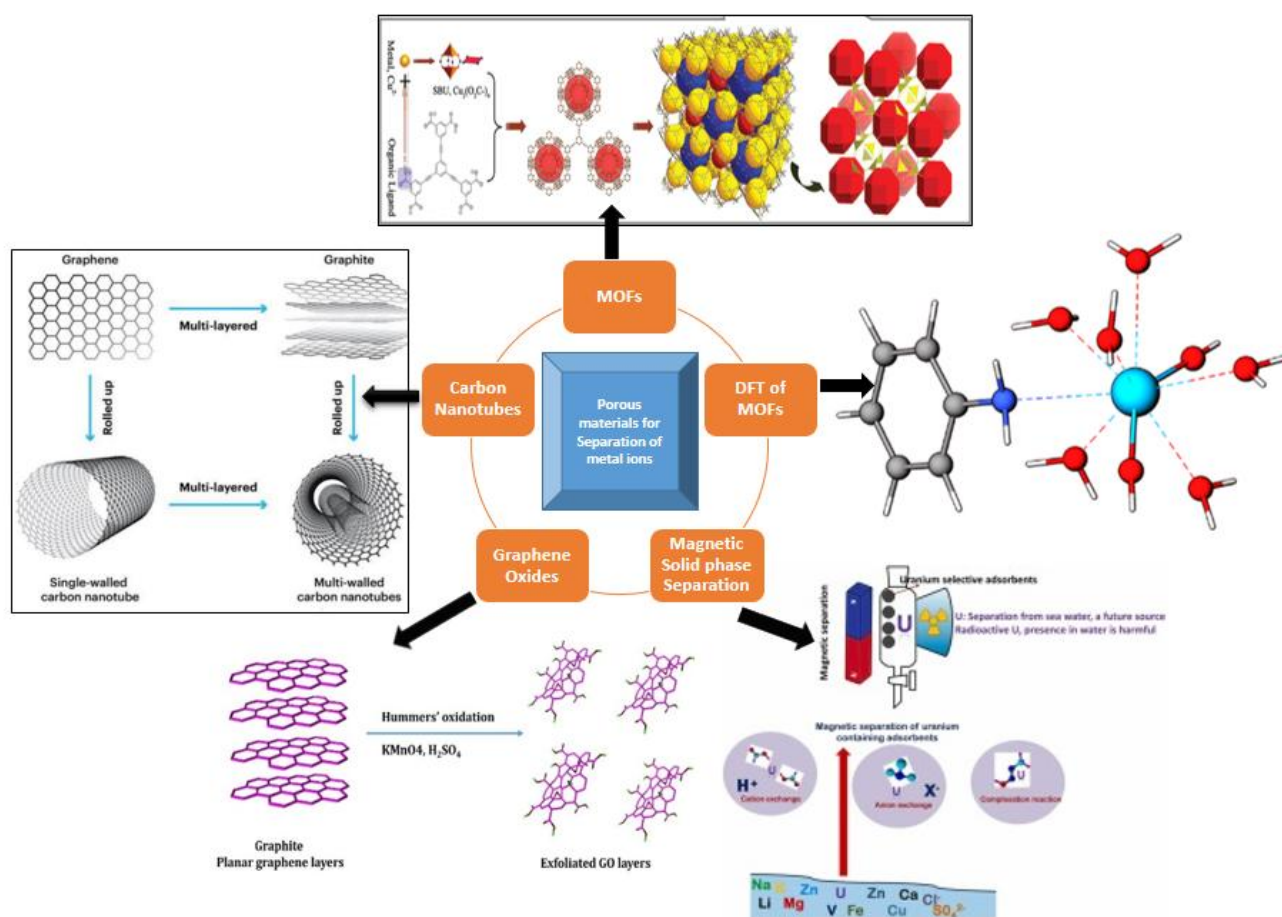




Separations of Lanthanides, Actinides and Fission Products using Porous Materials



Message

Guest Editor, ASSET Bulletin on "Separations of Lanthanides, Actinides and Fission Products using Porous Materials"



Greetings to all the members of ASSET.

The separation and recovery of lanthanides, actinides, and fission products are of fundamental importance in advanced nuclear fuel-cycle technologies, radioactive waste management, environmental remediation, and the development of sustainable strategies for resource recovery. This Special Issue, "Separations of Lanthanides, Actinides and Fission Products using Porous Materials," aims to bring together recent advances in the design and application of innovative porous materials for selective separation and recovery of radionuclides and related metal ions. Particular emphasis will be placed on metal-organic frameworks (MOFs), graphene oxide based materials, carbon nanotubes, magnetic solid-phase separation material adsorbents, as well as their functionalized derivatives. Contributions addressing experimental investigations, adsorption and separation mechanisms, surface functionalization, selectivity, kinetics, thermodynamics, regeneration and recyclability are particularly discussed in detail. The Special Issue will also highlight the growing role of density functional theory (DFT) in understanding metal-ligand interactions, adsorption energetics, coordination environments and separation mechanisms in MOFs and other porous materials. By integrating experimental and computational approaches, this collection seeks to provide a comprehensive perspective on emerging porous-material platforms and their potential for efficient, selective and sustainable separations of lanthanides, actinides and fission products.

I sincerely thank the President for providing me the opportunity to serve as Guest Editor, and I express my gratitude to all the authors who contributed to this special bulletin on this important and timely subject.

Dr. B. Sreenivasulu

Message

President, ASSET



Dear Members,

Greetings from ASSET!

It gives me immense pleasure to present this latest issue of the ASSET Bulletin, dedicated to "Separations of Lanthanides, Actinides and Fission Products using Porous Materials."

Separation science continues to be a cornerstone for advancements across nuclear technology, resource recovery, and environmental stewardship. In recent years, the development of functionalized porous materials—including metal–organic frameworks (MOFs), graphene oxide composites, carbon nanotubes, and magnetic solid-phase sorbents—has fundamentally transformed our capability to achieve high-selectivity radionuclide separations. Integrating these innovative physical matrices with Density Functional Theory (DFT) modeling provides unprecedented microscopic insights into metal–ligand interactions, bridging fundamental coordination chemistry with practical engineering solutions.

This special theme perfectly complements our broader ongoing national focus on securing critical elements and strategic minerals. Advanced separation technologies not only underpin nuclear fuel cycle management and actinide partitioning but also play a pivotal role in purifying high-purity rare earths and critical metals vital for green energy transition, high-tech manufacturing, and national security.

I express my sincere appreciation to our Guest Editor, Dr. B. Sreenivasulu, for compiling a fine collection of contributions that highlight these cutting-edge developments. I record my sincere appreciation to all the authors. I also extend my heartfelt gratitude to Dr. Arijit Sengupta, Editor, ASSET, Dr. P.G. Jaison, Prof. P.K. Mohapatra, Prof. V.K. Manchanda, and the Executive Committee members of ASSET for their continuous dedication to maintaining the technical excellence of our bulletin.

I hope our members, researchers, and students find the articles in this issue both informative and inspirational.

Dr. Jeyakumar Subbiah

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Synthesis and Evaluation of Novel Functionalized Metal-organic Frameworks for the Recovery of actinides from aqueous solutions

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1. Introduction

Uranium and thorium are important elements in nuclear energy systems, but their release into aqueous streams can create environmental and radiological concerns. Actinide-bearing solutions may arise during mining, ore processing, fuel fabrication, spent-fuel reprocessing and radioactive-waste management. Recovery of U(VI) and Th(IV) from aqueous media is therefore important for both resource recovery and environmental protection. Adsorption is attractive because it can combine simple operation with high uptake and can be applied to dilute aqueous streams [1-5]. Among available separation methods, adsorption offers operational simplicity and the possibility of regeneration. Conventional sorbents include activated carbon, inorganic oxides, clays and other porous solids; however, their selectivity and tunability can be limited. Metal-organic frameworks (MOFs) provide an alternative platform in which pore structure and chemical functionality can be deliberately engineered for actinide capture [6-8].

MOFs are crystalline porous coordination materials constructed from metal nodes or clusters and organic linkers. Their high surface area, ordered porosity, tunable pore dimensions and chemically addressable sites have enabled applications in adsorption, separation, catalysis, sensing and environmental remediation [8-11]. For actinide sorption, the principal advantage is the ability to position donor atoms and functional groups within an ordered pore environment rather than relying only on high surface area.

Post-synthetic modification (PSM) is particularly useful when the parent framework has suitable reactive sites but lacks the required actinide-binding functionality. Covalent modification of pendant $-NH_2$ groups can introduce carboxylate, phosphonate, sulfonamide, imine and other donor groups while retaining the parent topology [12-15]. This approach enables systematic tuning of chemical affinity, pore environment and stability. Amino-functionalized frameworks such as IRMOF-3 and UiO-66- NH_2 are useful starting materials for PSM. The present chapter focuses on functionalized IRMOF-3, MOF-LIC-1 and silicon-shielded amidoxime-functionalized UiO-66, highlighting their U(VI) and Th(IV) sorption, desorption and regeneration behavior [16-18]. The selected MOFs were characterized using spectroscopic, diffraction, thermal and microscopic techniques

and their actinide sorption behavior was evaluated as a function of pH, contact time and aqueous medium. The emphasis here is on the experimentally demonstrated sorption, desorption and recyclability results represented in the accompanying figures and tables [16-18].

2. Metal-Organic Frameworks: An Overview

Metal-organic frameworks are crystalline coordination networks constructed by linking metal ions or metal-containing clusters with organic ligands, as shown in Fig. 1. The metal-containing units function as nodes, while organic ligands act as linkers. Appropriate combinations of metal nodes and linkers generate one-, two-, or three-dimensional structures, with three-dimensional frameworks often providing interconnected channels and cavities.

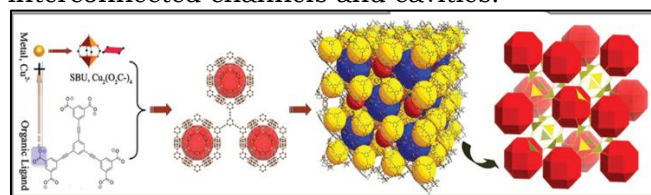


Fig. 1. Basic architecture of an MOF

The modularity of MOFs allows control over pore size, topology and surface chemistry. For actinide sorption, these features determine the accessibility of binding sites, diffusion of aqueous species and the local chemical environment around the target ion [4,8-10,15].

2.1. Important Properties of MOFs for Actinide Sorption

High surface area: Extensive internal pore networks provide a large accessible interface for interaction with aqueous actinide species. However, surface area alone does not determine sorption performance; functional-group density and accessibility are equally important [8,9,15].

Tunable pore structure: Pore dimensions influence diffusion, mass transfer, accessibility of binding groups and adsorption kinetics. Excessive functionalization can partially block pore openings, so an appropriate balance between functional-group density and pore accessibility is required [12,13].

Chemical stability: Stability is critical when MOFs are exposed to aqueous, acidic or radioactive environments. Strong metal-ligand interactions and robust framework connectivity can improve resistance to hydrolysis; Zr-based UiO frameworks are particularly attractive for demanding aqueous applications [12,19,24].

Thermal stability: Thermal robustness is relevant during activation, drying, regeneration and processing. PSM can change thermal stability; therefore, adsorption performance should be considered together with framework integrity [12,20,23].

