had demonstrated high irradiation stability, chemical compatibility and no swelling of fluorite structured lanthanide oxides like dysprosium titanate (Dy_2TiO_5) [1]. The chemical quality assurance (CQA) of any absorber material requires the investigation of neutron absorber concentration and material properties before being used in the reactor [2]. Also the characterization of trace critical impurities (elements other than Dy which have high σ_a values) in this matrix that affect the cumulative absorption cross section of the absorber material is one of the important aspect of CQA. These impurities can come directly from the precursors viz., Dy_2O_3 and TiO_2 or can be picked up during the synthesis process. This highly refractory material was dissolved by a clean and closed high temperature and high pressure environment in a microwave digestion system. After many permutations and combinations, a mixture of 2 mL of conc. H_2SO_4, 3 mL of conc. HCl, 5 mL of MilliQ water was found to completely dissolve 100 mg of sample. The dissolved samples were diluted in various proportions, spiked with analytes of interest and then analyzed in an inductively coupled plasma optical emission spectrometer (ICP-OES).

The emission lines of the matrix element Dy have interferences on a number of other lanthanides. Hence the maximum tolerable matrix concentration for determining minimum concentrations of other rare earth impurities was optimized. The emission lines of all analytes were chosen by considering their maximum intensity lines with minimum Dy interference. The matrix concentration was varied from 500 to 2000 mg L^{-1} for a minimum spiked analyte concentration of 0.25 mg L^{-1}. The results of the analysis were tabulated in Table 1. It was observed that a minimum of 0.25 mg analyte per g of Dy_2TiO_5 can be precisely determined (4-6% RSD) by the proposed methodology.

Table 1: ICP-OES analysis of spiked Dy_2TiO_5 sample solutions (percentage recoveries are in the paranthesis)

Element	Chosen emission line (nm)	Spiked analyte conc. (mg L^{-1})	Recovery at 500 mg L^{-1} matrix conc.	Recovery at 1000 mg L^{-1} matrix conc.	Recovery at 2000 mg L^{-1} matrix conc.
Nd	401.225	-- 0.25	0.32±0.01 0.56±0.02 (96)	0.65±0.02 0.90±0.04 (100)	1.35±0.05 1.62±0.06 (108)
Sm	356.827	-- 0.25	-- 0.26±0.01 (104)	-- 0.26±0.01 (104)	-- 0.32±0.02 (128)
Eu	381.967	-- 0.25	0.47±0.02 0.72±0.03 (100)	0.95±0.03 1.19±0.04 (96)	1.92±0.06 2.15±0.09 (92)
Gd	310.05	-- 0.25	0.62±0.02 0.87±0.03 (100)	1.20±0.03 1.43±0.05 (92)	2.38±0.05 2.63±0.07 (100)
Tb	350.917	-- 0.25	0.74±0.02 0.98±0.04 (96)	1.55±0.04 1.79±0.05 (96)	3.10±0.08 3.34±0.11 (96)
Ho	345.6	-- 0.25	0.27±0.01 0.42±0.02 (100)	0.54±0.02 0.79±0.03 (96)	1.10±0.04 1.36±0.06 (104)
Er	337.271	-- 0.25	-- 0.26±0.01 (104)	-- 0.26±0.01 (104)	-- 0.30±0.01 (120)

Keywords: Dysprosium, Titanium, Chemical quality assurance, ICP-OES

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Mo(VI) recovery from nitric acid medium using Amberlite IRA-743 resin: Column sorption-elution studies

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Molybdenum finds its wide applicability in the manufacturing of corrosion-resistant steel, catalysts and ceramic materials. In the context of radiopharmaceuticals industry, ^{99m}Tc the workhorse in nuclear medicine is produced from the radioactive decay of the ^{99}Mo which can either be produced from fission of uranium or activation of ^{98}Mo in a nuclear reactor. Due to its widespread range of applications, separation and purification of molybdate ion (VI) is of high significance and in turn necessitates the development of economical flowsheets for recovery of pure Molybdenum. In this paper, a detailed study has been carried out on the uptake and elution of Molybdenum into a commercial ion exchange resin Amberlite 743. The probable anion exchange mechanism of uptake of molybdate from dilute nitric solution on IRA 743 resin is shown in **Figure 1**. Mo sorption performance was evaluated from a simulated solution containing 0.1 M HNO_3 acid, 2 M $NaNO_3$ and 40 ppm sodium molybdate and spiked with ^{99}Mo tracer. The feed solution was passed at a flow rate of 10 bed volumes per hour in the column (bed volume 7 mL). The breakthrough curve of molybdenum uptake is shown in **Figure 2a**. The uptake performance of the column was calculated from feed and effluent Mo concentration. As evident, about 35 bed volumes of solution can be passed through the column with ~5 % breakthrough. The same experiment was repeated with a high Mo concentration (80 ppm) and it can be seen from **Fig 2a** that about 35 bed volumes of solution can be passed through the column with ~7 % breakthrough. The elution of Mo from the resin was done by passing 1.0 M NaOH elution at a flow rate of 5 BV/hr. The elution fractions were collected and Mo concentration was measured to calculate the elution efficiency. Around ~95% of total Mo was eluted in 7 fractions under this condition. The elution profile of Mo from the column is shown in **Figure 2b**. Quantitative sorption and elution of molybdenum onto the resin shows the possibility for its usage on a larger scale.

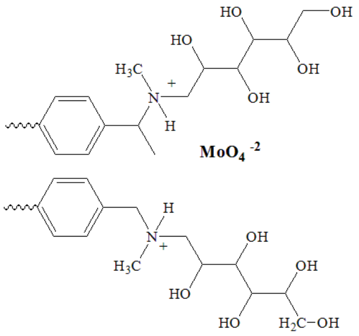

Figure 1: Sorption mechanism of molybdate ion on IRA 743 resin

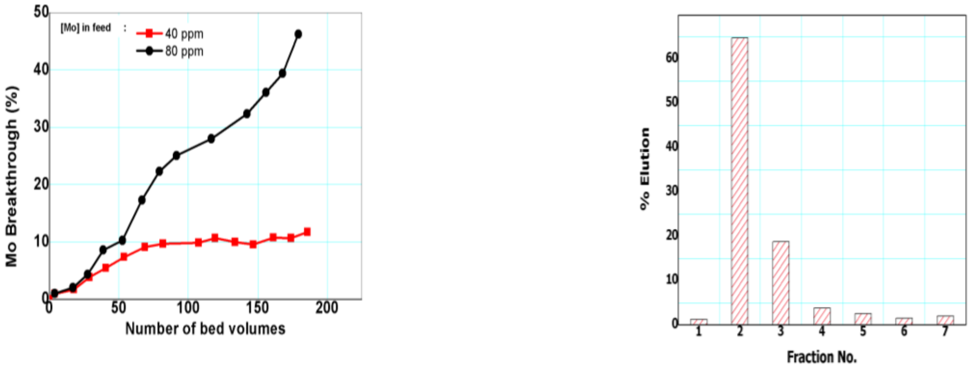

Figure 2: Loading(a) and elution(b) profile of molybdate ion in IRA 743 resin

Keywords: Molybdenum, Ion exchange, Separation and Column study.

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A novel extraction method development for lead(II) from alloys, ore samples and ayurvedic medicines by solvent extraction

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Solvent extraction is an ancient yet modern technique with an incredible scope of research due to the various intriguing phenomena in the system. Herein, we reported N-n-decylaniline as an efficient cation exchanger for the extraction of lead(II) from hydrochloric acid medium. The extraction of lead(II) was commenced at 0.01 M and grow to be quantitative at 0.16 M N-n-decylaniline in xylene from 1 M to 2.5 M hydrochloric acid. The extracted lead(II) was back extracted from the organic phase with an acetate buffer (pH 10) and determined complexometrically. The stoichiometry of the extracted species was determined by slope analysis method and it was found to be 1:3:1 (metal: acid: extractant).The influences of various parameters like acid and amine concentration, equilibrium time, loading capacity, diluents are discussed in this work. The extraction behavior of lead(II) was investigated at various temperatures. The result shows, as temperature increases the rate of complex formation increases consequently the extraction increases. The extraction process is exothermic and spontaneous in nature. The applicability of the developed methods was checked by the diverse ion study as well as binary and ternary mixture separation. This developed method was successfully applied for the analysis of lead(II) in real samples such as ores and ayurvedic medicines. Moreover, the developed method is simple, selective and reproducible.

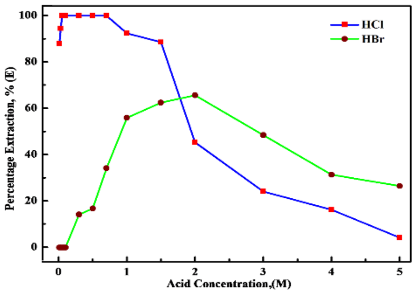

Fig. 1 Effect of acid concentration on extraction of lead(II),

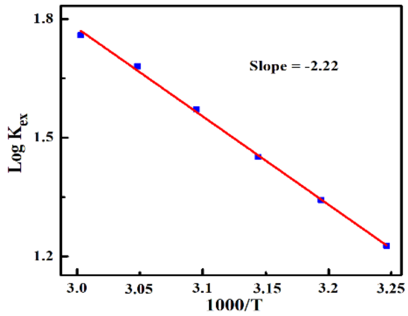

Fig.2. Extraction behavior of lead(II) as a function of temperature

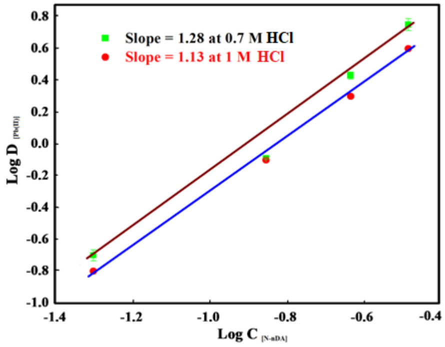

Fig 3. Log-Log plot of distribution ratio Log D$_{[Pb(II)]}$ *Versus* Log C$_{[N-n-DA]}$ at 0.7 M and 1.0 M HCl,

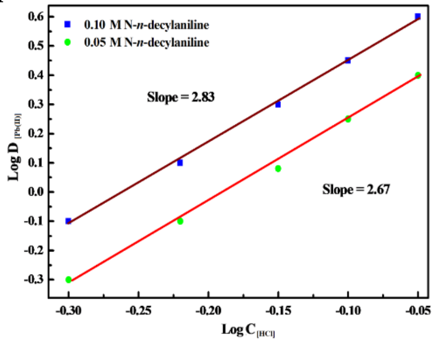

Fig 4. Log - Log plot of Log C $_{[HCl]}$ *Vs* Log D $_{[Pb(II)]}$ at 0.1 M N-n-decylaniline and 0.05 M N-n-decylaniline

Keyword: *Solvent extraction; Lead(II); N-n-decylaniline; hydrochloric acid media; Real samples*

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Development of a Chromatography Method for Quantitative Analysis of Calix-Crown-6

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1,3-dioctyloxycalix[4]arene-18-Crown-6 (Calix-Crown-6) is an extractant deployed at Waste Immobilization Plant (WIP), Trombay for the selective separation of ^{137}Cs from High-Level Liquid Waste (HLLW). The removal of ^{137}Cs from HLLW reduces the radio-toxicity and the heat load of the waste, and results in the advantageous utilization of radio-caesium as sealed gamma sources in multiple irradiation applications [1]. The extractant CC-6 undergoes radiolytic degradation during its use in the Plant which reduces its separation performance. Till date, to the best of author's knowledge, the solvent performance is monitored by the measured batch distribution coefficient values and no method is known for the quantitative estimation of the extractant in the spent solvent.

The present effort was therefore undertaken to develop an analytical method for measuring the undegraded CC-6 in the solvent system (i.e., 0.03 M CC-6 in 50% isodecyl alcohol-n-dodecane) during the various stages of Plant operation. Results of the study highlighted here include the development of a method for quantitative estimation of CC-6 in the presence of isodecyl alcohol and n-dodecane, and other degradation products using High-Performance Liquid Chromatography (HPLC). This method can also be used for evaluating the purity of calix-crown-6 during the synthesis of the extractant.

The study was performed on a C-18 reverse phase column (250 X 4.6 mm), coupled to a Diode Array Detector in HPLC. With the use of 100% acetonitrile as the mobile phase at a flow rate of 2 mL/min isocratically at room temperature, a well-separated peak of CC-6 was obtained at 30 min. Fig. 1 shows the chromatogram obtained for 0.03 M CC-6 in isodecyl alcohol-n-dodecane. CC-6 was determined at a wavelength of 268 nm (i.e., λ_{max}) based on its UV spectrum as well as 254 nm. It can be seen that both the chromatograms are identical and therefore the method can be used for the detection of CC6 when it is dissolved either in n-paraffin or iso-decyl alcohol. Further, the gaussian nature of the peak allows ease of quantitation. For quantitative estimations, standard CC-6 concentrations in isodecyl alcohol-n-dodecane were analyzed by HPLC under the above-mentioned parameters. The peak areas corresponding to the individual standard concentrations were plotted against the concentrations to obtain a linear calibration curve at both the wavelengths as shown in Fig. 2. From this calibration curve, CC-6 concentration in degraded calix solution is determined [2].

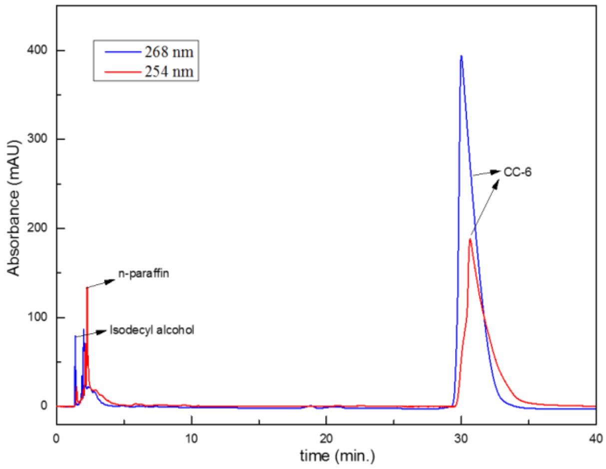

Fig. 1. HPLC – UV chromatogram of 0.03 M CC-6 in 50% isodecyl alcohol-n-paraffin

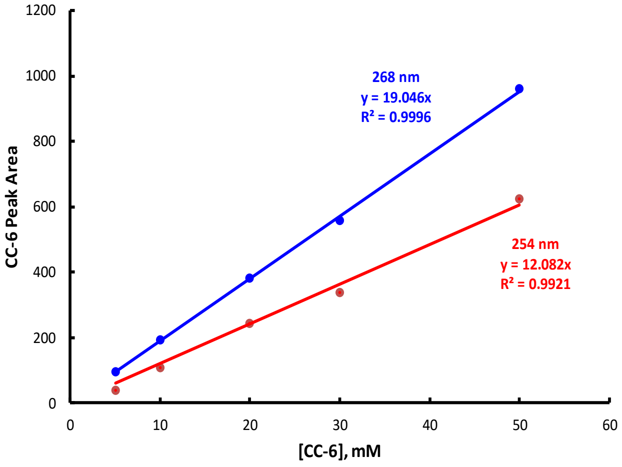

Fig. 2. HPLC – UV calibration curve for calix-crown-6

Keywords: HPLC, HLLW, calixarenes, calix-crown-6, quantitative analysis

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Performance evaluation of U^{3+}|U reference electrode for molten salt electrorefining operations

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In electrorefining operations, actinides are separated from fission products in spent metal fuel employing potentiostatic or galvanostatic methods. Control of anode and cathode potentials measured against Ag^+|Ag reference electrode is important to prevent contamination of lanthanides in cathode deposit and dissolution of noble metals from anode. Ag^+|Ag reference electrode is chosen due to its excellent stability over a wide range of temperatures. Same electrode was used for electrorefining of uranium in the High-Temperature Electrorefiner (HTER) at the PPRDF, IGCAR. However, potential data of anode and cathode were not reproducible. Subsequently, electrorefining runs were continued using metallic uranium as reference. Since performance of Ag^+|Ag reference is well understood in laboratory scale experiments and stable potentials were recorded across several hours of experimentation, failure of electrode in large scale electrorefining cell could not be well explained. It was therefore suggested to compare the performance of conventional Ag^+|Ag and U^{3+}|U reference both prepared exactly the same way. The latter electrode was prepared by loading LiCl-KCl-1wt%UCl_3 salt powder and uranium metal slices pieces into a 6mm diameter one-end closed quartz tube (Figure 1). 1mm diameter tantalum wire was inserted from the top open-end for electrical contact with uranium slices. The top-end was sealed with teflon plug and about 10 mm tantalum wire was projected out of plug for electrical connections.

Equilibrium potential of U^{3+}|U reference electrode was measured against standard Ag^+|Ag reference and bare uranium electrodes in LiCl-KCl-1wt%UCl_3 electrolyte in temperature range of 673-773 K. Figure 2 shows linear variation of equilibrium potential between U^{3+}|U and Ag^+|Ag reference electrode with temperature, and corresponding expression is described by Equation 1. In the given temperature range, equilibrium potential between U^{3+}|U and uranium metal electrodes was measured to be 3 mV, due to equal thermodynamic activity of uranium and UCl_3 in the concentration cell. Stability of equilibrium potential of U^{3+}|U *vs.* Ag^+|Ag also was checked at 673 and 723 K over a period of 12 and 30h, respectively as depicted in Figure 3. Corresponding equilibrium potential values are -(1.413 ± 0.002) and -(1.407 ± 0.003) V at 673 and 723 K, respectively.

$$E^{eq}_{\mathrm{U}^{3+}|\mathrm{U}}(\mathrm{mV})\ \textit{vs.}\ \mathrm{Ag}^{+}|\mathrm{Ag} = (-2677 \pm 100) + (1.77 \pm 0.14)T(K) \qquad (1)$$

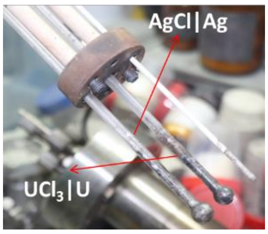

Figure 1: : Electrode assembly used in the present experiments

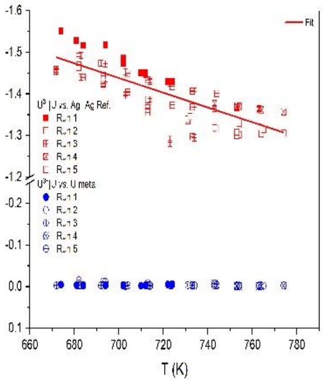

Figure 2: Temperature dependence of equilibrium potential of U^{3+}|U *vs.* Ag^+|Ag and U metal electrodes

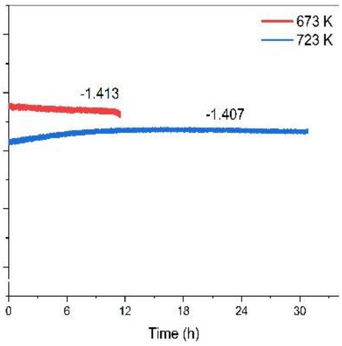

Figure 3: Variation of equilibrium potential of U^{3+}|U *vs.* Ag^+|Ag with time at 673 and 723 K.

Performance of U^{3+}|U reference electrode was found to be satisfactory over 120 h durations. Nernstian behaviour of equilibrium potential between U^{3+}|U and Ag^+|Ag electrodes, generation of stable and consistent potential values over extended periods at constant temperature, indicate the suitability of the U^{3+}|U as alternate reference electrode for application in electrorefining studies conducted in HTER at PPRDF facility.

Keywords: electrorefining, molten salt, reference electrode, high temperature electrorefiner

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A highly efficient Polyoxometalate (POM) based composite material for Actinide Extraction

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Polyoxometalates (POMs) are class of inorganic metal–oxygen clusters built from the connection of {MOx} polyhedral (M=V, Nb, Mo, or W, etc., x=5, 6). They have wide range of applications in different fields, such as medicine, catalysis, material science, radionuclide separation etc. The use of bare POMs as adsorbent for the separation of metal ion is limited due to their high aqueous solubility, easy aggregation nature, and small surface area. Therefore, it is very important to fix POMs onto a suitable solid matrix for its use as adsorbent. We make an attempt here to synthesize a phosphotungstate based POMs and make a composite material for the extraction of metal ions (UO_2^{2+}, Am^{3+}, Eu^{3+}) from acidic feed solution. The POM was synthesized according to the literature method [1]. The POM and the composite POM were characterized using different techniques such as NMR, FTIR, UV–Visible spectroscopy. The ^{31}P NMR data of the synthesized POM at pH 7.0 indicates a peak at -10.8 ppm suggesting the formation of $[PW_{11}O_{39}]^{7-}$ (PW_{11}) in the solution [1] which was also confirmed from its UV-Visible characteristic peak of mono lacunary PW_{11} at 252.9 nm [2]. The FTIR spectra of the solid synthesized POM showed peak at 1056 cm^{-1}(υ_{P-O}), 934 cm^{-1} (υ_{W-Ot}), 883 cm^{-1} (υ_{W-Ob}) and 742 cm^{-1} (υ_{W-Oc}) indicating the formation of PW_9 type POM [1]. The solid POM (PW_9) when contacts with water or pH 7.0 solutions converts to PW_{11} and this lacunary POM were adsorbed on the solid matrix to form a composite POM. The UV-Visible of the composite POM showed a peak at 252.9 nm suggesting its presence on the solid matrix. The FTIR data of the composite POM was compared with the literature data which shows peaks at 1053 cm^{-1} (υ_{P-O}), 957 cm^{-1} (υ_{W-Ot}), 805 cm^{-1} (υ_{W-Oc}) suggesting the incorporation of PW_{11} in the composite POM [3]. The composite POM was subjected to solid phase extraction of different metal ions (UO_2^{2+}, Am^{3+}, Eu^{3+}) from acidic feed solution which suggest very high extraction efficiency (>99%) within very short time for Eu^{3+}, Am^{3+} whereas it takes around 3 h for UO_2^{2+} at pH 7.0. The extraction of these metal ions by the POM is thought to be due to coordination of the unsaturated oxygen anion in the POM with the metal ions. The high extraction efficiency at pH 7.0 indicates these composite materials could be useful for the removal of radionuclides from biological and environmental samples.

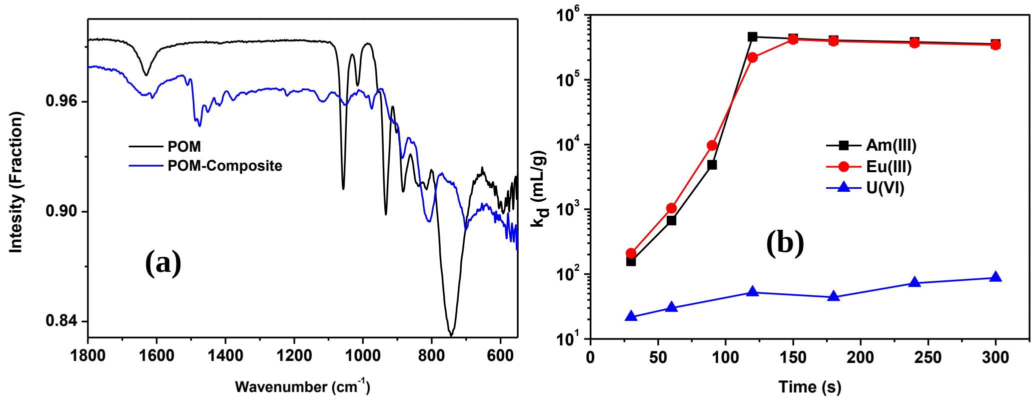

Fig. 1: (a) FTIR and (b) solid phase extraction of the synthesized POM Composite

Keywords: POM, FTIR, Lacunary, Extraction

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DAE-BRNS SESTEC-2024
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Efficient Separation of Actinides Using Extraction Chromatography Resin Containing TREN-DGA and RTIL

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Separation of the actinides such as Pu, Th and Np from the acidic effluents generated in reprocessing of nuclear waste is important for recycling and effective management of nuclear waste. Amongst the methods used for separation of actinides from effluents, solvent extraction is the work-horse of the nuclear industries. However, the method utilizes large volume of organic solvent which has several environmental implications. In this context, the extraction chromatography technique finds several advantages over the conventional solvent extraction such as lower solvent inventory, lower secondary waste generation and ease of operation when separation is performed in column mode [1].

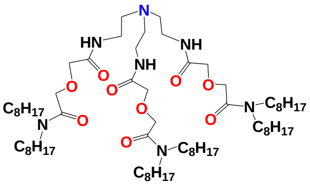

Fig. 1. TREN-DGA

Since the discovery of diglycolamide (DGA) ligands in 2001, they are the most widely studied ligands for actinide separation [2]. Recent studies have shown that the ligands containing multiple DGA units appended on a tripodal platform such as *C*-tripodal and *N*-tripodal have better actinides affinity than the normal DGA ligands like TODGA [1]. One of the such ligands is TREN-DGA (Fig. 1) where 3 units of DGA moieties are appended on the tripodal *N*-atom. Solvent extraction studies have shown excellent results for the separation of actinides with this ligand [1]. Additionally, use of ionic liquid (IL) as the diluent for TREN-DGA has further enhanced its extraction efficiencies for actinides [2]. Looking at results of solvent extraction studies, it was a curious attempt to study TREN-DGA/IL combination in extraction chromatography. Thus, an extraction chromatography resin was prepared using TREN-DGA and IL (C_4mim.Tf_2N) by impregnating on an inert solid support (Chromosorb-W) for the separation of tetravalent actinides, viz. Pu, Th and Np. The resin was characterized by FTIR (Fig. 2), TGA and SEM techniques. Separation of said radionuclides from acidic feed was studied by batch sorption method and column study.

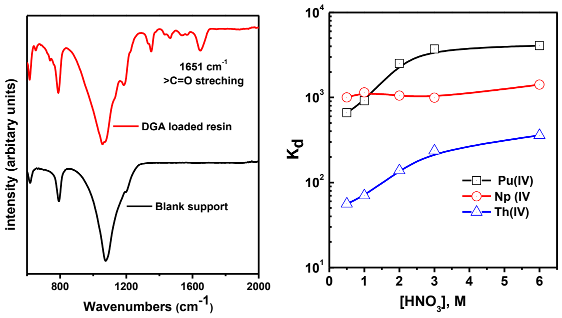

Fig. 2. Left: FT-IR spectra of impregnated resin and blank support. Right: K_d values of actinides vs. HNO_3 concentration.

Batch distribution data (Fig. 2) indicated highest uptake of Pu^{4+} followed by Np^{4+} and Th^{4+}. The K_d values at 3 M HNO_3 were 2514, 993 and 138 for Pu^{4+}, Np^{4+} and Th^{4+}, respectively. The K_d values of Pu^{4+} increased continuously with nitric acid concentration up to 6 M HNO_3. On the other hand, HNO_3 effect was not significant for Np^{4+}, though Th^{4+} K_d values increased with nitric acid concentration. The loading capacity of the resin at equilibrium was 46 mg/g determined at 3 M HNO_3. Detail sorption isotherm studies were performed with Th and the data were analysed in well-established Langmuir, Freundlich and D-R isotherm models. Column studies performed with 300 mg resin loaded on a 4 mm dia glass column (bed volume = 2 mL). In the column operation, about 22.85 mg/g of Th could be loaded without any breakthrough. The loaded Th from the column was successfully eluted with 0.05M EDTA + 1 M guanidine carbonate solution.

Keywords: *Extraction chromatography, actinides, ionic liquid*

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A novel extraction method development for lead(II) from alloys, ore samples and ayurvedic medicines by solvent extraction

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Solvent extraction is an ancient yet modern technique with an incredible scope of research due to the various intriguing phenomena in the system. Herein, we reported N-n-decylaniline as an efficient cation exchanger for the extraction of lead(II) from hydrochloric acid medium. The extraction of lead(II) was commenced at 0.01 M and grow to be quantitative at 0.16 M N-n-decylaniline in xylene from 1 M to 2.5 M hydrochloric acid. The extracted lead(II) was back extracted from the organic phase with an acetate buffer (pH 10) and determined complexometrically. The stoichiometry of the extracted species was determined by slope analysis method and it was found to be 1:3:1 (metal: acid: extractant).The influences of various parameters like acid and amine concentration, equilibrium time, loading capacity, diluents are discussed in this work. The applicability of the developed methods was checked by the diverse ion study as well as binary and ternary mixture separation. This developed method was successfully applied for the analysis of lead(II) in real samples such as ores and ayurvedic medicines. Moreover, the developed method is simple, selective and reproducible.

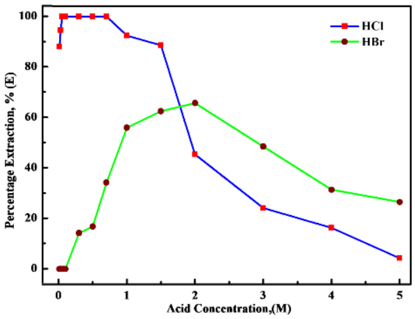

Fig. 1 Effect of acid concentration on extraction of lead(II),

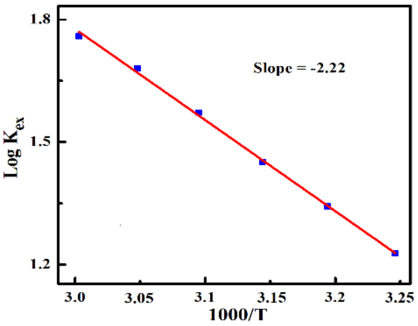

Fig.2. Extraction behavior of lead(II) as a function of temperature

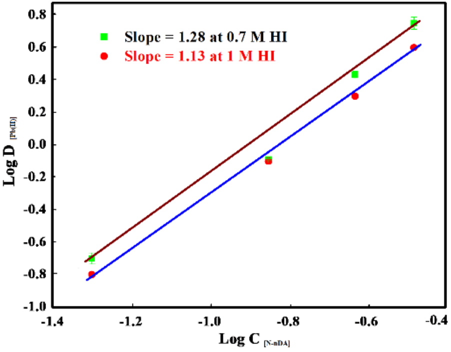

Fig 3. Log-Log plot of distribution ratio Log D$_{[Pb(II)]}$ *Versus* Log C$_{[N-n-DA]}$ at 0.7 M and 1.0 M HCl,

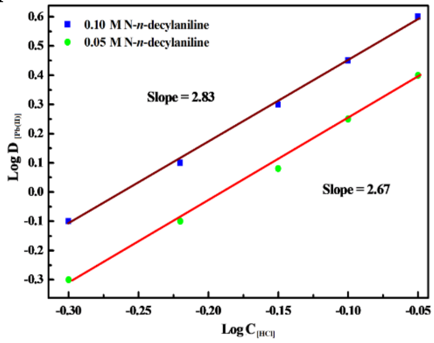

Fig 4. Log - Log plot of Log C$_{[HCl]}$ *Vs* Log D$_{[Pb(II)]}$ at 0.1 M N-n-decylaniline and 0.05 M N-n-decylaniline

Keyword: *Solvent extraction; Lead(II); N-n-decylaniline; hydrochloric acid media; Real samples*

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Electro-oxidation of hydrazine based waste stream generated during clean-up of degraded PUREX solvent

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PUREX (Plutonium Uranium Reduction Extraction) process is adopted worldwide for the reprocessing of spent nuclear fuel. The process uses 1.1 M tri-n-butyl phosphate in n-dodecane (TBP/ n-DD) as solvent. During extraction process, the solvent encounters highly ionizing radiation, decay heat and high concentration of nitric acid. Consequently, the solvent undergoes hydrolytic and radiolytic degradation leading to the formation of di-butyl phosphate (HDBP) in organic phase. Among the commonly adopted primary solvent clean-up reagents, hydrazine carbonate was proposed as a potential alternative to the conventional sodium carbonate for the clean-up of HDBP from the lean organic [1]. The management of the aqueous hydrazine carbonate based stream demands the separation of HDBP and recovery of metal ions followed by the complete destruction of hydrazine prior to its final disposal as waste. In our earlier study we have proposed suitable method for the separation of HDBP and recovery of metal ion resulted during cleanup of degraded solvent using 1.5 M hydrazine carbonate [2]. The present study deals with the possible method for the complete destruction of hydrazine in the waste stream prior to its final disposal as waste.

Previously we had studied the destruction of hydrazine in nitric acid solution by a chemical method using 1% &10 % NO_2 in N_2. But the rate of destruction of hydrazine was found insignificant. In the present case, the decomposition of hydrazine in nitric acid media was studied by electro-oxidation method. Preliminary studies using cyclic voltammetry (CV) suggested the possible oxidation of hydrazine in nitric acid medium as shown in figures 1. Two distinct oxidation peaks [Ia and IIa] were observed in the potential range -1V to 1V vs Ag/AgCl reference using Pt working electrode. The oxidation peak (IIa) around 0.5 V corresponds to hydrazine oxidation and peak (Ia) around -0.17 V corresponds to nitrous ion oxidation. The CV of nitric acid as inset is provided in the same figure for comparison. Electrochemical processes in the plant demand a simple experimental setup; hence, a two electrode cell arrangement with and without diaphragm was adopted for the electro-oxidation studies. Experiments with incremental current changes were carried out to determine the optimum current density using the setup shown in figure 2 for achieving efficient hydrazine decomposition. Polarization effects were minimized by mechanical stirring. Electro-oxidation experiments were carried out at the anodic current densities 10-90 mA cm^{-2} using divided cell set up and 20-60 $mA.cm^{-2}$ using un-divided cell set up and the optimized anodic current density for almost complete destruction of hydrazine was 40 $mA.cm^{-2}$ in both the cases based on the calculated current efficiency of the process. The results obtained using un-divided cell is plotted in figure 3. Based on the above studies, it can be concluded that, almost complete destruction of hydrazine in nitric acid medium can be achieved by adopting a simple un-divided cell set up.

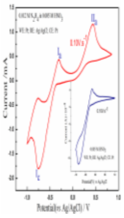

Figure 1 Cyclic voltammogram of $N_2H_5.NO_3$ and the CV of HNO_3 in the inset

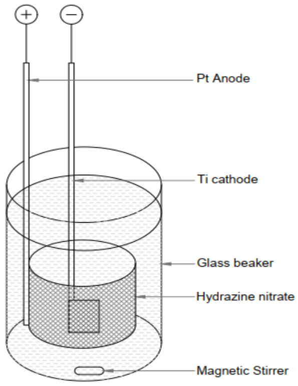

Figure 2 Un-divided cell set-up for hydrazine destruction

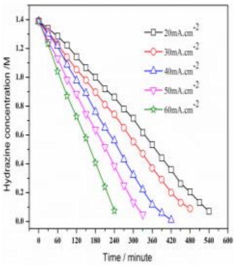

Figure 3 Decomposition of hydrazine w.r.to time at different current density by electrochemical method

Keywords: Hydrazine, cyclic voltammetry, electrochemical-oxidation, current efficiency

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Determination of krypton in Air at trace levels by gas chromatography method using an indigenously prepared chromatography column

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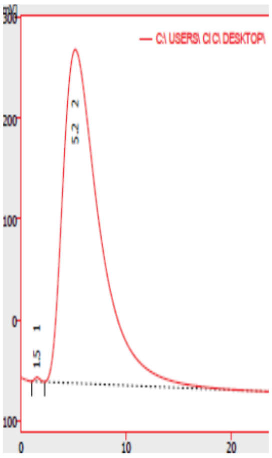
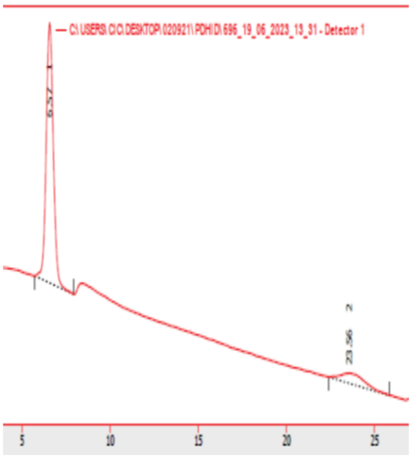
The assessment of composition of Air in and around Nuclear power plant is very essential and in particularly more for the presence of noble gases such as Krypton and Xenon in it. [1] Gas chromatography method offers a simplest way for accurate determination of Krypton in the air sample around Nuclear facility. Air samples are generally analyzed by using 5A Molecular sieve column [2] however for determination of trace level of krypton in air,on Molecular sieve column is not effective hence activated carbon along with alumina column is prepared in-house for separation of krypton from air. Owing to higher surface area of Activated carbon compared Mol sieve the adsorption of Krypton is high and lowering the temperature of column further enhances the adsorption of krypton yielding better results. For preparation of this column activated carbon granules and gamma alumina balls are crushed separately, sieved using 80/100 mesh size sieve and further activated at 300° C and filled in 2.5 meter S.S tube of 1/8 inch diameter the composition of activated carbon to alumina is (90:10).The prepared column is regenerated using helium gas for 24 hrs and used for separation of krypton from air using CIC make Chromatograph instrument with DID detector. The prepared column could be used for separation of krypton in air with concentration as low as 10 ppm using helium gas as a mobile phase at -40° C temperature and DID as a detector.

The experimental results of analysis of 99.99 % Kr and 10 ppm Kr in Air using the prepared column is showed in table no-1 and the chromatograph of the same in fig no-1.Thus one can easily to detect Kr in environmental air sample with concentration as low as 10 ppm using activated carbon column with excellent resolution.





Column	Component	Temp	T_r (MIN)	R
Carbon – alumina column	Kr (99.99%) Air	Room temp	1.5 5.2	1.0
Carbon – alumina column	Kr (10ppm) Air	-40° c	6.5 23.5	15

Keywords: krypton, carbon, alumina , Gas chromatography

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Analysis of selected volatile organic compounds (VOCs) in ambient air using SPME-GC-FID techniques

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Analyzing volatile organic compounds (VOCs) in ambient air is crucial for monitoring air quality, assessing health risks, and identifying sources of pollution. VOCs, originating from various sources including industrial activities and transportation, pose significant health hazards, with prolonged exposure linked to respiratory problems and environmental damage. Monitoring helps authorities enforce regulations, mitigate health risks, and implement targeted strategies to reduce emissions [**1**]. The increasing global apprehension regarding the impact of atmospheric pollutants on both climate and human health has spurred the rapid advancement of innovative analytical techniques for detecting VOCs in the atmosphere. In present study, air samples from corporate park, Kharghar Navi Mumbai were collected in 5-liter capacity tedlar bag using an air pump at a flow rate of 0.5 lpm. Subsequently, solid phase micro-extraction (SPME, SUPELCO 65µm PDMS/DVB fused silica) fiber was exposed to the sample for 20min to extract and preconcentrate the VOCs from the Tedlar bags. A VOC synthetic standard mixture (DW-VOC Mix #2, Restek) was used for optimization of chromatographic method. The SPME fibers were then analyzed by thermal desorption-gas chromatography flame ionization detection (GC-FID, Shimadzu 2010A). The novelty in analyzing volatile organic compounds (VOCs) using SPME coupled with GC-FID lies in its efficiency, sensitivity, and versatility for VOC analysis. We have also targeted a specific group of VOCs for analysis which can useful determining the combustion sources.

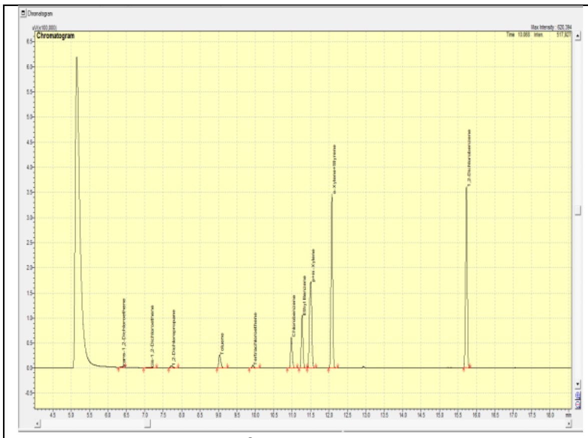

Fig 1: Chromatogram of VOCs mix using SPME-GC-FID.

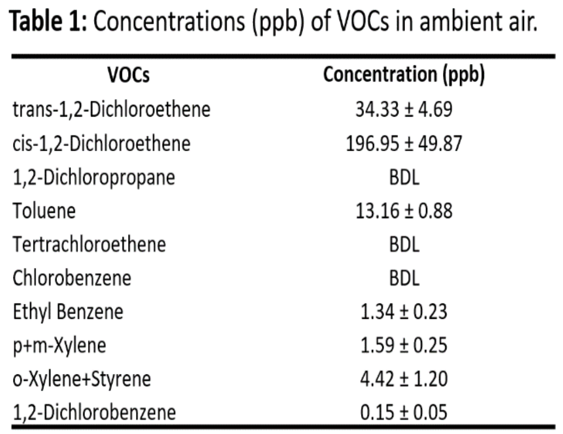

Table 1: Concentrations (ppb) of VOCs in ambient air.

VOCs	Concentration (ppb)
trans-1,2-Dichloroethene	34.33 ± 4.69
cis-1,2-Dichloroethene	196.95 ± 49.87
1,2-Dichloropropane	BDL
Toluene	13.16 ± 0.88
Tertrachloroethene	BDL
Chlorobenzene	BDL
Ethyl Benzene	1.34 ± 0.23
p+m-Xylene	1.59 ± 0.25
o-Xylene+Styrene	4.42 ± 1.20
1,2-Dichlorobenzene	0.15 ± 0.05

A 60 m long analytical capillary column (Rxi5 -MS, 60 m x 0.25 mm i.d., 0.25 µm, Restek) was used for separation of VOCs. The GC oven conditions was set at 40 ^{0}C initial for 2 min, ramping at 8 ^{0}C min-1 to 240 ^{0}C and holding for 8 min. Chromatograms for standard and sample are shown in Fig. 1. Total 12 VOCs were analyzed in the air sample (Table 1). Three VOCs i.e. 1,2-dichloropropane, tertrachloroethene and chlorobenzene were found below the detection limit (1 ppb) in ambient air. 1,2-Dichloroethene was the most abundant VOC among all the analyzed compounds. It is generally released to the atmosphere in emissions from contaminated wastewaters, contaminated waste disposal sites, and the pyrolysis and combustion of polyvinyl chloride and some vinyl copolymers [**2**]. Aromatic VOCs i.e. toluene, ethylbenzene, o-, m-, p-xylene and styrene were also detected in ambient air from 1.34 to 13.16 ppb; these compounds were most abundant in combustion sources [**3**]. Analyzing VOCs using SPME-GC-FID provide rapid, sensitive, and reliable analysis of complex sample matrices, making it a valuable tool for a wide range of applications in analytical chemistry and environmental science.

Keywords: *Air Quality, VOCs, SPME, GC-FID, Environmental Analysis.*

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Understanding the Separation of Sn(II) and Sn(IV) on Mixed Ion Exchange Columns

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^{99m}Tc pharmaceuticals necessitate labelling of organic molecules with Tc. Reduction of Tc(VII) to a lower oxidation state is imperative for high-yield, pure complex formation. While tin acts as the preferred reducing agent, its use presents challenges. Stannous compounds exhibit intricate solution chemistry, demanding maintenance of a minimum concentration for shelf-life [1]. Control of Sn(II) to Sn(IV) ratios is vital for effective reduction in addition to this, Sn(IV) persists as an inevitable impurity. Monitoring Sn(II) content is pivotal for quality control, with determination methods including titration, electrochemistry and spectroscopy [2].

Chromatographic techniques enable the development of separation procedures for different oxidation states of ions by controlling various parameters. In this study, the separation of Sn(II) and Sn(IV) was investigated on a mixed ion exchange column. Specifically, a DIONEX IonPac CS5A column, comprising both cation and anion exchange functionalities, was employed. Tin species were quantified utilizing PAR (4-(2-pyridylazo)resorcinol) as a post-column reagent, with detection at a wavelength of 530 nm. The eluent consisted of a combination of H_2SO_4 and Na_2SO_4 solutions. $SnCl_2$ salt was utilized for Sn(II) samples, while Sn metal was dissolved in concentrated H_2SO_4 for Sn(IV) solutions.

Separation experiments were conducted at different concentrations of H_2SO_4 and Na_2SO_4. Notably, at 0.04 M Na_2SO_4 and 0.15 M H_2SO_4, a difference in retention time between the two species was observed. Specifically, Sn(II) was eluted at 2.35 min, while Sn(IV) was eluted at 3.03 min (fig 1). Furthermore, decreasing the concentrations of both H_2SO_4 and Na_2SO_4 resulted in increased retention times for both species. Further investigations were undertaken to evaluate the influence of column temperature on the separation process. It was observed that the retention time for both species increased with rising column temperature. This observation suggests that the equilibrium involved in the separation process is endothermic.

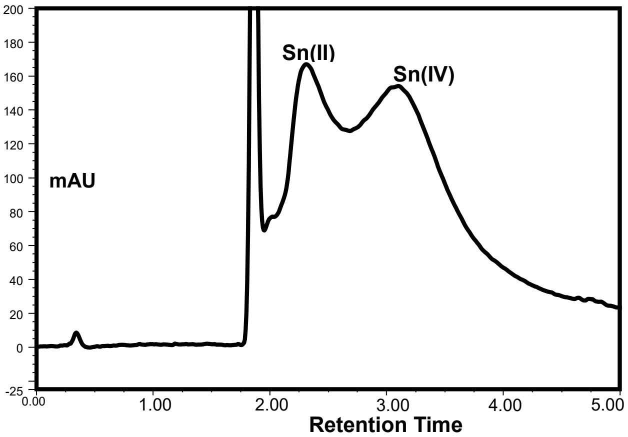

Fig 1: Separation of Sn (II) and Sn(IV) on IonPac CS5A column. Eluent: 0.04 M Na_2SO_4 and 0.15 M H_2SO_4, PCR: 0.5mM PAR, λ_{max}: 530nm

Keywords: Ion Chromatography, Tin speciation, mixed ion-exchange column

Reference:

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HPLC separation of Th and U in Molten Salt Reactor Fuel

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Thorium, a fertile material, can be utilized in both solid and liquid-fueled reactors, with the latter being of particular interest in India's nuclear energy program(1). The Molten Salt Reactor (MSR) is a Generation IV reactor design that employs fuel in molten form, typically consisting of fissile (such as UF_4) and fertile (such as ThF_4) elements dissolved in a fluoride medium of alkali and alkaline earth metal fluorides. In this concept, nuclear reactor uses fluoride liquid salt as either a coolant (in combination with solid fuel) or as both coolant and fuel (in the case of liquid-fueled MSRs). This design offers several potential advantages over traditional water-cooled reactors, including improved safety, reduced waste, and enhanced fuel utilization (2). The mixture of fluoride salts (CaF_2-LiF-ThF_4-UF_4) has been proposed as a suitable fuel for MSR applications. However, in view of the high corrosive nature, it is challenging to develop analytical methodologies for the chemical quality control of these fuel salts. The present work aims at the development of a high performance liquid chromatographic (HPLC) method for the separation and determination of thorium and uranium in the dissolved solution of fuel salt mixture. A C18 reversed phase column (Chromolith 4.6 mm x 100 mm) was used in combination with alpha-hydroxy isobutyric acid (HIBA) as an eluent. The eluted fraction was detected at 653 nm using a UV-Vis detector after reacting with a post-column derivatizing reagent, Arsenazo (III). The individual solutions of uranium and thorium prepared from their respective standards were injected for studying the chromatographic conditions. The optimized mobile phase condition for the separation of thorium and uranium consisted of 0.2 M HIBA of pH 4 and 5% (v/v) of MeOH. Two fuel salts of different compositions viz. (a) 70% LiF +8%CaF_2 +20.6%ThF_4 +1.4%UF_4 (mol%) and (b) 70%LiF+ 8%CaF_2 +22%UF_4 (mol%) were digested and dissolved in aqueous medium. Aliquots from these stock solutions were diluted with the mobile phase and injected into the HPLC system. Figure 1 shows the chromatogram obtained for the separation of thorium and uranium from 70% LiF +8 % CaF_2 + 20.6% ThF_4 +1.4% UF_4 salt. Figure 2 shows the chromatogram obtained for uranium from 70% LiF + 8% CaF_2 + 22% UF_4 salt. It is seen that present method offers good tolerance to the presence of high salt content in these samples.

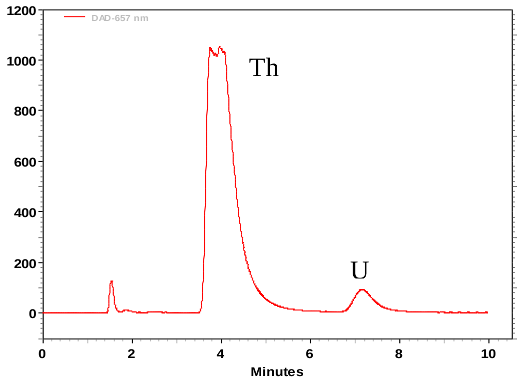

Figure 1: Chromatogram obtained for 70% LiF +8%CaF_2 +20.6%ThF_4 +1.4%UF_4

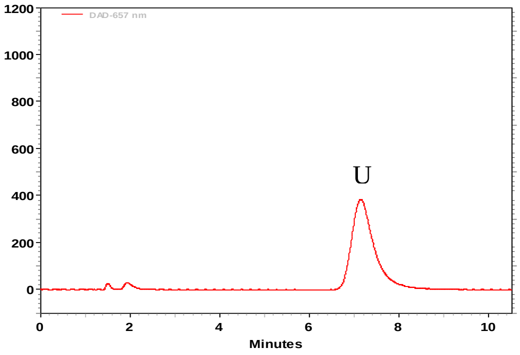

Figure 1: Chromatogram obtained for 70% LiF + 8% CaF_2 + 22% UF_4

Keywords: Molten salt, Thorium, Uranium

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Separation of thorium from bulk of plutonium using high performance liquid chromatography

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In view of their similar chemical behavior, separation of Th(IV) and Pu(IV) is a difficult task. Determination of small amounts of Th in a bulk of Pu by most of the analytical techniques requires prior separation of the matrix element due to potential interferences. Different methods such as solvent extraction, ion exchange, extraction chromatography etc. have been reported for the separation of Th and Pu [1]. However, many of these methods are suitable for samples having similar proportions of thorium and plutonium. The present work aims to develop a method for the separation and determination of Th in presence of large amounts of Pu. High-performance liquid chromatography (HPLC) was employed for the separation studies in view of its advantages viz. high resolution, sensitivity, and multi-elemental capabilities.

A C18 based reversed phase column was used as the stationary phase and mandelic acid was employed as the mobile phase. The fractions eluted from the column were monitored by a UV-Vis detector using Arsenazo (III) as a post-column derivatizing reagent. In view of the strong hydrophobic nature of thorium-mandelic acid complex, acetonitrile was also introduced in to the mobile phase for improving the peak-shape and faster elution. The effects of concentration, pH of mandelic acid and the composition of acetonitrile in the mobile phase on the separation of thorium and plutonium were studied. Figure 1 shows the chromatogram obtained for the separation of thorium and plutonium under the optimized conditions. It is seen that plutonium is eluted prior to thorium which is contrary to the pattern expected based on the ionic potential values of Th and Pu. Though plutonium is expected to form stronger complex with mandelic acid and be retained stronger onto the column than thorium, the elution order observed in the chromatogram was different. The smaller ionic radius of Pu(IV) compared to Th(IV) makes the former to be more susceptible for hydrolysis. This difference in hydrolysis behavior explains why Pu elutes prior to Th. Chromatograms were recorded by injecting mixtures of Pu and Th having different amount ratios. The peak area of Th was found to be linear with its concentration in the range 1 – 50 ppm, as shown in figure 2. Under the optimized HPLC conditions, separation and quantification of Th could be carried out in the mixtures having Th to Pu amount ratio up to 1:300.

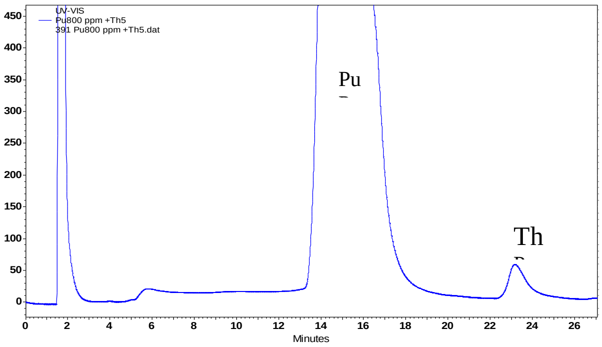

Figure 1: Separation of Th(IV) and Pu(IV) using mandelic acid

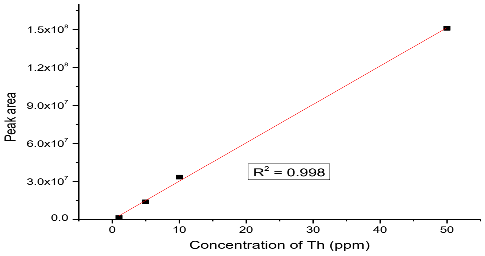

Figure 2: Peak area of Th(IV) as a function of its concentration

Keywords: Thorium, Plutonium, HPLC, reversed phase

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An overview of recycling of Lithium ion batteries involving Hydrometallurgical and Pyrometallurgical separation and its impact on environmental

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Abstract:

Lithium-ion batteries are increasingly being used to store energy, power electric vehicles and provide backup power. However, the environmental impacts of lithium-ion battery production are often overlooked. In this article, we will explore the hidden environmental consequences of lithium-ion batteries, from the high cost of lithium extraction to the toxic waste they produce. The present paper also tries to discuss the health hazards posed by lithium-ion batteries and will throw light on the ways to separate, recycle and re-use the waste lithium-ion batteries.

Electrorefining behaviour of U-Mo-Zr alloy in LiCl-KCl-UCl_3 melt

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In electrorefining of spent metal fuel, Zr and Mo, which are two of the major fission products, can also co-dissolve along with U and Pu if higher current densities are applied. Presence of Zr and Mo in melt may lead to side reactions as they exist in variable oxidations states. In order to study the limit of co-dissolution of Zr and Mo under electrorefining conditions, U-Mo-Zr ternary alloy was prepared and its electrochemical behavior was investigated in LiCl-KCl eutectic melt in temperature range 673-798 K. Total [Mo+Zr] in alloy was limited to 6 wt.%. U-2Mo-4Zr and U-4Mo-2Zr alloys were prepared by vacuum arc melting and characterized by XRD (Figure 1). Equilibrium phases in both alloys were established to be UZr_2, U_2Mo and α-U from XRD patterns. Alloys were further analyzed by equilibrium and transient electrochemical methods in LiCl-KCl eutectic melt. In former method, equilibrium potential of U-Mo-Zr alloy was recorded against $Ag^+|Ag$ reference electrode having the following cell configuration:

$$\text{Ta,U-}x\text{Mo-}y\text{Zr} \,||\, \text{LiCl-KCl} \,||\, \text{Ag}^+|\text{Ag}$$

Equilibrium potential of ternary alloys measured in temperature range of 673-798 K is shown in Figure 2 and temperature dependence of equilibrium potential is expressed as a linear relationship:

$$E^{eq}_{\text{U-Zr-Mo}}(\text{mV}) = (-1955 \pm 23) + (0.84 \pm 0.03)T(K)$$

Electrochemical dissolution of U-Zr-Mo alloy in LiCl-KCl eutectic melt was investigated by cyclic voltammetry (Figure 3) at 773 K employing a three-electrode assembly with $Ag^+|Ag$ and graphite as reference and counter electrode, respectively. Voltammograms were characterized with onset of dissolution of alloy at -1.316 V, followed by oxidation peak at -1.195 V that refers to U dissolution. Beyond -1.195 V, there is a linear increase in anodic current density that may involve co-dissolution of Zr and Mo although discernable peaks corresponding to their respective dissolution did not appear in the voltammograms (Figure 3). Zr is known to have two stable states in melt; Zr^{4+} and Zr^{2+} whereas Mo is known to be present in Mo^{+5} and Mo^{+3} states. During electrorefining of alloy fuel, anodic potential is controlled at -1.35 to -1.19 V to avoid co-dissolution of Zr and Mo. Presence of Zr and Mo ions in melt after electrorefining was studied using cyclic voltammetry. Voltammetric features revealed redox behaviour of U^{3+} and U^{4+} ions but there were no additional peaks due to Zr or Mo ions in melt. If U from UZr_2 and U_2Mo phases from U-Mo-Zr alloy does eventually dissolve in melt, Zr and Mo are expected to fall off into anode basket. Stability of chloride of U and Zr are very close (-236.9 and -188.2 kJ/equiv C at 773 K, respectively) so there is a possibility of Zr dissolution at around -1.10 V but since stability of chloride of Mo is only -56.9 kJ/g-equiv Cl at 773 K, it is not expected to dissolve until around -0.30 V. Therefore Zr dissolution is far easier than Mo since it requires a smaller overpotential relative to onset of dissolution of U.

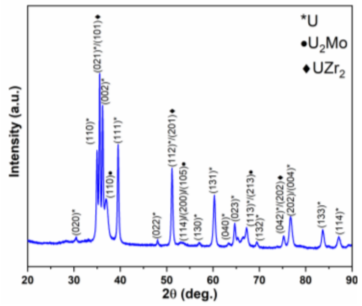

Figure 1: : XRD pattern of U-4Mo-2Zr ternary alloy

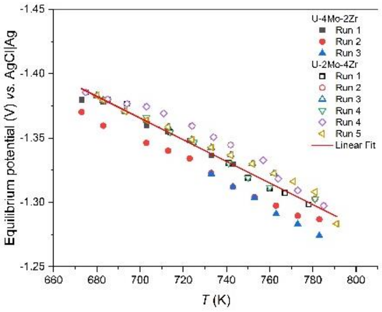

Figure 2: Temperature dependence of equilibrium potential of U-Mo-Zr ternary alloys in LiCl-KCl melt

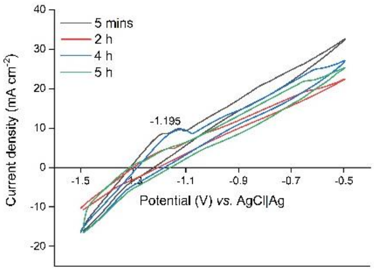

Figure 3: Cyclic voltammograms of U-4Mo-2Zr in LiCl-KCl eutectic melt at773 K, scan rate: 10 mV s^{-1}

Keywords: pyroprocessing, molten salt, electrorefining, equilibrium potential, metal fuel

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Analysis of anions in environmental water samples around upcoming uranium mine at Rohil, Rajasthan

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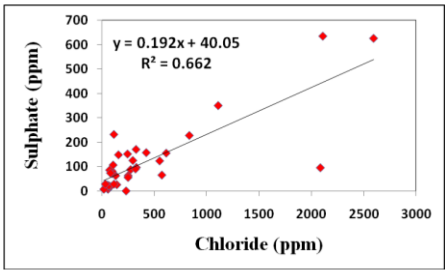
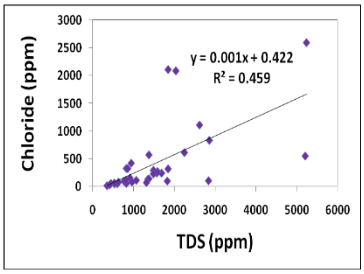
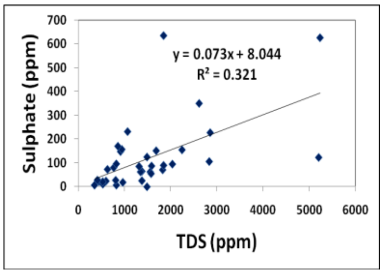
Baseline studies are required for impact assessment studies during the operational stages and decommissioning stages of any nuclear facility. These studies are carried out for uranium mining facilities only after economically viable grades of uranium deposits are ascertained. The information collected during such studies serve as connecting feature between regulatory compliance and technical information. A low grade polymetallic (U, Cu, Mo, Ni, Co) vein type uranium deposit has been found at Rohil in Sikar district of Rajashan. Uraninite is the main uranium mineral associated with pyrite, chalcopyrite, pyrrohotite and molybdenum. Operations have been planned by Uranium Corporation of India Limited at this site after completion of baseline investigations such as reserve, economic viability, waste management features and ecological considerations. Geologically, the area falls under Delhi Super Group of rocks of Mid Proterozoic Era of the North Delhi Fold Belt (NDFB). In the present study, as a part of preoperational survey of the site, environmental groundwater samples were collected around the site for determination of prevalent trace elements, cations, anions and radionuclides. This paper presents the anionic study of the groundwater samples collected from the site.

Many natural factors can affect environmental water quality; primary factors being the source and chemical composition (cations and anions). By measuring the concentrations of these ions, the chemical quality of the water can be assessed. A total of 36 water samples were collected around the study area and analysed by Ion chromatographic (IC) system 840 professional Metrohm system using anion exchange column. The mobile phase used is a mixture of millimolar solutions of Sodium carbonate and Sodium bi-carbonate. 100 mmol solution of H_2SO_4 is used for regeneration of suppresser. The samples were diluted using Millipore ultra-purified water. IC system is calibrated with 0.5 ppm, 1.0 ppm and 5 ppm of mixed anion standards (Fluka). Calibration curve was obtained for each anion and routine instrument blank, standards and duplicate sample analyses were carried out for anions like fluoride (F^-), chloride (Cl^-), bromide (Br^-), nitrite (NO_2^-),nitrate (NO_3^-), sulphate (SO_4^{2-}) etc. for quality control and quality assurance. The level of sulphate and nitrate in 83% and 66 % of the samples were found to be below limit i.e., 200 ppm and 45 ppm, respectively, whereas, that of fluoride varied from <0.15 ppm to 3.8 ppm, with mean of 1.91 ppm. Concentrations of chloride varied from 18.74 ppm - 2592 ppm, with average concentrations of 415 ppm. Concentrations of chloride were found to be well within the BIS and WHO guideline values (WHO, 2011; BIS, 2012) for 58% of the collected samples. For Fluoride only 22% of the samples are found to have concentration value within BIS limits. Higher percentage of fluoride and chloride anionic concentrations crossing the prescribed limits can be attributed to the high mineralisation of the region. From the data obtained, positive correlations between concentrations of Cl^- and sulphate (0.66), that of TDS and SO_4^{2-} (0.32) and TDS and Cl^- (0.46) were observed confirming their natural origin (Martinez, 2020).







Keywords: Uranium mine, Groundwater, Anions, Ion chromatography

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Separation of boron and fluoride in borosilicate glass materials by Pyrohydrolysis

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Borosilicate glasses have wide applications in optical lenses owing to their low dispersion and high refractive index. Further the properties of these glasses can be adjusted through appropriate modification of the constituents. Addition of alkaline earth metals in borosilicate glasses has been reported for altering thermal properties of the glasses. Alkaline earth borosilicate ternary systems are represented by a general formula ($RO-B_2O_3-SiO_2$ (where RO = alkaline earth element). Out of the all alkaline earth borosilicates, barium borosilicate, $BaO-B_2O_3-SiO_2$ shows the minimum immiscibility region. Composition of the barium borosilicate plays imperative role in ascertaining the chemical durability and homogeneity. High level waste (HLW) generated during the reprocessing of spent nuclear fuel contains significant amount of fluoride which in turn forms the corrosive HF. Barium borosilicate glass can take up F^- up to 4 wt % and can exist as F-Na(x) Ba (y) structural unit. Presence of F^- in glass affects physico-chemical properties of glass such as melt temp, glass transition temp, viscosity, coefficient of thermal expansion and chemical durability [1]. At higher temp F^- loss can occur in its volatile forms such as SiF_4 or BF_3 or alkali metal fluoride. Studies are being carried out to investigate the retention of F in the glass (during and after vitrification) to prevent the structural damages of the glass due to fluoride loss from the glass material. This demands an analytical methodology to estimate F^- in the vitrified glass material. Since F loss can occur through the formation of BF_3, the present study aims at developing a method for the simultaneous separation of boron along with fluoride F for their analytical quantification.

Many analytical methods have been reported for the independent determination of boron and fluoride in various matrices. However, these methods require pre-separation of boron and fluoride. Present study is aimed at simultaneous extraction of boron and fluorine from barium borosilicate glass and their determination by using Ion Chromatography (IC). It is observed that direct pyrohdyrolysis of borosilicate glass attacked the sample boat and hence, the observed recovery of both B and F are low. To circumvent this issue, U_3O_8 was used as a blanket as well as accelerator for enhancing the recovery. The optimum pyrohdyrolysis conditions that realize the simultaneous separation of boron and fluoride from glass matrix were identified. Quantification of boron and fluoride was carried out by IC.

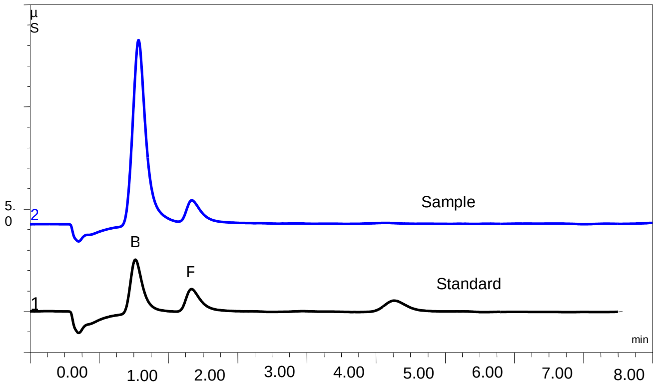

Fig 1: Typical ion chromatograms obtained for a barium borosilicate glass sample after pyrohydrolysis. Column: Waters IC Pak Anion; Eluent composition: 0.56 M d-mannitol in 6.5mM $NaHCO_3$; Flow rate: 1 mL/min; Detection: Suppressed conductivity.

Table-1 Optimum pyrohydrolysis conditions

Sample amount		*~ 30 mg*
U_3O_8 bed		*300 mg*
PH temperature		*950°C*
Time of Pyrohydrolysis		*120 min*
Carrier gas (moist O_2) Flow rate		50 cc/min
Trapping solution		60 mM NaOH
Distillate Collection rate		0.7 ml /min

Keywords: barium borosilicate glass, pyrohydrolysis, boron, fluoride, ion chromatography

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Separation of uranium and thorium as their quinic acid complexes by ion chromatography

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Liquid chromatography (LC) separation of actinides plays an important role from the analytical point of view and there is a growing interest in developing reliable and rapid methods using high performance liquid chromatography (HPLC) and ion chromatography (IC). The separation of actinide ions in HPLC or IC is a challenging problem as they exhibit very close selectivity coefficients among them and also with some of the lanthanide ions. Therefore, to separate the actinide ions, simple carboxylic acids are used as complexing agents, formation of metal complexes and their conditional stabilities are leading to their separation [1]. Among the complexing agents known for separating actinides and lanthanides, α-HIBA is a widely used hydroxy carboxylic acid [2]. Mandelic acid, an aromatic acid, is also used for separating U and Th. The elution order obtained in the case of α-HIBA may not be useful in many cases. For instance, U and Th are getting eluted in between the elution of lanthanide ions.

Quinic acid, another hydroxyl carboxylic acid, forms complexes with metal ions similar to α-HIBA. In the present study, the retention characteristics of U and Th as their quinic acid complexes on a reversed phase column dynamically modified into cation exchange surface by using Camphor-10 sulphonic acid (CSA). The effect of [QA] on the retention of U and Th was studied and an elution order of U followed by Th was obtained when [QA] < 15 mM whereas the order got reverted when [QA] > 15 mM. This separation condition will find applications in rapid separation of U and Th in several matrices including water, effluents and environmental samples.

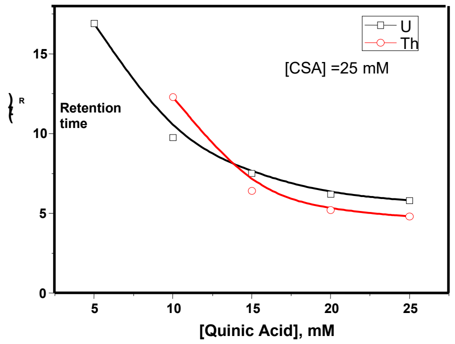

Fig.1 Effect of quinic acid concentration on the retention of U and Th

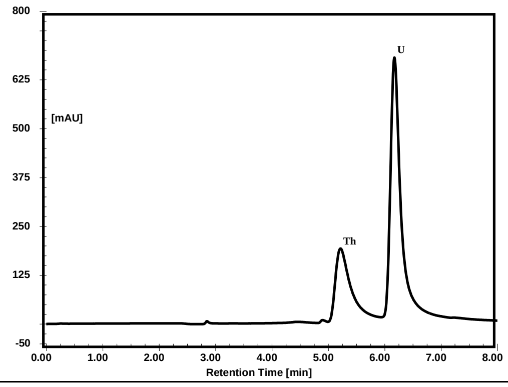

Fig.2 Chromatogram showing separation of U and Th. Column: Hypersil ODS-2, Eluent: 20 mM quinic acid in 25 mM CSA; pH 4. Detection: Arsenazo (III) as PCR at 656 nm.

Keywords: Uranium, Thorium, Quinic acid, Ion chromatography

Reference

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Separation and determination of alkali and alkaline earth metals in soil samples by ion chromatography

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Separation and Quantification of alkali and alkaline earth metals present in soil is important to evaluate the soil condition and its chemistry with respect to plant nutrients. Potassium is one of the main nutrients for plants whereas calcium and magnesium are essential secondary plant nutrients. Although sodium is not a nutrient, excess of sodium destroys soil structure which is undesirable for plant growth. In view of this, methods have been developed to for their separation and quantification in soils. Soils are digested and quantification of alkali and alkaline earth metals is achieved by techniques like flame photometry [1], inductively coupled plasma atomic emission spectroscopy [2]. However, ion chromatography offers simultaneous separation and quantification of alkali and alkaline earth metals. Since these metal ions are present in percentage level (minor/major), the chromatography is one of the preferred methods for accurate determination and desired precision. In present study, an analytical procedure comprising a microwave assisted digestion followed by ion chromatography (IC) separation of metal ions on a cation exchange column.

The soil samples were collected and prepared as per standard procedure. Accurately weighed samples (~ 100 mg) was added with a combination of Conc.H_2SO_4, Conc. HCl, Conc. HF and subjected to microwave assisted digestion. The digested solutions were treated and finally taken in 1% HNO_3 for IC analysis. The IC separation was carried out on a cation exchange column with methane sulphonic acid as eluent. Fig.1 shows typical chromatogram obtained for the standard and a sample.

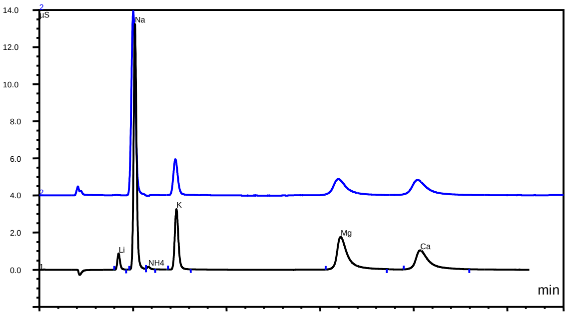

Fig.1 Chromatogram overlay obtained for (1) standard and (2) sample.

Table 1. Results obtained for soil samples

	Soil-1	Soil-2	Soil-3
	Concentration %		
Li	0.004 ±0.0001	0.004 ±0.0001	0.003 ±0.0001
Na	6.0 ±0.1	4.8±0.1	3.50 ±0.08
K	2.5±0.05	2.1±0.05	1.2±0.03
Mg	1.2±0.05	1.0±0.03	0.5±0.01
Ca	1.9±0.05	1.1±0.03	0.5±0.01

Keywords: Alkali metals, Alkaline earth metals, Soil, Ion chromatography

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Feasibility study on the individual separation of lanthanides using quinic acid by ion chromatography

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There is a growing interest in determining lanthanide impurities in one of the lanthanide matrices. For instance, determination of trace level concentrations of rare earth elements in Gd and Dy based materials are important from the chemical characterization as well as quality control point of view. Separation of the matrix lanthanide(s) is a prerequisite prior to the determination of lanthanide impurities due to matrix intolerance in the analytical determination. However, such separations are difficult with conventional separation methods. Liquid chromatography techniques such as HPLC/IC have scope of realizing such separations because it can provide high resolution between the individual lanthanides [1].

In the present work, feasibility of separating lanthanides individually was explored by converting them into their in-situ quinic acid (QA) complexes. Separation was carried out on a reversed phase column modified with camphor-10-sulfonic acid (CSA). The preliminary studies showed the feasibility of separation. Effect of concentration of QA and CSA has been studied and the results showed appreciable resolution among the lanthanides. Fig.1 shows a typical chromatogram obtained for a standard solution having all 14 lanthanides. It is also observed that the quinic acid complexes have shown strong retention and therefore, the separation time is too long, which is desirable especially while dealing with separating the matrix lanthanide from other impurity lanthanides. Further the chromatogram obtained shows the feasibility of modifying the elution depending on the application.

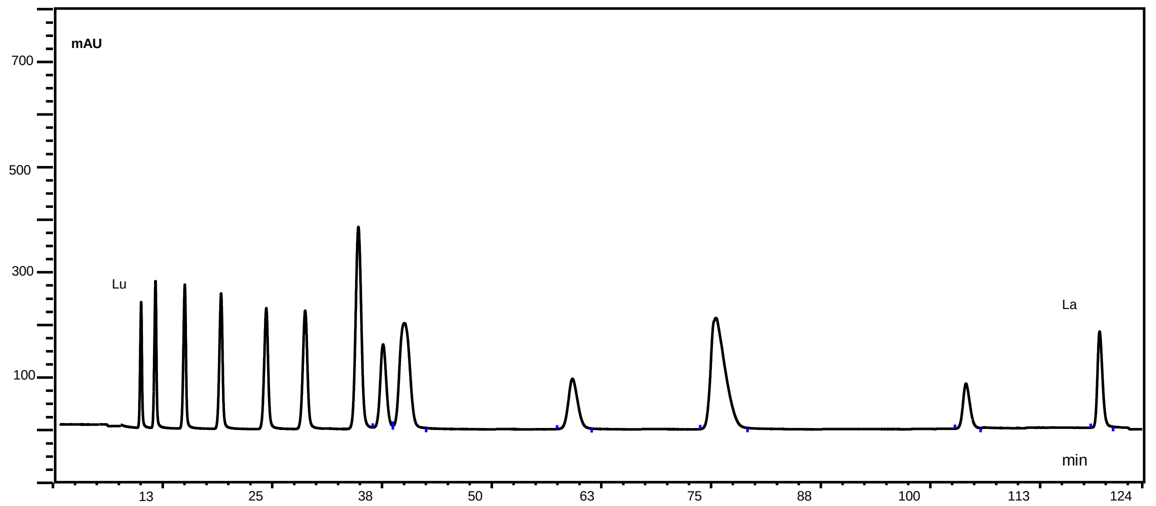

Fig.1 Chromatogramobtained with individual separation of lanthanides. Column: Hypersil ODS-2, Eluent: Concentration gradient of quinic acid from 10 mM to 80 mMin 25 mM CSA; Detection: Arsenazo (III) as PCR at 656 nm.

Keywords: Lanthanide, Quinic acid, Ion chromatography

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Simultaneous separation and determination of Gadolinium and Zirconium in Gadolinium Zirconate

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Gadolinium Zirconate ($Gd_2Zr_2O_7$) doped with niobium is used as burnable poison (BP) in nuclear reactors. The accurate determination of its constituents is essential for its chemical characterization. Knowing the concentration of Nb is absolutely necessary to evaluate the desired performance in the reactors. The sample preparation required for the determination of constituent elements is a difficult task because the dissolution of $Gd_2Zr_2O_7$ is challenging owing to its refractory nature. Mineral acid dissolution of $Gd_2Zr_2O_7$ is tedious and results in high acidity thereby making it unamenable to subsequent analysis. Recently, a simple solid state fusion method for $Gd_2Zr_2O_7$ using ammonium bifluoride has been developed, where in selective dissolution of Nb and its quantification by spectrophotometer has been demonstrated [1]. This study aims at developing an ion chromatography method of simultaneous separation of Gd and Zr for their determination after the complete dissolution of $Gd_2Zr_2O_7$ by bifluoride dissolution. The ABF fused mass of $Gd_2Zr_2O_7$ was initially dissolved in 8 M HNO_3 and finally taken in 1% HNO_3. To prevent the hydrolysis of the metal ions in low acidity, tartaric acid was added.

The prepared sample solution was injected into IC for separating Gd and Zr after appropriate dilution. IC separation was carried out on a reversed phase column using pyridine dicarboxylic acid (PDCA) in KNO_3 and HNO_3. Effect of PDCA, KNO_3 and HNO_3 on the retention of both Gd and Zr was studied and based on the results, the final composition of the mobile was arrived at. Mechanism of separation is found to be chelation exchange and the addition of KNO_3 is to minimize the ion exchange characteristics of the ligand expected to deposit on the surface of the column. Fig.1 shows a typical chromatogram obtained for a sample solution. Although the separation has been realized, their quantification with good reproducibility needs to be improved.

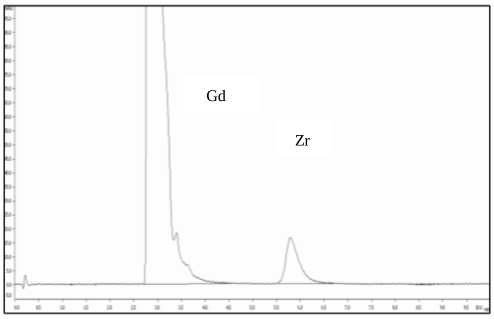

Fig.1 Chromatogram obtained for a sample. Column: Polymeric reversed phase; Eluent: 0.5 mM PDCA in 0.2M HNO_3 and 0.02M KNO_3. Detection: Arsenazo(III) as PCR at 656 nm.

Keywords: Gadolinium, Zirconium, Fusion, ammonium bifluoride, Ion chromatography

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Optical Recognition of Hazardous Chromium Ions in Environmental Samples Using a Low-cost Probe-threaded Hybrid Monolithic Matrix

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Industrial activities like mining, steel manufacturing, and leather tanning significantly degrade the environment, causing air, water, and soil pollution [**1**]. Consequently, heavy metal ions in these areas require strict monitoring due to their serious health risks over time. Among these metals, chromium is notably carcinogenic, with documented health hazards including respiratory issues, pulmonary carcinoma, renal dysfunction, immunodeficiency, and dermatitis [**2**]. This study addresses these concerns by developing a robust solid-state colorimetric sensor capable of detecting and quantifying hazardous chromium ions in real-world water samples. The sensor utilizes the chromoionophoric properties of an azomethine probe, named 4-((2-(benzo[d]thiazole-2-yl)hydrazono)methyl)-2-methoxyphenyl (BHEP), which changes color from white to dark red upon interaction with chromium ions. By incorporating the probe into ameso/macro-porous silica-polymer hybrid monolithic framework (poly(VTEO-co-EGDMA)), the sensor's sensitivity and selectivity are enhanced, with the absence of organic solvents during application is advantageous. Structural characterization of the sensor material is conducted using various analytical techniques, including p-XRD, FT-IR, BET/BJH, FE-SEM, and HR-TEM. Furthermore, the study explores optimal sensing parameters such as pH, probe concentration, sensing material amount, and metal ion concentration while examining potential interferences from other common metal cations in aqueous samples using UV-DRS analysis. The solid-state sensor, shows a linear range of 1.0–200 ppb, exhibited a detection limit of 0.52 ppb and a quantification limit of 1.32 ppb, respectively. Its practical utility with industrial and environmental water samples revealed excellent data reliability and reproducibility, with recoveries ≥99.3% and RSD ≤1.7%, ensuring accurate real-time monitoring.

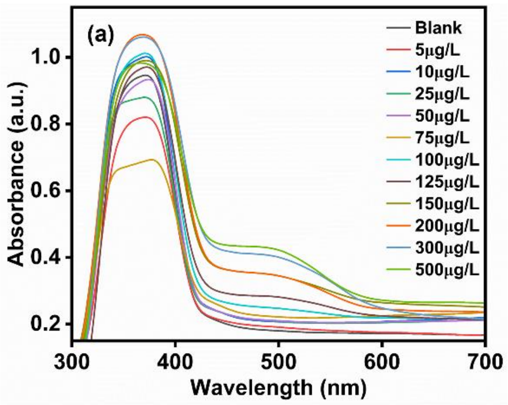

Fig. (a). UV-DRS signal response upon incremental addition of chromium ions.

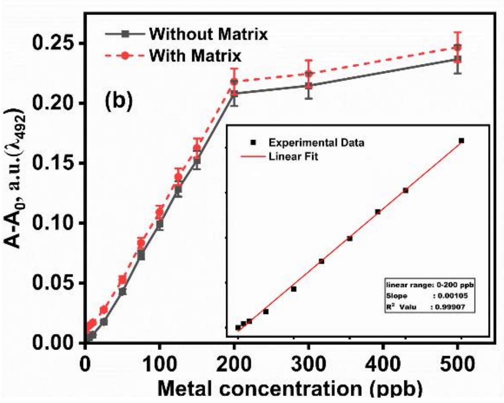

Fig. (b). Calibration plot (inlet linear response range).

Keywords:Solid-state sensor,Hybrid monolith, Chromoionophoric,Meso/Macro-porous,Chromium ions

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Structurally Engineered Chromoionophoric Probe Encapsulated Porous Polymer as A Solid-State Ocular Sensor Material for Mercury Ions

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According to the United States Environmental Protection Agency (USEPA) and the World Health Organization (WHO), mercury is one of the most toxic metal ions. The ultra-trace range of 1–10 µg/L is the maximum amount of mercury contamination that is allowed in different types of water resources [1].High levels of mercury exposure over an extended period can cause genetic mutations, carcinogenesis, Minamata illness, kidney failure, gastrointestinal disorders, and damage to developing fetal nerves. Previous research hasdemonstrated that drinking water tainted with mercury over allowable limits results in tremors, weariness, neuromuscular abnormalities, diarrhoea, nausea, elevated blood pressure, and an accelerated heart rate [2].The objective of this work is to create a novel solid-phase ocular sensor that can detect Hg^{2+} in aqueoussamples.Thechromoionophoric receptor molecule, (Z)-1,5-dimethyl-2-phenyl-4-(quinoline-4-ylmethylene)amino)-1,2-dihydro-3H-pyrrazol-3-one(DPQD), was encapsulated onto a porous polymer matrix. p-XRD, HR-TEM, FE-SEM, SAED, EDAX, and N_2 isotherm analysis are used to characterize the architectural and topographical aspects of tailor-made polymer monolith templates. The remarkable structural arrangement and network architecture of the porous polymer monolith allow for extremely quick dispersion of the target ions, facilitating simple interaction with the receptor active centers. The visible region experiences a bathochromic shift, resulting in a color shift from yellow to dark orange, due to a charge transfer process between the target Hg^{2+} ions and the DPQD probe. Furthermore, the chemo-sensor has exceptional sensitivity, faster kinetics, and superior.The solid-state sensor shows a linear range of 1.0–100 ppb, exhibited a detection limit of 0.67 ppb and a quantification limit of 1.90 ppb, respectively. Its practical utility with industrial and environmental water samples revealed excellent data reliability andreproducibility, with recoveries ≥99.2% andRSD ≤2.2%, ensuring accurate real-time monitoring.

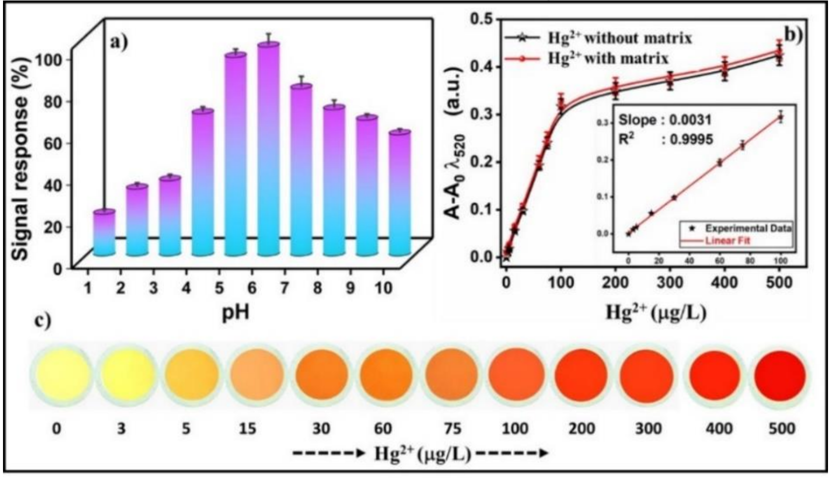

Fig.(a)Influence of pH, (b) calibration plot and linear fit (inset) and (c) gradual naked eye color shift of the sensor with an incremental concentration of Hg^{2+}.

Keywords: Mercury, Monolith, Mesoporous, Solid-State Ocular Sensor, Polymer.

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Laboratory studies on Strontium separation from water samples using hydroxyapatite

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Many water sources, including groundwater, have been reported to be contaminated with strontium in nations like Japan, the United States, and India [1]. In the pigment business as well as the cathode ray tube production processes, strontium is utilized [2]. Consequently, industrial wastewaters may be the primary source of strontium contamination in water [2]. This poses a serious threat to public health because it is known that ingesting a high concentration of strontium can be toxic to living things.

Various pollutant separation techniques such as reverse osmosis, precipitation, membrane filtration, ion exchange separation, electrochemical treatment, etc. are available for the separation of contaminants from aqueous media. However, many of these techniques are energy demanding, costly and does not work efficiently at low pollutant concentration. Adsorption is found to be one of the most effective separation technique for toxic metals from aqueous media.

In the present study, Hydroxyapatite (HA) (($Ca_{10}(PO_4)_6(OH)_2$) was synthesized and tested for its Sr removal from spiked water samples. The material was synthesized from natural bio-waste material i.e., egg shell using phosphoric acid as phase modifier. The material was characterized using XRD to confirm the formation of Hydroxyapatite phase. It was tested for adsorption kinetics and aqueous phase pH effect on Sr uptake. All experiments were conducted in duplicate by mixing 20 mg of HA with 10 ml of water. Initially, effect of aqueous phase pH on adsorption was studied by varying the pH from 6 to 9. Known amount of Sr ($SrCl_2$) was added and supernatant was separated after 24 hrs. The results (Table 1) indicates that maximum adsorption for Sr was observed at pH 9. Subsequently, adsorption equilibration time was established by interacting the HA with Sr spiked liquid (maintained at pH >9) for different time intervals ranging from 5 mins to 24 hrs. Supernatant was analyzed for Sr using Atomic Absorption Spectrometer (GBC Avanta). Analysis results show that, adsorption equilibrium was achieved at 18 hrs (Figure 1).

Table 1: Effect of aqueous phase pH on Sr separation

pH	**Adsorption capacity (mg/g)**
6	0.78±0.15
7	2.45±0.05
8	3.26±0.05
9	4.13±0.04

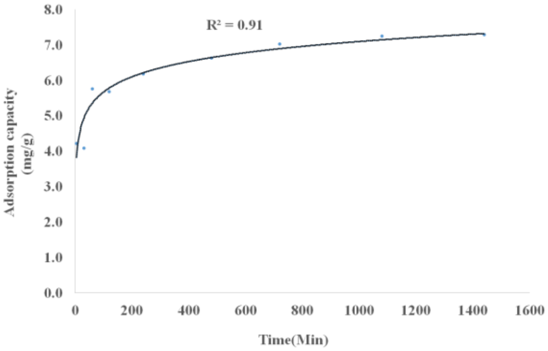

Figure 1: Sr adsorption variation with contact time

The results indicate that, HA has good adsorption affinity for Sr under studied experimental conditions and can be used for the treatment of conventional industry's waste water as well as low level liquid waste effluents from nuclear industry to sequester ^{90}Sr. As the material (HA) is synthesized from natural bio-waste, this method will be cheap and eco-friendly.

Keywords: Strontium, hydroxyapatite, remediation

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Wastewater Treatment: Complete Degradation of Prazosin using Newer Dual Activity Hydrodynamic Cavitation Reactors

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The present research reveals successful degradation of Prazosin, an Alpha-1 Adrenergic Blocker, commonly used in the treatment of Hypertension. A new cavitation technique employing a Dual Activity Reactor, a vortex flow-based cavitation device, suggests combination of cavitation and catalytic activity for enhanced degradation of the pollutant **[1]**. Two different types of vortex diodes were used for investigating comparative performance: a Non-Catalytic Aluminium diode and a Dual Activity Copper diode exhibiting catalytic properties **[2]**. The effect of different process parameters such as pressure drop, pH on Prazosin degradation and mineralisation was evaluated on a pilot-plant of capacity 1 m^3/h. Process Intensification was studied using Aeration, Hydrogen Peroxide, and pH modification. The results indicated significant improvements with aeration for the Cu-Vortex Diode compared to the Al-Diode. The use of H_2O_2 resulted in complete (100%) degradation of the Active Pharmaceutical Ingredient (API) pollutant within just 5 minutes of treatment. Interestingly, apart from complete degradation of the organic moiety, a very high extent of mineralisation, ~55%, was obtained with the Cu-Diode, compared to 34% using the Al-Diode indicating environmentally friendly process. The results also highlight a strategy for improving efficiency using Hydrodynamic Cavitation (HC) and Process Intensifications. Further, development of Hydrodynamic Cavitation technology, with the new concept of Dual Activity Reactor-Cu Vortex Diode as a cavitation device, represents a breakthrough in the field of industrial wastewater treatment, with possible real-life applications and for providing promising alternative to the existing cavitation devices. The technology can provide an efficient and practical solution for the degradation of various API pollutants and for wastewater remediation/ reducing the environmental pollution.

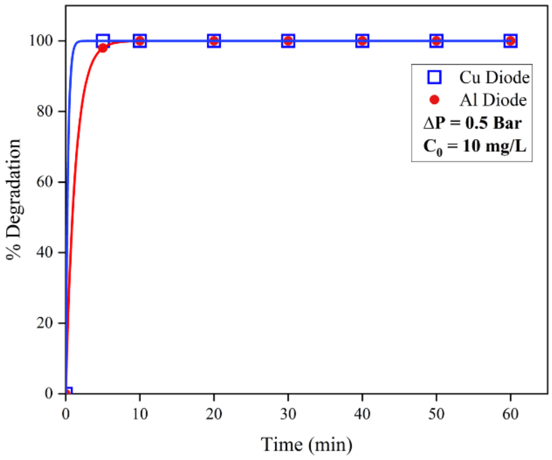

Fig1. Complete Degradation of Prazosin using H_2O_2

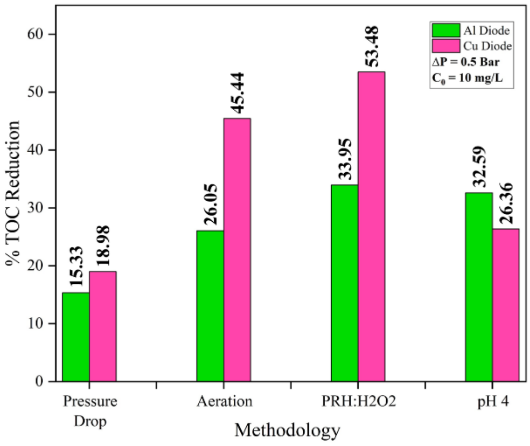

Fig2. Removal of Prazosin using different Methodologies

Keywords: Wastewater Treatment, Degradation, Pharmaceutical, Advanced Oxidation, Technology.

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Continuous flow mode adsorption and recyclability analysis of a functionalized cellulose based reusable adsorbent for effective U(VI) remediation in ground water

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Presence of Uranium in drinking water poses a severe health hazard in several parts of Northern and Southern India [1], with detected concentration levels well beyond the WHO permissible limits of 30 ppb. To provide a sustainable solution to this problem, a state of the art, green cellulosic adsorbent has been fabricated through surface functionalization of cotton cellulose fabric. ^{60}Co gamma radiation mediated Radiation Induced Graft Polymerization (RIGP) process was used to functionalize cotton cellulose in a single step using monomer bis[2-(methacryloyloxy)ethyl] phosphate (B2MP), a phosphate-based species well known for its selective uptake of Uranium [2]. Reusability of the adsorbent was established by studying the elution profiles of three different eluent systems to ensure multiple adsorption-desorption cycles on actual U(VI) contaminated ground water samples.

This work describes the ^{60}Co gamma radiation mediated grafting of B2MP onto cellulose, wherein parameters such as radiation dose, monomer concentration and solvent polarity were optimized to arrive at the desired grafting yield of ~25 %. U(VI) adsorption studies were conducted in continuous flow mode column operation by passing a 100 ppm U(VI) solution through a glass column packed with ~1 g of adsorbent at a flow rate of 1 ml/min (Fig. 1). Fractions were collected at regular intervals to determine the residual U(VI) concentration and the total adsorption capacity was calculated at ~135 mg/g. For regeneration and recovery of the adsorbent, three different eluents were studied, namely ammonium oxalate (AO), ammonium carbonate (AC) and sodium carbonate (SC), all concentrations being 0.5 M. Of the three, ammonium carbonate was observed to be the most efficient with over 85 % recovery of adsorbed U(VI) in 100 mL eluent volume from the saturated adsorbent column, at a flow rate of 1 ml/min. Ammonium carbonate was subsequently used to regenerate and reuse the adsorbent column for four cycles with minimum attrition losses. This novel process can be potentially upscaled as an efficient methodology for remediation of U(VI) ions in contaminated water.

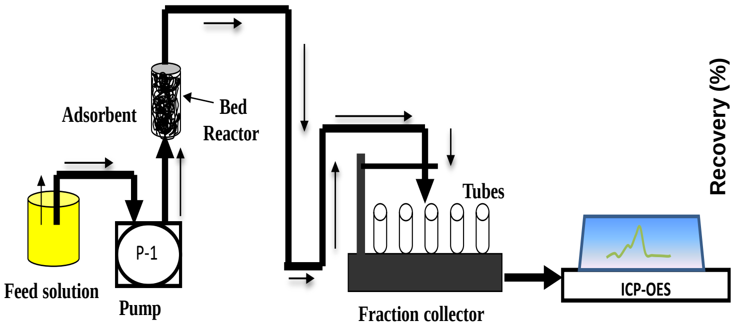

Fig. 1: Schematic of column mode continuous flow operation of U(VI) adsorbent [adsorbent wt. ~1 g, Flow rate: 1ml/min]

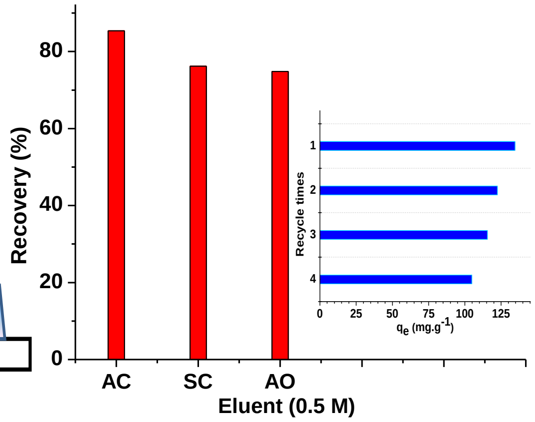

Fig. 1: U(VI) recovery (%) from saturated adsorbent by different eluents **Inset:** Recycling of adsorbent in column flow mode operation

Keywords: Radiation grafting, Cellulose, Uranium, Adsorbent, Recycle

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Synthesis of strong cation exchanger polymer matrix using radiation grafting method

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Porous polymer matrices, particularly PolyHEMA have been of great interest due to its unique properties like easy polymerization, crosslinking nature and biocompatible material [1]. Catalysts, electrodes, filtration systems, ion exchange resins and scaffolds for tissue engineering are some of the applications have been targeted by various researchers all over the world. In the present study, Super-porous polyHEMA has been synthesized through phase separation process in presence of a cationic polyelectrolyte as a porogen, using radiation induced crosslinking method. Further, the super-porous polyHEMA has been surface modified with strong cation exchanger sulphonate groups. Sodium salt of Polyvinylbenzene sulphonic acid (PolyVBSA) has been grafted using gamma radiation induced mutual radiation grafting method. The effect of three important experimental parameters, namely, absorbed dose, monomer concentration and volume (monomer) to weight (base polymer) ratio have been investigated. Grafting yield has been found to increase with the absorbed dose up to 3kGy and levelled off afterwards (Figure 1), while grafting yield was almost linear function of monomer concentration (inset figure 1b). Volume to weight ratio provided insight in to optimum volume required for achieve desired grafting yield (inset Figure 1a). Grafting yield of as high as 160% has been obtained under optimized experimental parameters. Equilibrium adsorption studies have been investigated by taking basic dye (positively charged) methylene blue (MB), as a model dye. Adsorption capacity has been found as a function of grafting yield which is due to increase in number of sulphonate groups as a chelating group (Figure 2) and Maximum Adsorption capacity of 522mg/g was achieved at 160% G.Y.

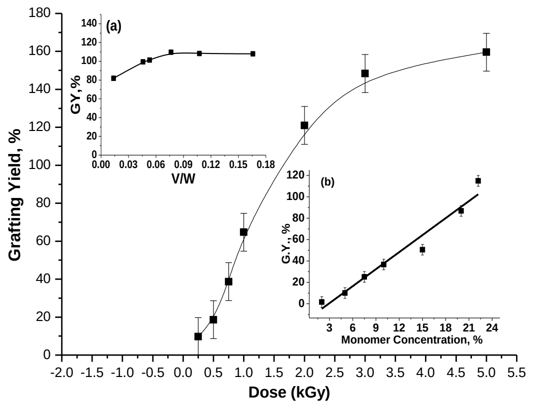

Fig:1 Effect of absorbed dose on grafting yield. Inset a) V/W ratio, b) Monomer Concentration

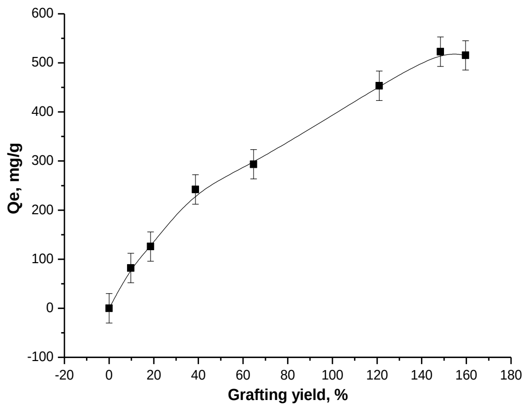

Fig:1 Adsorption capacity of adsorbent for MB dye as a function of grafting Yield

Keywords: *Grafting, Radiation, Adsorption, Dye*

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Radiolytically functionalized cellulose based biodegradable adsorbent for effective Hg(II) sequestration from ground water: Feasibility studies on simulated wastewater

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The presence of Mercury (Hg(II)) in water bodies poses a pressing threat not only to aquatic life forms but also human health, by virtue of its high neuro- and reproductive toxicities, biomagnification, non-degradability and long-distance transportability [1]. With practical applicability of most reported Hg(II) remediation methods being limited due to complex synthesis protocols, economic non-viability, upscaling or potential environmental risks, the use of radiation technology to develop adsorbents based on functionally altered surfaces is a novel proposition for achieving selective uptake of Hg(II) from contaminated water with high efficiency and viability [2]. Especially attractive is the concept of using biodegradable cellulose as the adsorbent base matrix to facilitate sustainability, ease of handling, processing and upscaling for large scale applications.

This work proposes the fabrication of a novel thiol (-SH), amine (-NH-) and carboxylic (-COOH) group containing trifunctional adsorbent for selective sequestration of Hg(II) from aqueous media. Polyacrylonitrile (PAN) was gamma radiolytically incorporated onto cotton fabric via Radiation Induced Graft Polymerization (RIGP) process, followed by chemical conversion of the nitrile groups using DL-Cysteine as the trifunctional agent. Grating parameters: radiation dose (Fig. 1) and monomer concentration (inset Fig. 1) were both observed to influence the Grafting Yield (G.Y.), with the trend in both cases being an initial increase followed by a saturation at higher values. The developed adsorbent was tested for Hg(II) removal in batch and continuous flow adsorption modes, followed by tests with Hg(II) spiked groundwater samples to determine the breakthrough characteristics (Fig. 2). The adsorption capacity was calculated at 174.3 mg.g^{-1}. Moreover, the adsorbent could be reused for >5 iterative cycles using an optimized HCl-Thiourea eluent system (inset Fig. 2). This novel process can be potentially upscaled as an efficient methodology for remediation of Hg(II) ions in contaminated water.