Functional-group tunability: O-, N-, P- and S-containing donor groups can interact with actinides through coordination, electrostatic attraction, chelation or ion exchange. Carboxylates, phosphonates, amines, amidoxime, sulfonamides and related functionalities have been investigated for selective metal-ion binding [2,3,12,19,22-23].

The ability to modify a common parent framework provides a convenient route to compare different binding chemistries while retaining a similar porous architecture.

2.2. Synthesis of MOFs

The synthesis route affects crystallinity, particle size, defect concentration, porosity and morphology. Common approaches include solvothermal, hydrothermal, microwave-assisted and mechanochemical synthesis [4-5].

Solvothermal synthesis: Metal precursors and organic linkers are reacted in a suitable solvent under controlled temperature and pressure, commonly producing crystalline MOF powders.

Hydrothermal and microwave-assisted synthesis: Water-based hydrothermal conditions and microwave irradiation can provide alternative routes with shorter reaction times or different particle sizes, depending on the framework [21,23].

Mechanochemical and greener synthesis: Solvent-minimized approaches can reduce solvent consumption and may facilitate scale-up. For practical actinide separation, precursor cost, solvent use, energy demand and reproducibility should be considered alongside material performance [21,23].

Room-temperature and green synthesis: The development of low-temperature and solvent-minimized synthesis is increasingly important for practical MOF production. For environmental and nuclear applications, future MOF synthesis should consider not only material performance but also precursor cost, solvent toxicity, energy consumption, waste generation and scalability.

3. Post-Synthetic Modification

Direct synthesis of a framework containing all desired binding functionalities can be challenging. PSM provides a modular alternative: the parent MOF is first synthesized and characterized, followed by selective reaction at accessible functional or metal sites as illustrated in Fig. 2a,b [12,20].

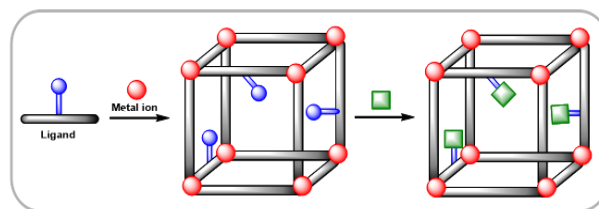


Fig. 2a. Integrate functionalities within MOFs.

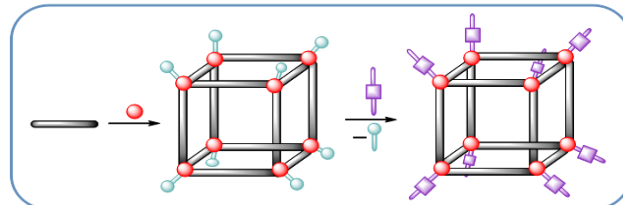


Fig. 2b. Exploiting functional properties of unsaturated metal centers (UMCs).

Amino-functionalized MOFs are especially useful because pendant -NH_2 groups can be chemically modified without necessarily destroying the underlying framework topology. The PSM strategy used for IRMOF-3, MOF-LIC-1 and UiO-66- NH_2 illustrates how the same framework concept can be adapted for different actinide-binding environments [16-18].

4. Actinide Chemistry Relevant to Sorption

Uranium(VI): Under oxidizing aqueous conditions, uranium is commonly present as the uranyl ion, UO_2^{2+} . Its aqueous speciation depends strongly on pH, carbonate concentration, ionic strength and competing ligands. Consequently, protonation/deprotonation of sorbent sites and changes in uranium speciation can produce an optimum pH for uptake rather than a monotonic increase.

Thorium(IV): Th(IV) is a highly charged hard Lewis acid and interacts strongly with oxygen-donor ligands. Hydrolysis becomes important as pH increases, making pH and ligand chemistry key factors in Th(IV) sorption [3,24].

5. Functional Groups for Actinide Capture

Carboxylate, phosphonate and phosphinic groups provide multiple oxygen donor atoms, whereas amine, imine, pyridine and amidoxime groups provide nitrogen-containing binding sites. Amidoxime is particularly attractive for uranium because its N/O donor arrangement can form strong interactions with uranyl species.

6. Mechanisms of Actinide Sorption by MOFs

Actinide ions can coordinate directly with donor groups located on the external surface or within MOF pores. Multidentate ligands can bind through two or more donor atoms, while proton/ion exchange and electrostatic interactions can also contribute. The porous framework can concentrate actinide species near chemically active sites, while hydrogen bonding and the local pore environment can further stabilize the adsorbed species. Thus, sorption is generally governed by a combination of framework accessibility and specific chemical coordination.

7. U(VI) Sorption Performance of Functionalized MOFs

Functionalized IRMOF-3:

The pH of the solution plays a very crucial role in sorption of U(VI) from aqueous (acidic/basic/neutral) medium, since it affects the specific state of uranium as well as the surface charge distribution of binding sites across sorbents. In order to investigate the influence of solution pH on the sorption behaviour of U(VI) onto IRMOF-3 and its PSM MOFs, studies were performed as a function of the pH of the solution in the range from 2 to 9. The results revealed that the sorption of U(VI) strongly depends on pH. Sorption of U(VI) onto MOFs is less up to pH 4 beyond which sorption of U(VI) increases up to pH 6 for all MOFs and then decreases after pH 7. Four PSM derivatives, IRMOF-PC, IRMOF-GA, IRMOF-SMA and IRMOF-DPC, were evaluated for U(VI) recovery. All materials showed high sorption at around pH 6, with the capacity following the order IRMOF-DPC (300 mg g⁻¹) > IRMOF-SMA (292 mg g⁻¹) > IRMOF-PC (289 mg g⁻¹) > IRMOF-GA (280 mg g⁻¹) > IRMOF-3 (273 mg g⁻¹) as shown in Fig. 3a,b. IRMOF-DPC also exhibited rapid uptake, reaching >99% U(VI) sorption within 5 min [16]. The improved sorption behaviour shown by IRMOF-DPC could be is due to the strong electrostatic interaction between hard Lewis acid U(VI) and hard Lewis base: phosphoryl oxygen (P=O). Furthermore, the bonding between IRMOF-DPC and U(VI) was confirmed by FTIR wherein the intensity of P=O (1127 cm⁻¹) decreases significantly with a peak shift due to bonding with U(VI). Additionally, the new intense strong sharp peak observed at 925 cm⁻¹ is attributed to the UO₂²⁺ ions. The IR analysis thereby confirms the formation of strong bond between P=O and U(VI). The kinetic studies confirmed that IRMOF-DPC responds quickly (~5 min) and has highest sorption efficiency towards U(VI) from aqueous medium. For IRMOF-3, IRMOF-PC, IRMOF-GA, and IRMOF-SMA the saturation sorption was observed after 3 h, however they exhibited higher efficiency beyond 60 minutes. IRMOF-DPC follow pseudo second order kinetics and all other MOFs also follow similar trend.

Functionalized MOF-LIC-1: MOF-LIC-DPPC, MOF-LIC-GA, MOF-LIC-PCA and MOF-LIC-SA were prepared through PSM. In order to investigate the influence of solution pH on the sorption behavior of U(VI) onto MOF-LIC-1 and its PSM MOFs, pH was varied from 2 to 9. The modified materials showed enhanced U(VI) sorption, with MOF-LIC-SA giving the highest capacity of about 298 mg g⁻¹ at pH 6. The corresponding sorption values and distribution coefficients are summarized in Table 1 [17]. The results revealed that sorption of U(VI) strongly

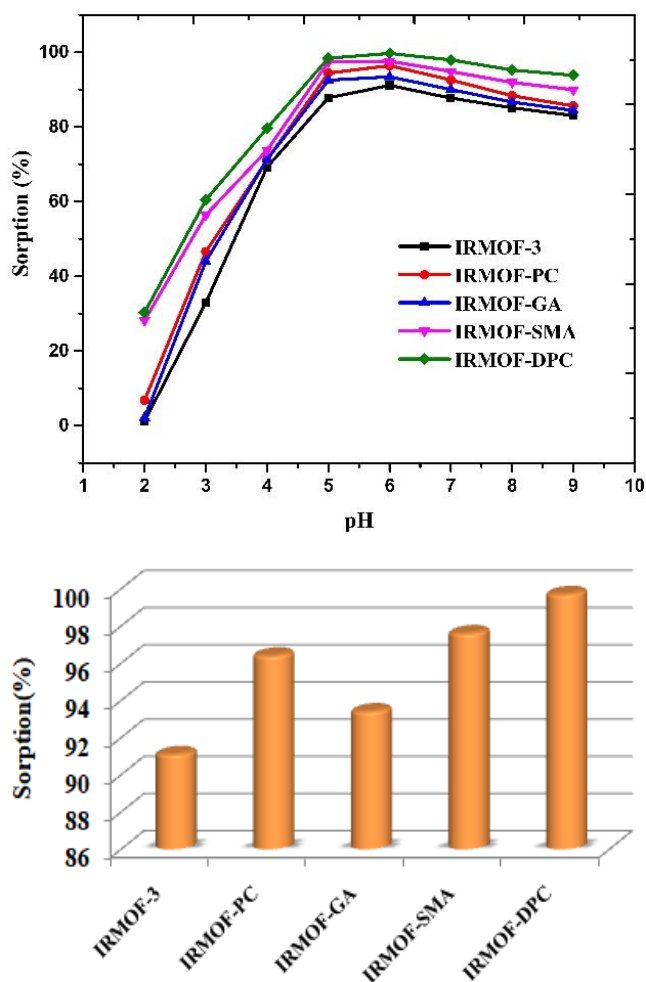


Fig. 3a. Effect of solution pH on U(VI) sorption (%) onto IRMOF-3 and its PSM MOFs, (b) U(VI) sorption (%) onto IRMOF-3 and its PSM MOFs at pH = 6. [Co = 1 mg/mL, t = 180 min, m_{sorbent} = 10.0 mg, V_{solution} = 3 mL and T = 25 ± 1 °C].

depends on pH of the solution and up to pH = 3 the sorption of U(VI) onto MOFs is lower and reaches a maximum at pH=6, and shows a decrease in extraction behavior. MOFs showed saturation sorption at pH = 6 except for MOF-LIC-DPPC (pH = 7), and the order of sorption efficiency of MOFs follows the order (Table 1): MOF-LIC-SA > MOF-LIC-GA > MOF-LIC-PCA > MOF-LIC-1 > MOF-LIC-DPPC. MOF-LIC-SA with sulphamide (-SO-NH) group showing enhanced sorption capacity towards U(VI) (298 mg/g) due to strong electrostatic interactions between sulphamide groups and U(VI). The lower sorption efficiency reported by MOFs at lower pH range could be due to protonation and deprotonation of incorporated functional groups. Moreover, at higher pH range uranium forms multinuclear complexes; therefore sorption efficiency decreases beyond pH 6. In order to avoid the formation of uranium hydroxides (at higher pH) and considering lower sorption efficiency (at lower pH), pH 6 was optimized for subsequent sorption experiments.

Uranium forms different species such as UO₂²⁺, UO₂OH⁺, (UO₂)₂(OH)₂²⁺, (UO₂)₃(OH)₅⁺,

$\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$, $\text{UO}_2(\text{OH})_3^-$, $\text{UO}_2(\text{OH})_4^{2-}$ depends on the solution pH. The fraction of uranium species increases in the following order $\text{UO}_2^{2+} < \text{UO}_2\text{OH}^+ < (\text{UO}_2)_2(\text{OH})_2^{2+} < (\text{UO}_2)_3(\text{OH})_5^+ < \text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$, $\text{UO}_2(\text{OH})_3^- < \text{UO}_2(\text{OH})_4^{2-}$ with increase in pH. There is a possibility of any of those above uranium species can be extracted by MOFs. The sorption of uranium is maximum at pH 6 may be due to the selective sorption of $(\text{UO}_2)_3(\text{OH})_5^+$ at pH 6. The fraction of UO_2^{2+} is maximum at pH 2 and it decreases with towards alkaline pH. The following sorption mechanism is also not ruled out - upon extraction of UO_2^{2+} by MOF, the fraction of UO_2^{2+} decrease in a medium; subsequent to this, the equilibrium adjusts to maintain an appropriate UO_2^{2+} percentage in the medium.

Table 1. Sorption of U(VI) onto MOF-LIC-1 and PSM MOFs.

MOF	pH	Sorption (%) [#]	q _e (mg U g ⁻¹)
MOF-LIC-1	6	91	244
MOF-LIC-DPPC	7	88	260
MOF-LIC-GA	6	96	269
MOF-LIC-PCA	6	93	256
MOF-LIC-SA	6	99	298

[#] Sorption (%) refers to the ratio of [U(VI)] in 10 mg of MOF to [U(VI)] in 3 mL of aqueous pH solution.

Silicon-shielded amidoxime-functionalized UiO-66: A second design strategy combined the chemically robust UiO-66 framework with amidoxime functionality and silicon shielding. The resulting Si/UiO-66-AO was developed for rapid U(VI) recovery from aqueous and acidic media [18]. The material showed capacities of approximately 217 mg g⁻¹ in aqueous medium, 65 mg g⁻¹ in acidic medium and 31.6 mg g⁻¹ in simulated seawater, as shown in Fig. 4. Substantial uptake occurred within about 5 min, demonstrating the usefulness of combining strong binding functionality with a robust framework [18]. It is important to understand the kinetics (saturation sorption and order of the reaction mechanism) of U(VI) sorption for practical applications. The significant increase in sorption rate of U(VI) by two MOFs was observed within 5 min, and the U(VI) saturation sorption efficiency reached to ~ 90 % for pristine MOF within 15 min. While, the highly acid resistant Si/UiO-66-AO showed the U(VI) saturation sorption efficiency

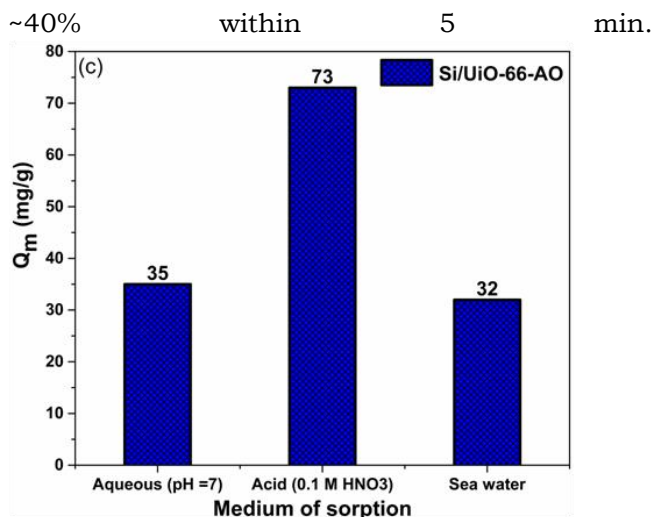


Fig. 4. Sorption efficiency (%) of U(VI) by Si/UiO-66-AO in aqueous, acidic and seawater media. ($m_{ads} = 10$ mg, $V = 3$ mL, $U(VI) = 200-1000$ mg L⁻¹, acid concentration = 0.1–6 M, $t = 0-360$ min, $T = 10-50$ °C).

The effect of temperature on sorption of U(VI) ($C_0=500$ mg/L) onto pristine and Si/UiO-66-AO MOFs at 283, 293, 300, 313, and 323 K was investigated. Both the U(VI) sorption efficiency and capacity for UiO-66-NH₂ are always higher than that of Si/UiO-66-AO. The sorption of U(VI) onto UiO-66-NH₂ and Si/UiO-66-AO significantly increases with increase in temperature up to 40°C, indicating that a higher temperature is beneficial for U(VI) sorption onto MOFs. However, from 50°C onwards, the drastic decrease in sorption efficiency was observed for both the MOFs towards U(VI). Such trends may be due to the partial reduction of linker free moiety at elevated temperatures. Interestingly, the variation of adsorption efficiencies is similar for both MOFs, i.e., first increases and then decreases. The value rapidly decreases from 323 to 333 K, indicating that the higher temperature plays a crucial role in the sorption efficiency. The maximum sorption capacity (C_s ; mg/g) was found to be 145 mg/g and 65 mg/g for UiO-66-NH₂ and Si/UiO-66-AO, respectively.

8. Th(IV) Sorption by Functionalized MOF-LIC-1 MOFs

The effect of solution pH on Th(IV) sorption behavior on four functionalized MOFs along with pristine MOF were investigated at pH 2-9. The studies revealed that, Th(IV) uptake follows the order (Table 2); MOF-LIC-SA > MOF-LIC-PCA > MOF-LIC-DPPC > MOF-LIC-GA > MOF-LIC-1. At lower solution pH (up to 3), Th(IV) uptake was found to be lower, while from pH= 4 onwards, all MOFs showed drastic increase in sorption efficiency and saturation occurred at pH=6, post to which a gradual decrease was observed. The MOF-LIC-GA showed saturation sorption at pH=7. The maximum Th(IV) uptake was exhibited by functionalized MOF-LIC-SA (149 mg/g) with 99% sorption at pH 6 (Table 2). The results

demonstrate that the same functionalized MOF platform can interact strongly with more than one actinide, while the magnitude of uptake depends on oxidation state, hydrolysis and coordination chemistry [17].

Table 2: Sorption parameters for Th(IV) adsorption by MOF-LIC-1 MOFs

MOF	pH	Th(IV) sorption	Capacity (mg g ⁻¹)
MOF-LIC-1	6	87%	131
MOF-LIC-DPPC	6	95%	144
MOF-LIC-GA	7	91%	137
MOF-LIC-PCA	6	98%	147
MOF-LIC-SA	6	99%	149

9. Desorption Studies

Desorption is important for the recovery of the sorbed actinide and regeneration of the sorbent. For IRMOF-DPC and other IRMOF derivatives, 0.01 M HNO₃ was the most effective eluent, giving up to 97% U(VI) recovery, as shown in Fig. 5a. For the MOF-LIC-1 derivatives, 0.01 M HNO₃ was effective for most materials, whereas 0.01 M Na₂CO₃ was more effective for MOF-LIC-DPPC, as shown in Fig. 5b [16,17].

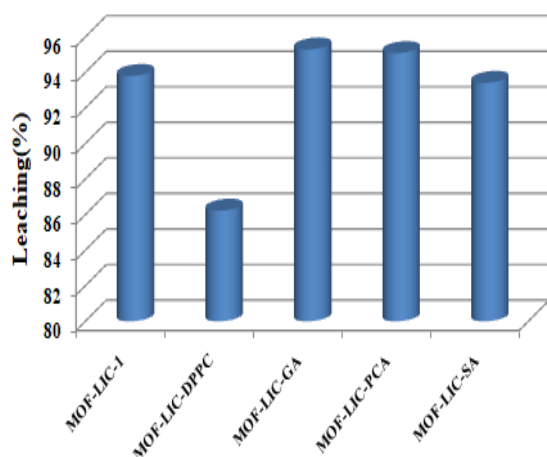
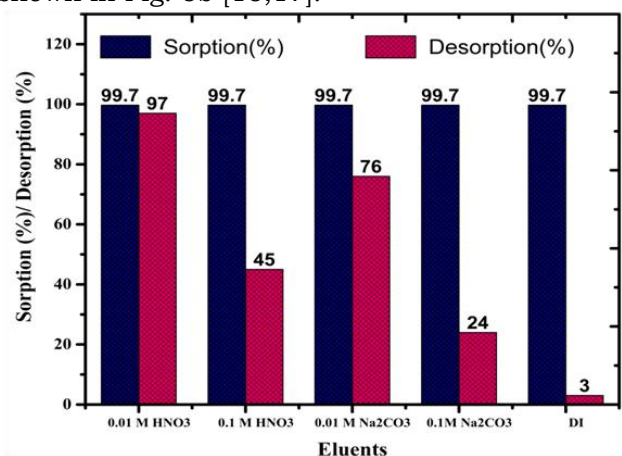


Fig. 5. (a) Sorption (%) and desorption (%) of U(VI) from IRMOF-DPC; (b) leaching (%) of U(VI)

from MOF-LIC-1 and its PSM MOFs using 0.01 M HNO₃.

For Si/Uio-66-AO, 0.1 M Na₂CO₃ provided the highest desorption, reaching approximately 99%, as shown in Fig. 6.

10. Stability and Regeneration of Synthesized MOFs

Recyclability was evaluated to assess whether the functionalized MOFs retained their sorption performance after repeated use. IRMOF-3 and its PSM derivatives showed only a marginal decrease after two cycles. A similar trend was observed for MOF-LIC-1 and its functionalized derivatives, indicating that the materials can be regenerated and reused under the tested conditions, as shown in Fig. 7a,b [16,17].

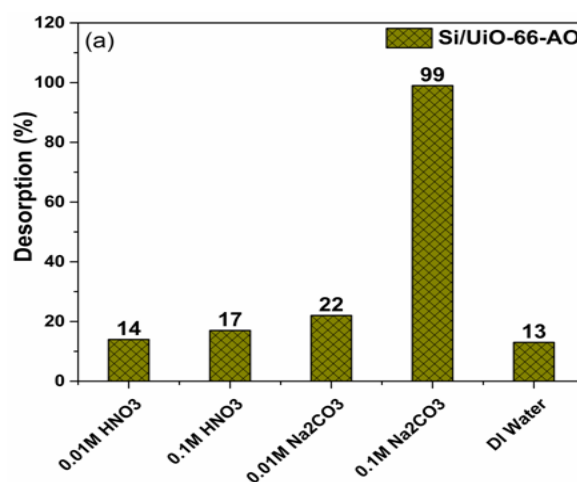


Fig. 6. Desorption (%) of U(VI) from Si/Uio-66-AO using different desorbing agents.

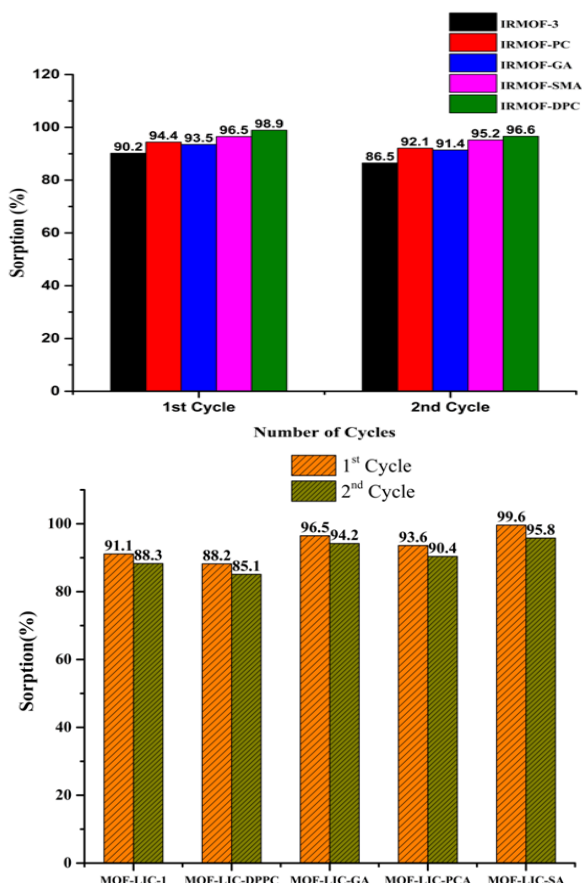


Fig. 7. (a) Recyclability of IRMOF-3 and its PSM MOFs; and (b) recyclability of MOF-LIC-1 and its PSM MOFs for U(VI) sorption.