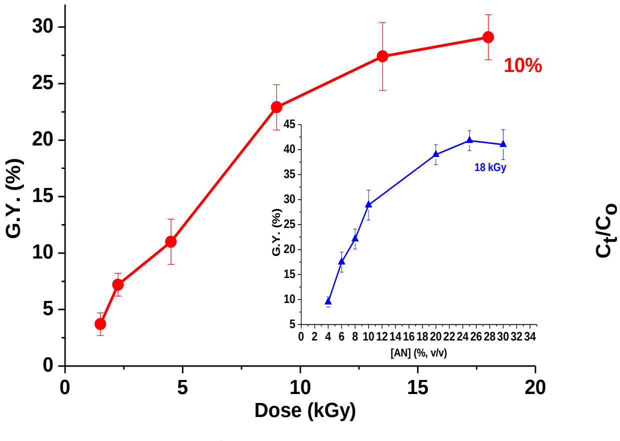

Fig. 1: Variation of G.Y. with absorbed dose. **Inset:** Variation of G.Y. with monomer concentration

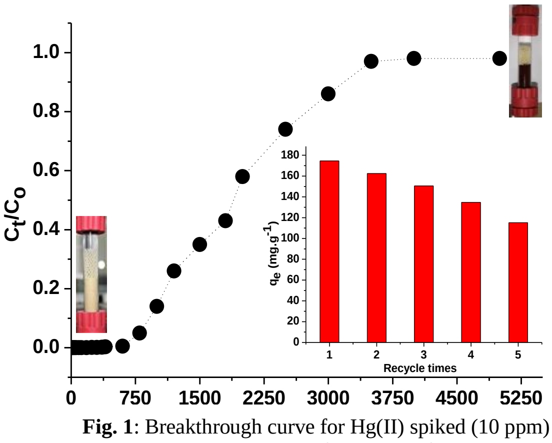

Fig. 1: Breakthrough curve for Hg(II) spiked (10 ppm) ground water adsorption in column flow mode (flow rate; 1 ml/min). **Inset:** Recycling of adsorbent in column flow mode operation

Keywords: Radiation grafting, Cellulose, Mercury, Adsorbent, Recycle

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Ion-receptor Immobilized Solid-state Opto-chromogenic Sensor for Ultra-trace Detection of Copper Ions in Environmental Samples

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Copper is the third most abundant element found in the human body and plays a crucial role as a trace element in biological processes [**1**].The main cause of elevated levels of copper contaminants in water resources is mainly attributed to mining, steelworks, metallurgy, and chemical manufacturing processes. According to the US Environmental Protection Agency, the limit of tolerable concentration of Cu^{2+} in drinking water is 1300 ppb. Hence, to ensure health and environmental safety, there is a need for a quicksensible and durable technique for the successful removal of Cu^{2+} in water contaminants[**2**].In this work, we carried out the selective detection of environmentally essential copper ions in aqueous solutions for application in industrial quality control and various environmental assays. The solid-state chromogenic sensor material is fabricated by exploiting the metal binding capacity of the probe, namely *(E)-1-((6-chlorobenzo[d]thiazol-2-yl)diazenyl)naphthalen-2-ol)*, i.e.,**CBNT**.The1:1stoichiometric ratio of CBNT-$Cu^{2+}$is confirmed byusing continuous variation method. The probe molecules were homogeneously dispersed on the tailor-made hybrid porous polymer monolith*poly (vinyltriethoxysilane-copolymer-pentaerythritoltetraacrylate)*, i.e.,**poly (VTES-co-PETA)**, which exhibited high surface area and porosity. The sensor material's structural features, surface morphology,and bare porous polymer monolith template were analyzed using p-XRD, FT-IR, XPS, FE-SEM and HR-TEM. The chromoionophoric sensor showed marked enhancement of UV-Vis-DRS absorbance at λ_{max}571 nm; the process was accompanied by a visible colour transition from orange to steel blue, which proves a sensitive detection tool for Cu^{2+} ions. The naked-eye detection and quantification limitswere3 and 5 ppb, respectively. Colorimetric data showed a linear response in a physiologically relevant range of 0−150 ppb of Cu^{2+}**(Fig. 1)**. The corresponding ocular color transitions and UV-Vis-DRS-spectral profiles obtained for individual cations are displayed (**Fig. 1(d))**.It was noticed that Co^{2+} interfered with the poly(VTES-co-PETA)-CBNT sensor at a concentration 15 times higher than Cu^{2+}(500ppb), which has been efficiently concealed by using 0.2 mM of oxalic acid and depicted in (**Fig. 1(e)**). Parameters like sensor dosage,amount of the sensor, pH, temperature, and kinetics essential for enhanced signal response were optimized. Real-time onsite analysis of the CBNT sensor was investigated with water samples and industrial waste effluents, and highly reproducible results were obtained (RSD≤1.2%). The proposed work provides a cost-effective, simple, and robust sensor for highly selective and sensitive detection of Cu^{2+}, which has the potential to be converted into a portable sensor kit.

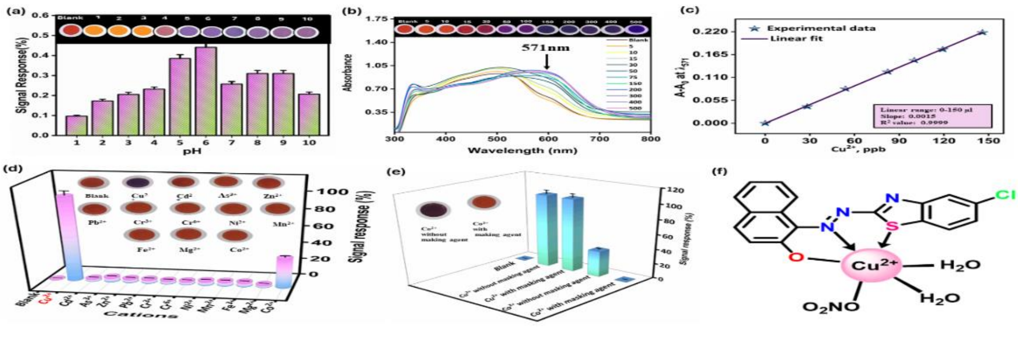

Fig.1. (a) Effect of pH, (b) & (c) Visual color transition of poly(VTES-co-PETA)-CBNT and linear fit data, (d) Ion Selectivity of poly(VTES-co-PETA)-CBNT sensor towards Cu^{2+},(e) Interference signal response of Co^{2+} with poly(VTES-co-PETA)-CBNT sensor in the presence of masking agent &(f) Complexation mechanism of Cu^{2+}-CBNT complex

Keywords: Chromoionophoric sensor, hybrid porous monolith, Naked eye detection, Copper, and onsite analysis

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Thiol based Zr MOF for the removal of cadmium from aqueous solution

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The relatively new field of Metal Organic Frameworks (MOFs) has attracted a considerable interest among the research fraternity due to their applications in diverse fields like sensing, catalysis, adsorption etc. The properties like high surface area and pore volume, easy functionalization etc. makes them a potential candidate for the removal of heavy metal ions from aqueous solutions **[1]**. Since heavy metal ions like Cd does not undergo degradation like dyes, there is an urgent need to develop adsorbents for the remediation. Keeping in mind the HSAB theory, we tried to separate Cd using MOF with thiol functionality from aqueous solution **[2]**. In this study, we have synthesized a thiol based MOF using $ZrCl_4$ as the metal source and meso dimercaptosuccinic acid as a linker at 90° C for 12 h under stirring conditions. The synthesized MOF was further characterized using techniques like XRD, FT-IR, SEM and B.E.T. The above mentioned MOF was utilized for the adsorption of Cd from aqueous solutions.

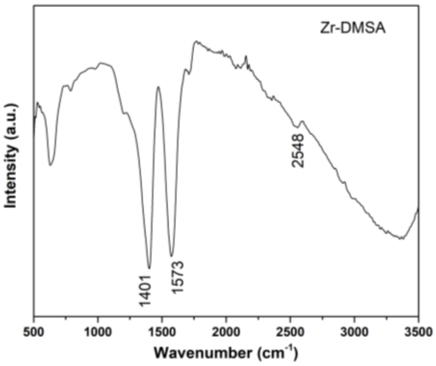

Fig. 1: FT-IR spectrum of Zr-DMSA

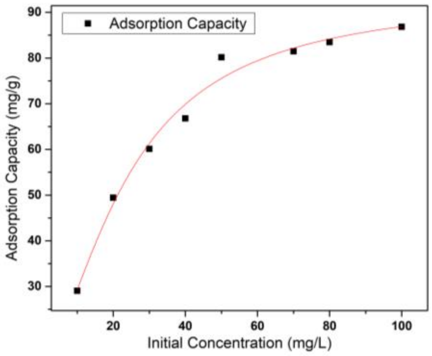

Fig. 2: Variation of adsorption capacity with change in initial concentration of Cd^{2+}

The XRD pattern observed was broad in nature which might be due to the presence of a flexible aliphatic linker or due to the crystallization of MOF in nano regime. The successful attachment of linker was established by observing the symmetric and asymmetric stretching of carboxylate group in FT-IR spectrum as shown in Fig. 1 where these stretching vibrations were found downshifted compared to the stretching vibrations of free linker. The specific surface area measured by B.E.T. analysis showed an area of 310 $m^2/g/$. The characterized MOF was utilized for the adsorption of Cd from aqueous solution. The pH dependence on adsorption characteristics of Cd (II) was evaluated by varying pH from 2-7 and the maximum adsorption was achieved at pH ~ 6. At low pH the thiol group would itself be protonated and hence unavailable for binding with Cd and as the pH is increased, the thiol groups become free and the adsorption capacity increases. All the further experiments like adsorption kinetics and adsorption isotherm were carried out at pH 6. These studies showed a maximum adsorption capacity of ~ 87 mg/g as shown in Fig. 2.

Keywords: MOFs, Cadmium, Adsorption, B.E.T., Isotherm

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Facile Synthesis of Novel Bi_2S_3-Nb_2O_5 Nanocomposites Decorated on Porous Polymer Monoliths for the Fast and Efficient Photocatalytic Reduction of Hexavalent Chromium

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Hexavalent chromium is considered to be a noxious contaminant discharged by leather processing, paint and pigment industries that interferes with human life, causing many health problems likeweakened immune system, nasal irritation, cancer and damage to the kidney and liver.**[1][2]**In pursuing environmentally responsible applications, this work aimed to synthesize Bi_2S_3-Nb_2O_5(BSNO) nanocomposite of variable stoichiometric proportions and the optimized BSNO (30/70) decorated on a porous polymer templateis innovatively applied as a new-age photocatalyst for the photocatalytic reduction of chromium. The porous polymer monolith-loaded catalyst has been prepared through in-situ polymerization ofethylene glycol dimethacrylate (EGDMA) monomer with BSNO (30/70) nanocomposite. The heightened efficiency of photoreduction of chromium with Bi_2S_3-Nb_2O_5 nanocomposite than the degradation efficiency of pristine nanomaterials(Bi_2S_3 and Nb_2O_5) can be attributed to the minimum recombination rate of electrons and holes.The chemical composition of these photocatalysts and their structural properties and morphology were characterized by field emission scanning electron microscopy, high-resolutiontransmission electron microscopy, powder X-ray diffraction, and X-ray photoelectron spectroscopytechniques.The UV-Vis DRS plot reveals that the polymer-dispersed BSNO (30/70)offers the optimal energy band gap for visible-light-induced photocatalytic activity. The optimized conditions for the photoreduction of chromium (5 ppm) involve a solution pH of 2 using 100mg of photocatalyst in the presence of formic acid as the sacrificial agent. Formic acid,like common organic additives, was used to elucidate the effect of hole scavengers on the photocatalytic reduction reaction. Among the different additives, the reduction rate of Cr(VI) was maximum achieved by formic acid due to the presence of the carboxylic acid group, which is bound to the surface of the photocatalyst and more prone to direct oxidation by photogenerated holes. Formic acid can effectively scavenge holes generated during the photocatalytic reaction,thereby enhancing the reduction efficiency.Under optimized conditions, the visible-light-induced photocatalytic reduction of hexavalent chromiumwas >96% within 2 h.The synthesized photocatalyst exhibited good structural stability and reusabilityfor the efficient photoreduction of toxic Cr(VI).

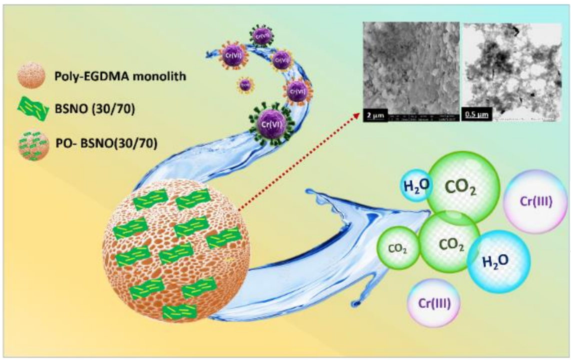

Fig.1: Graphical abstract

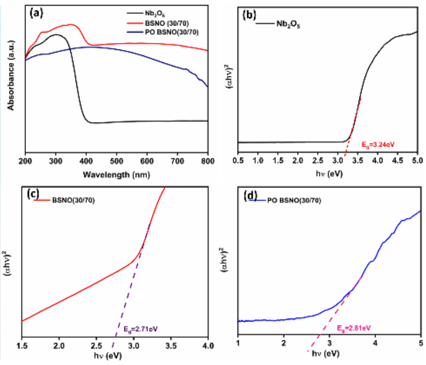

Fig.2: UV-Vis DRS plot(a) and band gap of Nb_2O_5(b), BSNO(30/70)(c), PO BSNO(30/70) (d)

Keywords:Bi_2S_3,Nb_2O_5, Heterojunction,Chromium reduction, Porouspolymer monolith

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Optimizing ReO_4^- (Surrogate for $^{99}TcO_4^-$) Sequestration: Unraveling Multifaceted Effects Using Surfactant Free, Synthesized-Zeolite Na-A

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Nuclear waste stream contains several toxic radionuclides, among which ^{99}Tc is of more concern owing to its pure beta emissivity with long $t_{1/2}$ of 2.11×10^5 y, biomagnification and environmental contamination [**1**]. Henceforth, technetium (existing as TcO_4^-) remediation becomes highly essential. Being adequately porous with high surface area, zeolites are promising adsorbent for the extraction of pertechnetate ions [**2**]. Literature study reveals that surface modification using organic surfactant leads to greater sorption capacity of zeolites [**3**]. Taking into account the carcinogenic impacts of surfactant, this study focuses on synthesis of surfactant free zeolite with similar sorption capacity. Zeolite Na-A appears to be effective adsorbent (pore size is comparable to ionic size of adsorbate) and hence been synthesized from Kaolin using multiple synthetic routes namely hydrothermal, alkali fusion and sonochemical. The formation of single phase pristine zeolites was confirmed by XRD, FT-IR, SEM and Raman. Specific surface area along with pore volume and pore size distribution was studied using BET analyzer. Rhenium as perrhenate (ReO_4^-) is widely being used as a non-radioactive surrogate for TcO_4^- owing to their similar chemical properties under aerobic conditions and has been synthesized by dissolving pure Re filaments in HNO_3 [**4**]. Effect of pH (~3-11), ReO_4^- concentration (~50-1000 ppm) and contact time (5-1440 min) was exhaustively studied to prove the efficient removal of perrhenate ions from aqueous solution.

Zeolite Na-A synthesized through sonochemical route was found to be the most suitable candidate among others for removal of ReO_4^- owing to its high surface area (24.773 m^2g^{-1}), adequate pore volume (0.032 m^3g^{-1}) and suitable pore size distribution (4.3-12.4 nm). With increase in pH, the removal efficiency reached up to 80% (at pH~11) for 500ppm of ReO_4^-. With rise in concentration of ReO_4^-, the sorption capacity increased to 318 mg g^{-1} (at 1000 ppm of ReO_4^-). The Langmuir and the pseudo-second-order models satisfactorily describes the sorption of ReO_4^- on zeolite Na-A. Study of contact time reveals the attainment of equilibrium sorption during the initial 60-90 min. Specifically, rapid adsorption of ReO_4^- occurred during the first 5 min and the extent of sorption duration up to 1440 min did not appreciably alter the equilibrium. Speciation of adsorbed rhenium using XPS confirms the absolute presence of Re (VII) in the zeolite matrix.

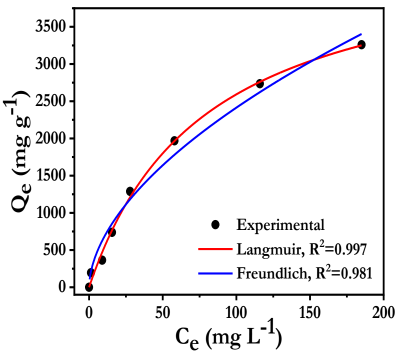

Fig. 1: Equilibrium adsorption isotherm plot for adsorption of ReO_4^-

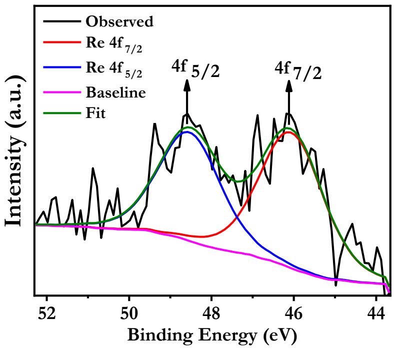

Fig. 2: XPS of Adsorbed Re(VII)

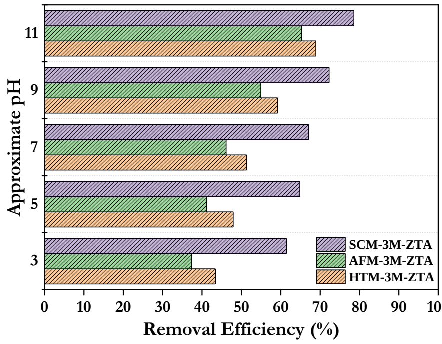

Fig. 3: ReO_4^- removal efficiency of synthesized zeolite Na-A at varying pH

Keywords: Surfactant free Zeolite Na-A, Kaolin, Perrhenate, Adsorption, Nuclear Waste

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Kinetics and Mechanism of Cadmium Sorption onto magnetic Fe_3O_4 coated Non-Stoichiometric Hydroxyapatite nanocomposite powder

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Cadmium, considered toxic even at low concentrations with a permissible limit of 3 ppb, necessitates effective removal from drinking water using economically viable methods like solid adsorbent. Therefore, aim of this study was to synthesize a novel magnetic nanocomposite and test its efficacy to remove Cd from simulated contaminated water. Magnetic nanocomposite (Fe_3O_4-nSt (non-stoichiometric)-HAP) was synthesized by using nSt-HAP (Ca/P = 1.34), $FeCl_3$ and $FeCl_2.xH_2O$. For the synthesis, solution of 4056.1 mg $FeCl_3$&1586.4 mg $FeCl_2.xH_2O$ (2:1 molar ratio of Fe (+3)/Fe(+2)) waspreparedin100 mL deionized water. After preparing the solution, 5011.2 mg of synthesized nSt-HAP was added to it and was stirred for 20 min. Subsequently, the pH of solution was maintainedto11and mixture wasallowedtoheatat82°Cfor90minutes, which resulted in a dark black colored solution. After magnetic separation the composite material was thoroughly washed with deionized water till near neutral pH was achieved. The washed composite powder was then allowed to dry in oven at 80°C and characterized using ATR-FTIR and FESEM to ensure synthesis of desired product. Batch sorption studies for Cd were carried for initial concentration of 200µg.L^{-1} and mass to volume ratio of 0.5 mg/10 mL (1:20) to investigate sorption kinetics. Kinetic data were tested with pseudo 1st order and 2ndorder kinetic models. Study revealed that equilibrium was achieved after 6 hours. The sorption kinetic parameters are presented in table 1 and R^2values suggest experimental data, best fit to the Pseudo 2nd order kinetics (figure 1.a), suggesting chemisorption. The sorption mechanism was studied by fitting the kinetic data with Boyd plot and Intra-particle diffusion model. The plots of the intra-particle diffusion (figure 1.b) didn't pass through origin, exhibits 2 step processes and linearity of the Boyd plot (figure 1.c) without passing through the origin indicates that film diffusion (External mass transfer) is the rate-determining step.

Figure1:a.)Pseudo2ndorderkineticplotb.)IDMplotc.)BKMplotforsorptionofCdiononFe$_3$O$_4$-nSt-HAP

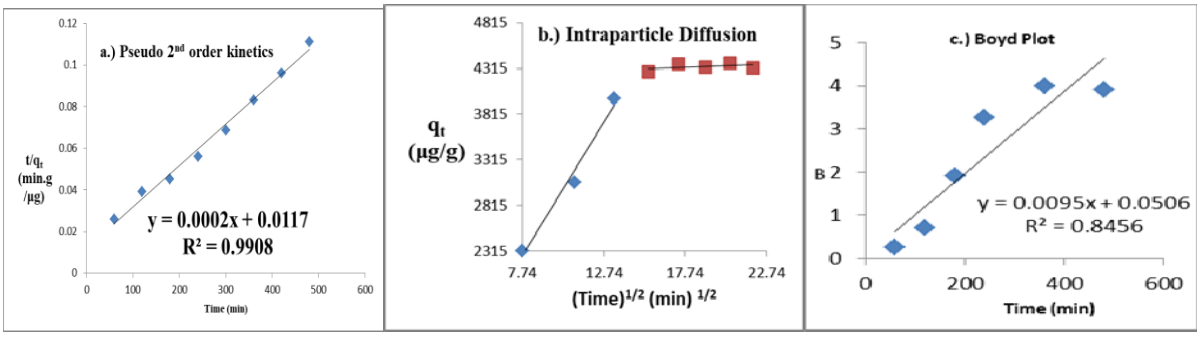

Table1: KineticparametersforsorptionofCdiononFe$_3$O$_4$-nSt-HAP

Pseudo1st order kinetic		Pseudo2nd order kinetic	
k_1(min^{-1})	0.0209	k_2(g/mg.min)	3.41x10^{-3}
q_e(µg/g)Theoretical	10287	q_e(µg/g)Theoretical	5000
R^2	0.934	R^2	0.990
q_e(µg/g)Experimental	4374.42	q_e(µg/g)Experimental	4374.42

Keywords:Fe$_3$O$_4$-nSt-HAP,Cd,sorptionkinetics

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An optimized liquid-liquid extractive spectrometric method for removal and determination of chromium(VI) from waste water

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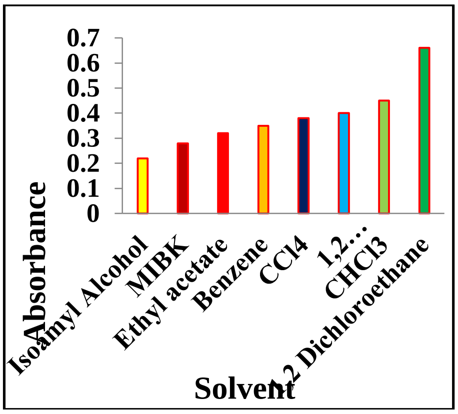
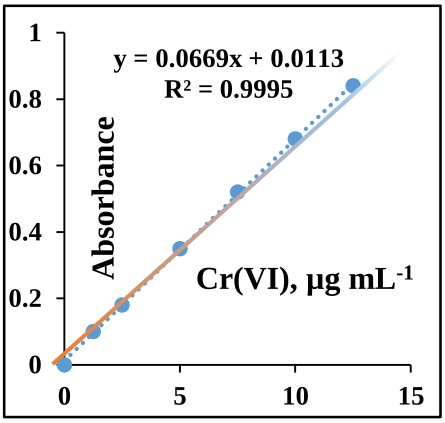
Many industrial processes or operations like metal processing, chromium plating, chemical dyes preparation, leather preparation and steel manufacturing uses chromium in large amount. Due to environmental and industrial conditions, chromium(III) gets converted into chromium(VI). So there is huge release of chromium(VI) into the environment. The anthropogenic discharge of chromium into the environment origins population exposure to occur by inhalation of contaminated air or ingestion of contaminated drinking water Owing to the inherent toxicity and carcinogenicity of chromium containing substances, the US Environmental Protection Agency and US Occupational Safety and Health Administration have determined exposure limits of 100 μg L^{-1} of total chromium for drinking water standards and 5 mg m^3 of Cr(VI)-timed weighted average for a normal work day (Pellerin and Booker 2000). It is well documented that exposure to chromium in the environment is pervasive and that chromium(VI) is a potent carcinogen, there are multiple mechanisms by which chromium exposure induces cellular damage and adverse health effects. Some studies have resulted that chromium(VI) is responsible to cause modifications in the DNA structure and genetic disorders [1].

In this work, a new methodology is designed for the liquid-liquid extractive removal and spectrophotometric determination of hexavalent chromium by using novel spectrophotometric reagent. 2-chlorobenzaldehyde thiocarbohydrazone in 1,2- dichloroethane is used as a complexing reagent for chromium(VI) in presence of potassium iodide to form yellow coloured complex at room temperature. This method has significant advantage of being a simple procedure where no further solvent purification or pre-concentration is needed. The ternary [Cr(VI)-CBTCH-iodide] complex was quantitatively extracted in 1,2- dichloroethane from 3.5 mol L^{-1} of hydrochloric acid medium which exhibited highest absorption at λ_{max} 415 nm and was stable around 72 h. The method presented excellent analytical response with a limit of detection of 3.2 μg L^{-1}, a wide working range up to 10.25 μg mL^{-1} and good precision (RSD = < 2%, n = 5). The molar absorptivity and Sandell's sensitivity of the ternary complex are as 0.3535×10^4 L mol^{-1} cm^{-1} and is 0.0147 μg cm^{-2} respectively. The enrichment factor is 2.496. The composition of the [Cr(VI)-CBTCH-iodide] complex was confirmed by log-log plot method and been found as 1:2:2. No substantial effects of potentially interfering ions are observed. This methodology was effectively used for the simultaneous removal and determination of chromium(VI) from polluted water, alloy samples and for separation of it from synthetic mixtures. The applied method has many advantages, such as simplicity, low cost, ease of operation, rapid detection, low-ligand consumption, and high sensitivity. The analytical method sensitivity was confirmed *via* the suitable selection of experimental circumstances.



Effect of diluent on [Cr(VI)-2CBTCH-iodide] complex.



Validity of Beer's law for [Cr(VI)-2CBTCH-iodide] complex.

Keywords: Alloys; 2-CBTCH; chromium(VI); extractive spectrophotometry; waste water.

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Benchmarking of 4E Parameters to develop an Energy Efficient Effluent Treatment System

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This paper examines the 4E (Energy, Environment, Exergy, and Economic) parameters crucial for developing an energy-efficient effluent treatment system tailored to challenges faced by solvent production plants, like the heavy water industrial unit of the Atomic Energy Industry. It is essential for the technology to meet strict environmental norms from State and Central Pollution Control Boards and ensure sustainable, eco-friendly industrial processes. The main goal is to investigate and analyse the 4E parameters enhancing efficiency and sustainability in effluent treatment, specifically for solvent production plant effluents. Research method (Fig.1) involves reviewing literature and assessing parameters influencing systems' performance on an industrial scale, aligning with state and central level statutory requirements. Moreover, the Process-Intensification method as described by Yaghy et al. [1] is also explored in this study to enhance efficiency and sustainability of operations in effluent treatment. The study analyses treatment technologies, including chemical, biological, physicochemical, and membrane options, as presented in [2,3] and many others, focusing on evaluating their performance relative to 4E parameters to establish benchmarks for energy-efficient effluent treatment. The outcomes of this research promise to provide valuable insights for the design and operation of energy-efficient effluent treatment systems in solvent production plants within heavy water facilities of Atomic Energy domain. By benchmarking essential parameters, the paper aims to contribute to the broader goal of aligning industrial practices in the Atomic Energy Industry with environmental sustainability objectives and regulatory compliance.

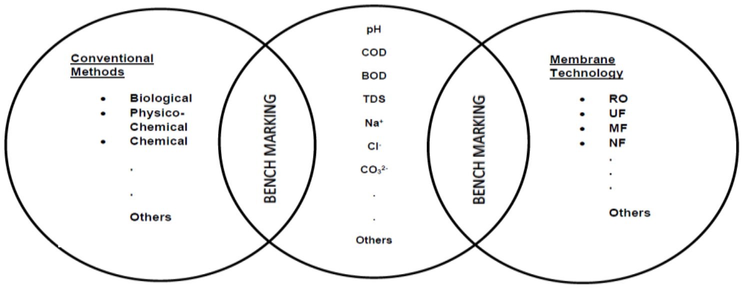

Fig.1: Methods in Benchmarking of Parameters to develop an Energy Effluent Treatment System

Keywords: Industrial effluents, COD, sustainability, benchmarking, Process Intensification, energy efficiency

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Design, development and practical implementation of a pilot scale "plug and play" tertiary treatment unit for persistent micropollutant degradation from real life pharmaceutical effluents

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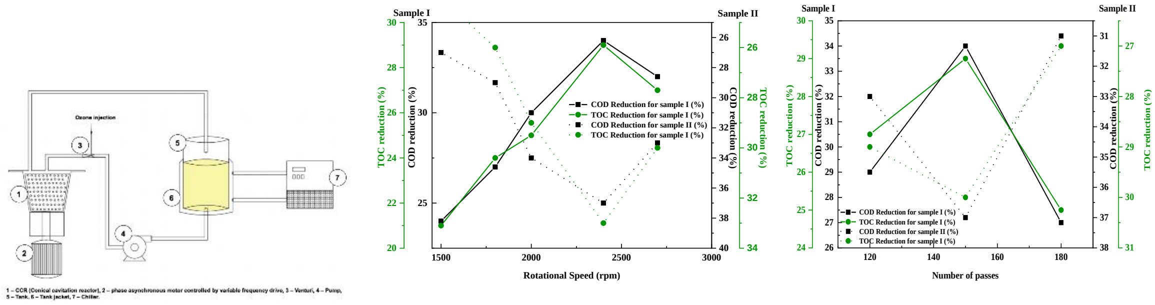
Realizing the strong inter-connection of water with life and energy cycle, it is our prime responsibility to fix the impact of impaired water throughout the world simultaneously with the scientific advancement. In spite of remarkable progress in wastewater treatment strategies over the past decades, degradation of micro-pollutant (present in ppb-ppt level in water) still remains a challenging domain to explore and often the treated effluent is disposed off without taking care of the same. One of the major categories of such organic micro-pollutants come from pharmaceutical industries, personal care products and wide use of different pesticides and herbicides. In this study, a conical plug and play hydrodynamic cavitation reactor is designed to be retrofitted into the existing tertiary treatment point for treating real life pharmaceutical effluents. It is observed that using intensified hydrodynamic cavitation process alone, a COD reduction of 37.11% was observed. Furthermore, the technology is coupled with other AOPs such as H_2O_2, Fenton's reagent and ozone for higher COD removal. At optimum levels, a COD reduction of 77.77, 79.41 and 87.03 % is achieved by 0.3 g/L of H_2O_2,1:3 ratio of Fe^{2+}: H_2O_2 and 3g/L of O_3 loading of AOPs. Further economic assessment is performed with break-even analysis study for financial estimation for incorporation of this technology.



(a) (b) (c)

Fig. (a) Process flow sheet of the Experimental Set-up (b) Effect of rotational speed on COD and TOC reduction (c) Effect of residence time on COD and TOC variation

Keywords: Tertiary wastewater treatment; Hydrodynamic cavitation; Conical rotor stator arrangement; AOPs; Micropollutant

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Synthesis of Crystalline Silico Titanate using anatase as the Titanium precursor

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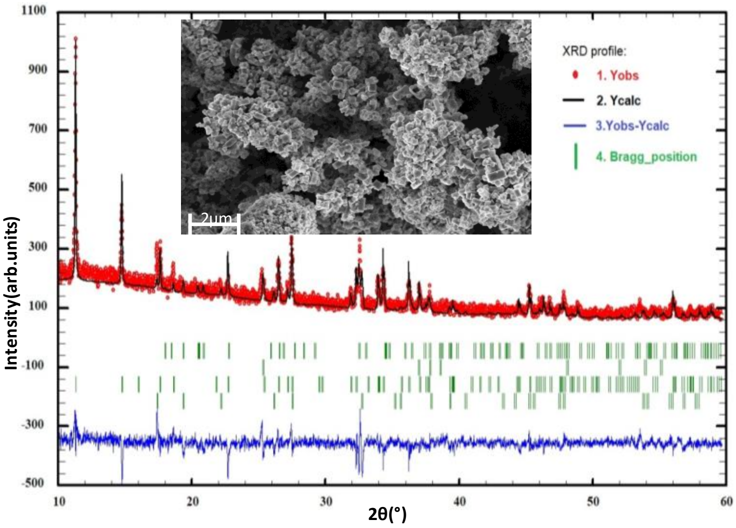
Crystalline silicotitanate (CST) is a well-known ion-exchanger with preferential affinity towards cesium and strontium. However, its wide usage is limited due to stringent synthesis procedures involve the use of unstable titanium precursors such as titanium tetrachloride or titanium isopropoxide[1]. In this report it is revealed that the desired phase can be obtained using easy to handle precursor anatase. The composition of active reagents used in the synthesis that yielded the highest CST phase composition (76%) was 6.875Na_2O: TiO_2: 1.98SiO_2: 13.6EtOH: 2HCl: 231H_2O however the presence other phases like natisite, paranatisite and residual anatase are noticed in the XRD (Fig.1) Ethanol was seen to have significant influence on the phase composition in the final product formed.[2] The SEM-EDX of the sample showed the presence of cubic morphology of CST. The phase composition of the cubic phase was found to contain Ti/Si~2:1. Treatment of the formed product with 1 M HCl and further with 1 M NaOH resulted in improved ion exchange property. The exchange capacity of the treated sample with respect to strontium was 2.46 meq/g.



Space group	**P4$_2$/mcm**
a	**7.8406(1)**
b	**7.8406(1)**
c	**12.0192(9)**
α = β = γ	**90.00000**
Rp	**26.3**
Rwp	**30.0**
Chi-Square	**2.78**

Fig(i) XRD and SEM image of the final product and Cell parameters of CST phase

Keywords: CST, Anatase, Sr exchange, CST synthesis, CST-Hydrothermal

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Adsorptive Removal of Crystal violet Dye from Aqueous solution using *Aegle marmelos* Fruit shell based Magnetic Composite

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The main cause of environmental pollution is rapid growth in population, urbanization, increased rate of industrial activities. The industries like textile, paper, paint, rubber, plastic, cosmetics and food industries directly discharge dye containing effluents in water body [1, 2]. The complex aromatic configuration in the structure [3] of dyes make them resistant to degradation. Thus, they are hazardous and stable. Among large number of cationic dyes, Crystal Violet (CV) is a triphenyl methane dye and is known to be carcinogenic and mutagenic. Excessive persistence of dye in body results in damage of kidney, respiratory disorders, eye irritation [4]. Hence, elimination of dye from waste waters is of prime importance. Among the various methods available for decontamination of dye, adsorption technique is most suitable due to its simplicity, low cost and efficacy [5].

The present work is focused on development of *Aegle marmelos* fruit shell based magnetic composite and its application for removal of CV dye from aqueous solution. The appropriate amount of fruit shell powder of *Aegle marmelos* was added in solutions of Fe(II) and Fe(III) which was prepared in the molar ratio of 1:2. Then addition of 5 M NaOH solution was continued to obtain black coloured precipitate. This was then stirred for 1 hour and separated by using simple disc magnet. The precipitate is made neutral by thorough washing with distilled water and finally dried and used as adsorbent for batch adsorption experiment of CV dye.

In batch adsorption study, 0.030 g of adsorbent was mixed with 10 mL of 100 mg L^{-1} CV dye solution taken in Erlenmeyer flask and agitated on orbital shaker for 90 min. After equilibrium Fe_3O_4 magnetic composite was separated by applying magnet and concentration of dye after adsorption was determined by using UV-visible spectrophotometer (Systronic 104, India) at 590 nm. The maximum adsorption capacity of prepared adsorbent was found to be 106.38 mg/g. The adsorption efficiency of prepared adsorbent was optimized by setting various experimental conditions like contact period, amount of adsorbent, initial dye concentration, temperature and agitation speed. The experimental data was used to understand various isotherms, thermodynamic parameters and kinetic models of adsorption technique. The study was also extended to characterize adsorbent with FTIR, SEM, BET, XRD, TGA analysis to know the adsorption process of CV dye.

In summary, the prepared *Aegle marmelos* fruit shell based magnetic composite was found as an excellent adsorbent for removal of CV dye from aqueous solution.

Keywords: Adsorption, Aegle marmelos, composite, Crystal violet dye, Kinetics, Isotherm

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MOF/COF hybrid material for photoelectrochemical degradation of textile wastewater

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The textile industry is a vital component of worldwide trade, producing a wide range of fabrics and materials used in everyday life. However, this industry is one of the major contributors to environmental contamination, primarily through polluted wastewater. Textile wastewater is a complex mixture containing colors, heavy metals, organic compounds, and suspended particulates, which poses substantial problems to environmental sustainability and public health. With the growing economy and population, the demand for fabrics has increased and so does the volume of wastewater discharged by the textile industry affecting the aquatic life, soil quality and human health. Recent developments in treatment technologies, such as advanced oxidation processes (AOPs), electrochemical methods, nanomaterial-based approaches, and hybrid systems, present promising alternatives for effectively removing refractory contaminants from textile wastewater. Photo electrocatalysis (PEC) is an electrochemical oxidation process that effectively removes organics from wastewater. Photo electrocatalysis is environmentally friendly, cost-effective, and simple to use.

We utilized a hybrid electrochemical advanced oxidation process (AOP) and photocatalysis system to eliminate Procion Brilliant Violet H-3R (PBV) from water in our study. To create a Fenton-like catalyst that can act as AOPs and aid in wastewater degradation, we synthesized a hybrid material of metal organic framework and covalent organic framework. We incorporated NH_2-MIL-101 (Fe) into covalent triazine framework (MOF/CTF) to create the catalyst, which we characterized based on its porosity, structure, crystallinity, and morphology. We also assessed its photoelectrochemical properties, which revealed that it absorbed energy in the visible range and had an energy band gap of 2.32 eV. In a quartz cylindrical beaker with a Teflon lid, we used the synthesized material as a photoanode and stainless steel as a cathode, connected to a DC power source, to perform photoelectrochemical degradation of PBV. About 83% degradation of 25 ppm and 70 ml of PBV solution at pH of 3.0 was observed, which was higher than photocatalysis or electrocatalysis alone, or with usage of only COF as working electrode through photoelectrocatalysis. The MOF@COF working electrode was illuminated with a 15 W white LED lamp with an applied voltage of 2 V between the working electrode and stainless-steel counter electrode. We optimized the degradation by varying the pH and voltage applied across the electrodes and studied the kinetics of the degradation. These findings demonstrate the efficacy of photo electrocatalysis for removing harmful textile dyes from water and highlight the importance of hybrid MOF@CTF electrodes as efficient and stable catalysts for photo(electro)catalysis.

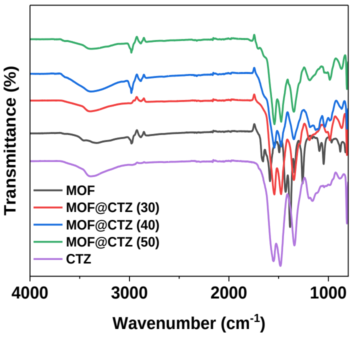

Figure 1: FTIR of MOF, MOF@COF and CTZ

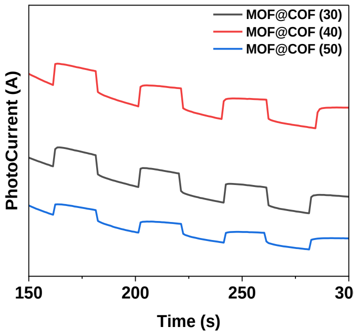

Figure 2: Photocurrent response of the catalyst

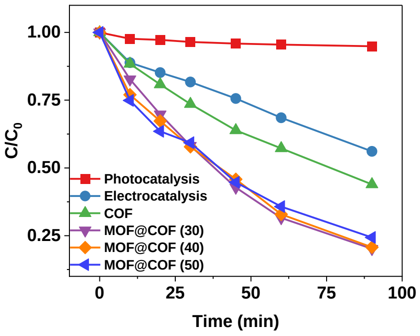

Figure 3: Performance of the material synthesized.

Keywords: Photoelectrocatalysis, Photoelectrochemical degradation, Textile wastewater, Photoanode

Biogenic, sustainable nano-ZVI@biochar for removal of Pb^{2+}: study of biorefinery of apple peel

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Large generation of apple peel wastes (to the tune of 17-20 million tonnes) especially from the food processing industries and the ensuing unscientific disposal methods has created environmental pollution, climate change and global warming [1]. Its biorefinery to value added adsorbents can help in alleviating the problem of waste management as well as can help in cost-effective sustainable separation of water based toxic pollutants. Its biochar was fabricated via pyrolysis at 500ºC with N$_2$ flow rate of 20ml/min. Keeping in view the wide acceptability of nano zero-valent iron (n-ZVI) as adsorbent, a green n-ZVI was fabricated using polysaccharide extract of mushroom. Hot water extraction was carried out at 60ºC for 3 hrs with subsequent centrifugation. Solubilization of concentrated supernatant in 80% ethanol followed by centrifugation resulted in water soluble polysaccharide extract. Dropwise addition of extract onto 0.1M FeCl$_2$ aqueous solution at 80ºC under continuous stirring for 80mins at pH of 10 resulted in the fabrication of black precipitate of n-ZVI. Composite of (n-ZVI@biochar) was fabricated by co-precipitation method. Fe-SEM studies revealed the heterogenous porous surface morphology and the nano dimension of its particles. Biogenic nature of the composite was evident from its carbonaceous nature from EDAX studies. FTIR studies revealed not only the successful incorporation of biochar and n-ZVI on the composite but also helped in the identification of suitable surface functionalities that helped in the binding mechanism. Pb^{2+} was selected as the model adsorbate mainly on account of its toxicity to the aquatic community and to humans [2]. Batch isotherm studies were carried out using 0.25 g/L of composite and 50 ml of Pb^{2+} solution with different initial concentration of 20-100 mg/L at neutral pH and at constant temperature of 25°C following by its shaking on an orbital shaker for fixed contact time of 60 mins. The set-up was repeated at temperatures of 35°C and 45°C. Similar set-ups were conducted for batch kinetic studies in which 0.25 g/L of composite and fixed Pb^{2+} concentration of 60 mg/L maintained at fixed pH of 7 and at fixed temperature of 25°C were contacted with varied contact time of 10 mins to 270 mins. Similar set-up was repeated for adsorbate concentration of 100 mg/L. The % removal of Pb^{2+} was recorded as 76 and 82 at adsorbate concentrations of 60 mg/L and 100 mg/L respectively at 90 mins of contact time and at a temperature of 45ºC. The sensitivity of the adsorption process was demonstrated from isotherm studies with highest adsorption demonstrated at higher temperatures. The maximum adsorption capacity determined was 370 mg/g at 25°C and increased to 667 mg/g at 45°C. The adsorption process was best fitted to the Langmuir isotherm model and the kinetics was best explained by Pseudo 1st order model. While the binding of Pb^{2+} was physisorption, its diffusion was both by particle and film.

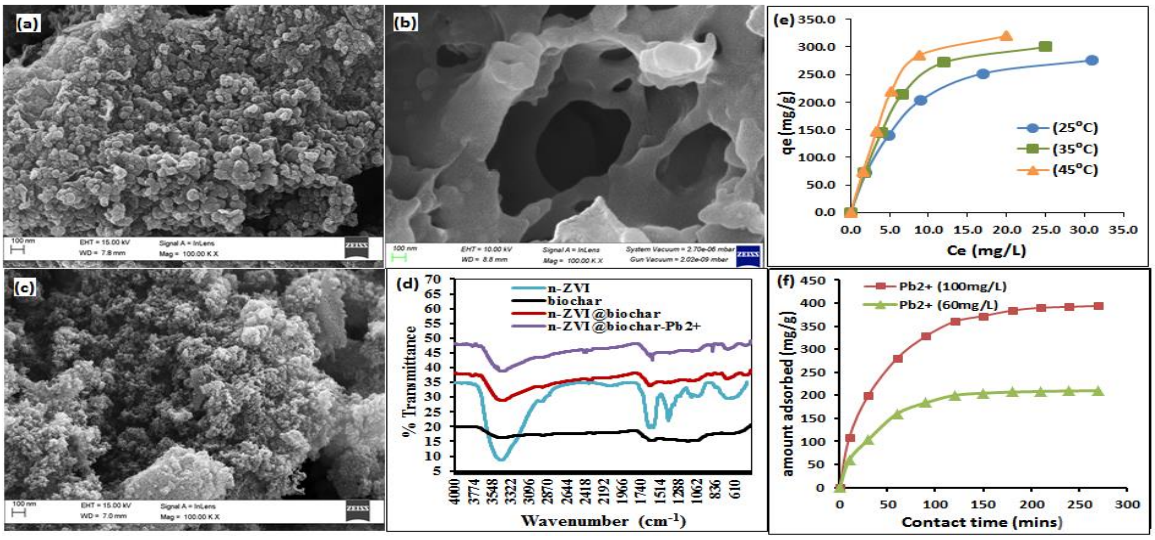

Fig 1 Fe-SEM of (a) n-ZVI (b) biochar (c) n-ZVI@biochar composite (d) FTIR spectra (e) isotherm studies (f) kinetic studies of Pb^{2+} onto composite

Keywords: apple peel, biochar, n-ZVI, adsorbent, Pb^{2+}

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Sorption of Eu and Zr in nano-hydroxyapatites

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Uranium is one of the special nuclear materials. It is also a well-known nephrotoxic element having a maximum permissible contamination level of only 30 ppb in drinking water. The treatment and recovery of uranium from lean streams during uranium ore processing and recovery of uranium from effluents of fabrication and reprocessing operations is quite challenging. Most of the techniques are expensive, need pre-treatment of the sample, large contact time, non-selective and have low sorption capacity. Hydroxyapatite (Hap) with chemical formula $Ca_{10}(PO_4)_6(OH)_2$ is a biocompatible mineral widely known as the main inorganic component of bones and teeth. Hap's unique structure and inherent properties have garnered significant interest across various fields, including biomaterials, biomedicine, optoelectronics and nuclear waste management.

The present study aims at investigating the potential of hydroxyapatites towards immobilization of radionuclides from the low level aqueous nuclear waste. In this regard, detailed characterization of the as-synthesized hydroxyapatites was carried out using electron microscopy, energy dispersive X-ray fluorescence (EDXRF) and X-ray diffraction (XRD). The sorption studies of Zr and Eu ions on hydroxyapatite were carried out in aqueous medium over a wide concentration range (10–1000 mg L^{-1}) in batch equilibration mode. For the present study, Zr was taken as a surrogate for uranium and plutonium while Eu was taken as a surrogate for the trivalent lanthanides and actinides due to their similar chemical properties. The effects of different physico-chemical parameters like pH (1-12 range), ionic strength etc on the uptake of Eu and Zr were studied. Solution ionic strength and temperature was found to have very little effect on the sorption at normal ambient conditions. The percentage uptake, decontamination factor, and distribution factors (K_d values) were found to be very high in the pH range (pH 2-12). Results show that hydroxyapatites are good sorbents and potential candidate for low level aqueous nuclear waste treatment.

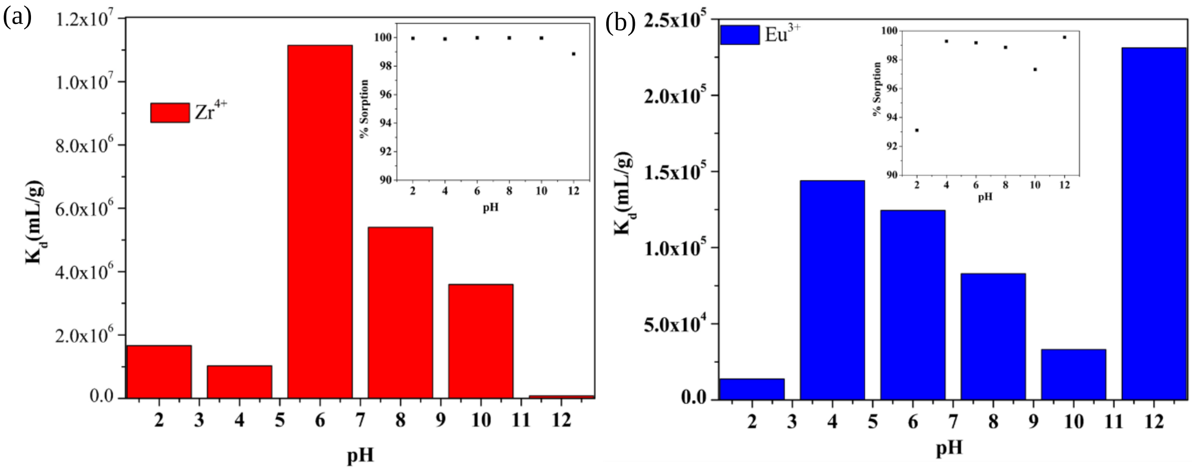

Fig. 1 Variation of Kd values as a function of pH for (a) Zr^{4+} ions and (b) Eu^{3+} ions

Keywords: Hydroxyapatites, Sorption, K_d Value, Nuclear Waste

Acknowledgements: Authors are thankful to Dr. G. Sugilal, Head, FRD and Dr. R. Tewari, AD, Materials Group for their keen interest and constant encouragement in this study.

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Wastewater remediation by pineapple waste

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Reactive azo-dye effluents generated from dyestuff industries and reported to exhibit obstruct light penetration and oxygen transfer into water thereby affecting aquatic life on aquatic organisms and humans. Hence, the objective of this study is to investigate the capability of pineapple waste garbage enzymes to degrade the Reactive azo dye using the pineapple waste enzymes. The effluent contained 0.08 g/L of TDS (90 % of which is NaCl and 8-9 % is Na_2SO_4 along with dyes and amines), neutral pH. The results indicate that enzymes from pineapple waste garbage successfully decolorized the dye, whereas enzymes from the edible part of the pineapple did not have the same effect. This work proposed that pineapple waste garbage enzymes can effectively remove Reactive azo dye in wastewater applications. The decolorization of reactive azo dyes presents a significant challenge due to their complex chemical structures and recalcitrant nature. In this study, we investigated the potential of pineapple waste as a cost-effective and eco-friendly alternative for the decolorization of Reactive azo dyes. Pineapple waste, a readily available agricultural by-product, was utilized as a source of enzymes and bioactive compounds capable of degrading azo dyes. Our results demonstrate that pineapple waste exhibits remarkable decolorization efficiency, achieving decolorization of reactive azo dye within 48 hours under ambient conditions and the absence of light. Overall, this study highlights the potential of utilizing pineapple waste as a sustainable and efficient solution for the treatment of wastewater contaminated with reactive azo dyes, offering promising prospects for eco-friendly dye remediation technologies. In this study, it was also observed that small particles of the waste pineapple peel which were smaller than the filter pores adsorbed the red azo dyes. The initial and final absorbance was measured using a UV spectrophotometer. Decolorization ranging from 80% to 87% was observed by varying the dilution parameters of wastewater from 0.005-0.01g/L and days. When the concentration of the pineapple enzyme was changed from 0.9-0.9285g/liter, a decolorization of 33% to 47% was observed. A wide range of decolorization percentages(3-54%) was obtained by varying the wastewater concentration from 0.005-0.1785g/liter

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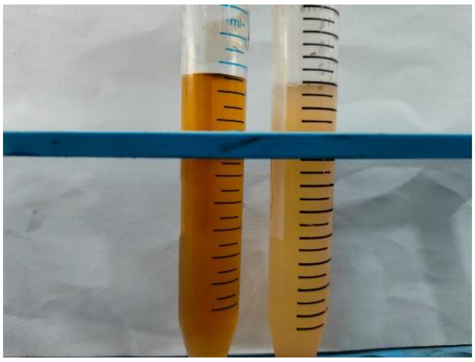

Figure1. The left sample illustrates its native coloration before decolorization

Fertilizer Grade Ammonium Sulphate from the Acidic Byproduct Stream of Methyl Methacrylate and Methacrylic Acid Plants

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Methyl methacrylate (MMA) is an important raw material for the production of acrylic sheets, acrylic powder, and paints (1-3). Methacrylic acid (MAA) is the intermediate for the production of MMA. During the production of MAA and MMA by cynohydrin process, huge quantities of acidic byproducts are generated. The byproduct stream consists of water, free Sulphuric acid, Ammonium Bisulphate, Ammonium Sulphate and organic impurities. The waste stream cannot be discharged to water bodies due to its high acidity (with a pH of less than zero) and high salt content. However, it can be a potential source of fertilizer namely Ammonium Sulphate.

The waste stream was neutralized with Ammonia to produce organic contaminated Ammonium Sulphate and it is not suitable for fertilizer application. In order to find a commercially viable solution for the preparation of fertilizer grade Ammonium Sulphate, several methods were adopted such as solvent extraction, adsorption and recrystallization. Solvent extraction method was least preferable owing to the lower solubility of the organic impurities in solvent. Different grades of activated carbons were used to adsorb the organic impurities and it was found that powder grade activated carbons were more effective in producing fertilizer grade Ammonium Sulphate. However, handling of powder activated carbon and their disposal were two challenges encountered during this study. Hence, a more viable solution was found by making a saturated solution of Ammonium Sulphate and skimming the top organic layer followed by recrystallization to produce fertilizer grade Ammonium Sulphate with minimum Ammonical Nnitrogen 20.6 wt%, maximum free Sulphuric acid 0.04 wt% and minimum Sulphur 23 wt%.

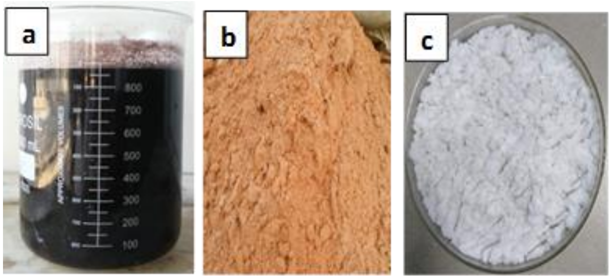

Figure 1: (a) Waste stream from MMA and MAA plant (b) Organic contaminated Ammonium Sulphate (c) Fertilizer grade Ammonium sulphate

Keywords: Methyl methacrylate, Methacrylic acid, Waste water, Fertilizer, Ammonium sulphate

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Effect of cross-linking method on the poly(vinyl alcohol)-poly(ethylene imine) anion exchange membrane

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The green hydrogen, produced using solar energy is the long term viable option to store the solar energy for use during the night. The hydrogen thus produced can be used directly into Internal Combustion (IC) engine, fuel cells for transport or stationary power generation purposes. In contrast to cation exchange membranes, anion exchange membranes based electrolyser use cheap electrode material like Ni, Co etc. They can offer high purity hydrogen at high pressure. However, the anion exchange membranes, face a challenge of stability, due the quaternary ammonium groups which are inherently unstable thus limiting the lifetime of these membranes at high temperatures. Therefore, development of stable, robust anion exchange membrane is highly warranted. Recently, Poly(vinyl alcohol) (PVA) and Poly(ethylene imine) (PEI) anion exchange membranes are reported to give good thermo-mechanical stability & conductivity[1]. However, authors have not optimized the crosslinking methods. In the present researchwork, anion exchange membranes are synthesized using PVA:PEI varying ratios (1:0.25 to 1:1.5), and both the polymers are cross-linked using gluteraldehyde by three different methods, i.e., acid treated, heat treated, and without treatment followed by quaternization. It is found that the polymer with PVA:PEI of 1:1 ratio having 12% gluteraldehyde gave higher conductivity and also found that conductivity was dependent on the method of treatment, and that followed the order of the conductivity conductivity$S_{untreated}$>$S_{acidtreated}$>$S_{heat\ treated}$.

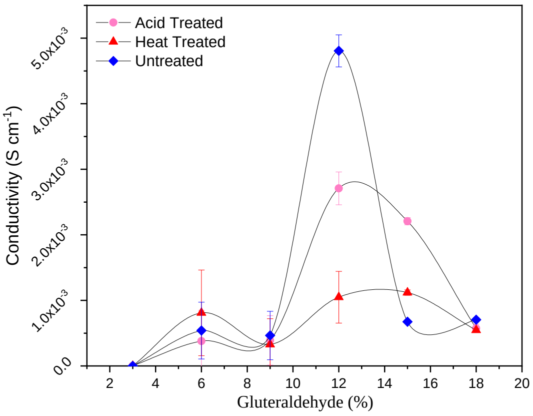

Figure 1: Comparison of PVA:PEI (1:1) membrane conductivity with varying gluteraldehyde %, effect of pre-treatment method

Keywords: *Anion exchange membrane, polymer electrolyte, polyvinyl alcohol*

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DAE-BRNS SESTEC-2024
July 10-13, 2024
F-02

Radiation assisted fabrication and characterization of functional adsorbent for potential application in iodine capture

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Iodine capture is highly relevant in the context of nuclear waste management as well as environmental protection. The primary concern associated with iodine pollutants is owing to their potential to harm human health. Radioactive isotopes of iodine (e.g. iodine-131), in particular, pose significant risks. Their sources include nuclear reactors and medical wastes. Due to their tendency to accumulate in the thyroid gland, their exposure to humans leads to an increased risk of thyroid cancer and other thyroid-related diseases. Moreover, iodine compounds tend to accumulate in soil and water bodies, eventually affecting the flora and fauna. Therefore, efficient capture and management of iodine is very important [1]. Additionally, it is also desirable to come up with the remediation strategy that do not generate secondary pollution in some other form. Pyrrolidone is considered an efficient functionality for capturing and storing iodine [2]. Therefore, a functionalized adsorbent was fabricated by gamma radiation assisted mutual irradiation grafting of N-vinylpyrrolidone (NVP) onto cellulose. Different substrates including nonwoven cellulose, woven cellulose, PP, and PE were studied for grafting of NVP to determine the most promising substrate for functionalization. Woven cellulose substrate provided the best results and was selected as the substrate. The grafting process was optimized by studying the effect of several different process parameters including absorbed dose, monomer concentration, type of solvent, and solvent composition (Fig. 1) on the grafting yield (G.Y.). However, even under optimized conditions, the maximum G.Y. of only ~18 % could be achieved using the conventional single step grafting. To overcome this limitation, an efficient process of multistep mutual irradiation grafting was employed that provides higher G.Y. for the same total absorbed dose compared to the conventional single step grafting, by introducing the sample to fresh grafting solution in each cycle. The grafted samples were characterized via C-13 NMR, FTIR, TGA (Fig. 2), SEM, etc. The appearance of carbonyl peak of NVP monomer at 1650 cm^{-1} in the FTIR spectra of the functionalized samples confirmed the functionalization of cellulose substrate with NVP (Fig. 3). Iodine capture experiments with the functionalized adsorbent were conducted in batch mode at ~75° C and the adsorption capacity was determined gravimetrically. The adsorption capacity was found to increase with increase in the G.Y. of the adsorbent. An adsorption capacity of ~300 mg/g could be achieved for the NVP functionalized cellulose with G.Y. of ~44 %.

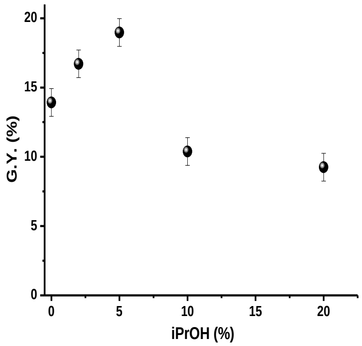

Fig.1: Variation of G.Y. with % iPrOH

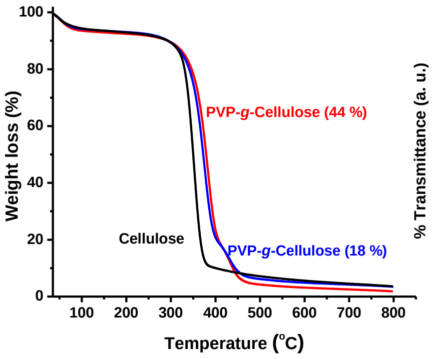

Fig.2: TGA Thermograms

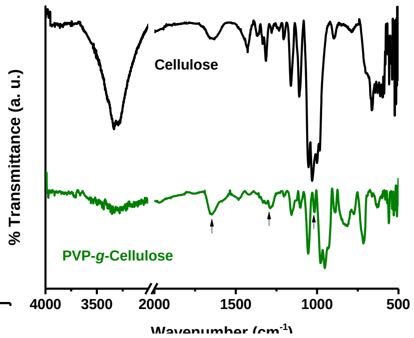

Fig.3: FTIR Spectra

Keywords: Radiation grafting, Iodine capture, N-vinylpyrrolidone

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Segregation of factors leading to temperature dependent ion transport in bi-ionic systems

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It is reported that the diffusion coefficients (D_i) of multivalent ions (Ba^{2+} / Eu^{3+}) in cation-exchange membranes (CEM) are affected significantly by the presence of monovalent ions (H^+ / Na^+).[1] In order to segregate the factors responsible for this behavior, herein, we have investigated the temperature-dependent (10-60 °C, radiotracer based method) variations in the D_i of Ba^{2+} and Eu^{3+} within CEM, particularly in the presence of hydrated monovalent ions (X^+: H^+ or Na^+). Notable differences were observed in diffusion coefficients between Ba^{2+} and Eu^{3+} ions, as well as within Ba^{2+} -X^+ and Eu^{3+} -X^+ systems, suggesting a complex interplay between ion valence, membrane composition, temperature, tortuosity, and electrostatic interactions. Based on the results, an equation, inclusive of the distinct effects of the tortuosity factor (τ) and electrostatic interaction parameter (φ) on the ionic diffusion is proposed (eq. 1) and subsequently validated.

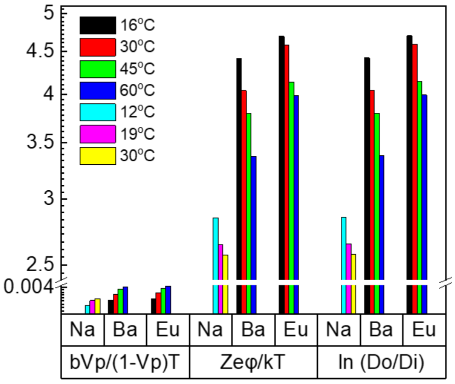

Figure 1. Segregation of parameters, tortuosity (bVp/(1-Vp)T) and electrostatic interaction (zeϕ/kT). The y axis is in contributing to D_i. 'b' is a fitting parameter.

$$D_i = D_0 \times e^{-\frac{\tau}{T}} \times e^{-\frac{ze\phi}{KT}} \qquad (1)$$

Results indicated that the D_{Ba} in the Ba^{2+} and Ba^{2+} -X^+ systems, as well as D_{Eu} in the Eu^{3+} and Eu^{3+} -X^+ systems, varied with the ionic composition of the membrane and temperature. Significant increase in D_{Ba} and D_{Eu} with rising temperatures were observed across all systems due to increase in the thermal energy (kT) of the ions. D_{Ba} and D_{Eu} in the Ba^{2+} -X^+ and Eu^{3+} -X^+ systems were lower than in the pure Ba^{2+} and Eu^{3+} systems. This varied temperature-dependent behavior in single and bi-ionic forms can be explained as a function of τ and φ. The inclusion of the term containing 'τ' in eq. 1 was based on the linear increase of the polymer volume fraction (V_p) with increase in temperature for the single-ion systems. This temperature-induced expansion of the polymer phase likely originates from alterations in its superficial structure, thus altering the τ and consequently impacting ionic diffusion. Increased polymer content (for Ba and Eu), which translates to a reduced water volume fraction, creates a more tortuous (than Na and H) pathway for ions, hindering their movement. This explains the lower D_{Ba} and D_{Eu} values compared to D_{Na} and D_H. Notably, despite having higher water content, the bi-ionic systems (Ba^{2+}-Na^+, Ba^{2+}-H^+, Eu^{3+}-Na^+, and Eu^{3+}-H^+) exhibit lower D_{Ba} and D_{Eu} values compared to their single-ion counterparts. This unexpected behavior in the bi-ionic systems can be attributed to the stronger coulombic interaction between the multivalent ions and the functional groups within the polymer. This study introduces the charge-standardized effective interaction potential (zφ), derived from eq 1, to quantify the extent of electrostatic interactions between the membrane and the ions. Results indicated variations in zφ for Eu^{3+} and Ba^{2+} ions as a function of temperature and ionic composition. Notably, zφ(Ba) exhibits significantly higher values (0.106 V and 0.148 V) compared to previous reports (0.038 V and 0.066 V) for single ion and Ba^{2+}-Na^+ systems respectively, highlighting the stronger account of interaction between Ba^{2+} ions and the membrane in our systems. The temperature dependence of zφ (Eu) was less prominent than that of the decrease in zφ (Ba). This can be attributed to the interplay between two key factors: the long-range electrostatic interactions within the membrane and the increased thermal energy of ions. A comparison of the tortuosity parameter and the electrostatic effect on D_i, reveals a substantially greater impact from the electrostatic interactions, especially for the multivalent ions. This is represented in the Figure 1, where the parameters contributing to D_i in case of the single ions systems are segregated. This enhanced understanding of ion diffusion has profound implications for various applications such as ion exchange processes, membrane separations, and the design of electrochemical devices.

Keywords: interaction potential, temperature dependence, Nafion, Multicomponent transport

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Molecular layer deposition on ion-exchangeable polymer films for selective ion separation

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Membrane-based selective ion transport plays a critical role in the water-energy nexus, and various fabrication techniques are under consideration to achieve this goal. Among these techniques, the generation of metal-based organic-inorganic thin films, often referred to as "metalcones" films, using molecular layer deposition (MLD), offers promising prospects for developing suitable selective layers.[1-2] These thin films enable steric and electrostatic sieving of ions, facilitated by the material's tuneable porosity and surface charge, which varies as a function of the precursor functionality and subsequent post-synthetic modification. In this context, hybrid organic-inorganic (Ethylene Glycol-Al) thin film was deposited via MLD to create an active layer aimed at converting an ion exchange membrane into an ion-selective membrane. Specifically, EG-Alucone (thickness ranging from 10 to 30 nm) was deposited onto commercial Nafion 117 membrane within the range of 5 to 100 MLD cycles, following optimization of process parameters using quartz crystal microbalance (QCM) and X-ray reflectometry (XRR) measurements at 75°C. Radiotracer based transport and electrochemical impedance spectroscopy (EIS) analysis was carried out with the as synthesized membrane (tagged as 'A' in Figure 1) as well their corresponding 'water etched' (or hydrated, tagged as 'H' in Figure 1) versions. As seen from Figure 1, the hydrated EG-Alucone system at 70 cycles showed a 2.5x improvement in Cs^+/Na^+ selectivity and a 1.5x improvement in Cs^+/Ba^{2+} selectivity compared to the pristine Nafion membrane. 70 MLD cycles is thus found to produce the optimum active layer thickness leading to superior selectivity compared to 50 and 100 MLD cycles. Furthermore, membrane stability was validated through three-stage separation studies, wherein the separation factor remained consistent. Notably, FEG-SEM results indicated that the EG-Alucone is partially converted to Alumina during hydration post-MLD (Figure 2.b) which improves the porosity and smoothens the MLD layer. The contact angle measurement of water on the active layer showed increasing hydrophilicity with increase in thickness of the MLD film in case of as-synthesized membranes, while the hydrophilicity reduced post-hydration irrespective of the initial film thickness. Cross-sectional SEM of the membranes revealed diffusion of MLD precursors into the Nafion substrate and XPS studies confirmed formation of an Al-F bond during the deposition process. These aspects are being further examined in detail using theoretical as well as other characterization tools. Overall, these findings highlight the potential of MLD-deposited EG-Alucone thin films for enhancing ion selectivity in membrane-based applications, with implications for various fields, including water treatment and energy conversion.

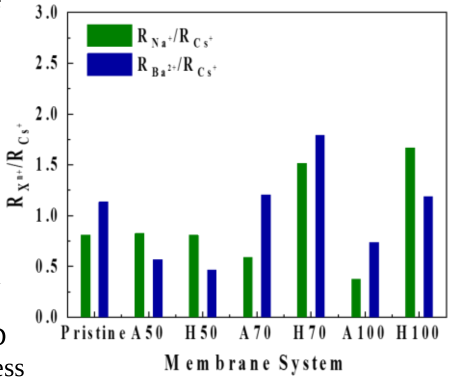

Fig 1. Transport selectivity as a function of cycle number

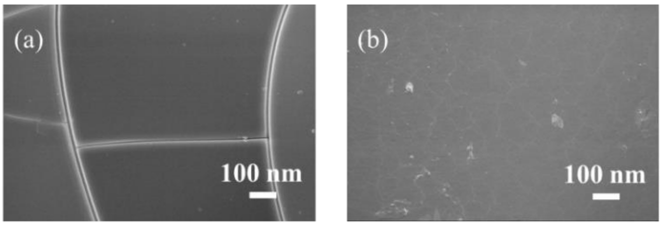

Fig 2. FEG-SEM of as-synthesized and hydrated membrane at 70 cycles

Keywords: Transport selectivity, ion selective membrane, Molecular layer deposition

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DAE-BRNS SESTEC-2024
July 10-13, 2024
F-05

Preparation of Polypropylene membrane via Thermally Induced Phase Separation process and their application as Supported Liquid Membrane for Recovery of Uranium

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In recent years, membranes have gain wide acceptance in various non-aqueous (organic & aqueous-organic) applications along with their regular use in aqueous based separation. Supported liquid membrane (SLM) based solvent extraction is one such application where highly hydrophobic materials with inertness towards organic solvent is required for its successful use. Among others, polypropylene (PP) & polyethylene (PE) polymers have tremendous potential for preparation of such membranes which offer good thermal stability and chemical resistance [1]. PP offers advantages over PE such as more resistant to high temperatures, abrasive agents and chemical solvents. The preparation of PP membranes via nonsolvent-induced phase separation (NIPS) method is difficult owing to its immiscibility in a suitable organic solvent to get viscous casting solution for membrane preparation. Hence, dry stretch and thermally induced phase separation (TIPS) are employed for preparation of PP membrane wherein TIPS offers controlled phase separation [2] for optimization of the preparation condition to achieve required pore size. In the present study, PP membranes were prepared via TIPS method, wherein PP in bead form is melted along with diluents namely myristic acid (MA) and diphenyl carbonate (DPCm) in different composition (PP: 20-30%, MA:DPCm = 3/2 to 2/3). The casting was done on polyester fabric (~100μm thick) with melt dope casting at various temperatures between 150 to 200^{o}C with optimized temperature of 158^{o}C. After optimization of casting parameters in laboratory set up (Fig.1), continuous sheet membranes were prepared in custom-made pilot scale melt casting unit (Fig. 2). The membranes were characterized with respect to pure water flux, water contact angle and surface images. The water contact angle obtained was in the range 122^{o} – 132^{o} (Fig. 3.b). SEM images of a representative membrane is shown in Fig.3.b, wherein pores in the size of ~2-9 μm can be observed. The membranes were further used to demonstrate recovery of Uranium from uranyl nitrate raffinate (obtained from UED, BARC) using 30% Tributyl Phosphate in dodecane as extractant and 1M sodium bicarobonate as stripping solution. The Uranium recovery achieved was ~60% in four hours.

Fig.1 Lab. Setup for preparation of PP flat sheet membrane &
PP membrane

Fig.2 Pilot Scale continuous PP flat sheet membrane preparation machine

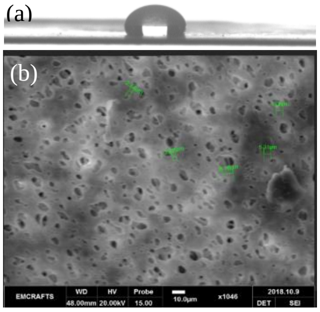

Fig.(3a) Water contact angle (~125^{o}) and (3b) SEM image of PP flat sheet membrane

Keywords: Polypropylene, Thermally Induced Phase Separation, Supported Liquid Membrane, Uranium

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Ultrafiltration membrane preparation from Polyvinyl chloride polymer waste and its application for Oil-in-water separation

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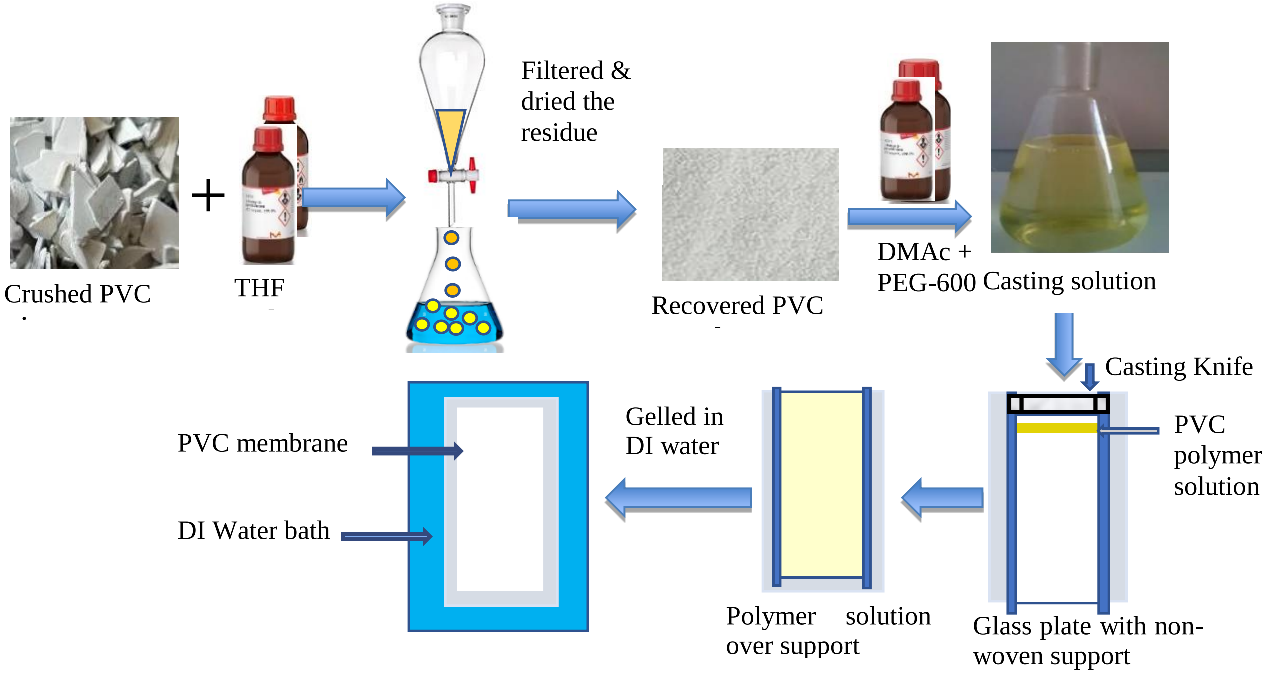
Plastic solid waste (PSW) disposal is a burning issue worldwide as it results serious environmental problems. The 'recycling and reuse' in an environmental friendly way is considered as the best PSW management route than their disposal through incineration and burying the waste. PSW having specific properties like film-forming ability, lower cost and easy processibility can be reuse by manufacturing of filtration membranes. Polyethylene terephthalate (PET), polyvinyl chloride (PVC), polystyrene (PS), polycarbonate (PC) etc. are some of the PSWs that can be used to fabricate useful membranes for filtration applications [1]. Among others, PVC is one of the polymers having several advantages such as low cost, robust mechanical strength, resistant to chemicals like many alcohols, fats, oils, common corroding agents including inorganic acids, alkalis and salts. In the present study, PVC was recovered from the waste PVC and ultrafiltration membranes were prepared. The used PVC waste were dissolved first in Tetrahydrofuran (THF) and the undissolved portions were filtered. Then the dissolved PVC solution was precipitate in water and recovered the PVC for membrane making. Casting solution of PVC were prepared in N, N-dimethylacetamide (DMAc) solvent with polyethylene glycol (average MW 600Da (PEG-600) as pore former [2] & membranes (size: 30×21cm) were casted over the glass plate. Prepared membranes were characterized in terms of pure water permeability, separation of single uncharged solutes like polyethylene oxide (PEO) and water contact angle. Membranes were tested using synthetic oily waste water (1000 ppm oil-water emulsion) as feed at 2-3 bar pressure. By optimization of casting solution composition and casting parameters, ultrafiltration membranes capable of giving 50 L.m^{-2}.h^{-1} flux with >98% oil removal efficiency have been achieved.



Scheme of membrane preparation starting from PVC polymer waste

Keywords: Polyvinyl chloride, Polymer waste, Membrane, Ultrafiltration, Oil-water separation

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Development of Composite Pd-Cu Membrane for Enhanced Production &Recovery of Hydrogen from Coal Gasifier

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In a coal gasifier, coal is partially oxidized with steam and O_2 to produce syngas, mainly consisting of H_2 and CO. This CO is converted to CO_2 in a water gas shift reactor producing H_2, which is equilibrium limited. To circumvent this limitation, metal membrane is a potential candidate that would cause*in situ* separation and recovery of H_2 from coal gasifier, in addition to the enhancement of equilibrium conversion. Mostly, Pd-based membranes on ceramic supports have been utilized for H_2 recovery [1]. However, ceramic support is unable to withstand high-pressure conditions (typically 20 to 40 bar).Moreover,Pd is not compatible with the coal gasifier environment (owing to presence of sulphur). This work focuses on the development of Pd-Cu membrane on SS-316 porous support using DC Magnetron sputtering, for high pressure applications. The morphology of SS-316 support was characterized using optical microscopy (Fig. 1). To avoid intermetallic diffusion between the top metal membrane layer and SS support, a coating of SiO_2 (both acid and base-catalyzed) as an intermediate layer was provided on SS support by sol-gel method. The slurry was characterized for viscosity and thermal stabilityusing a rheometer (Anton Paar) and thermal gravimetric analysis (SETARAM), respectively. The optimum set of coating parameters: dipping and withdrawal speed: 0.5-1 mm/s, time for coating: 60s, temperature of coating: RT, sintering temperature: 180°C, heating time: 5 hrs. The SS-SiO_2 composite support was used to coat Pd-Cu membrane using magnetron sputtering technique under the optimized set of parameters: power: 200 W, base vacuum: 5×10^{-6}torr, vacuum during coating: 1×10^{-2} Torr, temperature: 500°C. Gas permeation studies of SS, SS-SiO_2 composite support was carried out (Fig. 2). Flux and selectivity (H_2/N_2) of support were found to be 4.73×10^{-3} m^3/m^2.s and 2.07, respectively. Flux and selectivity (H_2/N_2) of composite (SS-SiO_2) support were found to be 6.03×10^{-3} m^3/m^2.s and 6.80, respectively. The dense nature of sputter-coated metal membrane was ensured by helium permeation studies, which was found to be impermeable to helium at RT. The permeability of hydrogen was determined to be. The application studies of in-house developed metal membrane for production & recovery of hydrogen from coal gasifier is taken up.

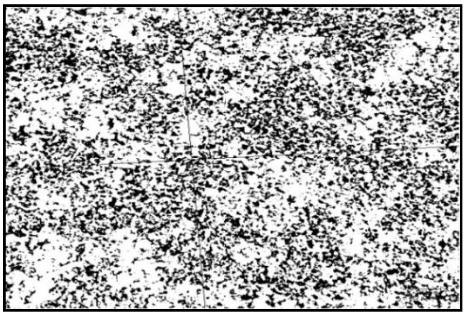

Fig 1: Optical image of composite support.

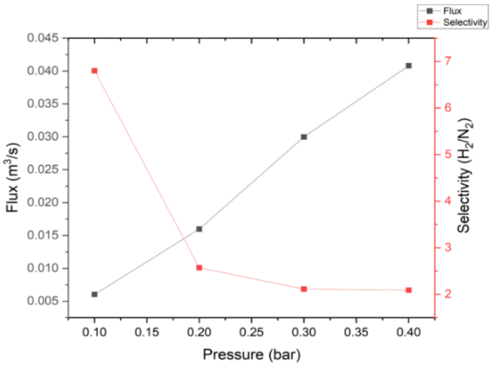

Fig 2: Gas permeation studies of composite support.

Keywords: Metal membrane, hydrogen, Coal gasifier, Sol-gel technique

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CFD Studies on Hydrogen Recovery from High-Temperature Steam Electrolysis Process Using Pd-Cu Alloy Membrane

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High-temperature steam electrolysis is pursued as an efficient route of hydrogen production at a high temperature of ~800°C. However, complete water splitting does not take place leading to the formation of a hydrogen-steam mixture, which can be separated using the condensation of steam. This causes a huge thermal load on the entire process. In this scenario, dense metallic membranes are potential candidate materials for hydrogen separation and recovery from this hydrogen-steam mixture [1]. In this work, a CFD model has been developed to study the separation of hydrogen-steam mixture using a Pd-Cu alloy membrane (developed in-house), utilising equations for momentum, energy and species transport. Using literature data [2], the model was validated and was used to predict the performance of the membrane for hydrogen-steam separation. The effect of various operating parameters [feed velocity & temperature (Fig. 1), pressure (Fig.2)] and geometrical parameters [length (Fig. 3) and diameter (Fig. 4)] on the recovery of hydrogen were studied. It was observed that decreasing the feed velocity and annular diameter lead to higher recovery, while an increase in length and temperature would increase the hydrogen recovery. Interestingly, pressure is not seen to have any considerable effect on hydrogen recovery. The optimum set of parameters for ~80% hydrogen recovery was found to be: wall temperature ~ 1073K, outlet pressure ~ 2 bar, inlet velocity ~ 0.0003m/s, length ~ 38cm and diameter ~ 8cm.

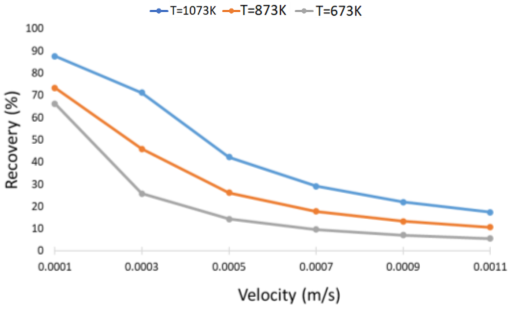

Fig. 1: Effect of velocity on recovery of H_2at different temperatures
[Pressure: 2 bar, Length: 33 cm, Diameter: 8 cm]

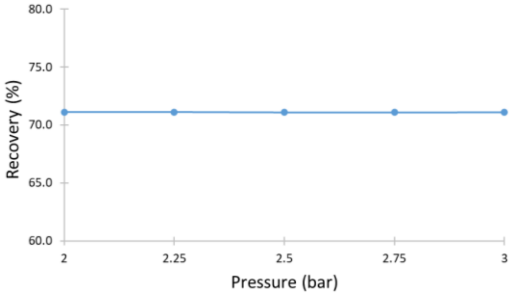

Fig. 2: Effect of pressure on recovery of H_2
[Length: 33 cm, Diameter: 8 cm, Velocity: 0.0003 m/s, Temperature: 1073K]

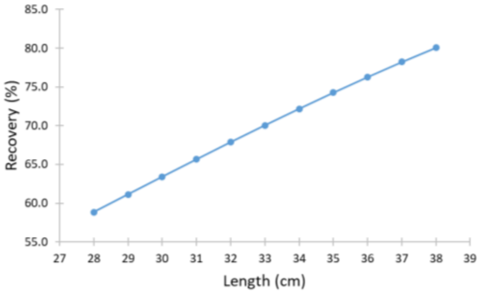

Fig. 3: Effect of length on recovery of H_2
[Pressure: 2 bar, Temperature: 1073K, Diameter: 8 cm, Velocity: 0.0003 m/s]

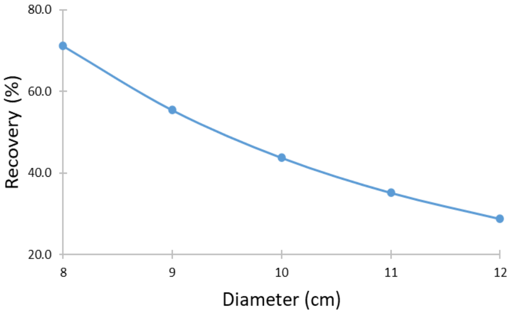

Fig. 4: Effect of diameter on recovery of H_2
[Pressure: 2 bar, Length: 33 cm, Velocity: 0.0003 m/s, Temperature: 1073K]

Keywords: Green hydrogen, Metallic membranes, Palladium-alloys, HTSE

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Development of a Radiometric Nanosensor for Trace Assay of Actinides in Aqueous Samples

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Detection and assay of actinides in environment is crucial to monitor environmental contamination caused by accidental release of actinides and to recognize residual nuclear footprints as a mark of illicit trafficking of nuclear materials. Sensors thus became an indispensable tool in the field of nuclear security, nuclear forensics, nonproliferation, and environmental monitoring. Although, the detection and assay of actinides is principally an analytical focus, separation science and technologies can offer numerous ways to improve the limit of detection by deploying advanced materials for selective sequestration or separation of actinides from dilute aqueous samples. Sequestration without selectivity is the prerequisite for nuclear forensic analysis in order to preserve the information of elemental ratio in a given sample, which could be a potential forensic fingerprint to trace the possible origin from which the sample is derived. Thus, development of sensors for gross alpha activity measurement with elemental and isotopic analysis is of paramount importance. Nanoparticle-based sensors, often called nanosensors, have emerged as potential sensors in recent years for sensitive detection and assay of actinides at ultratrace level, while utilizing the fascinating physico-chemical properties of nanoparticles. Nanomaterials also exhibit significant ability for efficiently sequestering actinides from dilute solutions and detecting them at low level [1]. In our previous work, optically transparent and water dispersible inorganic aluminosilicate nanotubes (imogolite NTs) were demonstrated for one step sequestration and assay of uranium ions from dilute aqueous solution at ultratrace level using its novel self-scintillating properties in contact with microporous polyethersulphone (PES) membrane [2]. In this work, the same has been extended further for low level detection of plutonium from dilute aqueous solution. The imogolite nanotubes with hydrophobic internal core and hydrophilic external surface were synthesized by hydrothermal route and used in the present study. The nanotubes efficiently capture actinide ions from aqueous solutions at alkaline condition (pH = 8), which was then filtered through a microporous polyethersulphone (PES) membrane, resulting in the formation of a pre-concentrated ultrathin transparent film of imogolite backed on PES surface. The imogolite-PES films after drying at room temperature was subjected to scintillation photon counting at dark using photomultiplier tube. In addition, the films were also tested as sample platform for alpha spectrometry in vacuum. The recorded pulse height spectrum in the scintillation counting shows a well resolved peak at higher pulse height due to the alpha particle scintillation compared to the background. Also, the alpha spectrometry of the substrate gives characteristic well resolved peaks of actinides present in the sample, with minimum alpha particle energy degradation in the substrate (see Fig. 1). The resolution of the alpha spectrum could be further improved by reducing the imogolite film thickness. Plutonium sample with lowest activity upto 200 mBq/mL (~87 ppt) was studied. The efficiency of the nanotubes for sequestration of actinides has been found to be close to 100% with negligible selectivity between actinide elements, which makes the present nanosensor suitable for quantification of total alpha activity with elemental composition in an aqueous sample at trace level. The potential of imogolite nanotubes for rapid actinide sequestration from dilute aqueous solution followed by radiometric assay shows strong promises for “in-field” environmental monitoring and nuclear forensic applications.

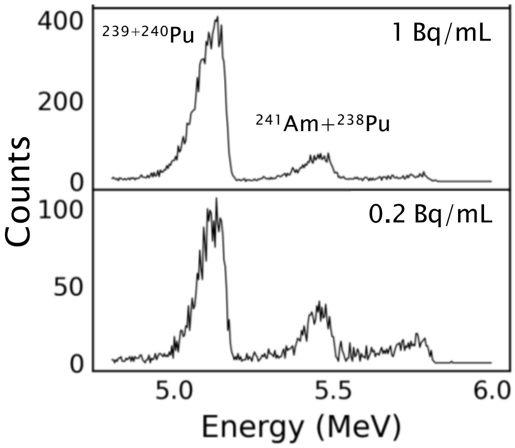

Fig. 1. Alpha spectra of the actinides captured in PES-Imo thin films. Pu concentration 1 Bq/mL (a) and 0.2 Bq/mL (b).

Keywords: Actinide, Nanosensor, Scintillator, Alpha spectrometry, Imogolite

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Reverse Osmosis Membrane Technology for Industrial Wastewater Treatment

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The wastewater from the industry has become a growing concern due to its toxic environmental impacts and hazardous nature of threat to the surrounding environment. Remediation of wastewater is most important goal in saving the environment from toxic pollutants as well as reusing of produced water for various cleaning and gardening purposes [1]. The Reverse Osmosis advanced membranes plays a crucial role in treatment of various Industrial wastewater and emerged as a promising alternative for wastewater reclamation [2] by fulfilling an alternative energy efficient sustainable solution [3]. This research paper investigates the experimental performance of Reverse Osmosis (RO) system feasibility in treating the effluents of Industrial zone in Tuticorin for water reuse. For our study the Polyamide membrane of Reverse Osmosis system was examined with effluents sample in aqueous solution form the chemical Industries at Tuticorin, Southern India. The various operating parameters effects such as transmembrane pressure, cross flow velocity and temperature on membrane performance with respect to water flux and COD (Chemical Oxygen Demand) rejection were studied. It is important to note that COD removal (Fig.1) was increased from 60 to 100% as temperature increased from 20℃ to 43℃ for the transmembrane pressure of 20 bar and cross flow velocity of 1.7 m/s; this elucidates the deposition of macromolecules from Total Dissolved Solids (TDS) is deposited on the membrane surface and triggers the hydraulic resistance by decreasing the flux but when the temperature is increased the permeate flux is also increased due to its diffusivity phenomenon. The high rejection of COD is due to the increase in solvent flux and stable nature of solute flux at the time of filtration. The scope of the current research work is to introduce the RO membrane technology (currently being used in Municipal Wastewater Treatment plants and Desalination plants) for filtering the effluents in Chemical Industry to overcome the limitations of current existing treatment in terms of energy efficiency and sustainability to filter the effluents compatible with the regulatory limits of state and national pollution control boards.

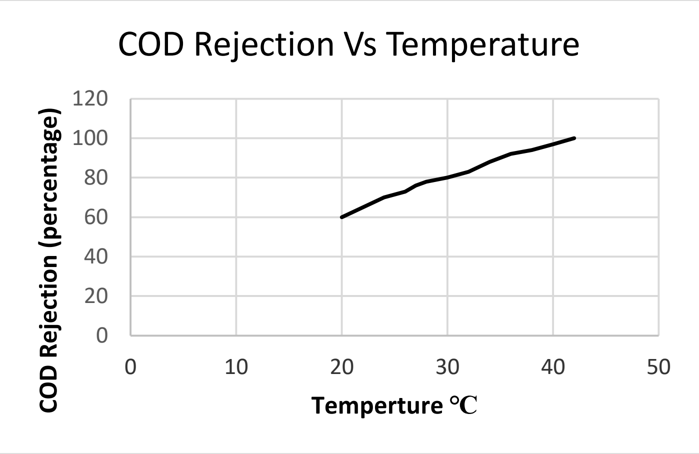

Fig.1: COD Rejection Rate vs Temperature

Keywords: Environment, Membrane technology, Reverse Osmosis, Industry, Wastewater, COD

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Transport studies of Np(IV) using three different bezene centered tripodal diglycolamide ligands

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The public acceptance of future nuclear energy programme largely depends on the management of long lived minor actinides (Np, Am, Cm) present in the high level waste (HLW). The currently acceptable strategy is partitioning of these minor actinides followed by transmutation in fast reactor or accelerated driven sub critical (ADSS) system. The recovery of Np from HLW will not only help to avoid long term surveillance of the vitrified waste in the deep geological repository but also it is considered as a wealth from waste as it is the precursor of ^{238}Pu. Diglycolamide (DGA) based extractant, particularly multiple DGA based extractant are known as promissing extractant for trivalent and tetravalent actinides. Here, three novel benzene centered tripodal diglycolamide (DGA) ligands (L_I, L_{II}, L_{III}, Fig. 1) [1, 2] were evaluated for the pertraction of Np(IV) across PTFE flat sheet membranes. Np oxidation state was adjusted to +IV by using ferrous sulfamate and hydroxyl amine mixture as reducing agent. The solvent extraction data suggest the kinetics of extraction of the metal ion is quite fast at 3 M HNO_3 (Fig. 2, a). Similarly the stripping kinetics was also fast with 1 M alpha HIBA (within 10 minutes). The solvent extraction data also suggest the formation of 1:1 (M:L) with L_I, mixed species (1:1, 1:2) with L_{II} and 1:2 species with L_{III}. The feed phase contained a tracer (^{239}Np) spiked nitric acid solution (3 M), while the receiver phase contained 1M α-hydroxyisobutyric acid (AHIBA).The supported liquid membrane (SLM) study with these ligands suggest the transport of Np(IV) is more (~90%) with the ligand, L_I with ethyl groups appended to the benzene ring at the 1,3,5-positions and two spacer atoms between the ring and the DGA group. The ligand, L_{II} with ethylamide linkage has somewhat lesser transport compared to L_I, however has better transport than L_{III}, with butoxy tether between the ring and the DGA unit (Fig. 2, b). The stability study of the ligands suggest out of the three ligands L_{II} showed best stability over five days of transport.

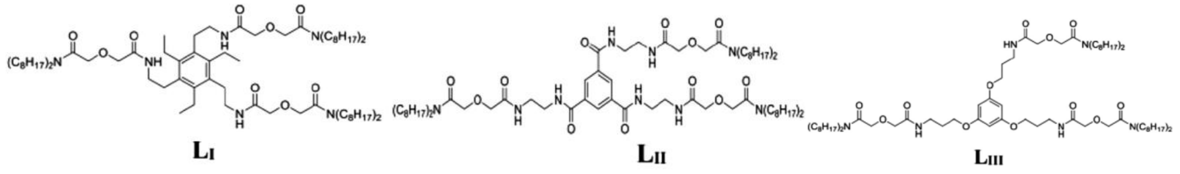

Fig. 1: Structural formulae of the three ligands

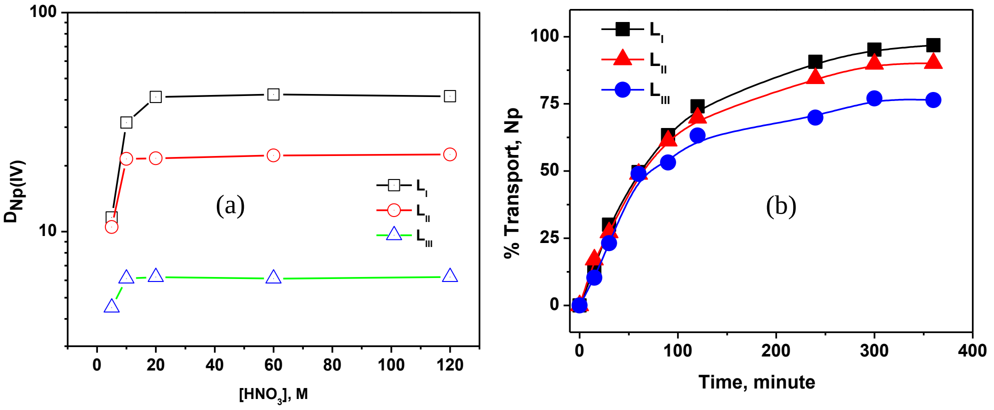

Fig. 2: (a) Kinetics of extraction of Np(IV), (b) Transport studies of Np(IV) at 3 M HNO_3

Keywords: *Supported liquid membrane, Neptunium, transport,*

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Analyzing the Quantum Yield of Carbon Dots and its Dependency on Dialysis Filtration Efficiency: A Real-TimeEvaluation

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Carbon quantum dots(C-dot), three-dimensionally confined particles with less than 10nm size, show excellent luminescent properties and have a wide variety of applications in diverse fields. In this study, the green and blue luminescent carbon quantum dots have been synthesized via the hydrothermal method. Weare mainly focusing on plant-derived green synthesised CDs, which are obtained through the hydrothermal method of synthesis. The bottom-up method, hydrothermal approach has been followed for the synthesis, where biomolecular species under certain pressure and temperature undergo polymerisation and carbonisation reactions[1].As the quantum yield of C-dot materials depends on the filtration process/impurity removal, it is initially analyzed using quinine sulfate after 0.22µm PVDF syringe filtration, followed by a hydrothermal reaction. The final stage of purification is the dialysis membrane separation process, whichremoves all the impurities and unreacted particles and results in better quantum yield. The impurities/unreacted molecular species, such as fluorophores/ other impurity particles may show quantum confinement effect, can lead to manipulated results like enhanced PL intensity.The purification processes in the CD studies are still lacking a standardised procedure for better yield[2]. This gap has been identified and tried to resolve with better results. Here, we are proposing a method, to check the filtration efficiency of carbon dots, once they are in the ultra-filtration stage. The filtration process in which dialysis membranes with different pore sizes have been used in different literature. We are performing the filtration with different membrane filters of Molecular Weight Cut Off (MWCO) to identify which is efficient. Rather than the optical evaluation using PL quantum yield and UV- Visible analysis, we have observed the change in the EIS spectrum every 30 minutes for 48 hours. The ferricyanidesystem-based error calculations and ENM (electrochemical Noise Measurement) have been evaluated and the results of EIS and ENM have been analysed using RMS (root mean square) relationships[3]. The filtration process in which dialysis membranes with different pore sizes have been used in different literature. We are performing the filtration with different membrane filters of Molecular Weight Cut Off (MWCO) to identify which is efficient. Rather than the optical evaluation, we have recorded the EIS spectrum every30 minutes for 48 hoursand the filtration efficiency has been calculated comparing the data. The Cyclic Voltammogram studies were also performed in regular intervals of time for the system detection in a specially designed cell with two channels of electrochemical workstations performing simultaneous reactions. The change in quantum yield has been recorded using the photoluminescent (PL) spectrum. The optical absorbance intensity over time during filtration was done using UV-visible spectroscopy to interpret the system. The percentage purity of as-synthesized samples was determined and compared with the hydrodynamic particle size evaluation using the Dynamic Light Scattering (DLS) technique. The membrane stability and structural changes were evaluated and compared using different techniques such as Fourier Transform Infrared Spectroscopy (FTIR), X- Ray Diffraction (XRD)and Brunauer-Emmett-Teller(BET) analysis, after different studies.

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Study of diffusion characteristics of ammonium phosphomolybdate modified Nafion membrane in different acidic conditions

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Nafion® membranes have attracted special attention due to their high proton conductivity and chemical stability even at elevated temperature [1]. However, due to the electrostatic interaction between the sulfonic acid groups and the hydrated cation, the selectivity of the membrane is not very high for a particular ion, which is not desirable for any separation based application. Radiocesium is one of the major environmental concern in radioactive waste waters owing to its long half-life (30 y) and its separation from other monovalent and multivalent ions is needed [2]. In this study, an attempt was made to synthesize ammonium phosphomolybdate (AMP) inside the pores of the Nafion-117 membrane. This was aimed to achieve Cs ion selectivity in the Nafion-117 membrane in highly acidic conditions, where due to the ion-exchange process, no cations except protons are taken up by the membrane. For AMP synthesis, a two compartment cell with Nafion as a separator was used with ammonium molybdate and disodium orthophosphate in the two compartments. Uniform formation of AMP in the membrane was observed and confirmed using XRD and FTIR. Fig. 1 shows the XRD of the AMP powder, blank Nafion and AMP modified Nafion membrane wherein characteristic peak of AMP is observed. The effect of reactant and acid concentration in the formation of AMP in the membrane was also studied. The diffusion characteristics of the AMP modified Nafion membranes were studied and compared with the pristine Nafion membrane. The studies were carried in water, 0.1 M and 0.5 M nitric acid concentrations and the diffusion of Cs^+ and Ba^{2+} ions were studied at trace as well as bulk concentrations of these ions. The studies were carried out by equilibrating the membrane with the solution spiked with the desired tracer for a well-defined time and counting the membrane in a NaI(Tl) detector. There was no significant difference in the diffusion and uptake behavior of the Cs^+ and Ba^{2+} ions when the ions were present in bulk concentrations in all the three solution conditions. However, at trace ion concentration, while the Ba^{2+} diffusion and uptake is unaffected due the presence of AMP in the membrane, it was observed to be significantly different for Cs^+ ion. At trace Cs^+ ion concentrations, the equilibrium uptake of Cs^+ ion was found to be much higher for the AMP modified Nafion membranes for all solution conditions, with no effect on the diffusion kinetics. This was also implicit from the much higher partition coefficients of the Cs^+ ion in the modified membrane relative to blank Nafion membrane as shown in Fig. 2. To see the effect of presence of other monovalent and trivalent ion, representative diffusion experiments with the trace concentration of the Na^+ and Eu^{3+} ions was also carried out. No difference in the diffusion and uptake behavior of the two ions was observed for the modified and the blank membranes. The study shows that the Cs^+ selectivity in the membrane has been achieved in the modified membrane even in presence of other monovalent, bivalent and trivalent ions. Further studies of Cs^+ extraction in samples containing other ions is in progress.