Comparison of the Three MOF Design Strategies

The three approaches illustrate complementary design principles (Table 3). IRMOF-3 and MOF-LIC-1 emphasize covalent PSM to introduce chemically diverse binding groups, whereas Si/Uio-66-AO combines amidoxime functionality with silicon shielding to improve chemical robustness. Together, these studies show that practical MOF design requires simultaneous consideration of framework stability, pore accessibility, binding chemistry, regeneration and processability [16-18].

11. Challenges in MOF-Based Actinide Sorption

Despite the strong sorption performance demonstrated in the figures and tables, practical deployment requires balancing capacity with stability and pore accessibility. Functional-group density can improve binding but may reduce diffusion, while defects can increase accessibility at the expense of structural robustness [12, 23].

Laboratory concentration versus real water:

Many studies use relatively high uranium concentrations. Future work should emphasize trace-level actinides, realistic competing ions, natural seawater, and groundwater, mining wastewater and nuclear-process solutions.

Table 3: Comparison of various properties of all three MOFs

Parameter	Function alized IRMOF-3	Functionali zed MOF-LIC-1	Si/Uio-66-AO
Parent MOF	IRMOF-3	MOF-LIC-1	UiO-66-NH ₂
Main strategy	Covalent PSM	Covalent PSM	Sequential PSM
Target ions	U(VI)	U(VI), Th(IV)	U(VI)
Key function alities	P, N, O, S-containing groups	P, N, O, S-containing groups	Amidoxime + Si
Maximum U(VI) capacity	300 mg g ⁻¹	298 mg g ⁻¹	217 mg g ⁻¹
Th(IV) capacity	Not investigated	149 mg g ⁻¹	Not investigated
Rapid uptake	5 min	5 min	5 min
Acid stability	Stable in aqueous medium (pH 1-10)	Stable in aqueous medium (pH 1-10)	Up to 6 M HNO ₃
Radiation stability	Not investigated	Demonstrated	Up to 500 kGy
Addition al property	Multiple binding functionalities	Multiple binding functionalities	Luminescence

12. Regeneration:

A practical sorbent should retain capacity and structural integrity over repeated adsorption-desorption cycles. Dilute nitric acid or carbonate eluents can facilitate recovery depending on the binding chemistry.

Mechanical strength: MOF powders are convenient for laboratory studies but may require shaping as pellets, beads, monoliths, membranes or polymer composites for continuous-flow operation. The shaping process should preserve pore accessibility and actinide-binding functionality [18,23].

13. Future Directions

The next generation of MOF-based actinide sorbents should be designed around practical process requirements: moving from high-capacity powders toward application-specific materials for trace-level capture, rapid mass transfer, regeneration and process integration [25,26]. A future workflow could combine DFT screening, ligand selection, MOF synthesis, PSM,

characterization and sorption testing *to reduce experimental trial and error*. Controlled defects can increase pore accessibility and expose additional active sites; recent research shows that ligand-defect engineering can enhance the kinetics and uranium uptake of amidoxime-functionalized MOFs. Combining micropores with mesopores can reduce diffusion limitations while retaining a high density of chemical binding sites. Integration with polymers can improve mechanical strength, processability, shaping and column stability. Magnetic MOFs can facilitate solid-liquid separation using an external magnetic field and MOF membranes may enable continuous uranium separation rather than batch adsorption; for industrial applications, batch adsorption should ultimately be translated into fixed-bed systems.

14. Broader Applications

MOFs designed for actinide sorption can support uranium recovery, thorium separation, process-stream purification and radioactive-waste treatment [27,28], with tunable pores and binding sites that also offer opportunities for selective recovery from seawater, groundwater and other complex aqueous systems. *More broadly*, the development of MOFs for actinide sorption lies at the intersection of coordination chemistry, materials science, environmental engineering and nuclear technology and their principal advantage is modularity: the metal node and linker define the framework, while PSM determines the chemical environment available for interaction with the target ion. Functionalized IRMOF-3 and MOF-LIC-1 demonstrate how diverse donor functionalities can be introduced into related porous platforms, while Si/UiO-66-AO demonstrates the value of combining strong uranium-binding chemistry with framework protection. Together, these studies indicate that successful sorbents should be engineered for selectivity, stability, regeneration and processability rather than for surface area alone and that future MOF design should move not simply toward increasingly high surface areas *but toward application-specific architectures in which structure, functionality and stability are deliberately optimized*.

15. Conclusions

MOFs are very promising materials for actinide sorption because their structure and chemistry can be precisely controlled. They have high porosity, adjustable pore environments, diverse structures, and can be modified after synthesis, offering advantages over many traditional adsorbents. For the recovery of uranium and thorium, *it is* crucial to include donor functionalities that can form strong bonds with actinide species; groups containing oxygen, nitrogen, phosphorus and sulfur can provide coordination sites and amidoxime is especially effective for capturing uranium. The study on

functionalized IRMOF-3 and MOF-LIC-1 shows that post-synthetic modification is a flexible way to enhance actinide sorption: among the materials tested, IRMOF-DPC and MOF-LIC-SA had the highest capacities, reaching 300 and 298 mg g⁻¹ for U(VI) respectively, while MOF-LIC-SA showed a Th(IV) uptake of about 149 mg g⁻¹ with fast kinetics. The creation of Si/UiO-66-AO highlights the importance of stability engineering: combining amidoxime functionality with a strong UiO-66 framework and silicon protection enabled quick uranium extraction from aqueous, acidic and simulated seawater media, along with resistance to harsh conditions.

These results show that MOFs can go beyond their usual role as high-surface-area porous materials and act as chemically selective molecular recognition platforms. For practical use, future research should focus on trace-level actinide extraction, real water environments, competing ions, long-term radiation exposure, repeated regeneration, mechanical shaping and continuous-flow operation. Ultimately, the development of stable, selective, rapidly acting, regenerable and processable MOF-based sorbents could provide an important materials platform for uranium and thorium recovery, radioactive wastewater treatment and future nuclear fuel-cycle technologies.

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ASSET Bulletin on "Separations of Lanthanides, Actinides and Fission Products using Porous Materials"

Biodata



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Application of Functionalized Carbon Nanotubes for the Extraction of f-cations from Aqueous Streams

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Introduction

Nuclear energy, as a sustainable and reliable energy resource, is in the forefront to satisfy the increasing demand of energy requirement driven by population growth, economic development and rapid industrialization. However, utilization of nuclear energy and associated nuclear fuel cycle generates radioactive nuclear waste that contains varying inventory of actinides, lanthanides, fission and corrosion products. Among them, actinides are of worth mentioning. Actinides like Uranium (U), Thorium (Th) and Plutonium (Pu) are of particularly important from the view point of nuclear fuel cycle. Several long-lived radioisotopes of minor actinides like Neptunium (Np), Americium (Am), Curium (Cm) possess half-life ranging from hundreds of years. They should be partitioned for prior conditioning required for either disposal in deep geological repository (DGR) or transmutation in accelerator driven subcritical system (ADSS) or in fast reactor¹. Many radioisotopes of the minor actinide have technological significance. Am²⁴¹ is an alternative candidate that can be used in radio thermoelectric generator (RTG)², major component of smoke detector³ and a well-known neutron source. Np²³⁷ is a precursor of Pu²³⁸ which is a primary component in radioisotope power systems.⁴ Presently solvent extraction is one of the primary processes employed in nuclear plant for actinide and lanthanide separation from aqueous stream⁴. But there are

multifaceted issues associated with solvent extraction process like organic handling, radiolytic and chemical degradation of organic solvents and diluents, third phase formation during solvent extraction and the secondary organic waste management⁵. Therefore, solid phase extraction is gaining attention as one of the alternative processes of solvent extraction. Solid phase extraction has lower ligand and organic solvent inventories, minimal requirement of liquid-liquid phase separation unlike conventional solvent extraction and can be easily operated in column mode⁶. A variety of solid phase sorbents like carbon nanotube (CNT), Metal Organic Framework (MOF), Covalent Organic Framework (COF), and other carbonaceous compounds like active charcoal and bio char have been investigated for actinide and lanthanide extraction. Among them, CNT draws significant attention due to its high surface area, tunable surface property, easy functionalization and higher thermal and chemical stability.⁷

Carbon Nanotube: What it is and why functionalization matters

Carbon nanotube is the cylindrical nanostructure of single or multiple graphene sheets rolled at specific and discreet angles. There are two types of Carbon nanotubes. One is Single walled carbon nanotube (SWCNT) that is made up by one graphene sheet rolled into a seamless cylindrical structure. The other one is Multiwalled Carbon Nanotube (MWCNT) consisting of multiple concentric

graphene like cylindrical walls rolled around a common hollow axis.

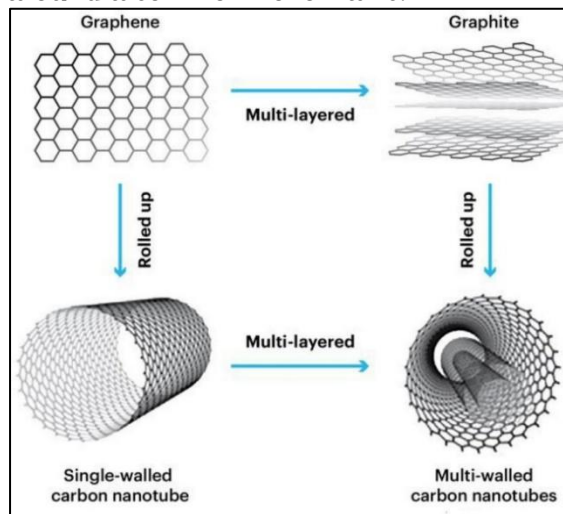
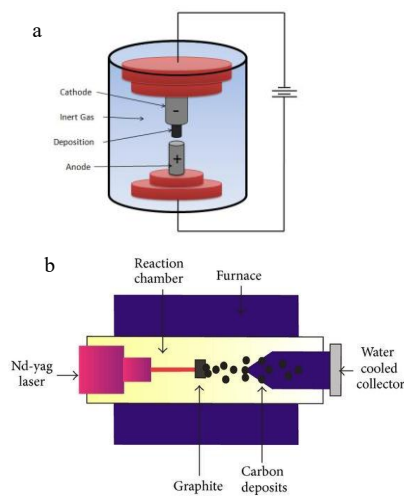


Figure 1: Schematic representation of structure of SWCNT and MWCNT

MWCNT is generally robust due to multiple graphitic cylindrical structure compared to SWCNT and easier to produce in large scale. CNT has very high surface area compared to conventional graphitic carbon material. Typical BET surface area of graphite is reported to be $\sim 5\text{--}20\text{ m}^2\text{g}^{-1}$ while that of SWCNT and MWCNT are in the range of $\sim 400\text{--}1000\text{ m}^2\text{g}^{-1}$ and $\sim 100\text{--}600\text{ m}^2\text{g}^{-1}$ respectively depending on the nanotube morphology, diameter, aggregation and functionalization. CNTs show aspect ratio in the range of $10^2\text{--}10^5$. This extremely high aspect ratio provides an extended one-dimensional platform for surface functionalization and interface to interact with dissolved metal ions.⁵⁰ But pristine CNT has very limited application as a solid phase extractant due to its intrinsic hydrophobicity and it is prone to agglomerate in solution. Surface functionalization overcomes that problem by grafting hydrophilic and chemically active group to the CNT surface. Moreover, task specific functionalization can transform the CNT from a carbonaceous nonspecific adsorbent to an engineered interface that interacts with selective metal ions.⁵¹ As for example, Polyamidoamine dendrimer (PAMAM) functionalized MWCNT shows high affinity towards Am^{3+} while it is reported that diglycolamide functionalized MWCNT can extract U and Th from aqueous solution¹². But how CNT can be synthesized and then functionalized?

Synthesis of Carbon Nanotube

CNTs can be synthesized primarily by three methods: electric arc discharge, laser ablation and Chemical Vapor deposition (CVD). Basic principle to synthesize CNTs for all the above methods remain similar, that is to convert Carbon containing precursor into Carbon species that nucleates and grows into tubular graphitic structure. In electric Arc and Laser ablation method, the vaporization process is done by intense electric arc and high energy LASER respectively. The vaporized Carbon then condenses and cools down to form CNTs. But in CVD method, it is done by the thermal decomposition of carbon containing gaseous precursors like acetylene, methane or other hydrocarbons catalysed by the nano-sized transition metal catalysts mainly Iron (Fe), Cobalt (Co) or Nickel (Ni). Subsequent diffusion, dissolution and precipitation of carbon occurs on or from the catalyst nanoparticles leading to the nucleation and growth of carbon nanotubes. CVD offers scalability, more control over CNT morphology and suitability for large scale production. The operational parameters in CVD like particle size of the catalyst, operating temperature, gas flow rate etc. can directly influence the physical properties of CNT like tube diameter, defect density, length, no. of walls etc. These structural characteristics can influence the susceptibility of the CNT surface to oxidation, functional group density and indirectly affects the mass transfer characteristics of the CNT-solution interface.^{8,9,10}



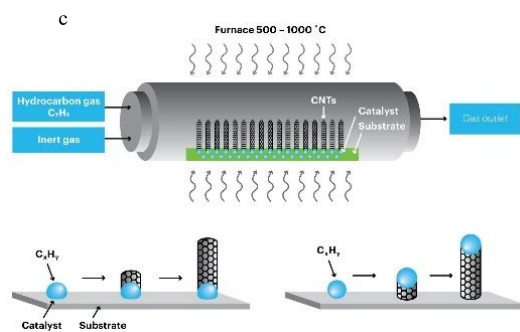


Figure 2: Schematic representation of the principal methods for carbon nanotube synthesis: (a) electric arc discharge, (b) laser ablation and (c) chemical vapor deposition (CVD)

Functionalization of Carbon Nanotube

Though pristine CNTs have high surface area but due to graphitic sp^2 carbon framework they are inherently hydrophobic and chemically inactive. Surface modification by functionalization introduces hydrophilicity and more coordinating sites to interact with metal ion in solid liquid interface. Oxidation of MWCNT by conc. HNO_3 or with a mixture of conc. HNO_3 and conc. H_2SO_4 under reflux condition generates higher density of defect sites and edge sites than pristine MWCNT and introduces functional groups like $-COOH$, $-OH$, $-C=O$ and $-O-$ groups¹¹. Oxidised MWCNT is more hydrophilic, provides greater no. of binding sites than pristine CNT and an increase in the specific surface area. Diglycolamide (DGA) functionalization in MWCNT involves sequential process like carboxylation, acylation, amidation and DGA fixation¹².

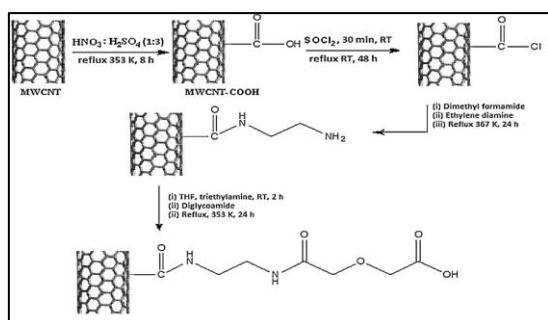


Figure 3: schematic representation of synthesis route of MWCNT-COOH and MWCNT-DGA (reproduced from ref. 51)

For different generations of Polyamidoamine functionalized MWCNT, first amidation coupling reaction was done between carboxylic acid group of MWCNT-COOH and amine group of Ethylene Diamine (EDA) in presence of activating

agent DCC and coupling additive agent DMAP to synthesize Amidoamine functionalized (AMAM) MWCNT. It is then reacted with methylacrylate in methanol medium to make MWCNT-PAMAM_{0.5}. It then undergoes amidation reaction with EDA to synthesize MWCNT-PAMAM_{G1} and MWCNT-PAMAM_{G2}.¹³

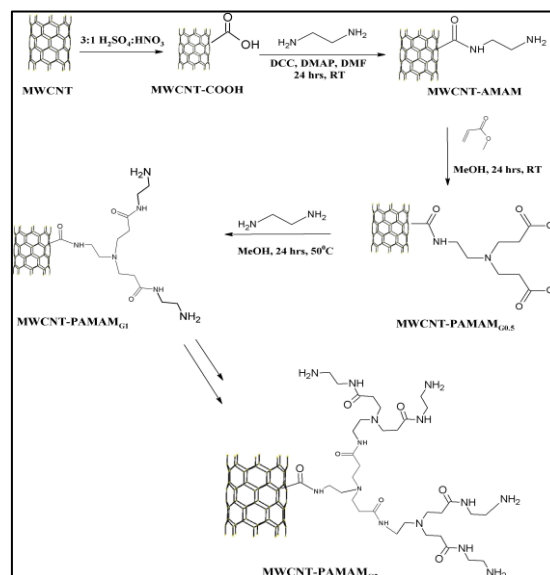


Figure 4: schematic representation of synthesis route of MWCNT-PAMAM_{G1} and G2 (reproduced from ref. 41)

For thiol group introduction, amidation reaction can be done between MWCNT-COOH and Cysteamine hydrochloride in ethanol solvent in presence of EDC/NHS activating agents.

Apart from chemical reaction, plasma induced grafting method is another useful tool for functionalization. In order to improve the water dispersibility, carboxymethyl cellulose (CMC) can be grafted by plasma induced method on MWCNT surface.¹⁴

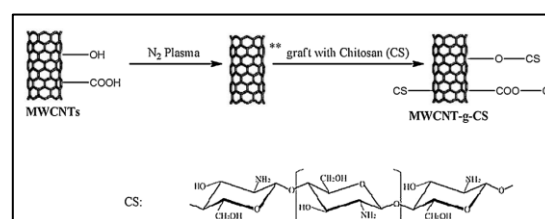


Figure 5: schematic representation of synthesis route of MWCNT-CMC (reproduced from ref 51)

Functionalized CNT and extraction of f block cation

Mechanism of extraction

To discuss the extraction mechanism, first we should define sorption process. Sorption is a general term encompassing the retention of a dissolved species at the surface or within the solid phase. The dissolved species retained by sorption is termed as sorbate and the solid phase as sorbent. Here, functionalized CNT, as for example, is a sorbent and the f block cations in aqueous solution is sorbate. During sorption, metal ion first has to migrate from the bulk solution to the interface of liquid and solid CNT surface. It interacts with the functional groups grafted on the CNT surface and then associates with the surface. Therefore, the macroscopic extraction of metal ion is a combination of several molecular processes that can occur sequentially or simultaneously. Besides, the f block metal ions, due to their high charge density, does not exist as bare ions in aqueous solution but are solvated with no. of water molecules. Besides, the surface of the functionalized carbon nanotube need not to be a homogeneous flat surface with identical binding sites. Therefore, the mechanism is a complex combination of several physicochemical processes. Process parameters also have profound influence on the sorption process.¹⁵ If we take the example of oxidized MWCNT, at high pH of the solution, the functional -COOH group can be deprotonated and form -COO⁻.¹⁶ Therefore, at different pH of the solution, oxidized MWCNT shows different sorption property to the same metal ion. The interaction mechanism of the f block metal ions with the functionalized CNT also differs. In some cases, interaction is predominately electrostatic, arising from coulombic attraction between positive metal ions and negatively charged sites on the functionalized CNT surface. Here the metal ion retains its hydration sphere and no coordination or covalent bond is formed between metal ion and functional group on CNT surface. This is called outer sphere complexation. It is reported that usually outer sphere complexation is strongly influenced by the ionic strength of the solution.¹⁷ The other mechanism where the

metal ion either sheds its partial or complete hydration shell or rearranges its hydration shell to form the metal ligand coordination bond is called inner sphere complexation¹⁸. Inner sphere complexation, in general is comparatively less sensitive to ionic strength variation of the solution medium. If the ligand of the functional group has one or more donor atoms with such spatial arrangement that those donor atoms from the same ligand can coordinate with the same metal ion (multidentate ligand) then it can form one or more chelate rings with that metal ion. Due to the chelate effect, resulted complex is generally thermodynamically more stable than complex formed with the monodentate ligand.¹⁹ Ion exchange can also occur where, H⁺ or the counter ion is released into the solution due to the metal - CNT interaction.²⁰

Physicochemical factors governing f-block extraction mechanism

There are several factors that govern the actinide and lanthanide extraction by functionalised CNT from aqueous feed. The first one is the inherent chemical nature of the actinide and lanthanide metal cations. The high charge density of the f block cations makes them hard acid and as per Pearsons HSAB principle, they generally prefer the hard donor atoms like Oxygen. Again, if we compare lanthanide and actinide cations with similar charge, 4f orbitals in lanthanides are strongly contracted and shielded, whereas 5f orbitals in actinides are comparatively more spatially extended and can participate more strongly in bonding. Therefore, interaction between actinide metal ion-CNT functional moiety possesses greater degree of covalent character than the corresponding lanthanide interactions. This property can be exploited during selective extraction of actinides from the solution of actinide and lanthanide by relatively soft donor atoms like S or N containing group.^{21,22} Again, because of lanthanide and actinide contraction, f block metal ions with same charge and in the same groups but with different positions across the series show different charge density.^{23,24} Charge density influences hydration energy and hydrolysis tendency of the metal cation as

well as CNT-metal ion interaction resulting in very different interaction mechanism.

Now let's discuss the effect of oxidation state of the actinide and lanthanide metal ions on the sorption mechanism. For lanthanides, primarily +3 oxidation state dominates in aqueous solution. But Actinides, especially Uranium (U), Plutonium (Pu) and Neptunium (Np) show variable oxidation states in solution. As for example, U exhibits several oxidation states in aqueous solution, major of them are +4 and +6. Again, under oxidizing condition, U^{6+} exists primarily as linear uranyl cation (UO_2^{2+}). Multiple oxidation states of Plutonium like +3, +4, +5, +6 can coexist in solution. Different oxidation states of the same metal ion show different charge/radius ratio that can influence hydrolysis behaviors, coordination geometry, speciation, hydration energy that ultimately governs the extraction mechanism.