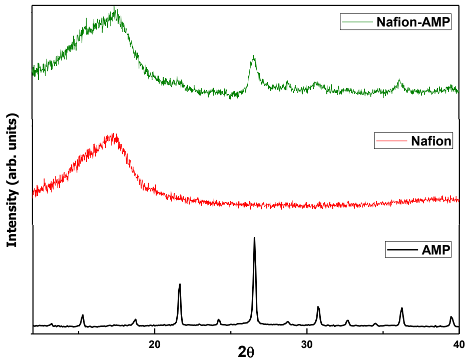

Fig. 1: XRD spectra of AMP powder, Nafion and NAfion-AMP membrane.

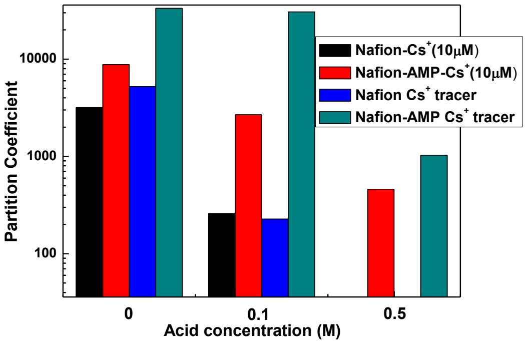

Fig. 2: Partition coefficient of Nafion and Nafion-AMP at different acid and Cs^+ concentrations.

Keywords: Cs-137, Nafion-117, Ammonium phosphomolybdate, diffusion

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Amidoximated Microporous Polymer for Physicochemical and Electro-Assisted Uranium Extraction from Seawater

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The access to clean, affordable and reliable energy has been a cornerstone of the world's increasing prosperity and economic growth since the dawn of the industrial revolution. Global energy-related CO_2 emissions grew by 1.1% in 2023, increasing 410 million tonnes (Mt) to reach a new record high of 37.4 billion tonnes (Gt). International Atomic Energy Agency (IAEA) submits the propelling significance of nuclear power in facilitating the transition to carbon-neutral energy, with projected contributions of 12% of global electricity by 2050. Considering the energy, climate and sustainability goals, the doubling of current nuclear capacity is projected. Current state-of-the-art nuclear technology utilizes Uranium (U) as the key element for power generation, and it is insufficient to fulfill the future demand at the existing rate of exploitation. [1] Uranium extraction from Seawater (UES) is among the seven separation challenges that will dramatically change the world. U is present in seawater in the form of $[Ca_2UO_2(CO_3)_3]$, as a source of sustainable and abundant fuel for the development of nuclear energy. Although, it is dilute with 3.3 ppb concentration but it is 1000 times (4.5 billion tons) more than the terrestrial reserves. [2] Decades of worldwide focused research in UES, guides well for the material design. Starting from the inorganic adsorbents, synthetic polymers, POPs, COFs, PAFs, MOFs, HOFs, bio-inspired proteins etc. and shifting towards nanostructured materials in quest for the representative materials in varied physical forms has afforded paradigm shift. The physical aspects of material design emphasize the use of downsized nanomaterials to have greater surface area, faster diffusion, accelerated migration and more efficient U capture.[3] The amount of uranium in seawater vastly exceeds that in land-based deposits; but separating it from other abundant metal ions require high affinity, selectivity and the ability to deal with an enormous volume of seawater. The polymers with intrinsic microporosity (PIMs) with highly rigid and contorted backbone addresses high surface area, diffusivity, solution processability and exposure of binding sites. Amidoxime functionalized PIM (AO-PIM) provides U-binding sites to overcome the challenge of 'high affinity & selectivity' amongst competing ions. Further, the assistance of electric field guides and accelerates the migration of U^{6+} towards the cathode for electrochemically boosted UES by means of reduction and precipitation of U^{4+}. [4]

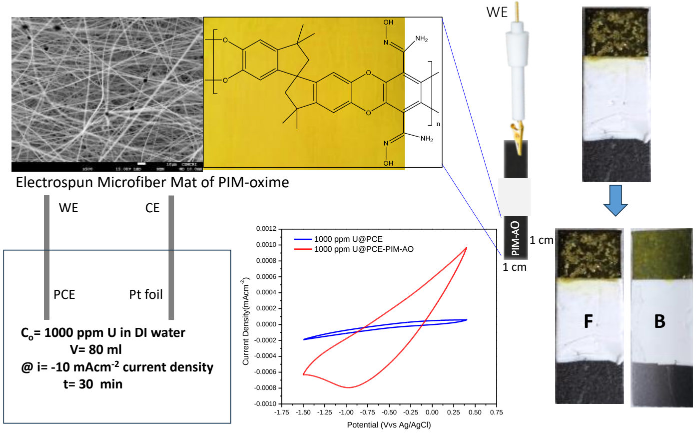

Figure 1. AO-PIM for Electro-assisted UES

Keywords: Sustainable Resources, U from Seawater, Microporous Polymer, U-Amidoxime binding, Electrochemical U-Recovery.

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Novel methodology for separation of ^{14}C and OBT (organically bound tritium) from biota samples and precise estimation the activity

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Tritium (^{3}H) present in atmospheric air gets exchanged with tissue free water of the organisms combines with oxygen, sulphur, nitrogen and carbon share of organic molecules and are termed as OBT. Similarly radioactive carbon (^{14}C), present in atmosphere, similar to other carbon gets incorporated into biota through the photosynthesis. ^{14}C and OBT activity estimation in the biota samples is a challenging task since it demands accurate analytical methods for its separation from environmental samples and sensitive radiation detectors for counting of low level activity. Main analytical methods for the determination of ^{14}C and OBT are (i) accelerator mass spectrometry (AMS) (ii) Samples combustion and conversion into benzene with subsequent counting in liquid scintillation counting (LSC) and (iii) thermal oxidation of the sample, collection of combustion water (CW) i.e. HTO and trapping of $^{14}CO_2$ in an amine-based absorber with LSC. The first two are highly sensitive and precise techniques. However, they have limitation of sample numbers and size to be analyzed on routine basis. Also complicated and time-consuming sample preparation procedure, high costs for analysis and absence of certified reference material enhance extra challenge. Methodology of thermal oxidation in a oxidizer system for separation of $^{14}CO_2$ and OBT having major issues like incomplete oxidation, acidification and particles contamination of trapped CW, and quenching of $^{14}CO_2$ absorber due to NO_2, SO_2 etc.. This issues result for higher background, lower sensitivity and accuracy of methodology [**1**].

To overcome these snags, a novel method has been developed, based on various optimized experiments. In this samples were oven dried, crushed into fine powder and combusted using Pyrolyser Trio-6 system (RADDEC, UK) and subjected to customized heating cycle for controlled oxidation (at 500-900℃). Air and pure oxygen were passed through quartz work tube, to separate carbon as $^{14}CO_2$ and OBT as HTO. Separated HTO and $^{14}CO_2$ were filtered by glass wool and condensed as normal ice and dry ice, respectively in empty bubblers maintained at -110°C in cryo cooler. Unwanted gaseous combustion products were vented out to prevent quenching. After the combustion process the dry-ice has been sublimed to $^{14}CO_2$ and collected by passed through the pre-weighed mixture of 10g each of carbon trap (3-methoxy propyl-amine) and Carbon count (1,2,4–Trimethylbenzene and 1-methoxy-2-propanol). Post-weighing the mixture, trapped $^{14}CO_2$ as carbamate was quantified. Collected HTO was distilled, neutralized to reduce the quench and mixed with scintillation solution. Prepared samples were dark adapted overnight to reduce chemiluminescence, and subjected to LSC for about 300min.

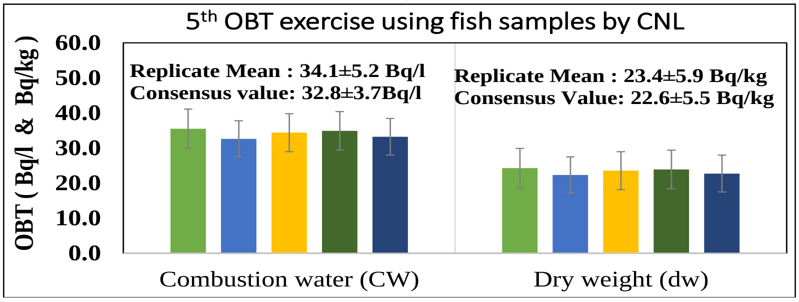

Fig. (1) Demonstration of precision and accuracy of methodology in OBT exercise

Application of method was demonstrated by participation in 5th OBT exercise. This was conducted by OBT International Group, CNL by distributing Largemouth bass fish collected from Chalk River and processed at Chalk River Laboratories, Canada. Results of five replicates reported by ESL NAPS (**Fig-1**), had a mean value of OBT as 34.1±5.2 Bq/l of combustion water (CW) and 23.4±5.9Bq/kg of dry weight (dw) sample (consensus mean value 32.8±3.7 Bq/l(CW) and 22.6±5.5 Bq/kg (dw)). ^{14}C activity in the terrestrial biota samples from clean air region GHAVP site, Haryana State as well as from the vicinity of a Pressurized Heavy Water Reactor (PHWR) NAPS were estimated[**2**]. Small excess activity in the samples in the vicinity of a NAPS site (225-249Bq/KgC) was observed compared to natural activity at clean air region site (224-228 Bq/kgC).

Keywords: OBT, Pyrolyser, Quenching, Oxidized, Combustion water.

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Low-Level Isotopic analysis of Plutonium using Solid Extraction Chromatography and Supported-Disk Liquid Scintillation

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Early determination of suspected Pu intake is essential for strategizing effective monitoring protocol and mitigation strategies [**1**]. This study aims to highlight a method for estimating low levels of plutonium isotopes in filter paper (FP) and nasal swab (NS), utilizing Supported-Disk Liquid Scintillation in conjunction with alpha spectrometry. The advantage of the adopted procedure is simplistic and efficient assessment of ^{241}Pu, low energy beta emitter in the presence of alpha-emitting nuclides from same electro-deposited planchette used for alpha spectrometry. For the purpose of standardization, known activity of Pu std (having $^{239+240}$Pu, ^{238}Pu, ^{236}Pu and ^{241}Pu activity) was spiked on blank FP and NS, and the spiked samples were acid digested. After matrix destruction the residue was taken in 15 mL of 3M HNO_3+1M $Al(NO_3)_3$ solution. $NaNO_2$ was added to the solution to convert Pu to Pu(IV) states. Purification of Pu from interfering matrix was carried out using solid extraction chromatographic resin (TRU column). Pu from resin column was eluted using 0.1M ammonium bi-oxalate solution [**2**]. The eluted Pu was electrodeposited on a 16mm SS planchette and initially subjected to alpha spectrometry. Later it was placed in Scintillation vial, covered with 5 mL of scintillator and directly counted in HIDEX 300 SL TDCR liquid scintillation counter (LSC) to assess ^{241}Pu. Pulse-shape discrimination technique was used to differentiate between alpha and beta-induced events. The method can precisely assess both gross alpha and beta emitters electrodeposited on the SS planchette thus, eliminating disruptions caused by chemiluminescence observed when digested sample is directly counted in LSC. Optimization of LSC parameters has yielded α and β efficiencies of 48 ± 2% and 7 ± 2%, respectively. Reduced counting efficiencies for alpha (approximately 100% to 48%) are observed due to the 2π geometry. However, for ^{241}Pu, there is significant reduction in counting efficiency (30% to 7%) because of 2π geometry and low average beta energy (E_{ave} 6.9 keV). The ^{241}Pu beta get further attenuated while overcoming a surface barrier existing at the planchette surface before it interacts with the scintillator. The LSC system gives only the gross alpha and gross beta counts of Pu. Alpha activity measured by both alpha spectrometry and LSC are within ±5%. Fig. 1 & 2 represents spectra observed in alpha spectrometry system and in LSC, respectively. MDA for low energy beta is 0.8Bq and for alpha is 0.07Bq with 30 min counting time in LSC. This low-level estimation technique offers a reliable and efficient means of assessing Pu isotopic composition in occupational settings, providing valuable insights for early detection and monitoring of internal contamination among radiation workers. The technique can also be efficiently be applied for fecal bioassay samples.

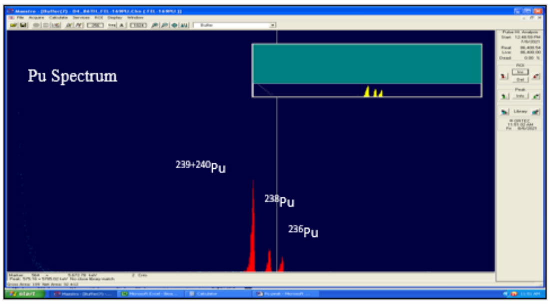

Fig 1: Pu spectra in alpha spectrometry

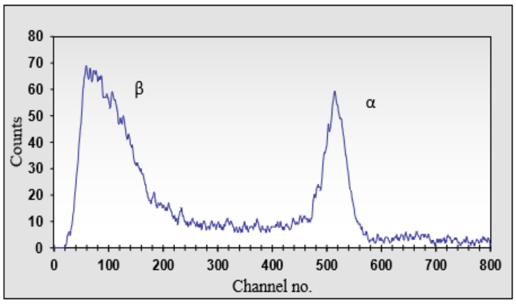

Fig 2: Pu gross alpha and ^{241}Pu spectra in LSC

Keywords: Plutonium, Nasal swab, Filter paper, LSC, Alpha spectrometry, MDA

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Selective Extraction of Trivalent Actinides and Lanthanides by Solid Phase Zirconia Extractants

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Solid zirconium oxide represents an applicable and robust inorganic ion-exchange material that has been used for radioactive waste separation with remarkable stability against radiolysis, heat and strong acids. Zirconia-based solid phase extractants (SPE) are developed for Ln/Ac separation as part of partitioning and transmutation (P&T) research relevant to the advanced nuclear fuel cycle. Decorating the zirconia support with organic task-specific ligands can be used to enhance the separation properties of the material.[1] The Ac/Ln selectivity is based on the 'Hard/Soft Lewis acid/base donors' effect of the ligand incorporated into the zirconia surface. In this study, we synthesized a range of hybrid zirconia materials that showed different affinities to Am/Eu. Phosphorous provides suitable linkages between organic and inorganic moieties and endures required harsh conditions. Free OH^- groups serve as functionalization spots on the zirconia surface. Ligand composition has been varied and tested in order to afford desired group selectivity for the material. Longer synthesis time has shown to increase the ligand loading while increase in the ligand size and length also result in a higher ligand loading**.** However, batch sorption studies have revealed a decrease in uptake of the materials loaded with bigger aminotrismethylene phosphonate (ATMP) derivatives (e.g. DTPMP and TTHMP). This is most probably due to the decreased surface area and the phosphonate group bonding between the layered metal oxide surface. The Zr-ATMP hybrid materials have showed preference for Eu in batch sorption experiments and gradient elution column process, in which Eu was sorbed nearly 50% more than Am (see Figure 1). In contrary, the 2,6-bis(1,2,3-triazol-4-yl)pyridine ligand (PyTri) has been recently used to form coordination complexes with f and d-metals.[2] The incorporation of PyTri ligands into zirconia surface afforded efficient extraction of Am^{3+} over Eu^{3+} in batch sorption experiments over a 24 h contact time with a separation factor of 29 at highest. The concentration of HNO_3 had a strong effect on the sorption properties of the materials, as expected due to increased competition from the acidic hydronium ions. Overall, this study provides an approach for the design of novel organophosphonate-based solid hybrid sorbents by utilization of the robust M-O-P linkage bonds with tunable Am/Eu selectivity.

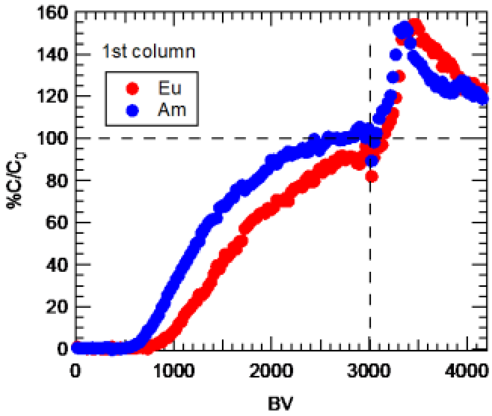

Fig 1. Column separation of ^{152}Eu and ^{241}Am with Zr-ATMP

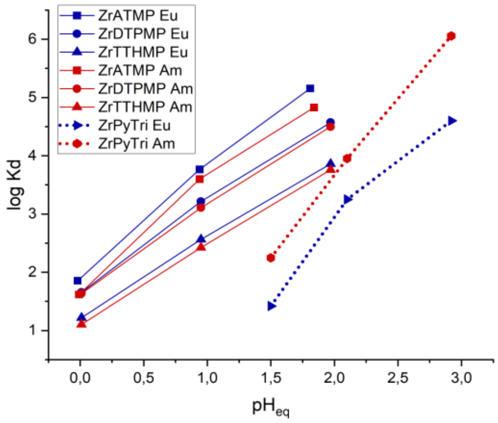

Fig 2. Separation of ^{152}Eu and ^{241}Am with selected hybrids.

Keywords: Solid phase extractants, Americium, Zirconia, Separation, Organophosphonates

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Emergency Bioassay for Uranium in Direct Urine using Extraction Chromatography and Liquid Scintillation Technique

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During any radiation incident, radionuclides released into the environment can enter the human body either through inhalation, ingestion, and / or wounds. Once into the body, some fraction of these radionuclides gets transferred to various organs and the rest is eliminated through body by biological processes. Bioassay monitoring techniques are, therefore, employed to estimate the intake of radionuclides as well as the committed effective dose (CED). However, during emergency situations rapid, highly sensitive, selective, as well as reliable methods are preferred. Various separation methods like ion-exchange, solvent extraction, and extraction chromatography [1] are available for estimation of radionuclides excreted in urine. In the present study, extraction chromatography method followed by Liquid Scintillation Spectrometry (LSS) was standardized for rapid separation of uranium in urine. The Derived Intervention Level (DALI) corresponding to intake of 1 ALI (CED 20 mSv) of uranium inhalation intake are listed in Table 1 for ICRP default parameters (particle size -5 µm AMAD and solubility type -Type M) [2]. The standardized method uses tandem column setup consisting of pre-filter and UTEVA resin for uranium separation in urine sample without any co-precipitation stage. Pre-filter resin is used for removal of organic components in urine before passing it through UTEVA resin. For standardization, twenty urine samples (50 mL each) collected from unexposed individuals were spiked with known amount of U(nat.) standard. Acidity of these samples was adjusted to 3M using conc. HNO_3 and samples were equilibrated for 15 mins. The samples were then passed through 10 mL plastic syringes containing pre-filter (1.5 g) & eluted urine was loaded on UTEVA resin (1.0 g), stacked one above the other. Both columns were previously preconditioned with 3M HNO_3. After sample loading, both these stacked columns were washed with 3M HNO_3. At this stage, the pre-filter column was separated from UTEVA column. Later, UTEVA column was washed sequentially with 9M and 5M HCl. The uranium retained on the column was then eluted using 1M HCl in 5 mL fractions (total elution was with 25 mL of 1 M HCl). To each 5 mL fraction, liquid scintillation cocktail was added and the eluted uranium was quantified using LSS technique (Hidex 300 SL). Fig.1 depicts gross alpha spectrum of U(nat.) obtained using LSS technique. It is observed that uranium gets eluted in the first two fractions, and the second fraction contained > 90% of the total spiked uranium activity. Thus, in case of emergency bioassay, it is sufficient if the first two fractions are collected and taken-up for LSS instead of the total elution volume of 25 mL. The average radiochemical recovery for uranium achieved in the present study was 96 % and the Minimum Detectable Activity (MDA) achieved for uranium was 1.3 Bq/L for 10 mins counting time. In case of annual chemical toxicity (limit = 10000 Bq), the sample need to be counted for a longer duration (15 mins). The total time required for uranium estimation, including counting was < 2 h. The method standardized is simple, rapid, and sensitive to detect uranium in urine even 30 d after the inhalation incident.

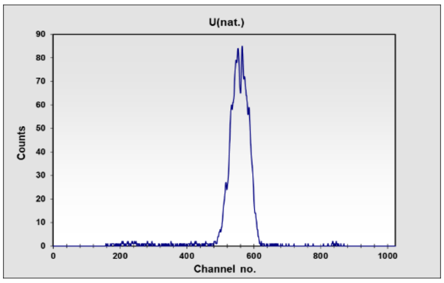

Fig.1 α-spectrum of U (nat) using LSS

Table 1: DALI of uranium isotopes in urine (Bq/L) for Type M uranium inhalation.

Nuclide	Day 1	Day 3	Day 5	Day 7	Day 10	Day 15	Day 30
^{238}U	113.6	6.2	4.8	4.2	3.6	3.0	2.1
^{235}U	113.6	6.0	4.5	3.9	3.4	2.8	2.0
^{234}U	96.2	5.4	4.0	3.6	3.1	2.6	1.8
U(nat.)	101.5	5.7	4.3	3.7	3.2	2.7	1.9

Keywords: Uranium, Urine, Extraction chromatography, LSS, Emergency

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Studies on the Extraction Behavior of Curcumin Towards Bulk Zirconium and No-carrier added Niobium Radioisotope

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The influence of green chemistry in radioanalytical chemistry has led to the replacement of organic solvents with environmentally benign nature resourced chemicals (NRC) [**1**] Curcumin, a natural polyphenol derived from turmeric powder, due to its multiple functional groups, may be a potential NRC in radiochemical separation. In this work, we have studied the potential of curcumin as an extractant in separation of no-carrier added (NCA) ^{90}Nb produced by proton irradiation of ^{nat}Zr target.

We have isolated and characterized curcumin as per the standard procedure [**2**]. For the production of ^{90}Nb, a zirconium foil of thickness 3.25 mg/cm^2 was bombarded by 10 MeV proton beam for ~ 10 h at Variable Energy Cyclotron Centre, Kolkata. Gamma spectrometric analysis showed presence of ^{90}Nb, produced via ^{90}Zr (p, n) ^{90}Nb reaction. Irradiated Zr target was dissolved in aqua regia followed by evaporation then reconstitution with deionized water. An yttrium foil of thickness 10.51 mg/cm^2 was irradiated by 11 MeV proton beam, which produced ^{89}Zr via ^{89}Y (p, n)^{89}Zr reaction. Separation of bulk Y from ^{89}Zr was done by our established procedure [**3**]. This ^{89}Zr was spiked with the solution containing ^{90}Nb and bulk Zr. Since curcumin is insoluble in water, SLX was carried out. 10 mg curcumin was added HCl (2.9 mL) solutions of varying concentration followed by the addition of 0.1 mL Nb-Zr stock solution. After 10 minutes incubation, the matrices were shaken for 5 minutes, centrifuged for 5 min and settled for 10 mins, The supernatant was collected separately in an Eppendorf which was then counted in a p-type HPGe detector. The weight of curcumin was varied at best condition.

It is concluded From Fig 1 that extraction of bulk Zr by curcumin depends on the molarity of HCl, while extraction of ^{90}Nb is more or less independent of acidity. Fig 2 shows that with increase in amount of curcumin, extraction of Zr was more compared to NCA Nb. Though at 1M HCl, separation factor ($S_{Zr/Nb}$) was more than 400, but in terms of separation and yield of NCA ^{90}Nb, the method was not satisfactory. Nevertheless, this experiment clearly demonstrates preferential selectivity of curcumin towards bulk zirconium over ^{90}Nb, which may be exploited in future to improve the separation of these two components.

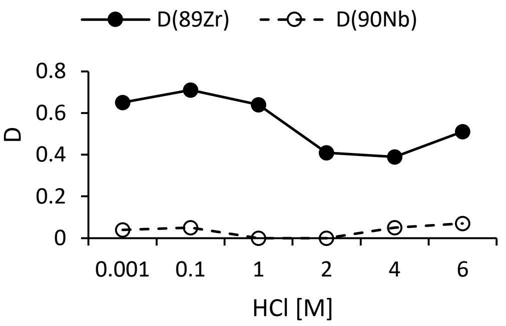

Fig. 1: D values for bulk Zr and ^{90}Nb at different concentration of HCl (fixed 10 mg curcumin)

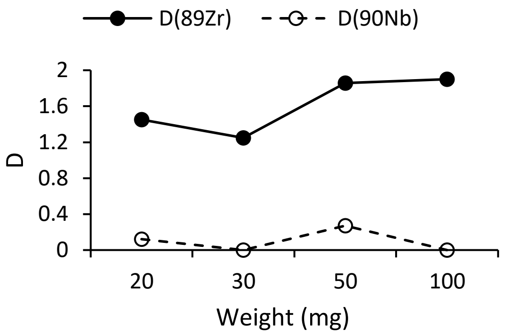

Fig. 2: D values for bulk Zr and ^{90}Nb at different weight of curcumin (fixed HCl conc. at 0.1 M)

Keywords: Nature resourced chemical, Curcumin, Zirconium, Niobium, SLX

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Application of solvent extraction and enhancement of miscibility of organic extract during uranium analysis in high level waste

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The determination of concentration of uranium and plutonium in the high-level wastes generated during reprocessing of spent fuel is essential for nuclear material accounting and to maintain the concentration of actinides below disposable limit. Generally, the typical concentration range of uranium and plutonium in high level wastes are in the range of 10-50 mg/L and 1-5mg/L respectively. The analysis of these nuclear materials in high level waste is challenging job due to presence of high fission product activity. Therefore, it is necessary to selectively extract uranium and plutonium from HLW using suitable solvent. Since, Tri-n-octyl phosphine oxide (TOPO) diluted with o-xylene exhibiting higher distribution ratio (in the order of 10^2) for U (VI) and Pu (IV) & Pu (VI), is generally employed for the selective and quantitative extraction of U(VI) and Pu(IV). The concentration of U(VI) in TOPO extract is the determined by a spectrophotometric method using Pyridyl azo resorcinol as a chromogenic agent. The chromogenic agent pyridyl azo resorcinol forms a stable complex with uranyl ion at pH in the range of 7.0- 8.5. Aqueous solution of tri- ethanolamine was employed as a buffer reagent to maintain the desired pH. The interference from tri and tetravalent metal ions are suppressed by adding aqueous solution of 1,2 diamino cyclo hexane tetra acetic acid and sodium fluoride during U determination. Due to the limited solubility of the TOPO/xylene phase in the ethanol mixture, addition of TOPO extract beyond 100 µL into the respective reference solution causes turbidity, which decreases the sensitivity of this method. The preliminary studies reveal that, the miscibility of nitric acid equilibrated 0.1 M TOPO in xylene is mainly dependent on the amount of water present in the reagent-ethanol medium and degree of miscibility decreases with increasing % of water content in the reference solution mixture. Since, triethanol amine is soluble in water as well as alcohol, alcoholic solution of triethanol amine was prepared and employed as buffer solution. Similarly, the volume of CyDTA and NaF is optimized to minimize the water content in the mixture. Under this condition addition of TOPO extract up to 40% volume of the reference solution does not cause any turbidity and homogeneous solution was obtained.

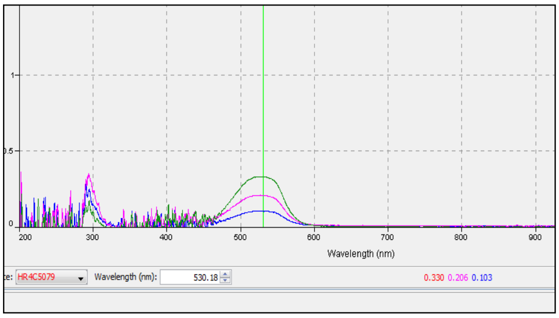

Fig.1 Calibration plot for 15-50 ppm U

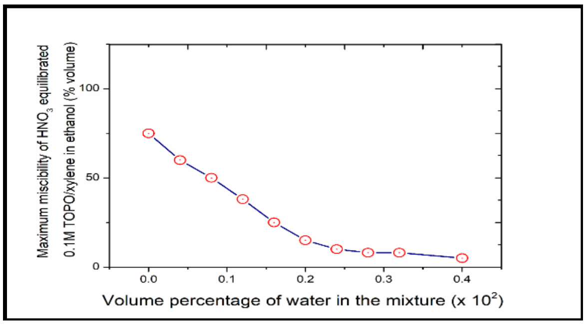

Fig.2 Effect of water content in reference solution on the miscibility of TOPO extract

Results of the present study showed that determination of uranium as low as 15 mg/L is possible in the HAW stream after the in-cell separation of U from fission product and subsequent spectrophotometric analysis of U loaded TOPO/xylene. As the in cell TOPO/xylene extraction is also suitable for the alpha radiometric analysis of Pu in the raffinate, this modified method is relatively easy for trace level U analysis with same TOPO layer transferred to the radioanalytical laboratory.

Keywords: uranium, raffinate, PAR, TOPO/xylene etc

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Polystyrene thin film scintillator based sensors for selective Pu detection in presence of alpha and beta-gamma activity

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Detection of low level of alpha emitting radionuclides is important not only for monitoring environment contamination, but for a variety of applications such as forensics, personnel monitoring, waste management, reprocessing etc. In many of these applications, especially in reprocessing, low level of Pu is present in high level of beta-gamma activity due to fission products. Along with this, other alpha emitters such as Am, Cm may also be present. Techniques such as mass spectrometry, alpha spectrometry require laborious sample preparation which includes multiple steps of separation and pre-concentration. These problems can be circumvented by the use of extractive scintillating sensors, wherein simultaneous pre-concentration and measurement is possible [1]. In our earlier work, phosphate functionalized polyethersulfone (PES) based polymer inclusion membrane with scintillator (PES-SPIM) was successfully tested for the low level Pu estimation [2]. While the scintillating PES thin films were found to have good pulse height but the pulse height distribution was observed to be broad and close to the low energy noise. This limited its alpha activity estimation in presence of a β-γ emitters. In the present studies, polystyrene film (PS) comprising of the fluor, 2,5-diphenyloxazole (PPO) and activator, 1,4-bis(2-methylstyryl)benzene (MSB) in its bulk matrix was chosen as the substrate owing to its good pulse height response. The Pu selective functional groups were introduced by surface grafting bis(2-(methacryloyloxy)ethyl) phosphate (BMEP) monomer using in-situ UV grafting. The poly(BMEP)-PS film was observed to extract Pu(IV) from 2 molL^{-1} nitric acid (~85 %) and as desired, a high pulse height with significantly narrow pulse height distribution was observed. The scintillation response of the film was found to be similar from both the surfaces of the film. The poly-(BMEP)-PS substrate was tested for estimation of Pu alpha activity in presence of different alpha and beta-gamma activities such as Am, Cm, ^{nat}U, Cs, Ba and Eu. The Pu activity was found to be within 8% of the expected activity, even in the presence of Am, Cm, Cs, Ba and Eu (Fig. 1). However, significant decrease in Pu activity was observed in presence of bulk U (10 mgmL^{-1}). A systematic study to see the effect of varying amounts of U on the response of the Pu loaded poly(BMEP)-PS film was carried and the results are given in Fig. 2. As seen, as the U concentration is decreased, the deviation in Pu activity from the expected activity also decreases with the deviation becoming less than 5% at 100 ppm of U(VI). This shows that the developed substrate is capable of simultaneous extraction and detection of Pu. The substrate was further checked for Pu uptake from a legacy dissolver solution of unknown history which was found to contain Pu, ^{241}Am and ^{137}Cs. The developed substrates were found to extract Pu (within 11%) in presence of high level of Am and Cs as measured by scintillation based counting and verified by alpha spectrometry.

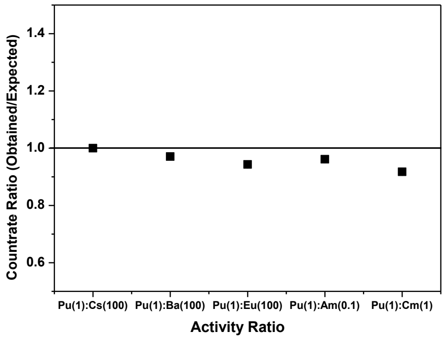

Fig. 1: Alpha count rate ratio of Pu loaded poly(BMEP)-PS film in presence of alpha and beta activity.

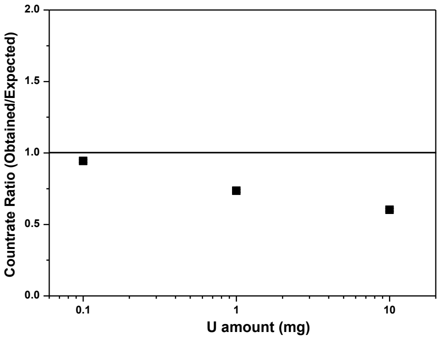

Fig. 2: Alpha count rate ratio of Pu loaded poly(BMEP)-PS film in presence of bulk U.

Keywords: extractive scintillation sensor, polystyrene, polymer, alpha, scintillation

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A Facile Method for Radiochemical Separation of Cyclotron Produced ^{211}At for Targeted Alpha Therapy

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Targeted alpha therapy (TAT) is now emerging in advanced cancer management due to the short range and high linear energy transfer (LET) of α-particles, which cause maximum damage specifically to the targeted cells while abating off-target effects on healthy tissues [1]. Astatine-211 has attained significant interest in the recent times as a promising radioisotope for TAT over other α emitters (e.g. ^{223}Ra and ^{225}Ac) as it emits just one α-particle per decay which alleviates certain concerns related to *in vivo* administration. Moreover, ~ 58.2 % of ^{211}At decays via electron capture (EC) to produce ^{211}Po, resulting in emission of 77-92 keV X-rays that permits counting of the radioactivity using standard gamma detectors and also in vivo visualization of the pharmacokinetics and localization of the administered radiopharmaceuticals by SPECT imaging. In this study, we have produced ^{211}At via ^{209}Bi (α, 2n) ^{211}At by irradiating natural Bi$_2$O$_3$ target with 30 MeV α-beam in an AVF cyclotron, VECC, Kolkata. The irradiated target was dissolved in 2 M HNO$_3$ and Bi was precipitated as Bi(OH)$_3$ using 2M NaOH followed by separation of ionic sodium astatide solution by centrifugation and membrane filtration. The batch yield of ^{211}At at the end of irradiation was ~ 6 MBq.µA^{-1}.h^{-1} and the separation yield was ~ 80%. The radionuclidic purity was >99.9 %, confirmed by γ-spectrum presented in **Figure 1a**, in which the peak at 687 keV corresponds to ^{211}At, peak at 569 corresponds to ^{207}Bi and ^{211}Po, and 897 keV also corresponds to ^{211}Po. Moreover, no extraneous radioisotopes were found in the γ-spectrum of the decayed sample (**Figure 1b**).

In order to successfully utilize ^{211}At in TAT, the radionuclide should be attached with a targeting vector. The conventional ^{211}At radiopharmaceuticals have low *in vivo* stability due to complicated radiochemistry and low conjugation efficiency. To circumvent these limitations, we have synthesized RGD conjugated gold nanoparticles (Au NPs) (particle size 8.4±0.8 nm) and labeled with ^{211}At adopting non-covalent approaches. The Au NPs is not only biocompatible but the RGD peptide also target the integrin $\alpha_v\beta_3$ receptors which are overexpressed on tumor endothelial cells of varying cancer types. The RGD peptide acted as both reducing and stabilizing agent and precluded the need for using toxic surfactants in Au NPs synthesis. The radiolabeling yield was found to be > 99 % and the radiolabeled nanoparticles retained their integrity under physiological conditions over a period of 21 h. Hence, the present strategy simplifies ^{211}At production in terms of purification and would increase affordable access to this radioisotope for TAT of cancer.

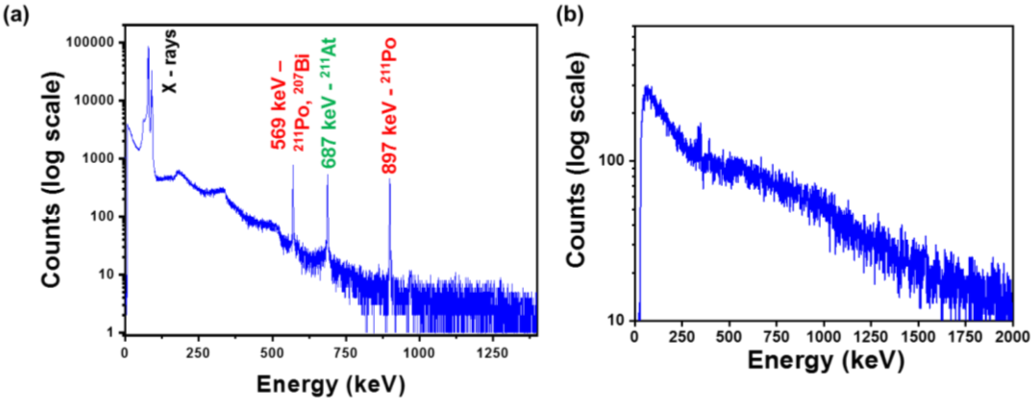

Figure 1. (a) γ- ray spectrum of ^{211}At after radiochemical separation; (b) γ - ray spectrum of decayed ^{211}At solution after radiochemical separation.

Keywords: ^{211}At; precipitation; radiochemical separation; gold nanoparticles; RGD peptide; targeted alpha therapy

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Production and Radiochemical Separation of Theranostic ^{44}Sc/^{47}Sc Pair for Potential Application in Cancer Management

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In recent times, scandium has offered a tremendous prospect in theranostics as suitable radionuclides of the element can be produced for both diagnostic imaging as well as therapeutic applications [**1**]. Three theranostically suitable radionuclides of scandium are being studied for their clinical application: ^{43}Sc [$T_{½}$ = 3.89 h; $E_{\beta+}$ = 476 keV (88.1 %); branching ratio β^+ = 88 %; E_γ = 372 keV (22.5 %)], ^{44}Sc [$T_{½}$ = 3.97 h; $E_{\beta+}$ = 632 keV (94.3 %); branching ratio β^+ = 94.3 %; E_γ = 1157 keV (99.9 %)] and ^{47}Sc [$T_{½}$ = 3.35 d; $E_{\beta-}$ = 162 keV (100 %); E_γ = 159 keV (68.3 %)]. Among them, both ^{43}Sc and ^{44}Sc exhibit positron emission, rendering them suitable candidates for positron emission tomography (PET) imaging [**2**]. On the other hand, ^{47}Sc has potential as a β^- emitter, making it a viable option for therapeutic applications. Furthermore, ^{47}Sc can be utilized for visualization through single photon emission computed tomography (SPECT) imaging due to its favorable γ-ray emission characteristics. In the present study, we report the production of ^{44}Sc and ^{47}Sc using a low energy linear accelerator (BARC-TIFR pelletron) and a medium flux research reactor (Dhruva), respectively. The nuclear reactions involved are: ^{44}Ca (p, n) ^{44}Sc in a cyclotron and ^{46}Ca (n, γ) ^{47}Ca → ^{47}Sc in a nuclear reactor. An efficient electrochemical method was optimized for the radiochemical separation of no-carrier-added (NCA) ^{44}Sc and ^{47}Sc from their respective bulk irradiated Ca targets. Near quantitative electrochemical separation of ^{44}Sc and ^{47}Sc was obtained when the applied potential was adjusted to 7 V for 20 min across the Pt-electrodes in HCl electrolyte medium maintaining pH ~ 6. The radiochemical separation yield was determined to be 92.1 ± 1.2 % in all the batches. After the separation, γ-spectrum of ^{44}Sc (**fig A**) and ^{47}Sc (**fig B**) was recorded. The radionuclidic purities of ^{44}Sc and ^{47}Sc were> 99.99 % and the radiometals were obtained in a form suitable for radiopharmaceutical formulation. As a proof of concept, [$^{44/47}$Sc]Sc-DOTA-E[c(RGDfK)]$_2$ was prepared with >98 % radiolabelling yield and its radiochemical stability was maintained under physiological conditions. The economic practicability of the process was ascertained by recovering the expensive enriched [^{44}Ca]$CaCO_3$ and [^{46}Ca]$CaCO_3$targets in the form suitable for reuse in future irradiations. Overall, the process is simple, efficient, reproducible and economically viable for obtaining ^{44}Sc and ^{47}Sc for theranostic radiopharmaceutical formulation.

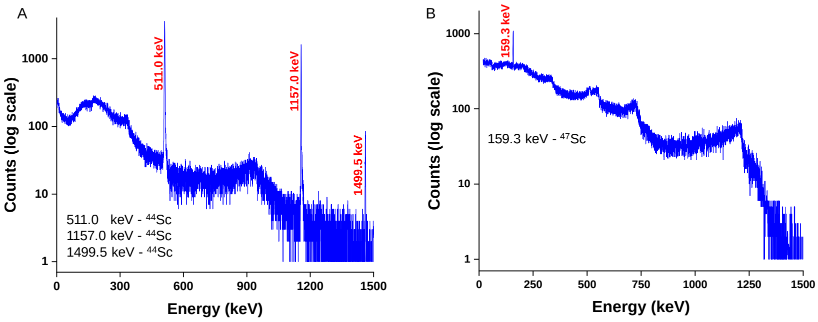

***Figure:* γ-ray spectra of (A) NCA ^{44}Sc after electrochemical separation, (B) NCA ^{47}Sc after electrochemical separation**

Keywords: ^{44}Sc; ^{47}Sc; electrochemistry; enriched ^{44}/^{46}Ca target recovery; radiochemical separation; theranostics

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Production, radiochemical separation and electrochemical concentration of no-carrier-added ^{52}Mn: a potent radionuclide for cancer diagnostics

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Manganese-52 (^{52}Mn) is an emerging radiometal that holds tremendous potential in nuclear medicine. The ^{52}Mn-based radiopharmaceuticals can be used in multimodal imaging involving positron emission tomography (PET) and manganese-enhanced magnetic resonance imaging (MEMRI), which provide accurate diagnosis of disease in various organs such as liver, pituitary glands, bone and intestine in preclinical settings [**1**]. Among various PET imaging radiometals used in radiolabeling with proteins or antibodies, ^{52}Mn ($T_{½}$ =5.6 d, $E_{\beta+max}$ = 575 keV; average $E_{\beta+}$ = 242 keV, branching ratio β^+ = 29.4 %) can be a better choice because it not only possesses similar chelation chemistry like ^{64}Cu but also possess longer half-life to show better pharmacokinetics when radiolabeled with proteins or antibodies [**2**]. In this regard, we have produced ^{52}Mn from natural Cr metallic powder target via ^{52}Cr (p, n) ^{52}Mn reaction in BARC-TIFR pelletron. The irradiation was carried out with 16 MeV proton at 110 nA current for 43 h. After irradiation, the target was cooled for 4 h before handling. The irradiated target was dissolved in 5 mL concentrated HCl medium by heating at 80 C. The average batch yield of ^{52}Mn was found to be 6.4 ± 1.3 MBq µA^{-1} h^{-1}. Then the solution was evaporated to near dryness followed by reconstitution in 10 mL of 0.1 M HCl solution. Subsequently, an efficient radiochemical separation method based on selective precipitation of Cr as $Cr(OH)_3$ was optimized for isolation of no-carrier-added (NCA) ^{52}Mn from the irradiated target. Finally, ^{52}Mn solution was concentrated using electrochemical method and obtained in a medium suitable for radiolebeling. The γ-spectrum was recorded before (**Fig. 1A**) and after (**Fig. 1B**) the separation and the peak corresponding to ^{51}Cr disappeared after separation, indicating complete removal of Cr from the solution. The overall radiochemical separation yield of the process was > 75 % with > 99.99 % radionuclidic purity and > 97 % radiochemical purity. The apparent molar activity of ^{52}Mn was determined to be 2.2±0.1 MBq/nmol and it was found suitable for preparation of radiopharmaceuticals.

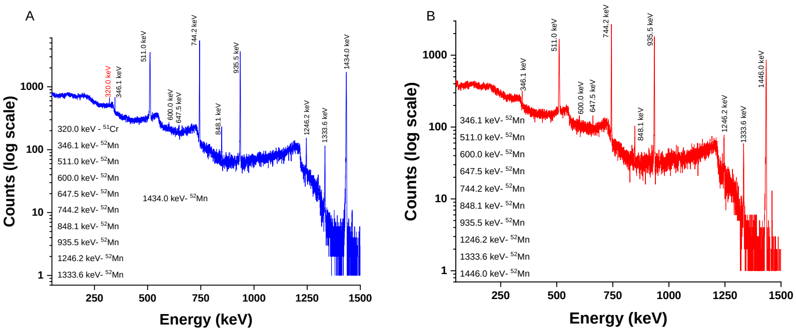

Fig. 1: (A) γ-spectrum of NCA ^{52}Mn before radiochemical separation and (B) after separation

Keywords: Manganese-52, *PET, MEMRI, no carrier added, precipitation, electrochemical*

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Development of an Efficient Separation Method for ^{90}Sr from Dissolver Solution and Radionuclide Generator for ^{90}Y Elution

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^{90}Y with a half-life of 64.05 h serves as a pure β-emitter, with a maximum β-energy of 2.2 MeV. ^{90}Y finds utility in the therapeutic management of hepatocellular carcinoma, leukemia, and lymphoma, with potential applicability in a broader spectrum of malignancies [1]. The major routes for producing ^{90}Y involve the neutron capture by ^{89}Y and the neutron-induced fission of fissile materials ^{235}U and ^{239}Pu i.e., ^{89}Y (n,γ) ^{90}Y and ^{235}U, ^{239}Pu (n,f) ^{90}Sr (β-) ^{90}Y respectively. Of particular interest is the latter pathway, which yields carrier-free ^{90}Y through the decay of its parent nuclide, ^{90}Sr ($t_{1/2}$ = 28.8 years) which are in secular equilibrium. Thus, a radionuclidic generator containing ^{90}Sr can offer a consistent supply of ^{90}Y through elution processes. The present work deals a novel method of ^{90}Sr separation from the nuclear fuel dissolver solution, followed by its immobilization onto a column to construct a radionuclide generator to enable the isolation of ^{90}Y to address tailored therapeutic requirements.

1.5 g of FBTR irradiated (U,Pu)C fuel with a burn-up of 105 GWd/t is dissolved in 11.5 M HNO_3 under reflux conditions at 120 °C for 24 h without evaporation loss. The dissolver fuel solution was subjected to solvent extraction to separate the Sr using crown ether i.e., 4,4'(5') Di-tert-butyl-dicyclohexano-18-crown-6 (DtBuCH18C6) in n-octanol diluent. Equal volumes of fuel dissolver solution and 0.1 M DtBuCH18C6/n-octanol were equilibrated and allowed 10 min for phase separation. A sample of the organic phase was assayed by high-purity germanium (HPGe) detector and found to contain traces of ^{137}Cs, ^{106}Ru, ^{125}Sb and ^{154}Eu. These impurities were minimized by scrubbing the organic phase with 12 M HNO_3. An aliquot of the organic fraction is subjected to back extraction with 0.001 M HNO_3 to bring the ^{90}Sr to the aqueous phase along with the trace impurities mentioned above. The aqueous phase was loaded onto a cation-exchange column prepared using 2 g of Dowex 50WX8 [100-200 mesh] resin. The column was eluted with a novel eluting agent i.e., tri-sodium tri-meta phosphate (SMP) to remove the impurities [Ru, Sb & Eu] along with the in-grown ^{90}Y in the first cycle of elution [2]. The ^{90}Sr was then allowed to produce its daughter ^{90}Y for a period of ten days and then eluted with SMP again to separate pure ^{90}Y. The collected ^{90}Y fraction was assayed by HPGe and liquid scintillation detectors and found to be free from any radionuclidic impurities. The activity of ^{90}Y was estimated to be 1 MBq. Three more such elutions were performed and results were always consistent. The purified fraction of ^{90}Y was loaded onto resin microspheres which were washed with 0.1 M HNO_3 to remove the chemical impurities of P and Na from SMP. The loading efficiency of ^{90}Y onto resin was found to be 95%. The chemical quality control of the final product was assured by removing the ^{90}Y from resin using 1 M HNO_3 and analyzed by ICP-OES. Average half-life of ^{90}Y from the four cycles of separation was found to be 63.1 ± 0.1 h which is in good agreement with literature. The present study established a flow sheet for separating ^{90}Y using a radionuclide generator.

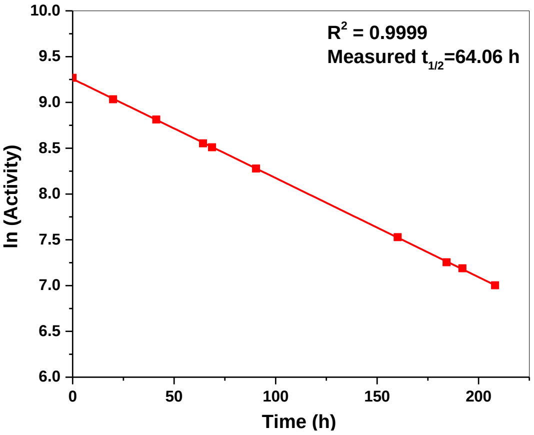

Fig.1: Decay profile of purified ^{90}Y.