Now it should be discussed that how hydration acts as a thermodynamic barrier for surface complexation off block metal ions.²⁵ Actinide and lanthanide metal ions do not exist as a bare ion in solution. Rather they exist as solvated cations with their hydration shell. Coordination with the CNT surface therefore requires rearrangement of that metal ion solvation shell or partial or complete shedding of its hydration shell. Spontaneity of the sorption therefore depends upon the free energy gains from the CNT-metal ion interaction that must compensate the energy cost to disrupt the hydration shell

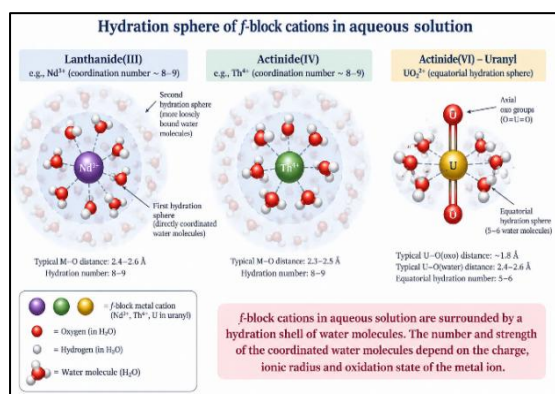


Figure 6: schematic representation of hydration sphere of f block cations in aqueous solution

of the solvated metal ion. stronger hydration of the metal ion can make

desolvation more difficult and therefore can reduce the tendency toward direct coordination with the CNT surface, unless the surface ligand provides a favorable compensating interaction.

Now we move to the next very important parameter that is pH of the solution. pH can influence both the CNT surface and the metal ion speciation. First, we should discuss the effect of pH on the metal ion speciation. Thorium as an example exists in solution as Th^{4+} as a dominating species and $ThOH^{3+}$ at $pH \leq 3.0$. As pH increases, the major species of Th that dominate in solution are $Th(OH)_2^{2+}$, $Th(OH)_3^+$ and at $pH \geq 8.0$, the predominately aqueous soluble species of Th is $Th(OH)_4$.²⁶ Again, the major species of U in solution is UO_2^{2+} at $pH \leq 4.0$. while at pH 5.0 many species of U can coexist in solution like UO_2^{2+} , $UO_2(OH)^+$, $(UO_2)_3(OH)_5^+$. While at pH 6-7, major species of U in solution is $(UO_2)_3(OH)_5^+$.⁵²

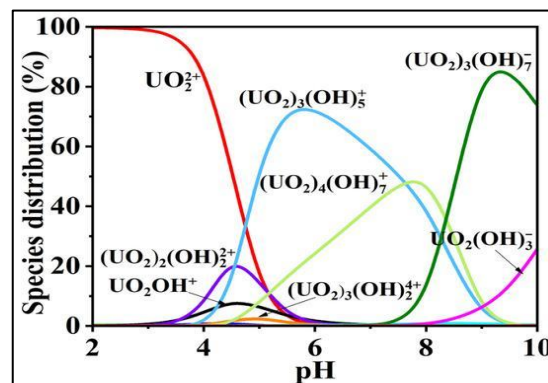


Figure 7: schematic representation of the distribution of speciation of Uranium with pH of solution

Same metal ion with different species shows different geometry, variable hydration energy and affinity towards the same functional group.

pH of the solution can also alter the nature of the surface charge of the same functionalized CNT. As for example -COOH group of oxidized MWCNT will be deprotonated at high pH and form -COO⁻. Therefore, at high pH, solvated metal ion will experience higher coulombic attraction towards the oxidized MWCNT surface. Here we should introduce the concept of point of zero charge (PZC). PZC is the pH at which the surface charge over the CNT is approximately zero under specified experimental condition. At the solution pH < PZC, the surface charge over CNT is

positive. Therefore, the metal cation will experience coulombic repulsion near the liquid-CNT interface. Whereas at pH higher than PZC, the surface of the CNT becomes negative and therefore the metal cation will face attractive interaction near the interface.³⁰ As for example, PZC of o-MWCNT is about 5.0,²⁷ while that of with chitosan group functionalized MWCNT is 4.8.²⁸ Ionic strength of the solution is another important parameter. Higher salt present in solution generally compresses the electrical double layer around the CNT surface and increases electrostatic screening. It can lower down Debye length i.e. characteristics distance over which the electrostatic potential created by a charged surface is screened by electrolyte ions. Moreover, change in ionic strength can affect the metal speciation, ligand protonation, competition among ions and can lead to ion pairing. Nature of background anions like Cl^- , SO_4^{2-} directly influence the speciation of the metal ion of interest and affects the extraction.

Nature of carbon nanotube also is an important parameter that can control the metal ion extraction. The higher specific surface area of the CNT can provide higher elongated liquid solid phase interface and potentially higher site for functionalization. Higher defect density over CNT surface can facilitate oxidative functionalization though very high defect can destroy the graphitic structure and reduce structural integrity.²⁹ The nature of functional group also determines the extent of extraction and selectivity towards f block metal ions. Hard donor like O atom generally exhibit stronger affinity towards f cations of high charge density and lower polarizability. While relatively softer and more polarizable donor atoms like S and N donor atom with tailormade group can enhance selectivity towards actinide metal cation over lanthanides.³¹ The density of functionalization over the CNT surface is a major factor. As the density of donor atoms increases, the number of chemically active and potential sites for metal ion coordination also increase. Accessibility of the ligands to the metal ion is another important factor. As for example, with the same no of donor atoms, all exposed donor atoms of functional group and donor atoms buried inside layers of same functional

group show different extraction behaviour. Ligand architecture and denticity also matters. Spatial arrangement of donor atoms affects the coordination geometry, chelation, binding strength and selectivity. As for example single amidoamine functionalized MWCNT and higher generation of polyamidoamine dendrimer functionalized MWCNT show different sorption behavior with the same actinide or lanthanide metal ion. Process parameters like solid to liquid ratio, temperature, contact time and mass transfer have to be mentioned. Mass of the CNT to volume of the solution affects utilization of the binding sites of CNT, the percentage removal and the equilibrium concentration of the metal ion of interest in the effluent. Temperature directly influences the diffusion, ligand conformation, metal hydration, metal ligand interaction and hence sorption equilibrium. Contact time and mass transfer are additional factors governing the extraction of f-block elements by functionalized CNTs. In a batch system, the observed time-dependent uptake represents combined contributions of metal species transport from the bulk solution to the CNT-solution interface, diffusion through the interfacial region or functionalized layer, and subsequent interaction with accessible surface binding sites. In a nutshell, the overall rate can be influenced by external film diffusion, surface or intraparticle diffusion, CNT aggregation, functional-layer architecture, ligand accessibility, solution viscosity, mixing conditions, and the intrinsic kinetics of interfacial complexation. This distinction is particularly important for ligand-functionalized CNTs, where the transport of hydrated f-block species to the surface may be followed by desolvation, ligand reorganization and metal donor coordination. Consequently, kinetic models such as pseudo-first-order, pseudo-second-order, intraparticle diffusion models can be useful for describing experimental uptake profiles.

Sorption kinetics and equilibrium Isotherm

Above mentioned factors can govern the extent and rate at which f- block cations can be interacted by the surface of functionalized CNT. Though the

physicochemical factors are very much important to understand the mechanism at molecular level, their combined effect must be evaluated through experimentally observable sorption behavior. Two aspects should be discussed in this context. One is the kinetics aspect which describes the time dependent approach to attain the equilibrium and the other is the concentration of the metal ion sorbed onto the CNT surface as well as retained into the feed solution at equilibrium. They together can give a picture of macroscopic behavior of the metal ion sorption by functionalized CNT. It should be mentioned that conformity of the experimental observables to mathematical models used for kinetics and sorption isotherm should not be interpreted as definitive evidence for mechanistic identification.³² As for example, rate behavior described by kinetic model may arise from a combination of mass-transfer and interfacial processes. Therefore, mechanistic conclusions should be supported by independent experimental or computational evidence, such as FTIR, RAMAN or XPS analysis of the functional groups, EXAFS to determine the change in local or geometric structure of the elements within functionalized CNT after metal ion sorption or molecular-level calculations using DFT or molecular dynamics.^{33,34,35}

Sorption kinetics

It described the extent of the metal ion uptake with time by functionalized CNT. During the contact between aqueous phase and the functionalized CNT, the metal ion transports from the bulk to the solid-liquid interface and interacts with the functionalized surface. The experimentally measured uptake of the metal ion q_t is the combined effect of mass transfer, diffusion, hydration shell reorganization and interfacial metal-ligand interaction. Typically, uptake is rapid at initial stage due to the large concentration gradient of metal ion in solution and accessibility of the vacant high affinity sites over the surface of the CNT. Progressively the rate slowly decreases due to lowering of that concentration gradient and a smaller number of unoccupied vacant sites for binding. Kinetic study can therefore provide information of the potential rate controlling step although empirical kinetic

models alone do not establish the molecular mechanism of sorption.

a) Pseudo 1st order model

The pseudo-first-order (PFO) kinetic model is one of the most widely used empirical approaches for describing the time-dependent sorption of metal ions onto solid sorbents, including functionalized carbon nanotubes. The model assumes that the instantaneous sorption rate is proportional to the difference between the equilibrium sorption capacity and the amount of solute sorbed at a given time.³⁶ For an f-block metal ion interacting with a functionalized CNT, the metal ion uptake by CNT at time (t) can be expressed as (q_t), while the corresponding equilibrium uptake is denoted by (q_e). The differential form of the PFO model is given by,

$$\frac{dq_t}{dt} = K_1(q_e - q_t)$$

where (q_t) and (q_e) represent the sorption capacities at time (t) and at equilibrium, respectively, and (K_1) is the pseudo-first-order rate constant. Integration of the rate equation gives the linear form:

$$\ln(q_e - q_t) = \ln q_e - K_1 t$$

Consequently, a plot of $\ln(q_e - q_t)$ against contact time (t) can be used to evaluate the applicability of the PFO model. The model provides a convenient description of the temporal approach of the sorption system toward equilibrium. An important limitation of the PFO model is that its successful fitting to experimental data does not, by itself, establish the molecular mechanism of sorption as mentioned before.

b) Pseudo 2nd order model

The pseudo-second-order (PSO) kinetic model is another widely used empirical model for describing the time-dependent sorption of metal ions onto solid sorbents, including functionalized carbon nanotubes. Similar to the pseudo-first-order model, the PSO model describes the approach of the sorption system toward equilibrium; however, it assumes that the instantaneous sorption rate is proportional to the square of the difference between the equilibrium sorption capacity and the amount sorbed at a given time.³⁷ For an f-block metal ion interacting with a functionalized CNT, the amount sorbed at

time (t) is represented by (q_t), while the equilibrium sorption capacity is denoted by (q_e). The differential form of the PSO model is given by:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2$$

after integration and rearranging it gives the linear form,

$$\frac{t}{q_t} = \left(\frac{1}{K_2 q_e^2} \right) + \frac{t}{q_e}$$

As stated earlier the sorption phenomena of the metal ion on CNT surface involves a no. of microscopic steps like migration, diffusion, rearrangement of the hydration shell of the metal ions, the PSO model should be used together with the experimentally measured equilibrium capacity rather than relying solely on the correlation coefficient of the linearized plot. In particular, the (q_e) predicted by the kinetic model should be compared with the experimentally determined equilibrium uptake. Significant disagreement between the calculated and experimental values may indicate that the model does not adequately describe the complete kinetic profile. Comparison of both PFO and PSO models can provide useful phenomenological information, but selecting a model solely on the basis of a higher R^2 value is insufficient for establishing the molecular mechanism. It should be supported by complementary experimental techniques and molecular-level calculations using DFT or molecular dynamics.