***Keywords**: ^{90}Y, ^{90}Sr, Dissolver solution, Resin, Radionuclide generator,* tri-sodium tri-meta phosphate

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Distribution of Polonium-210 (^{210}Po), Lead-210 (^{210}Pb), soil nutrients and physicochemical parameters in soil of tobacco growing places in Karnataka state

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The Polonium-210 (^{210}Po) and lead-210 (^{210}Pb) are radioactive progeny of Radon-222 (^{222}Rn), which are the daughter products of the Uranium-238 (^{238}U) decay series, with half-lives of 138.4 days and 22.3 years respectively. These are heavy metal ions that are more reactive, immediately attached to the aerosol in the atmosphere and return to the earth's surface as dry fallout or don't wash away by rain. These are deposited on tobacco leaves. Tobacco leaves are used in the production of cigarettes. The cigarette contains Polonium-210, which is an alpha emitter that depends on the energy of the alpha. Polonium-210 in cigarettes is volatilized at thetemperature characteristics of a burning cigarette and inhaled into the lungs along with the cigarette smoke. Lead-210 is a source of Polonium-210, it is also volatile and deposited in the lungs by smoking. When the smoke is inhaled, the activity of Polonium-210 causes lung cancer and damages DNA, different organs and tissues. Due tothis significance, the tobacco growing places were selected for the estimation of ^{210}Po an^{d} ^{210}Pb. Tobacco farmersused fertilizers such as Diammonium phosphate (DAP), Zinc sulphate, Potash, Urea etc. These fertilizers and soil contain nutrients for the growth and yielding of the plants. These fertilizers, soil, and rocks contain the naturally occurring radioactive nuclides of Uranium-238 and Thorium-232, which decay to release radon. Further radon decays into Polonium-210 and Lead-210. As the tobacco plant grows, this radon clings to the sticky hair on the bottom of the tobacco leaves called trichomes, where it decays into ^{210}Po and ^{210}Pb, which don't wash away by rain. Polonium-210 is extremely radiotoxic to humans, the cells and tissues of different organs are damaged and produce cancer. Therefore, this study is important for understanding the transfer of ^{210}Po from these materials to the tobacco plant and its dose to the public. The activity concentrations of Polonium-210 and Lead-210 were measured by radiochemical analysis using the ZnS (Ag) alpha counting system. Along with the activity of Polonium-210 and Lead-210, the soil nutrients and physicochemical parameters of the soil were also studied and analyzed. The soil nutrients were estimated by an Atomic Absorption Spectrophotometer (AAS). And physicochemical parameters were estimated by some standard methods. The activity concentration of Polonium-210 in the soil varies from 6.17±3.1 Bqkg^{-1} to 48.92±4.1 Bqkg^{-1}, and that of lead-210 varies from 17.09 ± 2.23 Bqkg^{-1} to 92.16 ± 1.32 Bqkg^{-1}. The ^{210}Po to ^{210}Pb ratio in this study is less than 1, indicating the presence of onlysupported ^{210}Po in this region. Polonium activity varies with the depth of the soil, as the depth of the soil increases, the activity of polonium decreases. The present study was able to assess the health risks from the alpha radiation emitted from the polonium and the relationship between the soil nutrients and physicochemical parameters.

Keywords: ^{210}Po, ^{210}Pb, Physicochemical parameters, Soil nutrients, Alpha counting system, Atomic AbsorptionSpectrophotometer (AAS)

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Incorporation of I-125 in 3D-graphene sponge for brachytherapy applications

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Graphene sponges are novel carbon-based nanomaterials exhibiting high adsorption capability along with excellent surface properties and robustness. Radiolabeled nanoparticles when injected intratumorally have important applications towards brachytherapy of tumoral tissues. The radionuclide I-125 having long half-life (60.14 days) and short tissue penetration range destroys tumor cells ($E_\gamma = 0.035$ MeV) effectively when placed near the tumor site without damage to healthy cells. Here graphene sponge was chosen as the nanomaterial for tagging with I-125. Preliminary radiolabeling studies and optimization of labeling parameters such as content of KI, pH of ^{125}I solution, incubation time, centrifugation etc. were optimized.

Graphene sponge (0.5 mg) was incubated with [^{125}I]NaI (0.2 mL, 37 μCi) for 24 h at room temperature with constant stirring. To separate unabsorbed, free [^{125}I]NaI, the reaction mixture was centrifuged at 5000 rpm for 10 min. where the radiolabeled graphene oxide settled at the bottom and the upper solution containing untagged [^{125}I]NaI was discarded. This process was repeated twice to completely remove any free I-125 in solution. I-125 incorporation efficiency was determined by measuring radioactivity of the graphene sponge as well of the solution containing [^{125}I]NaI. Reaction conditions such as incubation time (2, 4, 8, 24 h), centrifugation time (5,10 min.), pH of [^{125}I] NaI solutions (pH 1-14), amount of graphene sponge (0.1 mg -1.0 mg) and KI content (2 μg-100 μg) were optimized. Maximum yield (97%) could be achieved at pH 10 (Fig. 1) on incubation for 24 h. Particle size of ^{127}I-labeled graphene sponge was observed to be 250 nm as determined by dynamic light scattering (DLS) technique (Fig. 2). Experiments to ascertain the stability with different levels of radioactivity are planned in future.

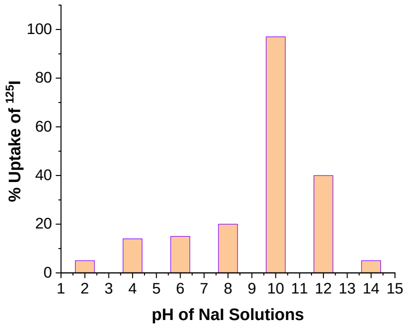

Fig.1: Incorporation of I-125 graphene oxide at different pH.

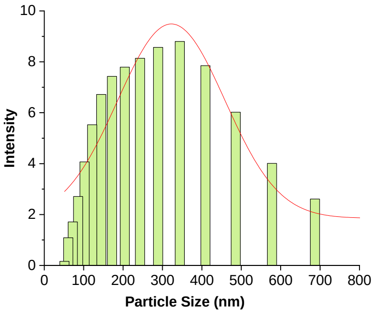

Fig. 2: Particle size of ^{127}I-labeled graphene oxide.

Keywords: Graphene sponge, ^{125}I, nanomaterials

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Estimation of Plutonium in FBTR irradiated U-Zr fuel using Radiochemical Gamma Spectrometry

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Metallic fuels such as U-Zr or U-Pu-Zr are indeed promising for future fast reactor applications due to their advantageous properties like high thermal conductivity, fissile atom density, breeding ratio and low doubling time etc. In this context, U-6wt% Zr metal fuel was irradiated in Fast Breeder Test Reactor (FBTR) in order to elucidate the properties of these fuels i.e., fuel swelling, fission product release, radiation damage during irradiation. The irradiated fuel was characterized for the U, Zr, fission product inventory, Am etc [1]. The total amount of Pu present in the irradiated fuel was determined by the Isotopic Dilution Mass Spectrometric (IDMS) method with TIMS. The present paper describes a radiochemical gamma spectrometry method for the estimation of Pu in the irradiated U-Zr fuel.

About 1.1 g of the irradiated U-Zr fuel was dissolved in nitric acid. An aliquot of the resulting dissolver solution underwent analysis by high-resolution gamma spectrometry employing a high-purity germanium detector. The obtained gamma spectrum revealed the presence of fission products such as ^{106}Ru, ^{125}Sb, ^{134}Cs, ^{137}Cs, ^{144}Ce, ^{154}Eu, ^{155}Eu etc [1]. However, estimation of low energy gamma radiation of plutonium i.e. 413.7 keV by gamma spectrometry is hindered by the formidable Compton background generated by highly intense gamma emitters such as ^{137}Cs, ^{106}Ru etc. within the dissolver solution which poses a significant challenge, rendering accurate estimation unfeasible under these conditions. Therefore, radiochemical separation of Pu is mandatory towards its estimation by gamma spectrometry. In this context, a portion of the dissolver solution was subjected to solvent extraction by 1,3-di-octyloxycalix[4]arene-crown-6 (CC6) to remove the Cs from dissolver solution [2] followed by the extraction of Pu by TBP. The extracted Pu in TBP was assayed by 50 % co-axial HPGe p-type detector (BSI) connected to standalone ORION 8 k MCA module and InterWinner 7.0 MCA acquisition software. The gamma spectrum of dissolver solution before and after radiochemical separation of Pu is shown in Fig.1. The spectrum showed a photo peak at 413.7 keV corresponding to ^{239}Pu after removing major Compton background due to fission products. A ^{152}Eu gamma standard source was also counted in a reproducible geometry by HPGe detector for arriving full energy peak efficiencies as a function of gamma energy. The acquired spectra were analyzed using BARC developed PHAST gamma spectra analysis software. The activity of ^{239}Pu was calculated using the obtained count rate of 413.7 keV photo peak and the respective efficiency. The total Pu content was found to be 6.42 ± 0.49 mg/g of irradiated fuel using the isotopic composition of Pu arrived from TIMS. The estimated Pu value by gamma spectrometry is in good agreement with IDMS reported value of 6.34 ± 0.10 mg/g [1]. Thus, the present method reports a quantitative gamma spectrometric estimation of Pu after its separation from dissolver solution.

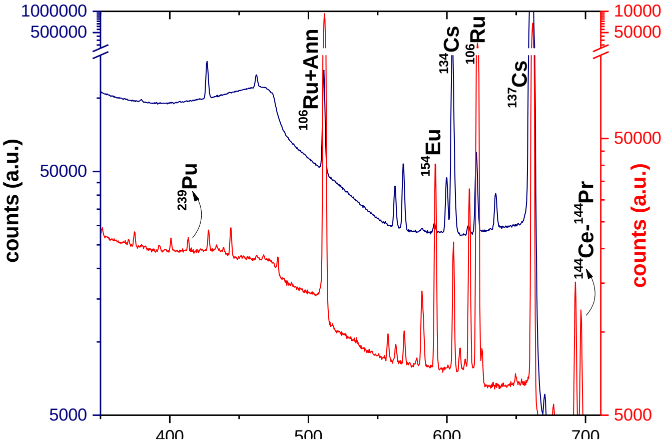

Fig.1. Gamma Spectra of dissolver solution before and after radiochemical separation of Pu

Keywords: *U-Zr fuel, Crown ether, TBP, Dissolver solution, plutonium, gamma spectrometry*

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Aqueous Biphasic Separation of ^{61}Cu from ^{nat}Co

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Aqueous biphasic extraction systems (ABS) comprising polymers and salts are recognized as green and environmentally benign technique as no carcinogenic organic phase is used and both the phases are soluble in water, biocompatible and less toxic [**1**]. We have designed an ABS for the separation of ^{61}Cu from natural cobalt target. ^{61}Cu is an emerging radioisotope in positron emission tomography owing to its half-life (3.33 h), decay properties (β^+=61%; EC= 39%), mean β^+ energy 500 keV, positron branching 51% and $E_{\beta max}$= 1.21 MeV [**2**].

A ^{nat}Co target of thickness 21.2 mg cm^{-2} was bombarded by 30 MeV α-particle to produce ^{61}Cu. Aiming at high yield of ^{61}Cu, we irradiated cobalt target for ~15 h (~5 half-life of ^{61}Cu) at Variable Energy Cyclotron Centre, Kolkata. The target was kept aside for 1 h. The irradiated foil was dissolved in concentrated HNO_3 followed by evaporation and redissolved in 0.01M HNO_3. For radiochemical separations, ABS comprising polyethylene glycol (PEG) of MW 4000 and 6000 and different salts like Na_2SO_4, $Na_2S_2O_3$ and $(NH_4)_2SO_4$ were opted. ABS was constructed using equal volume of 50% w/V PEG solutions and 2M salt solutions followed by addition of radioactive stock solution containing ^{61}Cu, ^{58}Co and bulk Co. The system was shaken for 10 min and settled for 5 min. After clear phase separation, the PEG phases and salt phases were counted in a HPGe detector for 300 s. Out of the three salts, $Na_2S_2O_3$-PEG4000/6000 showed a difference in extraction pattern. In $Na_2S_2O_3$-PEG4000 (3 mL: 3 mL), 34.5% bulk Co was extracted in the PEG phase along with 5.5% of ^{61}Cu. Since bulk Co was getting extracted in the PEG phase, the volume of PEG 4000 was increased to see the difference in extraction pattern. With 6 mL PEG 4000 and 3 mL $Na_2S_2O_3$, 98.3% of the bulk Co was extracted in the PEG phase. Fig 1 shows the retention profile of ^{61}Cu and bulk Co in $Na_2S_2O_3$ (extracted with 6 mL PEG 4000). At this condition, 95.1 % of ^{61}Cu was retained in $Na_2S_2O_3$ phase with ~ 1.7%. contamination from bulk Co. Separation factor obtained at this condition was $S_{(Cu/Co)} = 1.47 \times 10^3$. The minimum contamination from bulk cobalt can be avoided by second time extraction of salt-rich phase with fresh 6 mL PEG. The developed separation method used no organic solvent and reagent, therefore may be designated as green separation technique.

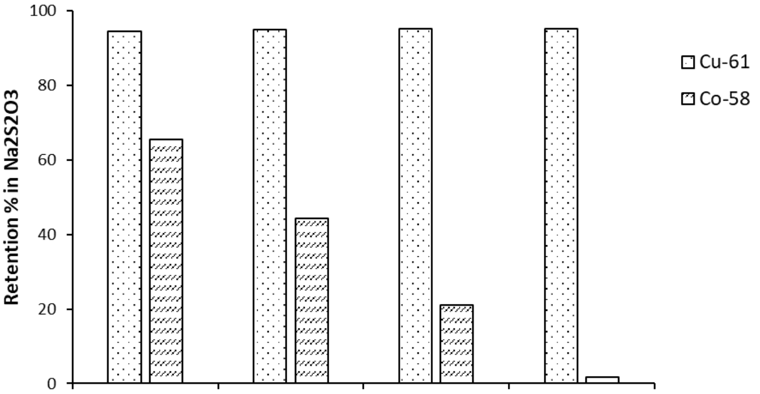

Fig. 1: Retention profile of ^{61}Cu and bulk Co in $Na_2S_2O_3$ phase with variation of PEG 4000 volume

Keywords: Radiochemical separation, ^{61}Cu, Aqueous biphasic system, Polyethylene glycol

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Measurement of radon activity concentration in water in the region of Chikkaballapura district, Karnataka, India

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Radon concentrations in water samples were measured in the various locations of Chikkaballapura district. Water samples were collected from bore well, hand pump, open well and ponds. About 37 samples were collected at different locations of the district. Samples were collected and filled completely in 200 ml airtight bottles to avoid aeration. The collected samples were carried to laboratory within 12 hours and the emanometry technique (Model PSI RBS 1 bubbler) was employed for the removal of bubbles [1- 3]. After that counts are noted by using alpha counter. Spatial variations of radon concentrations are noted. It was found that activity found of radon in greater than the WHO limit 11 Bql^{-1}. Inaminchenahalli bore well in Chikkaballapura taluk and Dibburhalli in Shidlaghatta Taluk were found to have highest radon concentration of 250.78 Bql^{-1} and 246.62Bql^{-1}, respectively. Paatpalya of Bagepalli Taluk (161.20Bql^{-1}), Hudugur of Gowribidanur Taluk (90.73Bql^{-1}), Enigadale (81.24 Bql^{-1}), Gudibanda Town (57.80Bql^{-1}) and Chintamani town (53.31Bql^{-1}) were also found to have significant values. The total effective doses were also found to be high in particular to the above locations in which the values obtained are 684.62μSvy^{-1}, 673.28μSvy^{-1}, 440.08μSvy^{-1}, 247.69μSvy^{-1}, 157.80μSvy^{-1} in Dibburhalli, Inaminchenahalli, Paatpalya, Hudugur and Gudibanda Town respectively. The higher value of radon in the study area was due the existence of Granites in the region. Activities of bore well water samples were found to be higher as in that of Pond water samples. In pond water the dissolved radon easily escapes into the atmosphere due to the temperature differences in the atmosphere. Physico-chemical parameters like electrical conductivity, pH and total dissolved salts were also determined. Electrical conductivity was higher in borewell water samples than that in pondwater samples which was due to the presence of dissolved salts in water samples. The correlation graph of Radon concentration was plotted with respect to pH and Electrical conductivity shows negative and positive correlation. Negative correlation due to pH and positive correlation was obtained with respect to Electrical conductivity.

Keywords: Radon, water, Chikkabalapura, Karnataka, emanometry technique.

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Leaching study of Technetium (^{99}Tc) from CWP Matrix after immobilized of active chemical sludge along with ^{99}Tc trapped in Goethite

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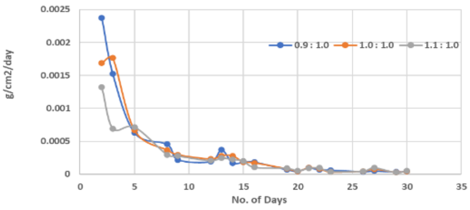
Technetium-99 is one of the fission products with very high yield (~6%) in thermal neutron induced fission of ^{235}U. The high solubility in water and high mobility of per-technate ions, coupled with very high half-life of ^{99}Tc ($t_{1/2} = 2 \times 10^5\, y$, βmax = 290 keV) makes it a potential candidate for long term hazard to the environment [1]. The major radionuclide present in the Low level effluent waste (LLW) from the IX column is ^{99}Tc. In one novel process, technetium has been made captured in goethite by making use of in-situ formed corrosion products of mild steel [2]. The leaching study of Tc99 from Cementised Waste Product (CWP) containing Tc99 trapped goethite has been published in NUCAR-2023. In this paper, a comparative study has been done between leaching study of Tc99 from CWP prepared from only goethite containing trapped Tc99 and active chemical sludge along with goethite containing trapped Tc99 generated during chemical co-precipitation process of treatment of low active liquid radioactive waste. The CWP were prepared with active chemical sludge along with captured Technetium (^{99}Tc) in Goethite and cement in the ratio 0.9:1, 1:1, 1.1:1. The curing time of CWP blocks was 28 days. Compressive strength was tested on different inactive cement blocks which were prepared using inactive chemical sludge in same proportion as active CWP blocks. Leaching study of ^{99}Tc from active cement blocks was done in distilled water up to one month. The active chemical sludge waste was characterized and the details is in Table 1. Primary investigation showed that, compressive strength (Table-2) of CWP blocks are less than that of cement blocks having no goethite and chemical sludge waste. Leach rate of the ^{99}TC from active CWP blocks are shown in Fig. 1 and after 30 days leach rate is given in Table 2. It has attained almost stabilized leach rate.

Table1: Typical properties of ^{99}Tc containing goethite and Active Chemical Sludge waste:

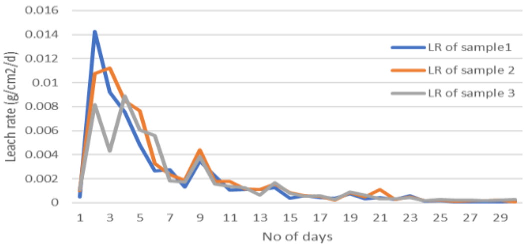
Waste code	Nature pH	Sludge (%)	TS (%)	B (mCi/L)	^{99}Tc (mCi/L)	Cs^{137} (mCi/L)	Sb125 (mCi/L)
Active chemical sludge waste	8.5	76	14.45	0.98	0.84	0.06	0.11
Goethite sludge waste	2	70	13	0.79	0.76	0.004	0.012

Table-2: Compressive strength & LR of CWP

Si no.	Waste to cement ratio	Compressive strength (N/mm^2)		Leach rate after 30 days, g.cm^{-2}.d^{-1}	
		Only goethite containing **^{99}Tc** 9	Active chemical sludge waste	Only goethite containing **^{99}Tc**	Active chemical sludge waste
1	0	5.6	5.6	--	--
2	0.9:1	3.3	3.5	$4.42 \text{ X } 10^{-5}$	$2.16 \text{ X } 10^{-5}$
3	1:1	2.2	2.6	$4.48 \text{ X } 10^{-5}$	$3.46 \text{ X } 10^{-5}$
4	1.1:1	1.5	1.8	$5.31 \text{ X } 10^{-5}$	$2.75 \text{ X } 10^{-5}$



Leach rate of ^{99}Tc from only goethite containing CWP



Leach rate of ^{99}Tc from active chemical sludge containing CWP

Conclusions: The CWP made from active chemical sludge waste is higher compressive strength and less leach rate than those of only goehite containing Tc99.

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Organically Bound Tritium Content in Major Food Crop around NAPS Narora site

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Tritium (^3H) is a radioactive isotope of hydrogen (T1/2 = 12.3 year), and it decays to ^3He by emitting low energy beta radiation with an average energy of 5.7 keV and a maximum energy of 18.6 keV . Tritium in the environment exist in several forms, such as gaseous (HT, HTO, CH_3T), liquid (HTO or organic molecules in solutions) or organically bound tritium (OBT) which can get incorporated into living organisms (vegetables, animals, humans). Tritium from air/water is incorporated into plant/animal biota as Tissue Free Water Tritium (TFWT) and Organically Bound Tritium (OBT) [**1**]. Narora Atomic Power Station (NAPS) has twin unit of Pressurized Heavy water type reactors (PHWR) with installed capacity of 220 MW_e each operational at Narora site and tritium is the radionuclide released to the water body [**2, 3**].In the present study, Major food crops such as Wheat, Corn and Bajra grain samples were collected from different off-site locations around the Narora Atomic Power Station (NAPS) Narora site during January 2022 to March 2022 and analysed for OBT. Quantification of OBT in the terrestrial biota and estimation of radiation dose due to its consumption by population is very important for implementation of regulatory guidelines. Samples were dried to remove moisture and crushed into fine powder and combusted in Pyrolyzer system (tube furnace) in the presence of oxygen and air mixture at 600-800˚C. Combustion water after distillation was mixed with scintillation solution and counted in ultra low level Liquid Scintillation Counter (LSC) for determination of OBT activity in the food crop samples.

Following formula was used for estimation of OBT activity in food crop samples.

$$C_{OBT}\left(\frac{Bq}{kg},\ DW\right) = \frac{\text{Net CPM}\times 10000\times WEQp}{[60\times \text{CE}(\%)\times \text{CW}(\text{l})\times \text{Rec}(\%)]}$$

Where CW (volume of combustion water) & CE (Counting Efficiency %) Rec. (Recovery %) of Pyrolyser System, DW (Dry weight), C_{OBT} (OBT Concentration), *WEQp* site specific water equivalent factor.

The site specific water equivalent factor (*WEQp*) in terrestrial matrices was evaluated using following formula:

$$WEQp, \frac{L}{Kg} = \frac{Combustion\ Water\ CW(l)\times 100}{Sample\ dry\ wt.(kg)\times Rec(\%)}$$

Table-1: OBT activity in various Food Crop

Matrices	No. of samples	OBT (Bq/kg Fresh Weight)	
		Range	Mean
Bajra	14	BDL-275.1	62.5
Corn	18	BDL-341.1	56.2
Wheat	40	19.8-731.3	90.2

Wheat crop is found to have slightly higher OBT concentration than other food crops, it may be due to larger growing period of wheat than other crops. The levels obtained in the current study are comparable to the studies carried out other nuclear sites of India [**3**]. Concentration of OBT in food crop sample is found to decrease with distance from the site. It is observed that OBT concentration depends on growth/maturity period of the matrices, variety of food crop, atmospheric HTO concentration etc. The resultant dose to member of public due to consumption of these crops is insignificant.

Keywords: Organically Bound Tritium (OBT), Food crop, PHWR type reactor

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Speciation study of major ions (Na, K, Ca and Mg) in geothermal waters at varying temperatures

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The temperature dependent speciation analysis of the major ions (Na, K, Ca and Mg) is very vital to ascertain the composition of the reservoir fluids in the geothermal systems. Although speciation study of the reservoir liquids in several geothermal systems situated in Iceland, Japan, New Zealand, Japan, Philippines regions are already been reported (Cioni and Marini, 2020 and the references cited therein), very few studies have been carried out in Indian geothermal systems. In this study, speciation analysis of the major ions (Na, K, Ca and Mg) are carried out in the temperature interval from 20 to 170°C in some of the thermal water samples from Gujarat geothermal area using GeoT computer code. Fig. 1 shows the variation in the activity of different sodium species in geothermal sample depending upon the aquifer temperature. The concentration of free Na^+ ion is found to decrease with increasing temperature. The fraction of free cation generally decreases with increase in temperature due to the increasing stability of the ionic complexes with relevant anionic ligands (Cioni and Marini, 2020). The concentration of NaOH is found to increases with increase in temperature. Concentration of the rest of the Na-species initially decreases with temperature and passes through a minimum before start increasing. At the reservoir temperature (~170°C) condition the concentration of the various sodium species is as follows: $Na^+ > NaCl > NaSO_4^- > NaHCO_3 > NaOH > NaCO_3^- > NaF$. The concentration of the most of the calcium species shows higher concentration in the reservoir condition (170°C) than in the surface discharge temperature (~55°C). At the reservoir temperature (~170°C) condition the concentration of the various Ca species is as follows: $Ca^{2+} > CaSO_4 > CaOH^+ > CaHCO_3^+ > CaCO_3 > CaCl^+ > CaHSiO_3 > CaF^+ > CaCl_2$ (Fig. 2). Similar trend is observed in case of magnesium and potassium ions also.

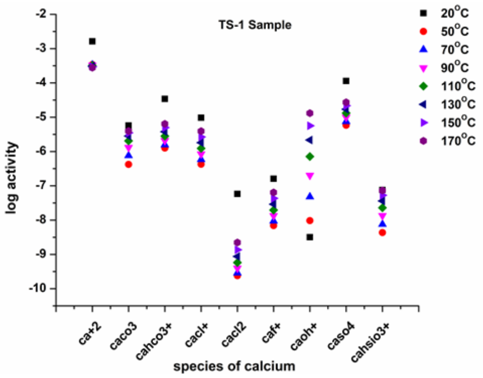

Fig 1: Speciation of Na in the range of 20-170°C

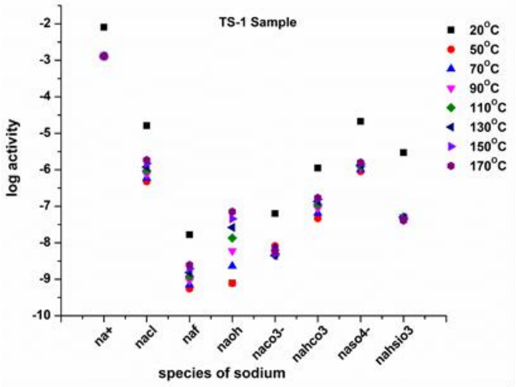

Fig 2: Speciation of Ca in the range of 20-170°C

Keywords: *Thermal waters, speciation, reservoir fluid composition*

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Complexation studies of thiazolidine-4-carboxylic acid with Europium(III)

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Thiazolidine-4-carboxylic acid (Thia4ca) has been clinically used for about 20 year specially in the treatment of liver diseases and related gastrointestinal disturbances [1]. Thiazolidine-2-carboxylic acid (thia2ca) derivatives are used as activator in horticultural crops, industrial crops, tropical crops and fruit trees [2]. This confirms the presence of thiazolidinecarboxylic acid ligands in the human body as well as in the environment. The complexation study of these ligands with actinides and lanthanides is important for environmental point of view as well as the ligands can be assessed for their performance as an actinide decorporating agent in human body. Keeping these facts in mind the thermodynamic complexation of thiazolidine-4-carboxylic acid was studies in detail. Eu(III) was chosen as an analog of trivalent actinides.

This work presents determination of thermodynamic parameters ((log K, ΔG, ΔH, ΔS) for complexation of Eu(III) with thia4ca. Thia4ca showed two protonations in the given experimental conditions. The log K_{P1} and log K_{P2} are 6.22 and 1.50 respectively. Potentiometric titrations were carried out to know the speciation and stability constant values for the Eu(III)-thia4ca complex species formed during the course of reaction. The thia4ca forms ML_1, ML_2 and ML_3 type of complexes with Eu(III) with log K values 5.2, 2.0, 1.76 respectively (Fig.1). The calorimetry studies gave information about the heat changes during complexation. Formation of all the three complexes were exothermic in nature and complexation is driven by both enthalpy and entropy. The density functional theoretical calculations were carried out to understand the complexation at molecular level and to confirm the binding modes of Eu(III)-thia4ca complexes (Fig. 2). The theoretical findings are in line with the obtained experimental results. Biological experiments using human erythrocytes and whole blood is in process to know the decorporation ability of thia4ca for trivalent actinides.

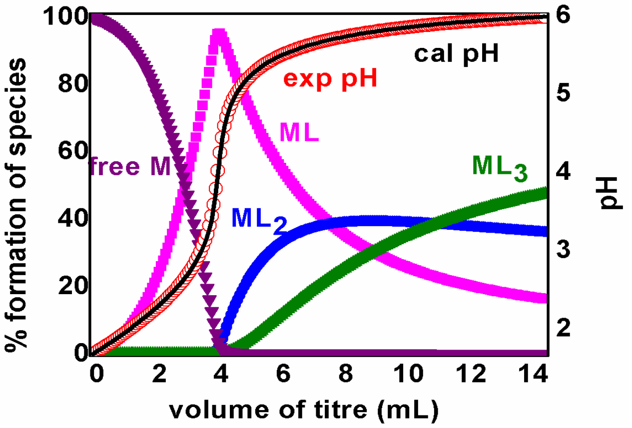

Fig. 1: Speciation of Eu(III) complexation with thia4ca

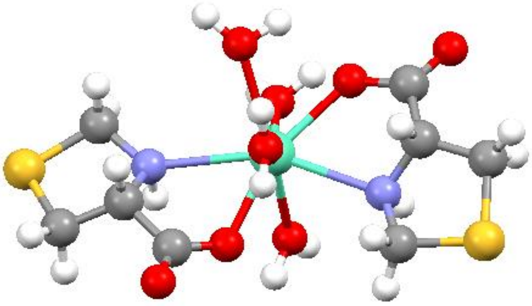

Fig. 2: Geometry optimized structure of Eu(III)-2thia4ca

Keywords: Europium, Thermodynamics, Complexation, Stability Constant, Calorimetry

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Spectroscopic Studies of Uranium binding forms in Human Urine

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Uranium is routinely handled in various stages of nuclear fuel cycle and can enter in human body via three major routes i.e. inhalation, ingestion, and injection. Once internalized it gets cleared to the body fluids depending on the solubility of the uranium compounds, and finally excreted through urine. Investigating uranium chemical binding forms (speciation) in human body fluids is crucial not only to understand its biokinetics but also its relevance in risk assessment and in designing effective decorporation therapy. In present study, Uranium speciation has been studied in simulated human urine (SU) through time-resolved photoluminescence spectroscopy (TRPLS) and compared with thermodynamic modelling results (VISUAL MINTEQ). For experimental studies, SU was prepared and the pH of all samples was adjusted to pH~5.5 based literature findings [1]. Small volumes (20 mL) of samples were spiked with uranium solution to get final concentrations of 50 µM U(VI) and samples were kept for 1 hour for equilibration. TRPLS technique was employed for spectroscopic investigation. All uranium (VI) species were excited non-specifically by a wavelength of 254 nm and the spectra were recorded from 380 to 750 nm. The readings were taken in duplicates and spectrum of blank SU and uranium in distilled water (DW) was also taken as control.

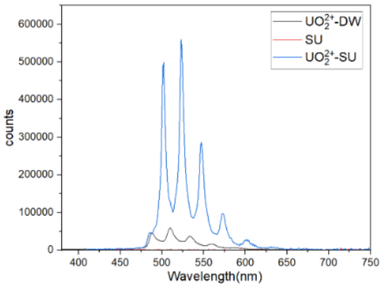

Fig. 1: Fluorescence spectra of (a) U(VI) in DW, (b) SU-blank, and (c) U(VI) in SU respectively.

Table 1: Fluorescence peak maxima of uranyl systems

System	Wavelength (nm)					Ref.
UO_2^{2+}-DW	488	509	533	559	589	Present work
UO_2^{2+}	488	510	533	560	--	[2]
UO_2^{2+}-SU	485	502	523	547	572	Present work
$UO_2PO_4^-$	--	502	524	548	574	[2]
$UO_2(Cit)^-$	475.3	491.8	513.5	537.0	561.9	[3]
$UO_2(Ox)_2^{2-}$	472.6	491.0	512.2	534.8	559.9	[3]

Thermodynamic modelling using VISUAL MINTEQ reveals that at pH 5.5, the predominant species present in UO_2^{2+}-SU system are $UO_2(Cit)^-$, $UO_2(Ox)_2^{2-}$ and $UO_2PO_4^-$ respectively despite high concentration of other ligands like urea, uric acid etc. The fluorescence peak maxima of UO_2^{2+}-SU system matches closely to $UO_2PO_4^-$ peaks as reported in literature [2]. No appreciable peaks/bands were observed for U(VI) citrate species as it does not show luminescence at room temperature. More sophisticated technique like cryo-TRPLS will be employed in future to study uranium speciation in actual human urine samples.

Keywords: Uranium, Speciation, TRPLS, Spectroscopy, Binding.

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Speciation of U in a tissue equivalent low Z_{eff} material $Li_2B_4O_7$ glass

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Lithium tetraborate (LTB) matrix is of wide importance as it has tissue equivalence with $Z_{effective}$ =7.2. Tissue equivalent materials are best suited for radiation dosimetry, as it mimics the nature of the human body [1]. Several materials like LiF are used for this purpose. Doping the material with heavy ions lead to better luminescence characteristics. In this study we have attempted to understand the impact of doping U in LTB matrix. Uranium is known to exist in many different forms in solids although in solutions, it is stable as hexavalent uranyl ion. Also, speciation of the actinide ion is essential to know the capability of the material as a dosimetric material in order to propose a suitable mechanism and understand the spectroscopic properties. Photoluminescence (PL) technique provides a unique, non-invasive and direct method for the speciation of actinide ions in various types of matrices [2]. In this study, four samples with uranium doping of 0.5, 1, 2 and 5 mol% were prepared from stoichiometric amounts of Li_2CO_3, H_3BO_4 and U_3O_8 via high temperature reaction route. The formation of the glassy phase was confirmed from the occurrence of a broad band in the XRD data. PL studies were carried out using an Edinburgh FLS-1000 series spectrophotometer.

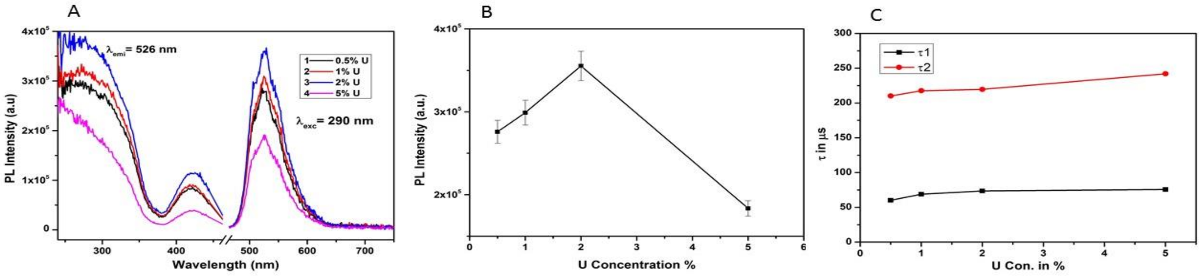

Fig 1 (A) Excitation and emission spectra of the U doped LTB systems, (B) Variation of PL intensity with increasing U concn., (C) Variation of life times with increasing U concn.

Fig 1 A shows the PL excitation and emission spectra for different concentration of U ion doped $Li_2B_4O_7$ glass.

The excitation spectra consist of a broad band around 290 nm and a small hump around 420 nm. The nature of the spectra suggested the stabilization of uranium in 6+ state. Maximum PL intensity was observed in 2 mol% of U ion concentration, then there was a decrease in intensity due to concentration quenching. The emission profile of uranium is directly related to the species. The first emission line or the zero-phonon line is observed to be present at 526 nm corresponding to UO_6^{6-}. Fig. 1C shows the variation of the two decay time data values with concentration. This is indicative of the fact that U exists in two different environments in the LTB matrix. Interestingly, even though there is concentration quenching of PL intensity and the life time values saturated after a slight increase initially.

Acknowledgements: Authors thank Group Leader, HP Unit, RLG, BARC; Head RPS(SF), HPD, BARC; Head HPD, BARC and Associate Director-RC&IG, BARC & Head, RCD, BARC for their unconditional help and support during the work.

Keywords: Lithium tetraborate, uranium doping, tissue equivalence, spectrophotometry

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Speciation of uranium in $LiZnPO_4$ (LZP): a potential ceramic host for nuclear waste immobilization

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$LiZnPO_4$ (LZP) has emerged as a potential ceramic host material for nuclear waste immobilization especially for its chemical and thermal stability. This allows the material to withstand high temperatures encountered during nuclear waste immobilization processes, such as vitrification or sintering without compromising the integrity over extended periods [1]. Further, LZP is capable to effectively accommodate a wide range of radioactive elements, including actinides and fission products, into its crystal lattice structure which is essential for preventing the release of hazardous radionuclides into the environment. Additionally, low leachability, radiation resistance, ease of fabrication, compatibility with nuclear waste streams earns the material much needed 'brownie points' among the other ceramic host competitors.

Uranium is one such actinide product which was doped in solid inorganic hosts, can exist in various chemical forms or species depending on factors such as oxidation state, surrounding environment, energetics etc. Understanding the speciation of uranium in solid inorganic hosts is crucial for assessing the stability, leachability, and long-term behavior of a particular radioactive waste form.

In this context, speciation of uranium in LZP host was investigated. The samples were prepared through a high-temperature solid-state reaction route at 1173 K at ambient condition as per the following chemical reaction.

$Li_2CO_3 + 2ZnO + 2(NH_4)_2HPO_4 \rightarrow 2LiZnPO_4 + 4NH_3 + 3H_2O + CO_2$

The samples were characterized by XRD, SEM, DLS techniques. Speciation studies of uranium were carried out using an Edinburgh FLS 1000 series time-resolved photoluminescence spectrometer.

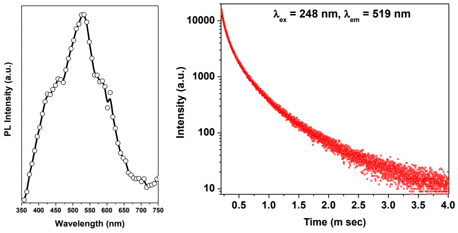

Fig 1 A and B: PL emission and decay time data for the U incorporated LZP host

XRD, SEM and DLS measurements confirmed the phase purity and the formation of homogenous sample with micron size particles. The DLS measurement was carried out to get an idea of the hydrodynamic radius or the average particle size of the syntheised samples. In case of a large variation in the particle size, a variation in the DLS measurements will be reflected. But in this case, the average variation was within +/- 20% range suggesting the formation of a homogeneous particle size sample. The emission profile of the 2% uranium doped LZP sample is shown in figure 1 A. As it can be seen, at least four maxima can be observed for the system at 460, 530, 590 and 610 nm with the maximum at 530 nm. This set of peaks is typical of uranium present in hexavalent state. However, unlike in solutions, uranium in 6+ state can exist in many forms in a solid matrix. It is well known that with 4,5 or 6 equitorial oxygen atoms, the position of the zero-phonon line shifts its position from 520 to 470 nm [2]. Here, in this case, based on the line position of the zero-phonon band, that is the band observed at 460 nm, it can be said that there are more than 5 and less than 9 oxygen atoms in the equatorial plane. Further confirmation about the species was achieved by the decay time measurements as shown in figure 1 B. This suggested a bi-exponential decay with life times of 200 and 320 microsec having 1:1 ratio. This value is relatively longer as compared to a tetrahedral uranate species like UO_4^{2-} and hence, the species was assigned as the octahedral hexavalent uranium that is – UO_6^{6-}.

Acknowledgements: Authors thank Group Leader, HP Unit, RLG, BARC; Head RPS(SF), HPD, BARC; Head HPD, BARC and Associate Director-RC&IG, BARC & Head, RCD, BARC for their unconditional help and support during the work.

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Stability of higher oxidation states of Americium in acidic medium: Effect of anions of mineral acid

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The Am^{3+} oxidation by $NaBiO_3$ in nitric acid is proposed way back in 1977 by Hara et al.,[1]. They have proposed rapid oxidation of Am^{3+} to higher-valent states (mainly AmO_2^{2+}) using $NaBiO_3$.[1] Rice et al.,[2] have also studied the oxidation of Am^{3+} to higher-valent states with $NaBiO_3$ in different acids, i.e. HNO_3, HCl, H_3PO_4 and acetic acid. The authors[2] have observed formation of different or mixture of oxidation state of Am in different acids. Quantitative formation of AmO_2^+ was seen in pH 1 HCl whereas, AmO_2^{2+} forms predominately in 1 M H_3PO_4.[2] Mixture of AmO_2^+ and AmO_2^{2+} was observed in 1 M acetic acid; however no oxidation of Am^{3+} is reported in HNO_3. Although, the possible scheme for the formation of AmO_2^+ and AmO_2^{2+} in acidic solutions in the presence of $NaBiO_3$ was reported, the stability of particular oxidation state in a given acidic media was not well understood. The authors[2] also suggested that a simple chemical equation (eq. 1) cannot be followed for Am^{3+} oxidation in HCl, where increasing acidic strength resulted in no observable oxidation of Am^{3+}.

$$3Am^{3+} + 3BiO_3^- + 10H^+ \leftrightarrow 3AmO_2^{2+} + 3Bi^{3+} + 5H_2O \tag{1}$$

The purity, stability or different side reactions of $NaBiO_3$ in the acidic media are suggested for the different reactions involving Am^{3+} oxidation in HCl, H_3PO_4 and HNO_3, but the experimental support in this direction was missing. The authors[2] have also reported enhanced stability of AmO_2^+ in HCl compared to that in the HNO_3 medium which was not well understood.

In the present work, we have carefully revisited the oxidation of Am^{3+} in different acid medium and the behaviors of the $NaBiO_3$ was also studied in the respective acidic solutions. Although, different mineral acids react differently with $NaBiO_3$, an increase in the initial pH was observed in all the cases. The highest pH variation was observed in the HCl medium (fig. 1). The treatment with different acids increased the pH to different extents either due to consumption of H^+ in the $Bi^{5+} \rightarrow Bi^{3+}$ conversion or due to the formation of different mineral phases containing Bi^{3+} (Fig. 1) The higher stability of the AmO_2^+ species in HCl was related to the poor disproportionation tendency of the former, whereas H_3PO_4 being a polyprotic acid behaved differently and stabilized AmO_2^{2+} by complexation.

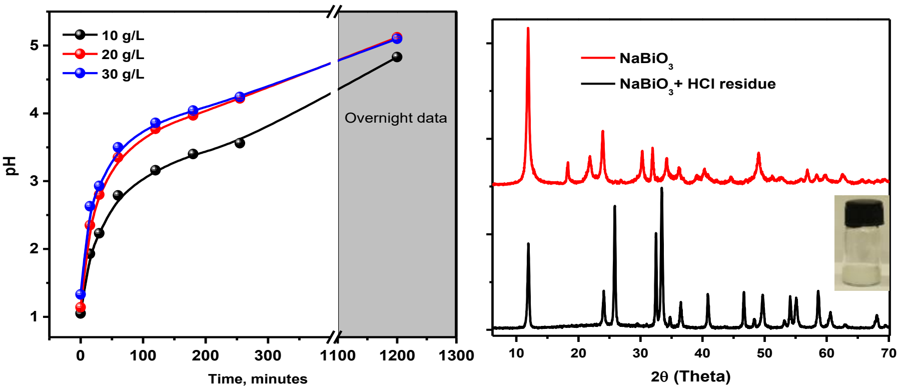

Figure 1. (a) The pH variation of $NaBiO_3.xH_2O$ (x= 2-3)-pH 1 HCl supernatant after equilibration at different solid to liquid ratio for different time intervals at 25 °C. (b) XRD of $NaBiO_3.xH_2O$ (x= 2-3) and the solid dried residue of HCl treated $NaBiO_3.xH_2O$ (x= 2-3), Inset: the color of the actual treated $NaBiO_3.xH_2O$ (x= 2-3)-HCl suspension before XRD.

Keywords: Am oxidation; sodium bismuthate, Am redox chemistry, Americyl ion, vis-NIR spectroscopy

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A novel complexant free method for Am oxidation to the pentavalent state for its effective separation from Eu and Cm

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The oxidation of Am^{3+} to its higher-valent states, i.e., AmO_2^{2+}/ AmO_2^{+} significantly changes its chemical properties leading to difference in its extraction, complexation, and migration behavior.[1] However, these changes coupled with the solvent extraction significantly eases the separation of Am from Eu^{3+} and Cm^{3+}as reported recently including the SESAME (Selective Extraction and Separation of Americium by Means of Electrolysis) process which are otherwise extremely difficult to separate by the conventional liquid-liquid extraction[2] using ligands relying on softer nature or size-based separation. Owing to the higher redox potential of $Am^{3+} \rightarrow AmO_2^{+}$ and $Am^{3+} \rightarrow AmO_2^{2+}$ couple direct electrochemical oxidation in aqueous medium is not feasible and suitable ligand-modified electrodes have been employed to do the task.[3] In principle, Am^{3+} can be oxidised to either AmO_2^{+} or AmO_2^{2+} to achieve efficient separation from other trivalent lanthanide or actinides. The higher redox potential for the Am^{3+}/ AmO_2^{+} couple compared to that of the Am^{3+}/ AmO_2^{2+} couple makes the former difficult but is advantageous if achieved. This can help in the better Am-Cm or Am-Eu separation due to the lower charge density of AmO_2^{+} compared to AmO_2^{2+}. Although both the AmO_2^{+} and AmO_2^{2+} ions have a linear geometry, the lower charge density of AmO_2^{+} makes its extraction or uptake difficult and hence, can be exploited in achieving better Am-Cm/Lns separations. Most of the literature reports for Am-Cm/Eu separation oxidizes Am^{3+} to AmO_2^{+} using $Na_2S_2O_8$ along with hypochlorite and Ag^{+} salts.[4] These reported mediums are complexing and interfere with the further separation of Am from other lanthanides or actinides.

The $AgBiO_3$ is reported for the first time for the exclusive oxidation of $Am^{3+} \rightarrow AmO_2^{+}$ under controlled chemical conditions at 25°C in a non-complexing medium (**Fig. 1**). Am-Eu and Am-Cm separation in a single contact with a separation factor $>10^4$ was achieved using $Am^{3+} \rightarrow AmO_2^{+}$ oxidation by the present method.

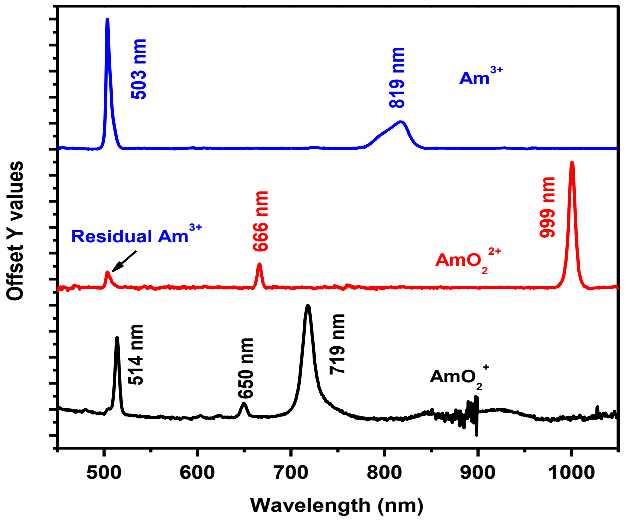

Figure 2. UV-vis spectrum of Am in different oxidation states; Am^{3+} (0.1 M HNO_3), AmO_2^{2+} (oxidation by $NaBiO_3$ at 0.1 M HNO_3), AmO_2^{+} (oxidation using $AgBiO_3$).

Keywords: Am oxidation; silver bismuthate, Am redox chemistry, vis-NIR spectroscopy

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Spectrophotometric Studies on Americium oxidation by sodium bismuthate and its stability in acidic solutions

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The mutual separation of trans-plutonium actinides (Ans) from lanthanides (Lns) or adjacent Ans is challenging as they exhibit great chemical similarity due to similar valence states and comparable ionic radii in aqueous acidic solutions. Selective Am oxidation-based separation strategies gives very high separation factors compared to those reported by the liquid–liquid extraction studies using soft donor ligands. Zsabka et al.,[1] have given a comprehensive overview of the hydrometallurgical chemical processes for Am separation from either Cm or lanthanides. Am oxidation-based separation strategies were recently reported by Wang et al., for Am-Cm and Am-Eu separation with separation factor $>10^4$.[2, 3]

Although, sodium bismuthate ($NaBiO_3$) based Am oxidation in HNO_3 is being studied from decades and still remains a preferred choice for Am-Cm or Am-Lns separation, the oxidation mechanism by $NaBiO_3$ in acidic medium is not well understood. In the present study we have revisited Am^{3+} oxidation by $NaBiO_3$ in acidic media. The XRD of pristine and acid treated $NaBiO_3$ (**Fig. 1(a)**) suggest loss of crystallinity after acid treatment. The equilibration of Am^{3+} with $NaBiO_3$ shows quantitative conversion of Am^{3+} to AmO_2^{2+} at pH 1 (HNO_3). The reduction of AmO_2^{2+} to Am^{3+} and AmO_2^{+} was followed spectrophotometrically following absorbance at 503 nm for Am^{3+} and 716 nm for AmO_2^{+}, respectively. The AmO_2^{2+} reduction in the HNO_3 medium is quite complicated due to the occurrence of several redox equilibrium simultaneously.[4] A careful investigation suggested that AmO_2^{2+} was probably converting to both Am^{3+} and AmO_2^{+} with time; however, AmO_2^{+} converts primarily to Am^{3+} **(Fig 1(b)-(d))**. The rate of conversion of AmO_2^{2+} to its lower oxidation state at 25°C suggested reasonably good stability of AmO_2^{2+} for >2 h before getting reduced to AmO_2^{+}**.**

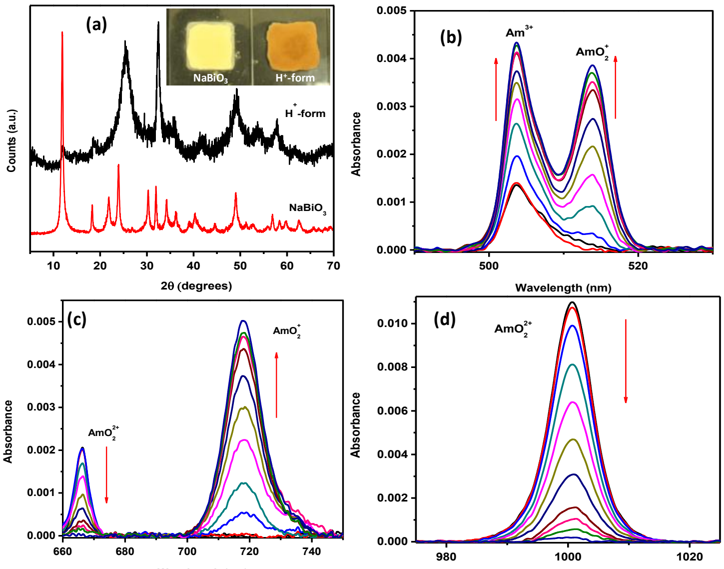

Figure 3. a) The color change and XRD of pristine (color: yellowish) and acid treated (H+-form, color: brownish)$NaBiO_3$; b-d) the spectra evolution in the Am^{3+}, AmO_2^{+}, AmO_2^{2+} regions with time after equilibration and separation from $NaBiO_3$ at pH 1.