C) Intraparticle diffusion model

The intraparticle diffusion model, commonly referred to as the Weber–Morris model³⁸, is widely used to investigate the contribution of diffusion processes to the observed kinetics of sorption. The commonly used form of that model is:

$$q_t = K_{id}\sqrt{t} + C$$

q_t =amount of f-block ion sorbed at time t (mg g⁻¹); K_{id} =intraparticle diffusion rate constant (mg g⁻¹ time^{-1/2}); t = contact time; C = intercept related to the thickness of the boundary layer; The plot of the q_t vs $\sqrt{t}$, if is a straight line passing through the origin, intraparticle diffusion may be the sole rate-controlling step under the experimental conditions. However, if the line does not pass through the origin, intraparticle

diffusion is involved but is not the only rate controlling process. For functionalized CNTs, this is particularly important because sorption can involve several sequential processes. Therefore, q_t vs $\sqrt{t}$ for f block metal cation and functionalised CNT show multiple linear regions. A larger C generally suggests a greater contribution from boundary-layer resistance, although C should not be treated as a direct quantitative measurement of boundary-layer thickness without an appropriate transport model.

Table 1: best fitted kinetic models for the sorption of various actinide metal ions onto different functionalized CNTs

Sorbent	Metal ion	Condition	Kinetic model
CNT-DHA ^{39,49}	Am ^{241 3+}	0.01(M)HNO ₃ ,300K, CNT-DHA=2mg contact time =2hr	Pseudo 2 nd order
	Th ⁴⁺ UO ₂ ²⁺	6(M)HNO ₃ , [Th ⁴⁺]=[UO ₂ ²⁺]= 10 ppm, contact time =2hr	Pseudo 2 nd order
MWCNT-AA ^{41,42}	Pu ⁴⁺ PuO ₂ ²⁺	6(M) HNO ₃ , contact time =2hr	Pseudo 2 nd order
	NpO ₂ ⁺ NpO ₂ ²⁺	3(M) HNO ₃ , contact time =2hr 300K, MWCNT-AA=2 mg	Pseudo 2 nd order

Equilibrium isotherm

Sorption kinetics describes the rate of the metal ion extraction from the aqueous solution to the solid CNT surface. But equilibrium isotherm establishes the distribution of the metal ion in solution and in the solid sorbent, after the system attains the equilibrium at a specified temperature and the definite composition. The isotherm study is particularly useful to evaluate the maximum sorption capacity of the given CNT for specific metal ion, selectivity and degree of heterogeneity over the CNT surface. If q_e is the amount of the metal ion sorbed per unit mass of sorbent

CNT at equilibrium, C_0 is the initial concentration of the metal ion in solution and C_e is the concentration of the metal ion remaining in solution after attaining the equilibrium, V is the volume of the solution contacted with the sorbent of mass m , then q_e can be experimentally measured by the following formula:

$$q_e = (C_0 - C_e) \times \left(\frac{V}{m}\right)$$

The resulting q_e vs C_e plot provides the equilibrium description of the sorption process under specific experimental condition. Several mathematical models have been developed to describe the equilibrium process like Freundlich, Langmuir and Temkin isotherm. They differ from each other in their assumptions concerning the distribution behavior and the property of the sorption sites.

- Langmuir isotherm

In Langmuir isotherm model, it is assumed that there are finite number of energetically equivalent binding sites available on the sorbent. Moreover, the adsorption is monolayer and there is no interaction among the sorbed species.⁴³ The relationship of the q_e and the C_e as per the Langmuir model is given by,

$$q_e = \frac{q_{max} \cdot K_L \cdot C_e}{1 + K_L C_e}$$

here q_{max} is the maximum sorption capacity of the sorbate predicted by Langmuir model, K_L represents the apparent affinity of the sorbate for the sorbent in the Langmuir isotherm description. When the $C_e \ll 1$, $q_e \propto C_e$ and at very high concentration of the metal ion i.e. $C_e \gg 1$, $(1 + K_L C_e) \sim K_L C_e$ and, $q_e \sim q_{max}$. So, at very high concentration of the metal ion, the vacant sites of CNT sorbent go to saturation.

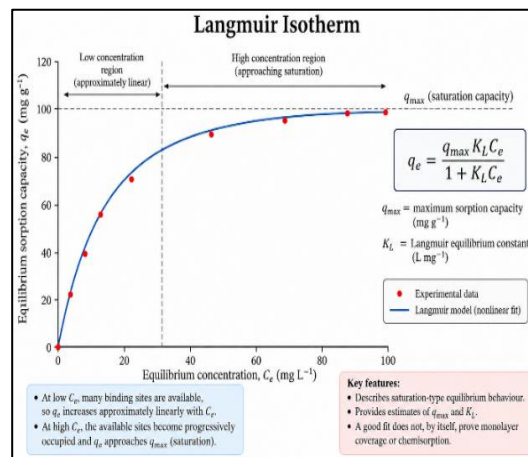


Figure 8: schematic representation of Langmuir Isotherm

- Freundlich Isotherm

While Langmuir isotherm assumes that all sites of the sorbent are energetically similar, Freundlich isotherm as an empirical model describes sorption on the heterogeneous surface of the sorbate.⁴⁴ CNT as for example can have heterogeneous surface due to uneven distribution of defect, inhomogeneity in the surface functionalisation, different conformations of the same functional group over the surface of same CNT. Freundlich isotherm takes into account this inhomogeneity of the sorbent surface. This model assumes that at low concentration of the metal ion in solution, metal ion readily prefers the high affinity binding sites on the sorbent. As the concentration of the metal ion increases in solution, progressively less favourable sites of the sorbent start to contribute. The relationship between q_e and C_e as per the Freundlich model is

$$q_e = K_F C_e^{\frac{1}{n}}$$

where K_F is the Freundlich constant that represents apparent sorption capacity and $1/n$ is empirical parameter related to sorption intensity/nonlinearity and is commonly related to surface inhomogeneity. if $n = 1$ then the q_e will increase linearly with increase in C_e . When $n > 1$, then the curve is concave downward and is commonly associated with favourable nonlinear sorption. When $n < 1$, curve becomes concave upward and progressively steeper with increase in C_e .

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That can correspond to progressive or sigmoidal type behaviour.

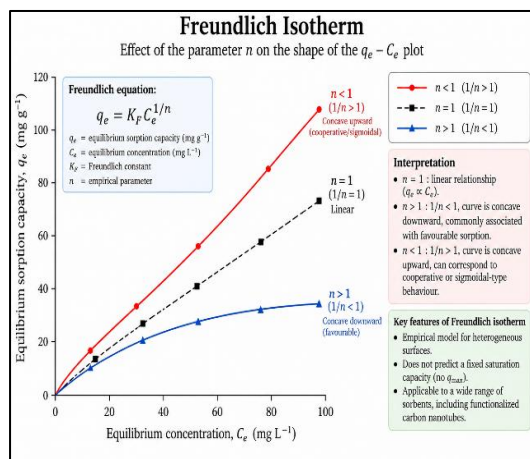


Figure 9. schematic representation of the effect of the parameter of n on the shape of $q_e - C_e$ plot

Linearized form of Freundlich isotherm and corresponding nature of the plot is schematically represented at Fig.10.

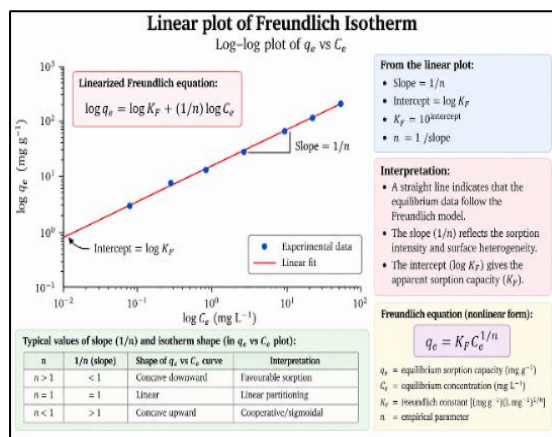


Figure 10: Schematic representation of the linear plot of Freundlich Isotherm

Temkin isotherm

Langmuir model assumes that energy of adsorption is independent of surface coverage because as per Langmuir model, all available adsorption sites of the sorbent are of equivalent energy. In reality, that adsorption energy can change with change in the surface coverage due to the interaction of neighbouring metal ions sorbed or change in electrostatic attraction between the metal ion in solution and the surface of the CNT as the surface coverage increases. Temkin model empirically takes into account this dependency of adsorption

energy with surface coverage⁴⁵ and gives the following equation:

$$q_e = B \ln(A_T C_e)$$

where q_e = equilibrium sorption capacity,

C_e = equilibrium concentration,

A_T = Temkin equilibrium binding constant and

B = Temkin constant related to the variation of adsorption energy with surface coverage.

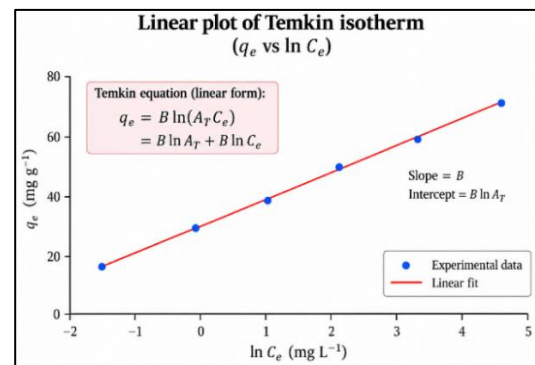
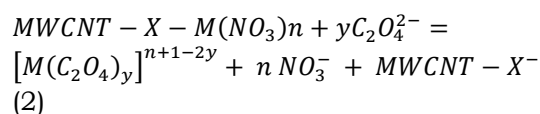
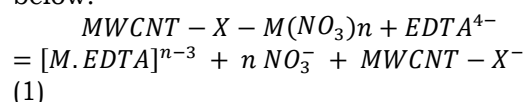


Figure 11: Schematic representation of the linear plot of Temkin isotherm

Regeneration

Regeneration of the functionalized CNTs is of much importance to reduce the volume of solid waste and to recover actinides and lanthanides metal ions sorbed into CNT for further treatment. As per literature, many functionalized CNTs show higher sorption with increase in pH. Desorption process therefore, has been done by passing solution of lower pH.⁵¹ Sometimes, agents such as Ethylenediamine tetraacetic acid (EDTA), Sodium Carbonate (Na_2CO_3), oxalic acid were used for desorption of actinides and lanthanides metal ions. These agents make complexation with desorbed metal ions in solution and lower down the free metal ion concentration in solution facilitating the desorption process thermodynamically feasible. The complexation reactions of the metal ions with the complexing agents are given below:⁵¹



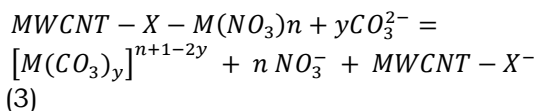


Table 2: best fitted isotherm models for the sorption of various actinide metal ions onto different functionalized CNTs

Sorbent	Metal ion	Condition	Isotherm model
CNT-DHA ^{39,49}	Am ³⁺	0.01(M)HNO ₃ , 300K, CNT-DHA= 2mg contact time =2hr	Freundlich
	Th ⁴⁺ UO ₂ ²⁺	6(M)HNO ₃ , [Th ⁴⁺]=[UO ₂ ²⁺] =10ppm, Contact time =2hr	Langmuir
MWCNT-AA ^{41,42}	Pu ⁴⁺ PuO ₂ ²⁺	6(M)HNO ₃ , contact time =2hr	Langmuir Langmuir
	NpO ₂ ⁺ NpO ₂ ²⁺	3(M), contact time=2hr T=300K, MWCNT-AA=2 mg	Langmuir Langmuir

Investigation of Radiolytic stability of the functionalized MWCNTs

In nuclear industry, structural and functional integrity of any sorbent in the presence of intense radiation field is of particular importance. Generally, the pristine graphitic CNT network is much more radiation resistant than the organic moieties grafted to the CNT surface. Usually bond breaking of the organic functional moieties takes place either by energy deposition of high energetic particles like α or β , interaction with gamma radiation or chemical attack by the reactive species (OH $\cdot$, HO₂ $\cdot$, H $\cdot$) formed by radiolysis of water. Radiation degradation of the functional groups on CNTs results in the deterioration of the sorption performance of the functionalized CNT. In recent years A. Sengupta et.al. and P.