Keywords: Am oxidation; sodium bismuthate, interlayer ion exchange; redox chemistry, vis-NIR spectroscopy

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Thermodynamic Complexation Studies of N-(2-acetamido) iminodiacetic acid with U(VI)

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Owing to the presence of multiple strongly binding functional groups, amino carboxylates have been extensively used for sequestration, decontamination and decorporation of actinides [1,2]. In order to understand the effect of N-(2-acetamido) functionality of iminodiacetic acid on its complexation strength with actinides, a systematic study on thermodynamics of complexation of N-(2acetamido) iminodiacetic acid (ADA) with U(VI) has been carried out. In addition, N-(2-Acetamido)iminodiacetic acid (ADA) is used for cell culture work and for other biochemical studies due to it's nontoxicity to biological systems [3]. Further, the ligand can be evaluated for decorporation of U(VI) owing to the reported biocompatibility of ADA.

In the present work speciation and stability constants (log K) for U(VI)-ADA complexes were determined by potentiometry and further confirmed by UV-Visible spectrophotometry. Further the energetics of complexation was determined by calorimetry. The ΔG and ΔS for U(VI)-ADA complexes were calculated using Gibb's free energy equation. The ADA showed three protonations in the given experimental conditions. Potentiometric titrations were carried out to know the speciation and stability constant values for the species formed during the complexation. The ADA forms ML_1, and ML_2, type of complexes with U(VI) with log K values 6.45 and 5.25 for respectively (Fig.1). The speciation and log K values were further confirmed by UV-Visible spectrophotometry and the obtained values are in good agreement with values obtained by potentiometry (Fig.2). Although the log K values for U(VI)-ADA are lower than the Th(IV)-ADA system. However, the log K values are showing the reasonably good stability of U(VI)-ADA complexes. The calorimetry studies gave information about the heat changes during complexation and also about the mechanism behind the complexation of ADA with U(VI). The complexation reactions were found to be exothermic in nature and favored by both entropy and enthalpy with ΔH_1 and ΔH_2 -10 kJ/mol and -17 kJ/mol respectively. The obtained thermodynamic parameters ((log K, ΔG, ΔH, ΔS) for U(VI)-ADA system were compared with complexation of U(VI) with other similar type of IDA based ligand to evaluate the role of acetamido functionality on complexation with U(VI). As revealed by thermodynamic studies, ADA forms aqueous soluble strong complexes with U(VI) and can be further studied biologically for decorporation of U(VI).

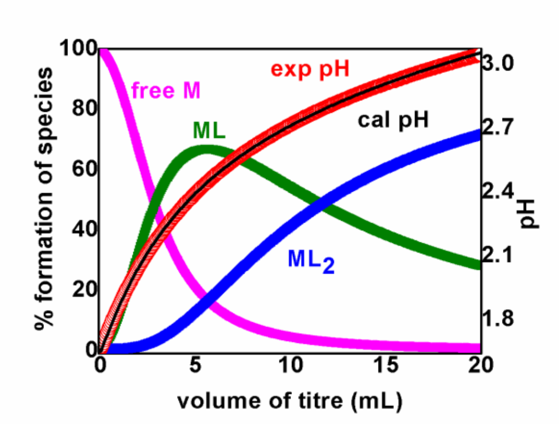

Fig. 1: Speciation of U(VI)-ADA by potentiometry

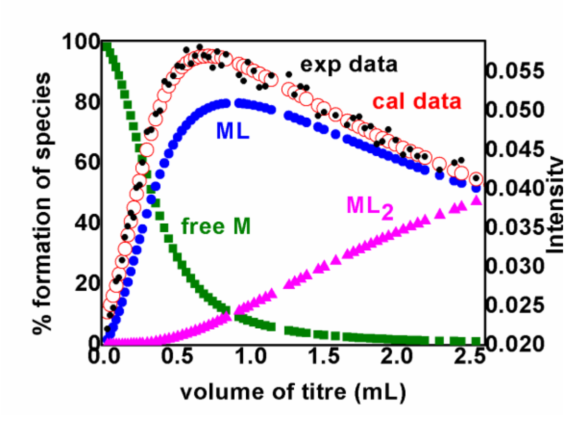

Fig. 2: Spectrophotometric studies of U(VI)-ADA complexes

Keywords: Uranium, Thermodynamics, Complexation, Calorimetry, Spectrophotometry

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Redox speciation of Uranium with Graphyne modified electrode in aqueous medium

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In recent years, carbonaceous based 2D materials have been highly explored as electrode materials by the researchers specially graphene due to low cost, light weight, high conductivity, and ease of preparation and tuneability. Although, graphyne is man-made carbon allotropes having layered 2D structure, the presence of unique structural and physical properties make it fascinating material. It possesses high conductivity owing to special arrangement of sp-sp^2 in its skeleton structure, where one acetylenic group (-C≡C-) is sandwiched between two sp^2 carbon of benzene rings and all the sp^2 carbon of benzene linked with sp carbon of acetylene, thus give rise to a radial star like structure which is very rich in conjugated π-electron, and high surface area with nanoporosity etc [1]. The theoretical application of graphyne has been reported but experimental based application still not reported yet. As we know uranium +VI is extremely soluble in aqueous media, highly toxic, and hazardous to living organism and may cause serious health issues. It released in the environment, specially, in aquatic sysyem through various anthrapogenic activities, such as mining and miling process etc. Therefore, detection, and speciation of uranium is very essential to avoid its adverse effects. Uranium possesses variable oxidation state ranging from +III to +VI which made it highly sensitive towards the redox speciation. It has great tendency to form complex with other compound having π-electron or some functional groups like hydroxyl group and their stability mainly depends on physiochemical parameters like pH, concentration etc. However, detection and speciation of uranium in aqueous media is very crucial on tracer level. Thus, we have found an electrochemical technique which is highly potent and feasible method owing to their great sensitivity (10^{-1} to 10^{-12} M), selectivity, and reproducibility for metal ions detection and monitoring its oxiadation state. Gaining information about redox speciation of uranium is highly challengeing at its trace level using conventional electrode because of slow redox kinetics [2, 3]. Herein, we design and develop an electrode by fabricating with graphyne to monitoring and studying the redox speciation of uranium in aqueous phase. The cyclic voltammetry [Fig. 1(a)] was used to redox energetics and kinetics parameters of uranium at Graphyne@GC electrode. The graphyne modified electrode shows notable peaks current response in differential pulse voltammetry (DPV) plot in the pH range from 1 to 4.6 and maxium current intensity is at pH 2. This results might be because of unique arrangement of sp-sp^2 π-electron in the sheet structure of graphyne. The detection limit for the present electrode for understaning speciation of uranium is $(4.04\pm0.04)\times10^{-10}$ M. The appreciable response of modified electrode towards the various uranium aqueous solution make it potential candidate for understaning the speciation and detection of uranium. The FTIR [Fig. 1(b)] illustrate the presence of Uranium peaks at 922 and 950 cm^{-1} confirmed the physical adsorption of uranium at Graphyne surface.

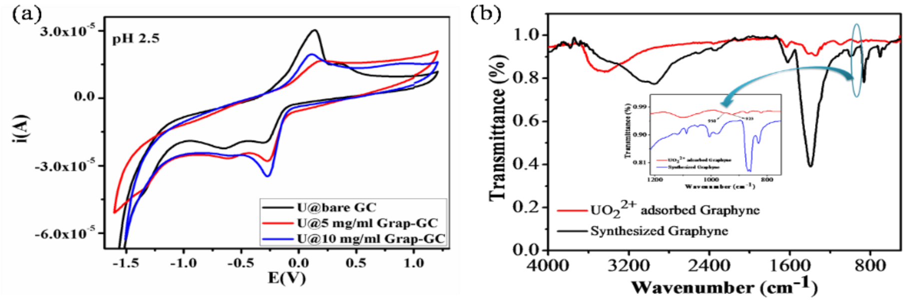

Figure 1: (a) Cyclic voltammetry (CV) plot for uranium redox speciation at bare GC and Graphyne@GC electrodes, (b) The FTIR spectra the presence of uranium

Keywords: *Electrocal redox speciation; uranium aqueous solution; modified electrode; metal detection*

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Probing molecular speciation of uranium in Ethaline

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In the framework of non-aqueous solution, deep eutectic solvents (DESs) have emerged as a neoteric green and sustainable solvent of 21st century with unique salvation potential and tuneable physicochemical properties. Deep eutectic solvents (DESs) were synthesized by combination of a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD) and the resultant mixture has the melting point lower than their individual components[1-2]. The combined eutectic mixture is environmentally benign and hence could be an alternate option of non-aqueous processes for reprocessing of spent nuclear fuel. One of the key questions when considering the reactivity of a metal in a DES is the species that form upon dissolution. Speciation of actinides in solution controls their reactivity and is essential aspects for understading their solubility, complexation potential, redox poptential and electrochemical behaviorare. In addition, due to their inherent ionic conductivity and excellent solubilizing properties, the DES solvents are being projected as novel electrolytic media.

Uranium being a nuclear material, it is important to understand its speciation in DES. In literature the speciation actinides in DES is limited. One of the most widely studied DES is based on choline chloride and ethylene glycol in 1:2 mole ratio (commonly known as ethaline), and this DES solvent was our choice of study for uranium. Studies included the complexation of ethylene glycol and choline chloride (individually) with uranyl perchlorate (in 1 M $NaClO_4$) so as to understand the speciation in DES with the support from EXAFS and FT-IR spectroscopy.

Uranyl nitrate or perchlorate salt was freely soluble in the DES. However, UO_3 could be dissolved by sonication. As confirmed by FT-IR and absorption spectroscopy, the uranium existed predominantly as UO_2^{2+} species in the present DES. Dissolution of UO_3 in the present DES indicated its probable complexation with the DES moiteis (ethylene glycol or chloine chloride). Individual complexation of chloine chloride and ethylene glycol with uranyl ion indicated the formation of UO_2/L species with both the ligands (Fig. 1). The formation constant with chloine chloride (0.23±0.01 mol^{-1}) was lower than those observed with ethylene glycol (0.46±0.01 mol^{-1}). The EXAFS studies [Fig. 1(c)] indicates the coordination modes of uranium is six, which is associated with the two axial oxygens and four chloride at the equatorial position. The DFT calculation provides the optimized structure along with bond lengths, coordination number, and Gibbs free energy and corroborates the experimental findings.

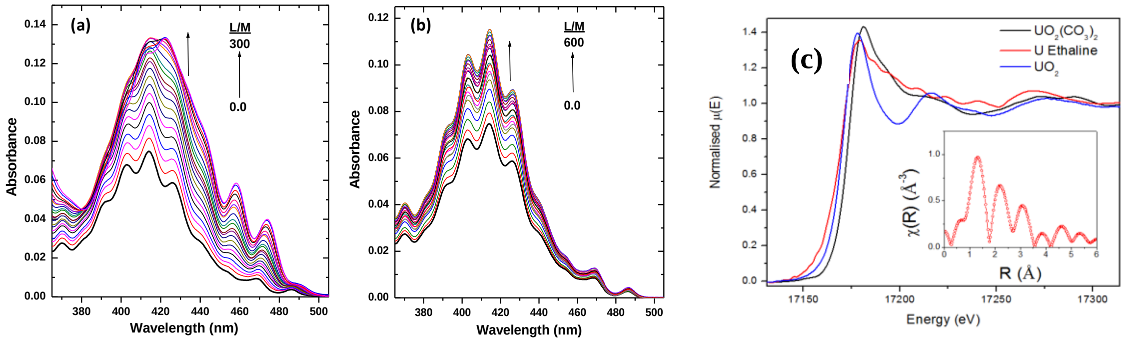

Fig.1. Spectrophotometric titration of $UO_2(ClO_4)_2$ with Choline Chloride (a), and ethylene glycol (b). Cuvette: 10 mmoles/L $UO_2(ClO_4)_2$in 1 M $NaClO_4$(1.5 mL); Titrant: 5.2 M Choline Chloride / 1 M $NaClO_4$or 10.3 M Ethylene Glycol (pure) (c) the EXAFS data of Uranium in Ethaline DES.

Keywords: *Deep eutectic solvents, Ethaline, Speciation, Uranium matrices*

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Bonding details of $K_4Pu(SO_4)_4.2H_2O$ solid

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In the Actinides series, *5f* electrons from thorium to neptunium show an "itinerant" or "delocalized" character, causing themselves available for covalent bonding.[1] By contrast, from americium to lawrencium they are more localized. Plutonium stands at the limit between the two behaviours. The crossover of the *5f* and *6d* frontier orbitals on the energy scale causes the rich redox and coordination chemistry of the actinides. Chemical trends within the periodic table have frequently been used as guides for predicting reactivity, structure and electronic properties of the elements. The periodic decrease in the metal-ligand bond length observed in the structural studies of the binary tetravalent oxides and halides of the actinides allowed Seaborg to propose his actinide hypothesis and actinides series as a separate group of elements in the periodic table. Ce and Pu crystallize in the α and β phases of $M(SO_4)_2(H_2O)_4$ and the complexes of $K_8M(SO_4)_8(H_2O)_5$ [M ≡ Ce, Pu] are isostructural. Besides these complexes, the profound similarity between other complexes of Pu(IV) and Ce(IV) with sulphate anions poses question if this indicates the localized nature of *5f* orbitals.[2]

In the present study, $K_4Pu(SO_4)_4.2H_2O$ salt was synthesized and analyzed using XAFS for the local structure around Pu(IV). Further, LDA based DFT simulations with spin – orbit coupling was carried out for Pu L_3 edge ($2p_{3/2} \rightarrow$ nd excitation; 18057 eV) XANES to delineate the (electronic) bonding characteristics. The Self-consistency cycle was run without core-hole in view of strong screening effect of the valence electrons.[3] This single – electron approach was carried out over a cluster of 114 atoms. Matching with the single crystal data reported for this compound,[4] the EXAFS based local structure of the plutonium sulphate salt was described by Pu-O and Pu-S backscattering shells at phase-corrected radial distances of 2.32 and 3.17 Å, respectively (Fig. 1). The XANES simulation (Fig. 2) matches the experimental data except in the splitting of the above edge features (30 - 60 eV). Different core-hole option and the role of periodic structure are being explored to reproduce this splitting. This splitting is attributed to strong excitonic effects in these correlated systems. In the interim result, it is obvious that 6d orbital contributes significantly in the bonding characteristics.

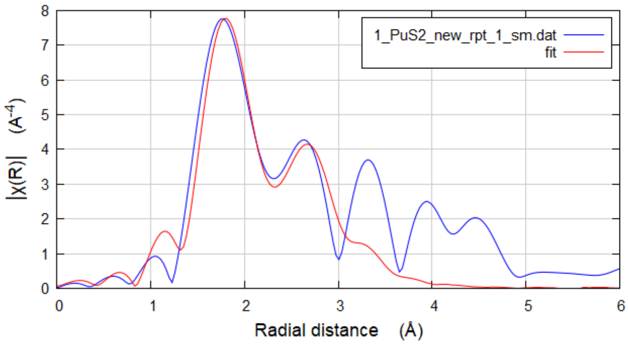

Fig. 1. Fourier transformed EXAFS spectra and simulation of $K_4Pu(SO_4)_4.2H_2O$

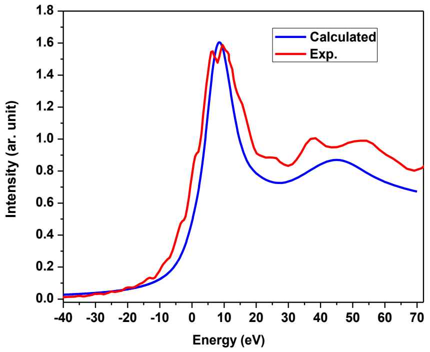

Fig. 2. Experimental and simulated Pu L_3 XANES spectra of the $K_4Pu(SO_4)_4.2H_2O$

Keywords: Plutonium, Sulphate, EXAFS, XANES, Electronic Structure

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Facility Development for X-ray Absorption Fine-Structure Spectroscopy Study of Radioactive materials, Indus-2 Synchrotron, India

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Coordinative and electronic details of actinides and important fission products are important information in regard to radionuclides sorption, separation and speciation studies. Synchrotron radiation based X-ray Absorption Fine Structure (XAFS) Spectroscopy studies are uniquely placed among spectroscopic techniques to delineate the local structure of the probe atom, be it in solid, liquid or gaseous state. Indus-2 synchrotron facility at RRCAT Indore hosts Scanning XAFS technique at beamline BL-09 in the X-ray energy range of 5 - 20 keV. To extend the capability of this beamline to actinides and important fission products, an experimental facility incorporating a glove box, exhaust facility and radiation monitoring systems has been developed by Radioanalytical Chemistry Division in collaboration with RRCAT authority. Unique capabilities of the other divisions of BARC were made best use to complete this project.

A brief scheme of the facility is as follows: The exhaust line starts from the glove box and ends at the top of the Indus-2 experimental hall employs charcoal filters, valves and HEPA filter bank. The blowers clubbed (in redundancy mode) in the exhaust line ensures one inch negative pressure of the 0.5 m × 0.5 m × 0.5 m sized glove box during the experiment. The glove box is equipped with solenoid valves at the inlet and outlet sides to ensure the negative pressure by their opening – closing as per the requirement. The box has a cubical 15 cm × 15 cm × 15 cm box having 8 cm diameter kapton window for aligning the box with the Synchrotron X-ray beam. This cubical will contain the sample at the centre position during the measurement. No direct sample handling is permissible at the experimental station, therefore samples need to be prepared at the parent laboratory and be transported to experimental station. Continuous air monitor present in the experimental hutch as well as clubbed to the final air release point ensures non-contaminated working environment.

With the AERB approval for the developed facility, with an aim to hot commission the facility an experimental run was carried out during 16 - 23 February 2024 during which XAFS (Pu L_3 edge; 18507 eV) measurement of Pu – 239 carrying solids samples - $Pu^{IV}O_2$(am), $K_4Pu^{IV}(SO_4)_4$ and $K_4Pu^{VI}O_2(CO_3)_3$ - were carried out in fluorescence mode of measurement. Representative spectra for the samples are shown in Figure 1. Facility was found satisfactory on all safety guidelines and operational requirements for many-days experimental run. The facility is thus successfully commissioned and will be available for collaborative work with RACD.

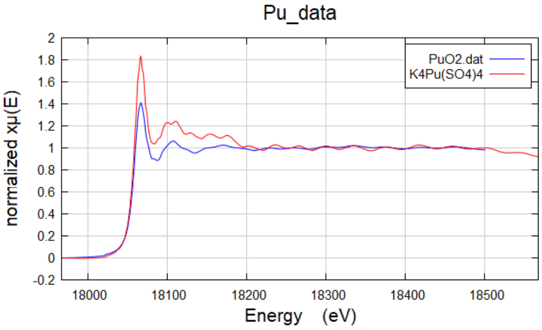

Fig. 4. Normalized XAFS spectra of Pu(IV) solids

***Keywords**: XAFS, Actinides, Fission Products*

Acknowledgement: Authors acknowledge the support and guidance provided by Dr. B. S. Tomar (RC & I G), Dr. P. K. Pujari (RC & I G), Dr. S. Kannan (RC & I G), Dr. S. K. Jha (BDS, BARC), Dr. R. D. Makde (BDAS, BARC), Dr. Saurabh Mukherjee (RCD), Shri T. C. Patil (HLU & ESS, RLG), Shri P. Nagaraju ((HLU & ESS, RLG), Shri R. K. Bhatt (BDAS, BARC), Shri B. K. Sahu (BDAS, BARC), Dr. Arnab Sarkar (FCD, BARC).

Solvation of spherical anions in alkaline medium: XAFS Study

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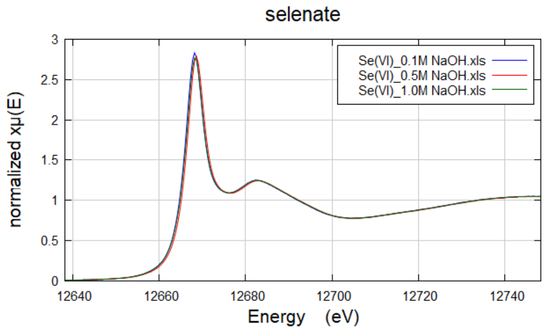
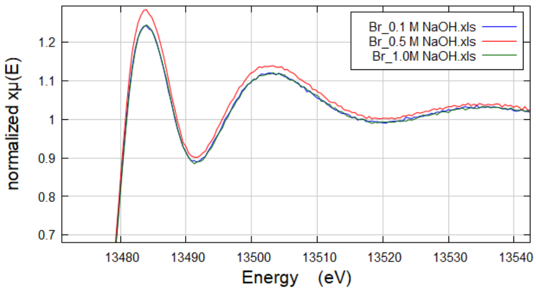
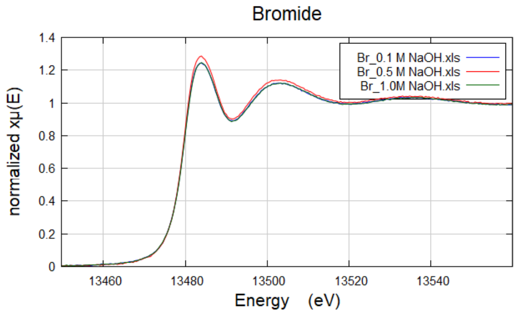
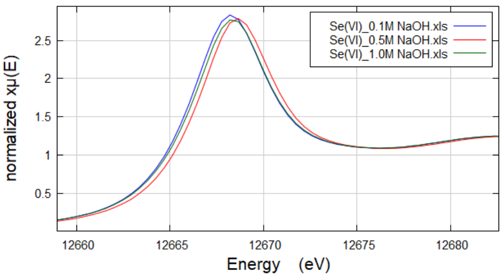
Anion recognition is pertinent to a range of environmental and industrial applications with regard to their efficient and selective estimation. Recent progress in this area has relied on advances in design of synthetic hosts incorporating a broad range of recognition motifs capable of effective binding. However, performance suffers a critical challenge in respect to the solvent effect. Understanding the effects of bulk and local solvent structure around anions is therefore the first step in delineating the role of solvents in effective and selective determination. In the present study XAFS studies of spherical anions, bromide and selenate, in NaOH medium (0.1 -1 M) was investigated at Se & Br K-edge with the presumption that increasing strength of the NaOH medium will disrupt H-bonding of the bulk aqueous medium and thereby the local solvation structure will vary. While EXAFS features were same for the both the anions in all the studied NaOH medium, there is steady high energy shift of the XANES features for selenate ions over 0.1 to 0.5 M NaOH. Beyond 0.5 M features starts to reverse back. Intensity decrease at the white line has been observed by Eklund and Persson (2014) with hydrogen ion association in the selenate ions (selenate – hydrogenselentate species) with no shift in spectral feature while energy shift to higher energy for the white line maxima was observed with the increasing formal charge on the selenium atom. For bromide ions energy shift in the Br K-edge was not noticed, rather similar pattern (reversal beyond 0.5 M NaOH) was noticed in terms of features intensity. Further, unlike bromide ions high unoccupied density of states near fermi level was observed in case of selenate ions. These studies clearly indicate subtle role of changing H-bonding in the electronic structure of the studied ions with the changing NaOH concentration.









Keywords: Selenate, Bromide, XANES

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Oxidative influence of Manganese in the adsorption of selenite oxyanion on doped hematite

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In the fate and migration of radionuclides in environment, their interactions with solid surfaces are very critical in immobilizing/mobilizing them. Nanosized inorganic particles in the aqueous medium have been reported to adsorb the radionuclides and contribute in their long range movement. As the nanoparticles are being synthesized as a result of the changing chemical conditions of the groundwater, observation of defects containing solid particles is general one. Extrinsic defects – formed on dopants presence in the solids - and intrinsic defects owing to missing cation/anion from stoichiometric ratio in the solids create the adsorption sites with interesting adsorption characteristics.[1] In the present study, role of Mn doping in hematite (Ht) matrix was evaluated towards the selenite adsorption using batch adsorption and electrochemical investigations. This study is important in view of the co-presence of various iron oxides with Mn dopant in environment. Ht and Mn-doped- Hematite (Mn-Ht) was synthesized using a precipitation method: Ferric nitrate (with Mn when Mn-Ht being synthesized) was hydrolyzed with KOH in presence of $NaHCO_3$ and the hydrolyzed mass was aged at 95 ^{0}C for 4 days. The XRF based composition of the Mn-Ht mass was determined to be ~ $Fe_{1.71}Mn_{0.29}O_3$, wherein Mn is mainly in (II) oxidation state, and thus carrying oxygen vacancy in the matrix. XRD measurement showed single phase formation of Mn-Ht with Fe(III) substitution in the matrix. In an interesting observation of kinetics profile of selenite (SeO_3^{2-}) adsorption, unlike the strong adsorbing character of Ht there was observed strong non-adsorbing characteristics on Mn-Ht (Fig. 1). It is postulated that surface induced oxidation reaction in the interfacial layer of case of Mn-Ht takes place which converts adsorbed selenite species to selenate and as this species has very small adsorption on hematite surfaces, they desorbed out to the aqueous behaviour. To prove this postulate, electrochemical investigation was carried out. Fig. 2 indicates oxidative peak at 0.51 V in cyclic voltamogram (CV) obtained with Mn-Ht deposited on glassy carbon electron which is totally absent with the Ht solid. The origin of the oxidative action of Mn-Ht was found to be in lowering of band gap with respect to Ht (2.0 to 1.8 V) which causes surface presence of photoholes to oxidize the surface adsorbed selenite species. This study establishes the migration facilitative role of dopants towards environmental contaminants.

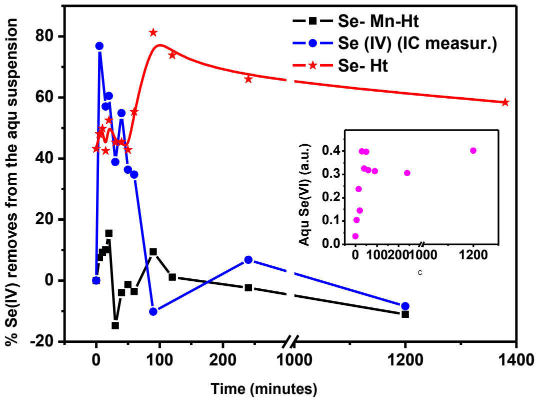

Fig. 1. Selenite adsorption kinetics on Ht and Mn-Ht

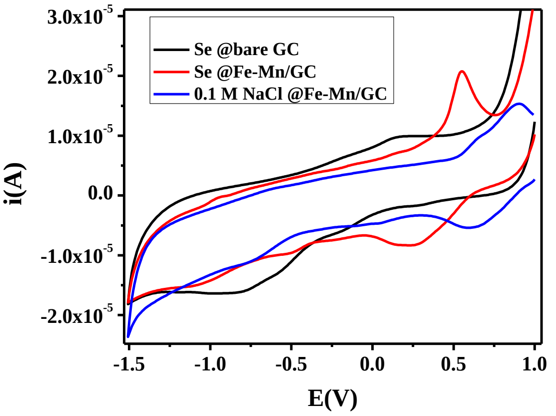

Fig. 2. CV study of selenite ions on Ht and Mn-Ht

Keywords: Hematite, Manganese, Selenite, Oxidation, Adsorption

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Luminiscent probing on speciation of Uranyl with Phosphonocarboxylate in aqueous medium

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Aqueous speciation of uranium with environmentally relevant ligands such as phosphonocarboxylate is essential to understand its migration behavior in geo-, chemo-, hydro-sphere [1-2]. Phosphonocarboxylate (PC) is important environmentally relevant hetero-bifunctional chelator which contains carboxylate and phosphonate organic moieties to bind metal ions [2] with higher stability. Since, the uranyl ion is very prone towards hydrolysis, a very sensitive technique is required for probing its solution speciation. Luminescence spectroscopy is inherently sensitive to work at low metal ion concentration and it provides the direct information about the the life time of the all possible species of metal-ligand complexation process. Because of its unique characteristics, the luminescence spectroscopy technique was used to understand the complexation of uranyl with three PCs which are differing in -CH2- spacer. The excitation at λ_{em} 534 nm and emission at λ_{ex} 261 nm was chosen for UO_2^{2+}. The fluorescence spectra of UO_2^{2+} (1 mM) with all three Phosphonocarboxylate ligands were measured by their successive addition in pure aqueous solution of UO_2^{2+} at I =1 M $NaClO_4$ and have conferred in Fig. 1. The observed emission bands correspond to the electronic transition S11→ S00 (473 nm) and S10→S0ν for ν= 0-4 (488, 510, 535, 560 and 587 nm). As evident from results, with PAA and 3-PPA the peaks intensity having the proportional relation with the added ligand concentration while reverse behavior in peak intensity was observed in case of PFA. It reflects that PFA having quenching effect over other two Phosphonocarboxylate ligands [PAA and 3-PPA]. The quenching of UO_2^{2+} peak intensity through PFA ligand might be due to absence of alkyl moiety –(CH_2)- (as n=0) between two functional groups and formation of compact/rigid 5-membered ring chelation with UO_2^{2+} moiety. The λ_{max} values reveal that bathochromic shift of UO_2^{2+} emission with PAA and 3-PPA. These shifts ([Δλmax]PAA = 8.53 nm & [Δλmax]3-PPA = 8.96 nm) in λ_{max} attributed the complexation of UO_2^{2+} with PAA and 3-PPA. In case of PFA small blue shift ($\Delta\lambda_{max}$ = 0.51 nm at λ_{max} =539.49 nm) was observed in UO_2^{2+} emission with the quenching effect. This also indicates the complexation of UO_2^{2+} with PFA. The logβ value of UO_2^{2+}-PC found to be 12.20±0.05. Stern-Volmer (SV) plot of fluorescence quenching of UO_2^{2+} (at λ_{max} =539.49 nm) by PFA has linear relationship between I_0/I and concentration of ligand. From the slope of SV plot the value of quenching constant value was found to be 4.26×10^2 M^{-1}. Time correlated single photon counting (TCSPC) was used to establish the emissive lifetimes of UO_2^{2+}-PC complexes by fitting the raw data obtained from the spectrometer with an iterative program. The decay profile of UO_2^{2+} in presence of PC have presented in Fig. 2. All the decay time curves showed the biexponential fitting and the respective lifetimes values of uranyl complex are 97.06 µS, 74.26 µS, and 93.7 µS for PFA, PAA, and 3-PPA, respectively. The biexponential behavior indicates presence of two species which could be due to existence of uncomplexed and complexed UO_2^{2+}.

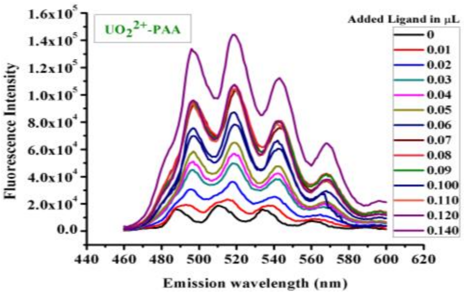

Fig. 1: Variation of D values with acidity of Pu extraction

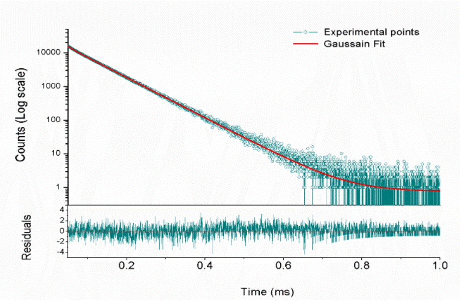

Fig. 2: Kinetic data for Pu extraction

Keywords: *Aqueous, Speciation, Phosphonocarboxylate, Luminiscence*

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Cesium sorption on Geopolymers

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Geopolymers are being explored as cost effective and eco-friendly sorbents for the removal of toxic metals from wastewater [1]. The present work is an exploratory study regarding the use of geopolymers for the management of nuclear waste. Geopolymers, GP1 and GP2, were synthesized using fly ash and blast furnace slag as aluminosilicate source. Characterization of synthesized geopolymers encompassed the determination of mineralogical composition, elemental composition, surface area, cation exchange capacity, morphology identification of characteristic vibrational bands and determination of dissolved metal ions from geopolymer matrix. Cesium, one of the high yield (~ 6%) long lived fission products (^{137}Cs = 30 y; ^{135}Cs = 2 x 10^6 y), has been chosen to evaluate the retention behavior of geopolymers, GP1 (FA: BFS = 70:30) and GP2 (FA: BFS =60:40).

Kinetics of Cs sorption on both GP1 and GP2 was found to be rapid and equilibrium was attained within 2 h. Sorption of Cs on geopolymers was found to be independent of pH while it decreased with increase in ionic strength, thereby signifying ion-exchange as the dominant mechanism for Cs sorption. The free energy of sorption, calculated using D-R isotherm, has been found to be 11-12 kJ mol^{-1} which also suggests ion exchange as predominant mode of Cs sorption on geopolymers. The adsorption isotherm of Cs on GP1 and GP2 exhibited linearity in the entire Cs concentration and temperature range investigated in present studies. Freundlich model gave better fit as compared to Langmuir model which indicates that sorption process can be regarded as multilayer.

The present results seem to be promising with regard to the sorption characteristics of geopolymers towards Cs. However, for thorough assessment of geopolymers, sorption other relevant radionuclides need to be studied.

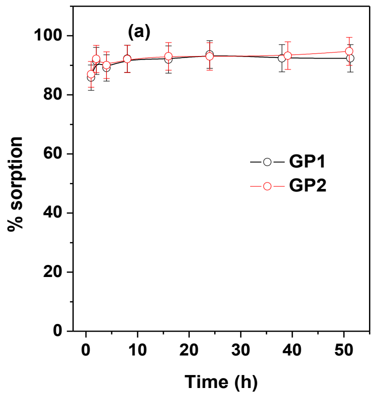

Fig. 1: Kinetics of Cs sorption on GP1& GP2; [Cs] = 4.2x 10^{-10} M, pH = 9.5 ± 0.2, Ionic Strength = 0.001 M.

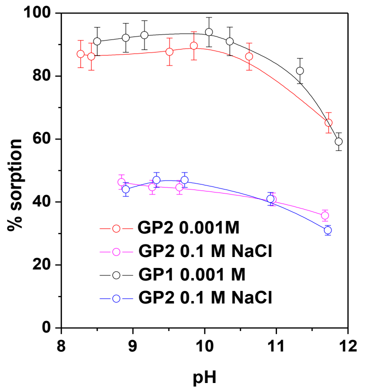

Fig. 2: Cs sorption on GP1 & GP2, as function of pH; [Cs] = 4.2 x 10^{-10} M.

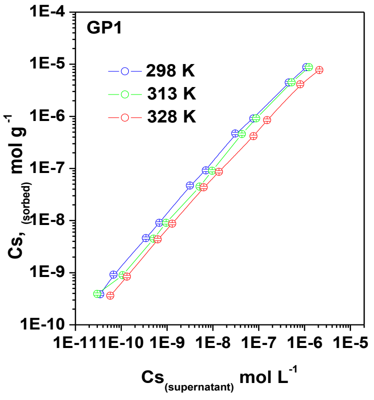

Fig. 3: Adsorption Isotherms of Cs on GP1. [Cs] = 4.2 x 10^{-10} M, pH = 9.5 ± 0.2, Ionic strength = 0.001 M

Keywords: Sorption, Cesium, Geopolymers

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Retention characteristics of bentonite of Jhilmil Region towards radionuclides

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Bentonite is one of the most preferred buffer / backfill materials for deep geological repository for disposal of nuclear high level waste worldwide [1]. In Indian context, bentonite of Jhilmil Region is being evaluated as prospective buffer /backfill. In the present study, sorption of Am(III) onto Jhilmil bentonite has been studied as function of time, pH, ionic strength and [Am(III)] and modeling of Cs(I) sorption profiles onto Jhilmil bentonite has been carried out. Sorption equilibrium of Am(III) (~10^{-9} and 10^{-5}) is attained within ½ hour. The pH variation studies at two different ionic strengths (IS = 0.01 M, 0.1 M) (Fig. 1) studies shows that log K_d for Am(III) is almost independent of pH in the entire pH range. The effect of ionic strength at two different [Am(III)] (~10^{-9} and 10^{-5}) demonstrates that Am(III) sorption decreases drastically at low pH (2,4) thereby confirming ion exchange as dominant sorption mechanism for Am(III). Am(III) sorption is found to be independent of ionic strength for pH 6,8 indicating that surface complexation is the dominant sorption mode at higher pH (Fig. 2). Modeling of Cs(I) sorption profiles at varying pH and [Cs (I)] was carried out by considering two ion exchange sites. Frayed edge sites (FES) were found to have major contribution towards Cs(I) sorption at low [Cs(I)] (< 10^{-7} M) while conventional ion exchange sites played a dominant role at higher [Cs(I)]. Fig. 3 shows the experimental and modeled Cs(I) profile along with the contribution of each ion exchange sites. Thus, present studies show that owing to higher sorption capacity, the bentonite of Jhilmil region is capable of retarding the migration of radionuclides.

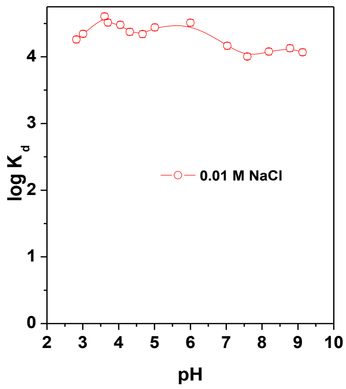

Fig. 3 Effect of pH on Am(III) sorption by Jhilmil Clay

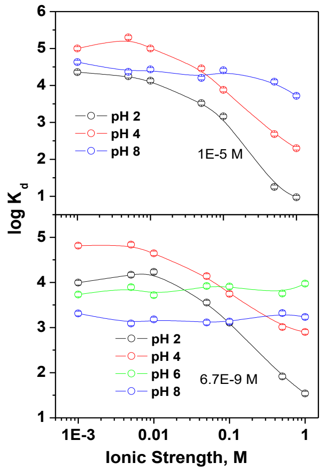

Fig. 2 Effect of ionic strength on Am(III) sorption by Jhilmil Clay

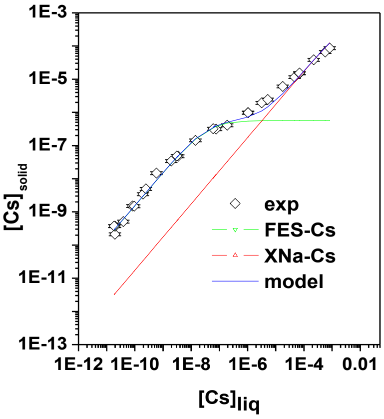

Fig. 3 Modeling of Cs adsorption isotherm using two ion exchange sites

Keywords: Sorption, Americium, Cesium, Jhilmil Clay

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Uniqueness of Nanoscale Confinement for Fast Water Transport and Prospective of Sea Water Desalination

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Immobilization of High Inspired by the enhanced water permeability of carbon nanotubes (CNTs), molecular dynamics simulations were performed to investigate the transport behavior through nanotubes made of boron nitride (BNNT), silicon carbide (SiC), and silicon nitride (SiN) alongside carbon nanotubes (which have different hydrophobic attributes) considering their implication for reverse osmosis (RO) membranes under different practical environments. According to our findings, not only do CNTs but also other kinds of nanotubes exhibit transition anomalies with increasing diameter. Utilizing the robust two-phase thermodynamic (2PT) methods, the current examinations shed light on thermodynamic origin of favorable water filling of these nanotubes. The results show that regardless of the nanotube material, the filling of water inside small nanopores (d < 10 Å) as well as within pores of diameter larger than 15 Å will always be favored by the entropy of filling. However, the entropic preference for filling nanotubes with a diameter of 10–15 Å depends on the constituent material. In particular, the enhancement in total entropy of confined water was mainly due to the increased rotational freedom of confined water molecules. The thermodynamic origin of water transport was correlated with the structural and fluidic behavior of water inside these nanotubes. The observed data for density, flow, structure correlation functions, water–water coordination, tetrahedral order parameter, hydrogen bonds, and density of states functions quantitatively support the observed entropy behavior. Of critical importance is that the present study demonstrates the effectiveness of RO filtration using nanotubes of boron nitride rather than carbon. Furthermore, it was found that one should avoid the use of silicon nanotubes unless filtration needs to be performed under harsh environments where nanotube of other materials cannot survive. Specifically, the results show that both the structural and dynamic properties of water confined in BNNTs are similar to those of CNT's, and for SiNT it is similar as SiC. Our results show that besides the nanotube material, the chirality index of the nanotube also plays a significant role in determining the structure, dynamics and thermodynamics of confined water molecules.

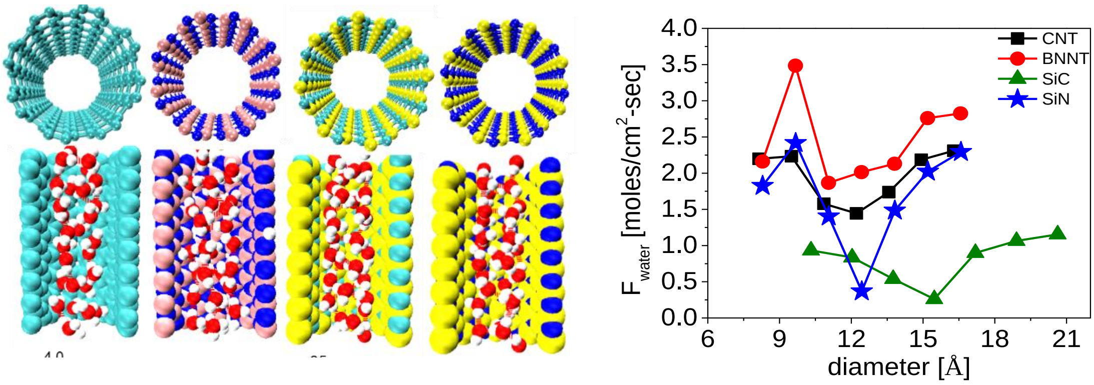

Fig. (left) Snapshot representing water flow through nanotubes made of carbon (CNT), boron nitride (BNNT), silicon carbide (SiC) and silicon nitride (SiN) and (right) the permeation rate of water through these nanotubes as a function of nanotube diameter.

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Complexation Behavior of Pd(II) and Zr(IV) with Tri-*n*-butyl Phosphate and Tri-*n*-butyl Phosphorotrithioate

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Transition metals Pd and Zr are both present in appreciable quantities in the spent nuclear fuel [1]. Therefore, it is crucial to understand their complexation behavior with phosphorous-based ligands commonly used in the solvent extraction of lanthanides and actinides during the spent nuclear fuel reprocessing. It is known that the complex formation step between the metal nitrate and ligand is a deciding factor in the extraction behavior of the ligand. Accurate computations have revealed the major interactions leading to complexation, such as dispersion and orbital interactions, and there is evidence that the electronegativity of the atom directly attached to the P atom also plays a role in deciding the complexation behavior of phosphoryl (P=O) group ligands [2]. In this context, we set out to investigate the effect of replacing the bridging oxygen atoms in the phosphate ligands with sulfur atoms and the complexation behavior of the resulting ligands with Pd(II) and Zr(IV). We have employed accurate quantum chemical methods, as implemented in the ORCA program [3], first to obtain the lowest energy geometries of tri-*n*-butyl phosphate (TBP) and tri-*n*-butyl phosphorotrithioate (TBPT) ligands and then their complexes with Pd(II) and Zr(IV) nitrates. The complexation energies were subsequently computed (cf. Table 1). Our results indicate that TBP and TBPT preferentially bind to Zr(IV) over Pd(II). Furthermore, we investigate the reasons for the observed trend in the complexation energies of these complexes using the energy decomposition analysis scheme implemented in the Amsterdam Density Functional (ADF) program package [4].

Table 1. Complexation energies of 1:2 complexes of TBP and TBPT ligands with Pd(II) and Zr(IV) nitrate computed at the RI-BP86-D3BJ/def2-TZVP-ZORA level.

Molecules	Complexation Energy (kcal/mol)
$Pd(NO_3)_2 \cdot 2TBP$	-30.34
$Pd(NO_3)_2 \cdot 2TBPT$	-33.64
$Zr(NO_3)_4 \cdot 2TBP$	-56.07
$Zr(NO_3)_4 \cdot 2TBPT$	-54.90

Keywords: Phosphate, phosphorotrithioate, transition metal, density functional, energy decomposition.

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Computational studies on the Extraction of Actinides by Tri-Alkyl phosphorotrithioate Ligands

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The challenges encountered during Spent Nuclear Fuel (SNF) reprocessing for the fast breeder reactor fuels, as well as the need to overcome drawbacks associated with Tri-*n*-Butyl Phosphate (TBP), motivates us to design new ligands. This drives us to explore various other extractants comparable to TBP. Our earlier theoretical predictions have indicated that using organophosphorous ligands, while maintaining the extracting ability of the phosphoryl group, and substituting P-O-C bonds in phosphate ligands with P-S-C bonds, can enhance extraction capability. To initiate theoretical understanding of phosphorotrithioate ligands such as Tri-*n*-Methyl PhosphoroTrithioate (TMPT), Tri-*n*-Ethyl PhosphoroTrithioate (TEPT), Tri-*n*-Propyl PhosophoroTrithioate (TPPT) and Tri-*n*-Butyl PhosphoroTrithioate (TBPT) and their extraction behaviour with actinide complexes, we began by examining approximately 20 possible complex structures of uranyl nitrate [$UO_2(NO_3)_2$] with these ligands. Ground state geometries of these complexes were determined using Density Functional Theory (DFT), and the identified stationary points were subsequently characterized as minima by calculating the harmonic vibrational frequencies.

$$UO_2(NO_3)_2 + 2L = UO_2(NO_3)_2.2L \qquad (1)$$

The complexation energies calculated for all these ligands, as in equation (1), were found to be in the range of approximately -66 to -81 kcal/mol, as expected with their similar phosphate analogues. This can be attributed to the increase in the basicity of the phosphoryl group, which was enhanced by substituting the oxygen in the tri alkyl chains with sulphur, aiding in better complexation with U(VI) ions. To further probe this reasoning, DFT calculations were applied to explore the conformational preferences and interconversion barriers of various C-C bond rotations in the metal-ligand complexes.

Ligands	TMPT	TEPT	TPPT	TBPT
Complexation energy (kcal/mol)	-66.3	-72.1	-73.6	-81.2

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An Artificial Neural Network based modeling for separation of Cadmium (II) using MOF from aqueous solution

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Cadmium is a toxic heavy metal which necessitates its removal from aqueous solutions to minimize the hazardous effects associated with it. Metal Organic Frameworks (MOFs) are one of the potential candidates for separation of toxic heavy metals due to their exceptional morphological characteristics such as high surface area, pore volume and pore tunability **[1]**. MOFs are hybrid materials composed of inorganic metal ions and organic linkers to form uniformly spaced porous apertures. In here we have successfully synthesized a Zr based MOF with dimercaptosuccinic acid as linker by conventional heating method. Fig. 1 shows the XRD pattern of the as prepared MOF. The broad peak appeared at ~ 9° confirms the formation of MOF **[2].**The as prepared MOF was employed for the separation Cd(II) from a simulated solution containing Cd. In the present study, we have employed an Artificial Neural Network (ANN) based methodology and modeled the controlling parameters for its efficient removal. The presently developed model showed its superiority in predictive capability of adsorption capacity by simulating the Cd(II) removal process from aqueous solution.

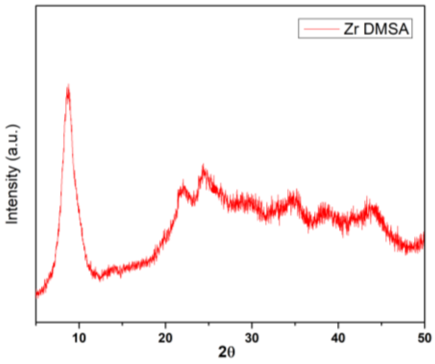

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Fig. 1: XRD pattern of the as prepared MO

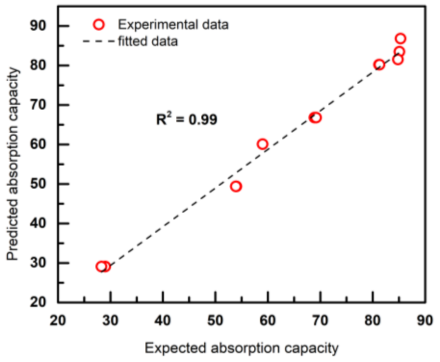

Fig. 2: Validation plot for optimized ANN model on test dataset

In the presently developed computational modeling, absorption data was simulated as a function of initial concentration, pH of the medium and time of contact of the solution with MOF using ANN based method. About 60 data points were collected and used to train, validate and test the ANN model. The input dataset was split into train, validate and test dataset in 50:25:25 ratio. The Python 3.9.7 version was used to implement the presently used ANN model. For handling data, an easy-to-use data structure and data analysis tool called Pandas was employed. After optimizing all the parameters (i.e. ANN architecture, activation function and epochs no), the relative error and precision for the prediction of absorption capacity in test dataset were evaluated using the optimized ANN model. A relative error and precision of 2.09% and 1.04% respectively were obtained by the regression on the test dataset. The model's validity on test data set was found to be accurate with the statistical parameter R^2which was equal to 0.99 (Fig. 2).

Keywords: Cadmium, MOF, Adsorption, ANN, Precision

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On the Complexation Ability of Water and Betaine with Pu^{4+}/PuO_2^{2+}: A DFT and an Ab-initio Born-Oppenheimer Molecular Dynamics Simulations Study

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Task specific ionic liquid protonated 1-carboxy-N,N,N-trimethyl-methanaminiumbis (trifluoromethylsulfonyl) imide, [Hbet][NTf_2][1] has been studied to characterize its dissolution and extraction abilities towards Pu(VI) and Pu(IV). In the current work, we aimed to investigate the complexing ability of these two ions with the de-protonated cationic part of the task-specific ionic liquid (TSIL) i.e., betaine and water. All the calculations have been performed in the gaseous phase using B3LYP and PBE functionals with Grimme's dispersion using Gaussian16, CP2K and Turbomole7.2.1 software. Harmonic vibrational frequency analysis was also performed to obtain the true minima of the complexes. Different parameters like structural parameters, reaction energies, binding energies were considered and it was found that betaine binds much strongly to Pu(IV) ion than Pu(VI) ion thus specifically extract Pu(IV) ions over Pu(VI) from a mixture having both ions. However, betaine showed stronger binding towards both the ions as compared to water. Non-Covalent Interactions (NCI), Reduced Density Gradient (RDG), Electrostatic Potential (ESP) and Density of States (DOS) analyses were also performed and it was found that VDW interactions and hydrogen-bonding contributed significantly in the stability of complexes. In PuO_2^{2+} ion complexes, region around the PuO_2^{2+} ion acted as a nucleophile and that around the ligands acted as an electrophile whereas in Pu^{4+} ion complexes, whole surface acted as an electrophilic surface and HOMO levels got more contribution from betaine ligands than water ligands[2]. Apart from static electronic structure calculations, ab-initio MD simulation had also been performed on $[PuO_2(H_2O)(bet)_4]^{2+}$ complex using a cubic box of 25Å, which was found to be the most stable complex among all the PuO_2^{2+} ion complexes in the static DFT calculations. In the MD simulation, GPW method with PBE functional and DFT-GD3 van der waals correction was employed. A time step of 0.5 fs was used to integrate the equations of motion using Velocity Verlet algorithm for ionic counterparts. The trajectories of the system were obtained at five different temperatures namely, 100K, 273K, 300K, 360K and 460K. To determine the thermal stability of the complex, different parameters like Pu=O bond length variation, ∠O=Pu=O angle variation etc. with time were evaluated. From the obtained data it can be stated that at these temperatures complex is stable and has not disintegrated, but there are dynamic changes in conformations and bonding linkages. Figure 1 depicts the most stable complexes in PuO_2^{2+} and Pu^{4+} ions complexes.

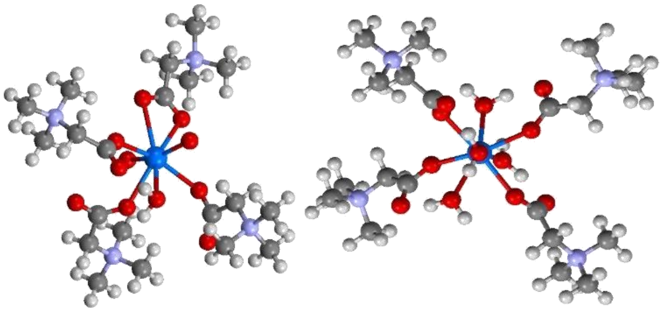

Figure 1. (a) $[PuO_2(H_2O)(bet)_4]^{2+}$ (b) $[Pu(H_2O)_4(bet)_4]^{4+}$

Keywords: TSIL, Plutonium, DFT, ab-initio MD.

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Metal Ligand Interactions in the Alkyl Phosphate and Uranyl Nitrate Complexes

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Tri-*n*-butyl phosphate (TBP) is the workhorse of the closed nuclear fuel cycle, serving well in the separation of U and Pu from spent nuclear fuel and aiding in the separation of minor actinides from high-level liquid waste (HLW). However, TBP has several drawbacks, such as high aqueous solubility, radiation degradation, and third-phase formation, necessitating the search for alternate ligands that overcome these issues. Recent studies indicated that the basicity of the phosphoryl oxygen in these ligands does not change with increasing alkyl chain length [1] or along the series phosphate, phosphonate, phosphinate, and phosphine oxide [2]. On the other hand, there are no experimental or theoretical investigations exploring the effect of symmetrical and unsymmetrical ligand substituents on metal-ligand complexation. In this context, we have applied quantum chemical calculations to investigate the electronic structure and complexation behaviour of unsymmetrical phosphate ligands resulting from modifying each alkyl chain (methyl, ethyl, propyl, butyl) in symmetrical trialkyl phosphates (e.g., ethyl methyl propyl phosphate (EMPP), *n*-butyl ethyl methyl phosphate (BEMP), *n*-butyl methyl propyl phosphate (BMPP), *n*-butyl ethyl propyl phosphate (BEPP)) with uranyl nitrate (1:1 and 1:2 complexes). The ORCA quantum chemistry program package [3] was used to obtain the lowest energy geometries of the ligands and complexes, while the charge and energy decomposition analysis were performed with the NBO [4] and Amsterdam Density Functional (ADF) program package [5], respectively.

Keywords: Phosphates, Uranium, DFT, ADF.

Ligands	NBO Charges		
	P	**O**	**Net**
EMPP	2.41	-1.05	1.36
BEMP	2.40	-1.05	1.35
BMPP	2.41	-1.05	1.36
BEPP	2.42	-1.05	1.37

Ligands	Binding Energies of various uranyl nitrate complexes (kcal/mol)	
	1:1	**1:2**
EMPP	-44.15	-73.69
BEMP	-44.21	-74.53
BMPP	-44.65	-75.58
BEPP	-44.83	-76.34

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Selective Gas Adsorption Using Graphitic Carbon Nitride: Exploring the Role of Molecular Descriptors and Fingerprints by Artificial Intelligence Frameworks and Quantitative Structure Property Relationships

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The research delves into the development of artificial intelligence (AI) frameworks cross-validated by quantitative structure property relationships (QSPR) for the selective gas adsorption on graphitic carbon nitride (g-C_3N_4). The frameworks evolved through the generation of molecular descriptors as well as fingerprints tailored by various conformations of g-C_3N_4. Graphitic carbon nitride (g-C_3N_4) was selected as the material of choice for selective gas adsorption because of its wide surface area, robust gas interactions, and environmentally acceptable nature. Given its potential for high selectivity and adsorption capacities, it presents a viable way to address environmental issues such as air pollution and greenhouse gas emissions. The study systematically investigates 60 g-C_3N_4 structures and contaminants to identify distinct molecular descriptors and fingerprints. Such a conformation of g-C_3N_4 is given in Figure 1. The central hypothesis posits that different combinations of g-C_3N_4 and contaminants exhibit unique molecular characteristics. These descriptors, along with interaction parameters, are utilized to construct QSPR models as well as AI formulations aimed at estimating the ideal g-C_3N_4 system for selective gas adsorption such as CO_2, O_2, NO, and CO. CO_2 is a major greenhouse gas contributing to global warming, and its selective capture are essential for mitigating climate change impacts. While NO is a pollutant emitted from combustion processes, posing health and environmental risks. CO is another important gas produced from incomplete combustion and can be hazardous in high concentrations. Leveraging Artificial Neural Network (ANN) integrated with Genetic Algorithm (GA), the research enhances modeling accuracy and efficiency. ANNs, known for their ability to capture complex nonlinearities, are adept at modeling gas adsorption behavior. When integrated with GA, optimizes the architecture and parameters of the neural network, facilitating the search network structure for the ANN. This interaction between ANN and GA enhances the performance of modeling complex systems such as gas adsorption processes. A schematic of AI showing fingerprints as input is shown in Figure 2. Specifically focusing on CO_2, O_2, NO, and CO, the study elucidates their preferences for open-hollow sites on the g-C_3N_4 system, demonstrating varying adsorption energies, ordered as $CO_2 < O_2 < NO < CO$. This is inline with the experimental observation [1]. Around 33 blocks of descriptors divided into constitutional, ring, and topological domains, etc. have been determined and analysed. Parameters related to size, shape, and connectivity relevant to particular gas binding are calculated inside the constitutional descriptors, offering information on the material's possible steric hindrance and available interaction sites for gas adsorption. This comprehensive exploration underscores the importance of molecular descriptors and fingerprints in explaining QSPR, thereby facilitating a deeper understanding of the intrinsic features and characteristics of molecular structures, and advancing the field of selective gas adsorption on g-C_3N_4.

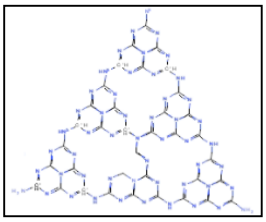

Figure 5. Representative structure of g-C_3N_4

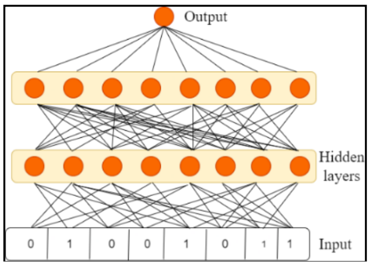

Figure 6. Schematic of AI

Keywords: Molecular descriptors, Quantitative structure property relationships, Gas adsorption, graphitic carbon nitride, Artificial Neural Networks

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Mass transfer modelling of cesium chloride adsorption on zeolite

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In pyrochemical reprocessing, high-temperature electrorefining of metal fuel results in accumulation of fission products in molten LiCl-KCl eutectic salt, increasing heat load and contamination. Adsorption is proposed to separate the fission products using zeolite and reuse the salt. Experimental work [1] show heat generating fission product like Cs-137 has relatively higher concentration and shorter breakthrough time with a high half life of ~30 years. Analytical model[1] predicts fission product uptake using empirically derived exchange factors that grossly under predicts uptake of some ions.

This brings in the requirement of a theoretical model to simulate the performance of the packed column for adsorption of CsCl on zeolite, without using any empirical exchange factors. Towards this model development, a numerical study has been carried out for simulating the adsorption of Cs ions on zeolite using the general rate model[2] in COMSOL 6.0. According to the model, the liquid phase mass balance equation for the solute is given by the following equation: $-D_L \frac{\partial^2 c}{\partial x^2} + v \frac{\partial c}{\partial x} + \frac{\partial c}{\partial t} + \left(\frac{(1-\varepsilon_b)}{\varepsilon_b}\right) \frac{3}{r_p} k_f \left(c - c_{p,r=rp}\right) = 0$

The diffusion of solute molecules in the pore phase of the adsorbent through pore diffusion process is given by the following mass balance equation: $\varepsilon_p \frac{\partial c_p}{\partial t} + \rho_p \frac{\partial q_p}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r}\left[r^2 \left(\varepsilon_p D_P \frac{\partial c_p}{\partial r}\right)\right]$

The equilibrium relationship between the concentrations of solute in the solid phase and the pore phase is given by the Langmuir isotherm as given by: $q_p = \frac{q_{max} K_L c_p}{1 + K_L c_p}$

The Langmuir adsorption constant K_L and maximum adsorption capacity c_p were determined from the batch equilibrium results of Tsukada et al[3]. For the numerical simulation, the same concentration of cesium was used as reported in the experimental work[1]. The properties of cesium, zeolite and molten salt were inputs to the model for solving the liquid and solid phase equations described above. The model is validated by comparing the breakthrough times from the experimental work[1]. The numerically predicted breakthrough times had error margins of 0.01% and 0.5% from the experimental data as shown in Figures 1 and 2, for superficial velocities of 3.3 cm/min and 0.5 cm/min respectively. The numerical model could predict the breakthrough behavior and concentration profile in the mass transfer zone (MTZ) for cesium adsorption on zeolite at a superficial velocity of 0.5 cm/min compared to 3.3 cm/min.

Parametric studies were carried out using the validated model. It is observed that changes in the salt composition has a small effect on the breakthrough time which rises by 6.67% on increasing bed height by 25%, and decreases by 14.6% when the particle size is increased by 87.5%. The breakthrough curves have a steeper slope at higher gas velocities. The results match with the experimental and theoretical data and the model may further be used to evaluate the performance of the ion-exchange column and for subsequent engineering scale up studies and validation.

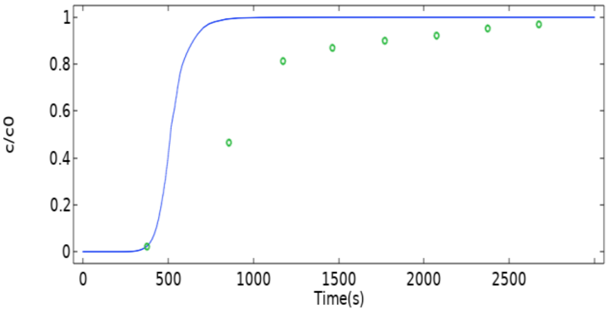

Figure 1

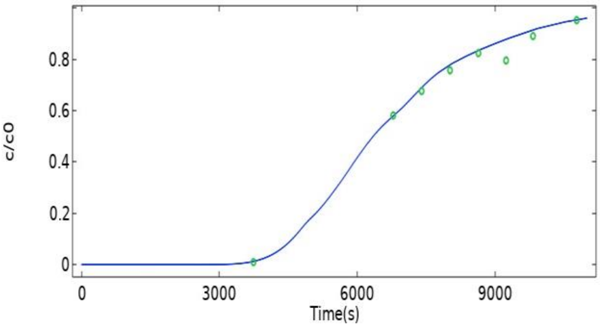

Figure 2

Keywords: Pyrochemical reprocessing, Fission products, Cesium adsorption, Breakthrough, Packed beds

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Back Extraction of Uranyl Ion into Aqueous Phase Using Molecular Dynamics Simulations

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The back extraction (stripping) of uranium from loaded organic is equally important as the extraction of uranium from aqueous feed solution to organic phase in PUREX process. The extraction of uranyl ions using TiAP as a potential ligand along with mass transfer parameters was investigated in our previous molecular dynamics (MD) simulations work.[1] The distribution coefficient (K_D) profile for uranyl ions as a function of aqueous phase acidity was established. Now, the back extraction of uranyl ion into the aqueous phase needs to understand to develop the entire process of fuel reprocessing. The recovery of metal ions depends on the de-complexation of uranyl – ligand complex in organic phase. The interface phenomena and the associated transfer mechanism are very much complicated and difficult to capture by experimental route and it is only possible through MD simulations studies. In the present studies, the K_D of back extraction and the % of recovery have been evaluated for complex biphasic system along with the interfacial properties.

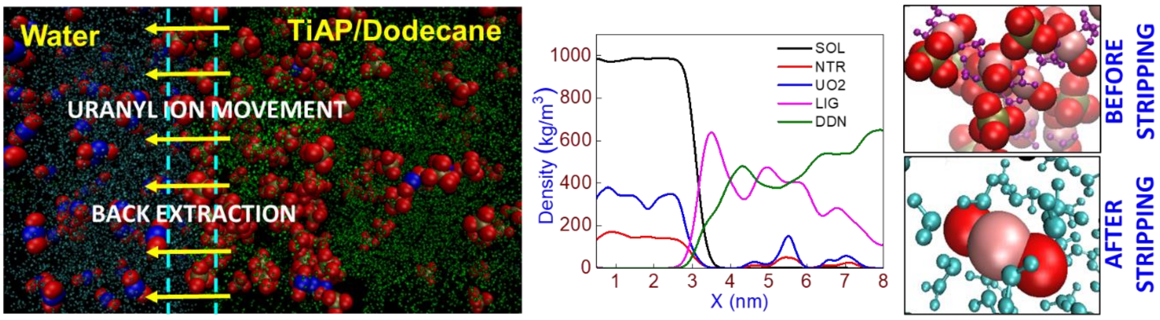

Figure 1. Snapshot of complex biphasic system showing the direction of uranyl ion movement during back extraction into the aqueous phase along with the density profile generated after 0.17 µs simulation length and the snapshots before and after stripping ensures the phenomena.

It has been observed that the packing density of TiAP is higher at interface and then it is diluted in the bulk dodecane phase. The interfacial tension (γ) and total interface thickness (w_t) have been computed using our proposed equation and the density profile. The proposed equation for multi-component system developed in our earlier work[2] which correlates the total interface thickness and the interfacial tension via the bulk correlation length as given below:

$$w_t^2 = C\,\frac{k_B T}{\gamma}\,\ln\left(\frac{L_{II}}{L_b}\right) \tag{1}$$

$$C = \frac{(\sigma_{Water} + \sigma_{TiAP} + \sigma_{dodecane})}{1.4\,\sigma_{water}} \tag{2}$$

$$L_b = L_{W-T} * x_{TiAP} + L_{W-D} * x_{Dodecane} \tag{3}$$

$$w_i^2 = w_t^2 - w_c^2 \tag{4}$$

where, k_B is the Boltzmann constant, T is the temperature, L_{II} indicates box dimension along the y or z direction and L_b provides the bulk correlation length in terms of the molecular length. Here the weighted average of bulk correlation length is used [see eqn. (3)] as discussed in our earlier work.[2] C is a constant which depends on the molecular sizes. The molecular volumes are calculated from COSMO-RS method.[3] The x_{TiAP} and $x_{Dodecane}$ denotes the mole fraction of TiAP and dodecane molecule respectively. The w_i indicates the intrinsic interface thickness coming from molecular contribution and it is the major contributor to w_t and w_c is the capillary thickness due to thermal fluctuations.

System	w_t (nm)	Interfacial tension (mN/m)	w_c (nm)	w_i (nm)	K_D	Q (%)
TiAP	1.47	22.91	0.17	1.46	0.15	87.1

TiAP shows very low K_D value which is preferable for back extraction and the recovery around 87% is observed when water is used as a stripping agent. Further, the passage of back extraction of uranyl ion is investigated through water chain assisted mechanism.

Keywords: Back extraction, TiAP, Uranyl ion, interfacial tension and interface thickness.

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Correlation between bond length and distribution coefficient: A DFT Study

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Rare earths (REEs) are indispensable key elements in new energy vehicles, wind energy sector, electronic information,and other high-tech fields[1]. Nowadays the focus on accelerating the energy transition to mitigate climate change, resulting in an increased demand for rare earth elements[2]. Rare earth elements are very similar to each other as per their chemical properties. Generally they occur in nature as groups. They form similar species in complex mixture. But individually they possess excellent properties as was mentioned in the above. Chemical recognition of the rare earth elements is necessary to separate them individually to make use of them. Various solvents of different types have been applied upon them for the separation purpose. Of late, there is a thrust on using non phosphorous based reagents to address separation issue and avoid waste management problem too. Thus, a migration was observed from phosphoric/phosphonic acid based extractants (like D2EHPA/PC 88A) for recovery and separation of the rare-earth elements. Also the separation factor of rare earths for the extraction by PC88A is not significant leading to requirement of more number of stages to achieve the same purpose. Thus there is a hunt for better extractant providing effective and easy separation of the rare earth elements. The diglolamide based solvents (DGAs) are the recent ones with latest developments. Here one type of DGA, tetra octyl di-glycolamide (TODGA) was used for REEs separation purpose[Fig. 1]. DFT study on that separation process shows that increasing distribution coefficient is supported by decreasing bond length as we go from lanthanum to gadolinium [Fig. 2]. The bond lengths obtained for europium are comparable with the literature[3].

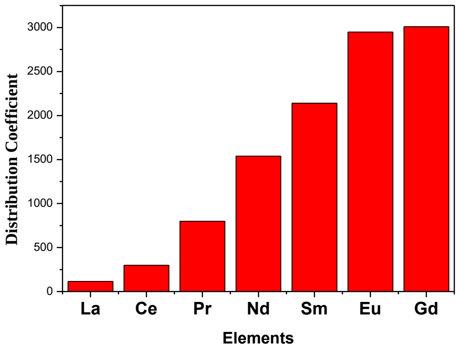

Fig. 1: Distribution coefficient for REE extraction by TODGA

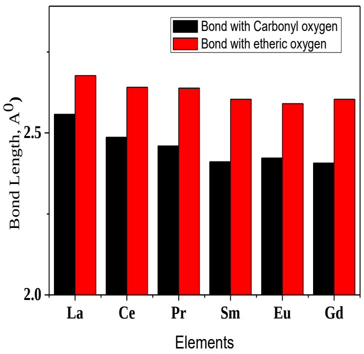

Fig. 2: Bond length in REE-TODGA complex

Keywords: Rare earths, TODGA, distribution coefficient, bond length, extraction

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Tuning the Selectivity of Carbamoyl Phosphine Oxides Towards Trivalent Lanthanide Nitrates

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Carbamoylmethylsphosphine oxide (CMPO) is utilized as the extractant in the TRans Uranium EXtraction (TRUEX) process [1]. Like other phosphine oxides, CMPO lacks selectivity and is known to extract lanthanides and actinides from their aqueous solutions. Over the years, many modified CMPO ligands have been synthesized and utilized to extract rare earth and actinide nitrates [2]. Experimental screening of these ligands is a tedious task, especially considering the added risk of handling radioactive materials such as actinide elements. However, it is a fact that the complex formation between the ligand and metal nitrate is a crucial step in the entire extraction process [3]. Hence, using the tools of computational chemistry, it is possible to explore the complexation behavior of any ligand without encountering the risks mentioned above, thereby enabling the screening of ligands for the selective extraction of desired metal nitrate from its aqueous solution. In this regard, we examine the complexation behavior of a modified CMPO ligand in which the butyl chain on the N atom is replaced with a 2-diphenylphosphinylethyl group with representative trivalent rare earth nitrates and compare it with the complexation behavior of the conventional unmodified CMPO ligand. Using the ORCA package [4], we first obtained the lowest energy geometries of the ligands, metal nitrates, and their complexes; for these geometries, the complexation energies were then computed employing different exchange-correlation density functionals (Table 1). Furthermore, energy decomposition analysis (EDA), implemented in the ADF program [5], was performed to elucidate the reasons behind the observed trend in the complexation energies.

Table 1. Complexation energies of 1:3 complexes of Ce(III) and Eu(III) with CMPO ligand (L_1) and the modified CMPO ligand (L_2) computed in the gas phase using various density functionals in conjunction with def2-TZVP basis set, including scalar relativistic corrections.

Complex	BP86	PBE	B3LYP	M06-L
$Ce(NO_3)_3{\cdot}3L_1$	-123.33	-110.14	-129.23	-115.98
$Ce(NO_3)_3{\cdot}2L_2$	-116.98	-101.49	-123.49	-113.03
$Eu(NO_3)_3{\cdot}3L_1$	-123.35	-105.11	-127.16	-113.70
$Eu(NO_3)_3{\cdot}2L_2$	-114.96	-94.39	-118.62	-113.46

Keywords: Phosphine oxide, lanthanide, actinide, selectivity, density functional, energy decomposition.

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Numerical Modelling and Optimization of H_2O^{18} Production Plant Based on Water Distillation Process

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O-18 is a key isotope as it is the precursor for medical radioisotope F-18 which is used in PET scanning (Positron Emission Tomography). There are various methods for isotope separation but fractional distillation proves to be industrially competitive and successful for production of O-18 of higher concentrations. Distillation is the most common separation technology in gas-liquid processing. Its widespread application in combination with a high energy demand makes the distillation process to be analyzed considering both an economic and an ecological perspective. The present work deals with the development of a rate-based model to study the dynamic behavior of a distillation column for O-18 separation using water distillation process. In the present study, heavy water having > 99.95 % isotopic purity(D/(D+H)) was taken as feed and and a multicomponent distillation process was modelled considering 4 components (D_2O^{16}, D_2O^{18}, HDO^{16} and HDO^{18}) in the feed. The governing equation in the model were solved numerically using Levenberg Marquardt Algorithm. Initially the process was simulated for a capacity of 10 kg/yr D_2O^{18} production and the simulation results were validated using the available data. This model was also used to compare the results using two different feeds i.e D_2O and Depleted Deuterium Water (DDW). Further this validated model was used to simulate a distillation cascade with a scaled-up capacity of 200 kg/yr. Parametric sensitivity analysis was performed by varying various column parameters such as column pressure, boilup ratio and results were analysed to see column performance. The validated model can be used to evaluate cascade choices for 200 Kg/yr capacity plant.

Solid Phase Extraction of Europium(III) by usingTulsionCH-93

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Europium (III) is a rare earth element with diverse applications in luminescent materials, medical imaging, and electronics. Tulsion CH-93 a phosphoric acid resin has been reported previous [1]. In this work, it was used for the sorption of europium (III) from hydrochloric acid media.

Using a batch method the influence of acid concentration, and time on the sorption of europium(III) was studied. The amount sorbed was determined from the amount present in the aqueous phase spectrophotometrically using Arsenazo (III) at 657nm. The sorption of europium (III) (20µg) was maximum using 0.01M hydrochloric acid (*Fig. 1*) with 30 min of agitation time (*Fig. 2*). The sorption of europium (III) was studied from 20µg to 2000µg.

Europium (III) sorption obeyed pseudo first-order and pseudo second-order rate kinetic model for the entire time range studied (*Fig. 3.0*). Both the Langmuir and Freundlich adsorption isotherms were followed for europium sorption.

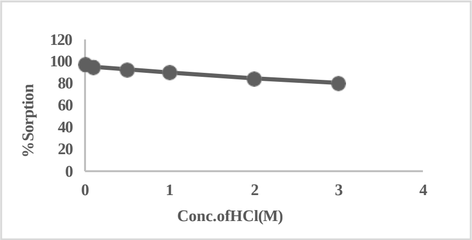

Fig.1.EffectofConc.HClvs %Sorption

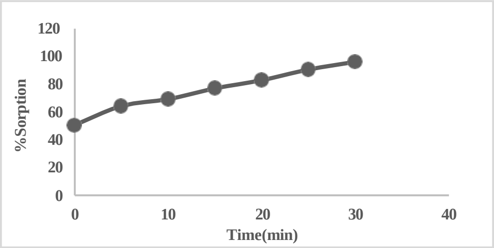

Fig.2.EffectofTimevs %Sorption

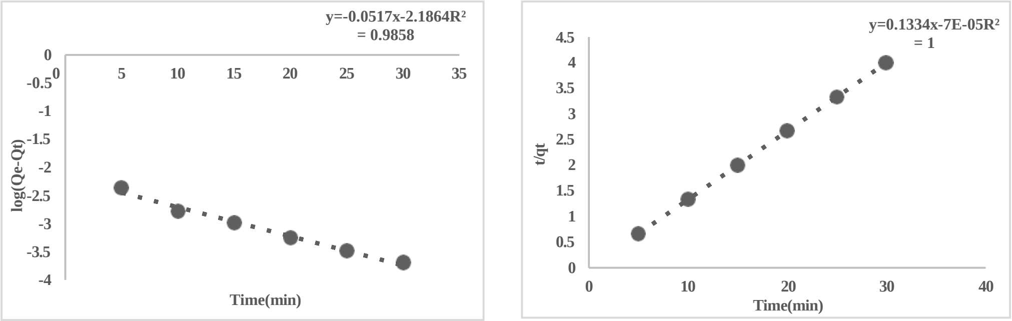

Fig.3. Kinetic rate models of pseudo first order rate and pseudo second order

***Keywords**: Solid phase extraction, europium, TulsionCH-93*

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Determination of Coordination Modes for Complexation of N-(2-acetamido) iminodiacetic acid with U(VI) by DFT

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N-(2-acetamido)iminodiacetic acid (ADA) was found to be very efficient for decorporation of Th(IV) from human blood and lung cells in our previous studies [1]. In order to evaluate it's decorporation efficacy for uranium (VI), it is prerequisite to study the complexation of ADA with U(VI). In the current paper density functional theory (DFT) calculations have been carried out to understand the interaction of U(VI)-ADA complexes at the molecular level by the determination of optimized geometries, bond distances, and partial atomic charges.

To get insight into coordination mode of U(VI)-ADA complexes density functional theoretical calculations were carried out. The geometries of ligand, and predicted complexes (ML and ML_2) were optimized at the DFT level of calculations using the TURBOMOLE program package. The geometry optimization for all the structures was performed without any symmetry restriction using the B3LYP functional with the triple-ζ valence plus polarization (TZVP) basis set, as implemented in the TURBOMOLE package [2]. The aqueous-phase energetics was calculated using a conductor-like screening model (COSMO) approach. The dielectric constant (ε) of water was taken as 78.4. The partial atomic charge distribution was calculated by natural population analysis in TURBOMOLE. The following equation representing the complexation of U(VI) with ADA was used to estimate the overall energetics of the complexation process.

$$[UO_2(H_2O)_5]^{2+} + m\text{ADA}^{2-} \rightleftharpoons [UO_2(\text{ADA})_m(H_2O)_n] + (5\text{-}n)\, H_2O \quad (1)$$

Based on different possible coordination modes of the ligand, the various initial guess geometries were used for structure optimization of the ML and ML_2 complexes of U(VI)-ADA. The binding energies were calculated for all of the possible geometries of U(VI)-ADA complexes in both gas and aqueous phases from the energies of individual species involved in the complexation process. The binding energies are becoming less negative with successive complexations; *i.e.,* the affinity of ADA is reducing upon successive complexations with U(VI). The optimized geometries of minimum energy for both the complexes are shown in Fig 1 and 2. The partial atomic charges on uranyl ion in $[UO_2(H_2O)_5]^{2+}$ is 2.146, in ML is 1.917 and in ML_2 is 1.895 in electrostatic unit. Optimized geometries showed that ADA binds to U(VI) in tridentate mode with two carboxylate oxygens and amine nitrogen in ML_1 while in ML_2 ADA binds to U(VI) in bidentate mode with two carboxylate oxygens only. In ML_2, the amide $-NH_2$ of both the ADA moieties form hydrogen bond with axial oxygen of U(VI). The bond distances and partial atomic charges were obtained from the optimized structures with minimum energies. In conclusion, the amide functionality of ligand is not binding with U(VI) in ML. However, in ML_2 amide group is strengthening the complexation by formation of hydrogen bonds with axial oxygen of U(VI) with bond lengths 1.99 and 2.00 A°.

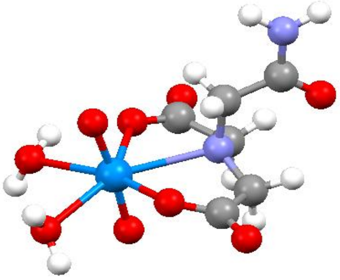

Fig.1: Geometry optimized structure for ML complex of U(VI)-ADA

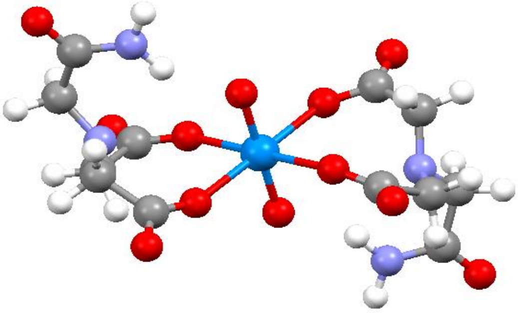

Fig.2: Geometry optimized structure for ML_2 complex of U(VI)-ADA

Keywords: DFT, Uranium, Complexation, Coordination modes, ADA

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Theoretical Investigation of Interaction of Phosphonate and Phosphate Ligands with Zirconium Nitrate

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The extraction of zirconium nitrate with phosphonates [di-*n*-butyl-*n*-butyl phosphonate (DBBP), di-*n*-amyl-*n*-amyl phosphonate (DAAP)] and phosphate [tri-*n*-butyl phosphate (TBP)] ligands was studied using density functional theory (DFT) methodology. The phosphonate ligands showed improved extraction of zirconium nitrate due to an increase in the basicity of the phosphoryl group. Ground state structures of the ligands and the complexes were established at DFT level (cf. Figure a-b) in a 1:2 stoichiometry, consistent with previous observations [1, 2]. The ligands were observed to be in a –*trans* orientation with respect to the metal atom in the respective complexes. Calculated highest occupied molecular orbital (HOMO) energies of the ligands indicated stronger complexation by the phosphonates than by phosphates. Calculated gas-phase and solvent-corrected extraction energies derived at the DFT level, considering the energy balance of stoichiometric equations (1), and (2), were in agreement with the experimental results. It is to be noted that since the ligands are neutral molecules, neither cationic nor anionic species are extracted by them. In this context, we have only considered neutral species for the calculation of complexation and extraction energies.

$$Zr(NO_3)_{4(gas)} + 2L_{(gas)} = Zr(NO_3)_4{\cdot}2L_{(gas)} \tag{1}$$

$$Zr^{+4}_{(aq)} + 4NO_3^-{}_{(aq)} + 2L_{\ (org)} = Zr(NO_3)_4{\cdot}2L_{(org)} \tag{2}$$

$$\Delta E_{comp}= E^{SP}\,[Zr\ (NO_3)_4{\cdot}2L] - E^{SP}\,[(Zr\ (NO_3)_4] + 2.\ E^{sp}\,[L] \tag{3}$$

Here, E^{SP} represents the single-point energies calculated for the respective systems (both gas-phase and solvent-corrected) at the corresponding theoretical level. The complexation energies are higher for phosphonates (ca. -61 kcal/mol) than for phosphates (-58 kcal/mol). To mimic the experimental situation, the effect of the solvent environment was considered using the conductor-like polarizable continuum model (CPCM) [3], employing dielectric constants of 2 and 80 for the aqueous and organic phases, respectively. The calculated extraction energies follow the same trend as the complexation energies (-53 kcal/mol for phosphonates and -50 kcal/mol for phosphates). Energy decomposition analysis (EDA) [4] revealed that the pristine metal nitrate undergoes a very high distortion (ca. 48-50 kcal/mol) upon complexation with the ligands, and this distortion is found to be independent of the nature of the ligands (phosphonates or phosphates). EDA also reveals that the effect of dispersion on the overall complexation process is minimal and does not vary when changing the ligands.

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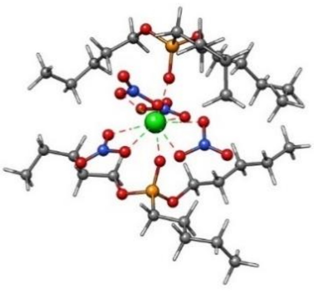
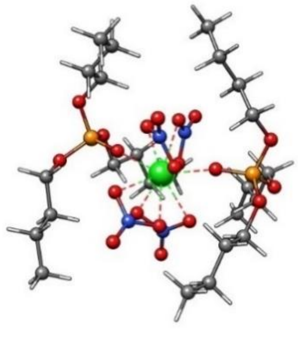


(*a*) Ground state structure of $Zr(NO_3)_4{\cdot}2DAAP$



(*b*) Ground state structure of $Zr(NO_3)_4{\cdot}TBP$

Keywords: Density Functional Theory, Phosphonate, Phosphate, Complexation Energy

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Chitosan-based composite beads for effective removal of heavy metals from aqueous solutions

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Addressing the critical challenge of heavy metal and radioactive contamination, especially prominent in developing nations, this research introduces an innovative approach using chitosan-based polymer beads. These beads, formulated with dry cowdung powder (DCP), humic acid (HA), and bentonite (B), demonstrate notable potential for selective adsorption of silver and zinc from aqueous solutions. The primary objective of this study is to assess the efficacy of these composite beads as biosorbents while exploring their reusability. The synthesis process is meticulously elucidated, accompanied by comprehensive characterization using advanced microscopy and spectroscopy techniques. Through systematic batch and column experiments, various parameters including pH, contact time, and metal ion properties were investigated for their impact on adsorption efficiency.

In batch experiments, Ag(I) and Zn(II) adsorption efficiencies reached 88±3% and 92±2%, respectively, within 30 minutes. Desorption using 0.1 M HCl demonstrated effective regeneration with recoveries of 79±2% for Ag(I) and 66±3% for Zn(II). Column adsorption studies using a 5 mL bed at a flow rate of 30 mL/hr and 6 bed volumes/hr achieved impressive removal efficiencies: 93±2% for Ag and 94±2% for Cs. Desorption experiments showed promising metal recovery rates of 79±2% for Ag and 72±2% for Cs, confirming the potential reusability of the composite adsorbent. The findings not only provide an effective solution for heavy metal removal but also contribute to sustainable practices through material recycling. Incorporating agricultural and fishing waste materials into chitosan-based composite beads highlights their eco-friendly nature and waste reduction benefits. These adsorbents show high adsorption capacity, rapid kinetics, and selective removal of Ag and Zn ions, enhancing practicality and cost-effectiveness in water treatment applications.

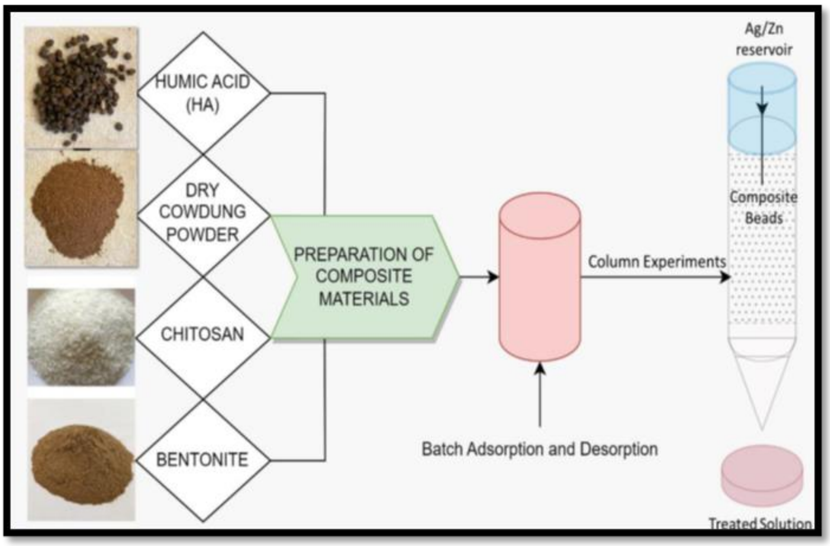

Figure 1. Methodology & experimental procedure of using DCP-HA(CB) beads for batch and column Study.

Keywords: Chitosan, Dry cowdung Powder, Humic acid, heavy metals, remediation

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Advancing Varietal Identification of Indian Honeys via Physicochemical Properties and E-Beam Irradiation to Enhance Antioxidant Properties

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Honey, a natural product with significant nutritional and medicinal value, is derived from the nectar of flowers and processed by bees. Its composition and properties can vary widely based on floral source, geographical location, and processing methods. Accurate identification of honey variety is crucial for quality control, authentication, and to prevent adulteration. Traditional methods, such as melissopalynology, which analyzes pollen content in honey, are time-consuming and require specialized expertise. Recent advances have highlighted the potential of using physicochemical properties as alternative indicators for honey variety. Properties such as color, pH, refractive index, and antioxidant activity can provide insights into the honey's floral source and processing history. Additionally, irradiation techniques, particularly electron beam (e-beam) irradiation, have been investigated for their effects on honey properties, including microbial decontamination and enhancement of antioxidant activity. This study aims to explore the efficacy of using physicochemical properties and e-beam irradiation as biomarkers for identifying varietal Indian honeys. By examining changes in these properties post-irradiation, we seek to establish a faster and more straightforward method for honey verification. Six samples of varietal Indian honeys collected from Manghar apiaries were subjected to e-beam Irradiation. Honey samples were irradiated with the electron beam of 10 MeV at dose rate 10, 20, 30, and 40 kGy using the linear pulse accelerator at Electron Beam Center, Kharghar. Post-irradiation honey samples were analyzed for physicochemical tests about their color, pH, refractive index, free radical scavenging activity, sugar analysis, and total phenolic counts (TPC), and compared with pristine honey samples' antioxidant capacity using the DPPH method. The total phenolic content (TPC) was determined via the Folin-Ciocalteu method. Pissa honey from Manghar exhibited the highest antioxidant activity, while multiflora honey from Mumbai showed the lowest.

The refractive index of honey was measured by a BRIX refractometer, and values were compared with the results of analysis of reducing sugars done by RP-HPLC with RI detector, to get the Fructose/Glucose (F/G) ratio. It was seen that the ratio F/G ratio remained higher than 1, which ensured that honey did not crystallize at room temperature. The pH measurements revealed a slight decrease from 10 to 40 kGy, which could be attributed to radiolysis-induced increase of free amino acids, hydrogen peroxide, and 5-Hydroxymethylfurfural (HMF). The lower pH is also expected to improve the anti-bacterial activity of honey. The color intensity of honey is due to polyphenols, and could thus be related to the antioxidant activity. The DPPH radical scavenging assay and Folin-Ciocalteau method and total phenolic content were carried out for the antioxidant activity, respectively. It was observed that these parameters varied with floral type and dose of irradiation. Thus, the color of all honey samples darkened post irradiation and a corresponding increase was noted in the antioxidant activity and total phenolic content. In conclusion, the irradiation dose of 30kGy sufficiently improved the antioxidant activity for all samples without significantly affecting other properties. Therefore, it can be concluded that physiochemical properties and e-beam irradiation can act as a biomarker for various honey samples. This activity is affected by the floral source and the geographical location from which the honey is derived.

Keywords: Honey; Biochemical composition; Biomarker; ; Antioxidant activity; Phenolics compounds; E-beam Irradiation

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Hydrophilic Deep Eutectic Solvent as Green Lixiviant for Leaching Heavy Metals from Beach Sand

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The increasing environmental concerns and the need for sustainable practices have propelled the development of green chemistry solutions for various industrial processes. This study explores the efficacy of hydrophilic DESs as environmentally benign alternatives for the extraction of heavy metals from beach sand. In the present work, the choline chloride (CHCL) based DESs with ethylene glycol (CHCL-EG=1:2), urea (CHCL-Urea=1:2), citric acid (CHCL-CA=1:1), lactic acid (CHCL-LA=1:2), malic acid (CHCL-MA=1:1), and oxalic acid (CHCL-OA=1:1) were used for leaching heavy metals from Kerala beach sand at 70 ºC for 6 h, and concentrations were measured using ICP-MS as shown in Table1. The leaching experiments were also carried out using 4 M HNO_3 for the reference. It is seen from the Table that CHCL-CA is the best DES as the lixiviant for leaching REE from Kerala beach sand. However, its efficiency of leaching is considerably lower than HNO_3. This may be attributed to the fact that leaching of REE requires treatment with caustic to convert REE in hydroxide forms, which are easier to leach with DES as reported elsewhere [1].

Table 1. Concentration (ppb) of heavy metals in leach liquors as obtained by ICP-MS after dilutions.

Elements	CHCL-EG	CHCL-UREA	**CHCL-CA**	CHCL-LA	CHCL-MA	CHCL-OA	**HNO_3 (4M)**
^{89}Y	0.004	0.008	**7.723**	1.211	0.067	0.638	**15.32**
^{139}La	0.004	0.034	**27.056**	6.567	0.555	22.001	**153.13**
^{140}Ce	0.002	0.020	**61.062**	8.070	0.258	7.058	**339.94**
^{146}Nd	0.002	0.012	**25.019**	3.409	0.117	2.462	**147.5**
^{147}Sm	0.004	0.008	**4.482**	0.658	0.019	0.418	**24.4**
^{157}Gd	0.002	0.005	**3.890**	0.591	0.023	0.375	**16.05**
^{163}Dy	0.002	0.004	**2.359**	0.394	0.014	0.192	**5.143**
^{165}Ho	0.003	0.005	**0.592**	0.096	0	0.041	**0.788**
^{166}Er	0.003	0.005	**1.234**	0.204	0.006	0.091	**2.456**
^{172}Yb	0.000	0.005	**1.117**	0.184	0.004	0.078	**1.82**
^{175}Lu	0.004	0.005	**0.224**	0.029	0	0.010	**0.273**
^{232}Th	0.044	0	**34.177**	5.105	0.147	5.411	**168.3**
^{238}U	0.005	0.013	**3.495**	0.671	0.032	2.321	**8.238**

Keywords: Deep eutectic solvent, Hydrophilic, Leaching, Rare earth elements, Beach sand.

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Immobilization of Deep Eutectic Solvent in Electrospun Polyurethane Nanofibers for Application in the Separation of Heavy Metals

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Deep eutectic solvents (DESs) have emerged as a promising alternative to conventional organic solvents due to their tunable properties, low toxicity, and biodegradability [1]. This study explores the innovative use of DES immobilized on electrospun polyurethane (PU) nanofibers for applications in separation science. Electrospinning, a versatile technique for producing nanofibers, was employed to fabricate PU nanofibers with high surface area and enhanced mechanical properties [2]. The DES, composed of a mixture of trioctylphosphine oxide (TOPO) and lactic acid (LA) in a 1:2 mol proportion, was successfully immobilized on the PU nanofibers, resulting in a composite material with unique physicochemical characteristics. After optimizing the electrospinning machine parameters, the fibers were made of PU with 10, 20, and 30 wt.% DES. The electrospinning machine used was obtained from E-Spin Nanotec as shown below in Fig.1.

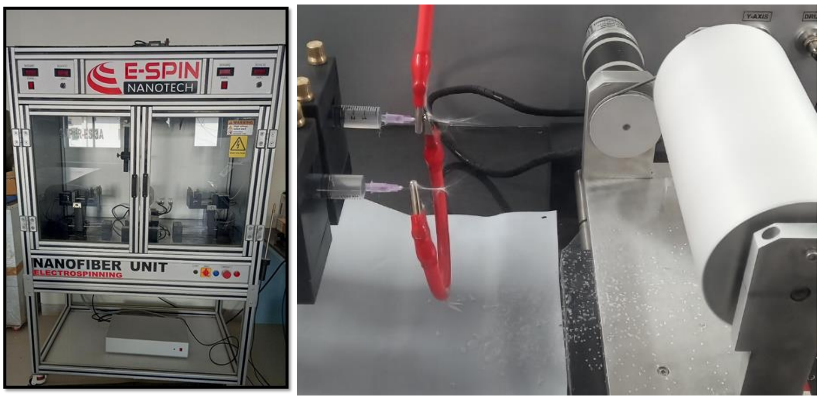

Fig. 1. Electrospinning machine from E-Spin Nanotec used to form PU nanofibers with DES.

Characterization techniques such as scanning electron microscopy (E-SEM), Fourier-transform infrared spectroscopy (FTIR), and EDS confirmed the successful immobilization of DES on the PU nanofibers and demonstrated the stability of the composite material as no swelling or loss of materials was observed in PU samples equilibrated in water, 0.5 M NaCl and 0.5 M HNO_3. The DES-PU nanofibers were evaluated for their efficiency in separation processes, specifically targeting the removal of heavy metals from 0.5 M HNO_3 leach liquor of Kerala beach sand.

Keywords: Polyurethane nanofibers, Deep eutectic solvent, Electrospinning, Separation, Rare earth elements.

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Dr. Sasi Bhushan K. joined the Fuel Chemistry Division in 2006 and earned his Ph.D. from the Homi Bhabha National Institute in 2022. His research focuses on developing precise and accurate methodologies for measuring isotope ratios of various nuclear fuel elements using Thermal Ionization Mass Spectrometry (TIMS). He also explores on adopting various mathematical correction methodologies to minimize isotopic fractionation and eliminate isobaric interferences. He has approximately 25 peer-reviewed international articles to his credit.

Dr. Shikha Sharma received her Ph.D. degree from HBNI in the year 2016 and awarded with national post doctoral fellowship by DST-SERB in 2017. She joined BARC as a KSKRA in 2018 and now working as SO E in RCD, BARC. She is working in the field of lanthanide-actinide complexation with organic ligands, complexation thermodynamics and theoretical studies. She has 18 publications in international journals of high repute.

Dr. Nimai Pathak has been employed as a Scientist at the Bhabha Atomic Research Centre in Mumbai, India since August 2012. He also served as a Fulbright visiting scholar at the Illinois Institute of Technology in Chicago from 2021 to 2023. Dr. Pathak's research interests include spectroscopic studies of inorganic materials, particularly trace metal assay in nuclear fuels, and the design and development of various light-emitting materials. He has authored approximately 70 international journal papers and 2 book chapters to date. Dr. Pathak has been honored with Young Scientist Awards from prestigious organizations such as The National Academy of Sciences, India, and the Department of Atomic Energy, Government of India, in 2020. Additionally, he received the Marie-Skłodowska-Curie Action Seal of Excellence (SoE) award from the European Commission in 2020.

Dr. Sumit Kumar joined Bhabha Atomic Research Centre (BARC), Mumbai following 46th batch one - year orientation course in nuclear science and technology. He received his Ph.D. degree from Homi Bhabha National Institute, Mumbai and continued his investigation on actinides speciation using X-ray Absorption Fine structure Spectroscopy (XAFS) during his postdoctoral assignments at University of Nice Sophia Antipolis, France and Karlsruhe Institute of Technology, Germany. Presently he is a staff scientist at Radioanalytical Chemistry Division, BARC and his research interest is in the XAFS study of actinides and long – lived fission products at the solid - water interface for characterising their sorption behaviour in predictive manner. He has developed a facility to carry out XAFS studies of radionuclides at Indus-2 synchrotron facility, RRCAT, Indore. He has over 55 publications in peer reviewed international journals. He also serves as a Ph.D. guide, Chemical Science Division, HBNI.

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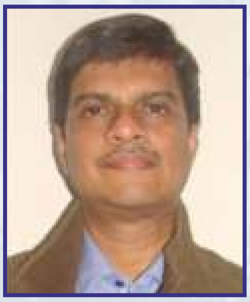

Dr. P. K. Mohapatra joined Radiochemistry Division, BARC in 1987 after graduating from the 30th Batch of the Bhabha Atomic Research Centre (BARC) training school. His research interests include separation of actinides and fission products using novel extractants, in ionic liquid based solvents and novel separation techniques including liquid membranes. A recognized guide of Mumbai University and Homi Bhabha National Institute (Deemed University), Dr. Mohapatra is an Associate Editor of Separation Science and Technology and one of the Editors of Radiochimica Acta. He is on the advisory board of several prestigious journals including Solvent Extraction and Ion Exchange. He has over 415 publications in peer reviewed international journals with over 8000 citations. Currently, he is Director, Radiochemistry and Isotope Group, BARC.