Kumar et.al. investigated the radiation stability of the functionalized MWCNTs. To investigate the radiation stability of the functionalized CNT, the CNT is exposed to the desired γ radiation dose in the ⁶⁰Co gamma chamber and then sorption performance of the irradiated CNT is compared with virgin CNTs. Sorption performance of dihexylamide functionalized CNT (CNT-DHA) for Am³⁺ reduced to 86% and 79% at 500 KGy and 1000 KGy respectively of γ radiation dose while at for Eu³⁺, it was 88% and 83%. 1st and 2nd generation of polyamidoamine functionalized MWCNT exhibited reduced sorption for Am³⁺ and the evaluated values were 81.4% and 80.4% at 500 KGy of radiation dose. The performance further reduced to 62.8% and 62.5% at 1000 KGy dose.^{13,41,42}

Sorption performance of functionalized CNTs

Dihexylamide functionalized MWCNT shows high sorption capacity for both tetravalent and hexavalent metal ions. It was observed that K_d of U and Th both increased upto 3(M) and then it did not increase much. Maximum K_d for U and Th reported was 10³ and 10⁴mlg⁻¹ respectively at 6 (M) HNO₃. Experimental result showed that sorption of both metal ions followed Langmuir adsorption isotherm as well as pseudo 2nd order kinetics model. The maximum equilibrium capacities for UO₂²⁺ and Th⁴⁺ were found to be of 32.5 mg g⁻¹ and 47.1mg g⁻¹ at the experimental conditions.⁴⁹ Maximum sorption of U and Th by diglycolamide functionalized MWCNT (DGA-MWCNT) was observed at pH=4.0 and K_d of U and Th found to be of 2.75×10⁵ and 4.59×10⁴ ml g⁻¹.⁴⁸ Oxidized MWCNT showed higher affinity of Th⁴⁺ at aqueous solution of pH 4.0-5.0. The reported (K_d)_{Th⁴⁺} of o-MWCNT is 6.34×10⁴ ml g⁻¹. Polyamidoamine functionalized (PAMAM) MWCNTs of 1st and 2nd generation showed Pu sorption from the acidic solution with K_d in the range of 1.2-2.24×10⁴ ml g⁻¹.¹³ Amidoamine functionalized MWCNT shows sorption of NpO₂⁺ and NpO₂²⁺ from acidic solution with K_d of 8×10³ and 1.5×10⁴mlg⁻¹.⁴² A rapid increase in the sorption capacity of Ln³⁺ onto oxidized MWCNT was observed at the pH range of 3-5 and the sorption capacity of La³⁺ was found 99.01 mg g⁻¹.⁴⁶ It was

comparable to the sorption capacity of the same metal ion onto CNT-DHA ($q_{max} = 86.2 \text{ mg g}^{-1}$) and much higher than Tannic acid modified MWCNT with maximum sorption capacity of 5.35 mg g^{-1} .

Conclusion

MWCNT showed highly efficient extraction of f cations, while proper functionalization induces the selectivity towards tri, tetra and hexavalent f cations (depending upon the nature of functional groups). They also showed good radiological stability and recyclability. However, most of the extraction processes were from aqueous streams in pH range. Therefore, attempts to be made to synthesize acid stable CNTs (3M -5 M HNO_3). Dendrimer functionalized CNTs have also been employed for improving the efficiency of the extraction.

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Biodata



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Unravelling Actinide Adsorption in Porous Metal–Organic Frameworks: Insights from Density Functional Theory

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INTRODUCTION

Metal–organic frameworks (MOFs) are crystalline porous materials composed of metal ions or clusters connected by organic linkers. Their high surface areas, well-defined pore structures, and chemically tunable functionalities make them attractive for the selective capture and separation of metal ions. For actinides, MOF pores can be engineered with donor atoms that interact with the metal centre and facilitate the displacement of coordinated water or other ligands. Actinide adsorption is therefore fundamentally a coordination-chemical process, making an understanding of the electronic structure of actinide–framework interactions essential for rational material design.[1]

Density functional theory (DFT) provides a powerful molecular-level approach for elucidating these interactions. It can predict optimized structures, binding energies, charge distributions, frontier molecular orbitals, and other electronic descriptors that reveal the nature and strength of actinide–ligand bonding. However, DFT calculations for lanthanides and actinides are particularly challenging because of their complex electronic structures, strong relativistic effects, and multiple closely spaced electronic states. [2,3]

Actinide adsorption can be viewed as a ligand-exchange process in which framework donor sites compete with water, nitrate, and other solution ligands for coordination to the metal centre. Thus, the interaction energy between an isolated actinide ion and a model framework site alone cannot fully describe the adsorption thermodynamics. Factors including oxidation state, aqueous speciation, coordination number, spin state, solvation, and framework flexibility must also be considered. DFT is particularly valuable in this context because it allows these contributions to be examined individually and correlated with experimentally observed adsorption behaviour.[4,5]

DFT DESCRIPTION OF ACTINIDE–LIGAND INTERACTIONS

The electronic structure of actinide complexes is governed by the interplay of electron–electron interactions, exchange–correlation effects, and relativistic interactions. Unlike the relatively localized 4f orbitals of lanthanides, the 5f orbitals of actinides are more spatially extended and can participate in metal–ligand bonding to varying degrees. The extent of 5f orbital participation, and hence the degree of covalency in actinide–ligand bonds, depends strongly on the actinide element, oxidation state, and ligand environment. Consequently, even the same donor group can interact differently with different actinide ions.[4,5,6]

The electronic structure of actinides is further complicated by strong relativistic effects arising from their high nuclear charge. Scalar-relativistic effects influence orbital energies and radial distributions and, consequently, affect bond lengths and bonding energetics. Spin–orbit coupling (SOC) can additionally alter the electronic structure, particularly for open-shell actinides where several electronic states may be close in energy. Relativistic effective core potentials or relativistic all-electron approaches are therefore generally required for reliable calculations. In open-shell systems, particular attention must also be given to the oxidation state, electronic configuration, spin state, and treatment of SOC, as these factors can significantly influence the calculated structure and energetics. [4,5,6]

Within this framework, DFT provides a powerful means of investigating actinide–ligand interactions at the molecular level. Although calculated binding or adsorption energies provide a measure of interaction strength, they do not by themselves reveal the underlying nature of the interaction. DFT-derived electron density and molecular orbitals therefore provide essential complementary information on charge redistribution, orbital interactions, and

metal–ligand bonding. Comparing the electronic structure of the isolated components with that of the resulting complex can, for example, reveal charge transfer and changes in orbital occupation associated with complex formation. [2,3,6]

A more rigorous analysis of the electron density can be obtained using the Quantum Theory of Atoms in Molecules (QTAIM). QTAIM characterizes chemical interactions through the topology of the electron density and provides quantitative descriptors at bond critical points. Parameters such as the electron density (ρ), Laplacian of the electron density ($\nabla^2\rho$), and local kinetic and potential energy densities can provide insight into the strength and nature of actinide–ligand interactions. In particular, these descriptors can help assess whether an interaction has predominantly closed-shell/electrostatic character or exhibits greater electron sharing and covalent contribution. QTAIM is therefore especially useful for comparing how different donor atoms or functional groups bind to actinide centres. [7]

Molecular orbital analysis provides a complementary perspective by identifying the specific donor and acceptor orbitals involved in metal–ligand interactions. It can help determine the extent to which ligand-based orbitals interact with actinide 5f, 6d, or other relevant orbitals and thereby provide qualitative insight into orbital-driven contributions to bonding. Charge-partitioning schemes can further quantify changes in electron distribution and charge transfer upon complex formation. [8,9]

The energetic origin of these interactions can be examined further using energy decomposition analysis (EDA), which partitions the overall interaction energy into physically meaningful components, such as electrostatic interactions, Pauli repulsion, orbital interactions, and dispersion. EDA is particularly valuable when comparing different actinide–ligand systems because similar binding energies may arise from substantially different combinations of these contributions. [10,11,12]

For actinide adsorption in MOFs, these complementary analyses are particularly important because the framework provides a heterogeneous coordination environment in which electrostatic interactions, coordination bonding, hydrogen bonding, and dispersion may operate simultaneously. Thus, a comprehensive interpretation of actinide–MOF interactions should ideally combine adsorption or binding energies with electron-density analysis, QTAIM

descriptors, molecular orbital analysis, charge-transfer information, and, where appropriate, EDA. Such an integrated approach can identify the dominant factors governing actinide binding and establish clearer structure–property relationships for the rational design of selective MOF-based actinide adsorbents. ^{10,12}

ACTINIDE SPECIATION AND COORDINATION ENVIRONMENT

Actinide adsorption from aqueous solution is governed initially by the speciation of the metal ion, which depends on factors such as oxidation state, pH, acidity, and the concentrations of competing ligands. Under these conditions, actinides may exist as aquo ions, hydrolysed species, nitrate complexes, or complexes with other solution ligands. Consequently, the species interacting with a MOF surface is often substantially different from a bare actinide ion. A realistic DFT investigation should therefore begin by identifying the predominant aqueous species under the experimental conditions and, where relevant, considering the competing solution ligands in the adsorption model. [13,14]

Uranyl, UO_2^{2+} , provides a representative example. Its characteristic linear $\text{O}=\text{U}=\text{O}$ unit contains two short axial U–O bonds, while the equatorial coordination plane is occupied by water molecules, anions such as nitrate, or other donor ligands. When uranyl interacts with an oxygen- or nitrogen-functionalized MOF, adsorption may involve the displacement of one or more equatorial ligands and formation of direct inner-sphere U–donor bonds. Electrostatic interactions may additionally contribute to stabilization of the adsorbed species. DFT optimization can therefore be used to examine alternative coordination geometries and evaluate parameters such as U–donor bond distances, coordination number, binding energies, and changes in the electronic structure. These descriptors help establish the preferred adsorption configuration and provide insight into the mechanism of actinide binding. [14,15]

The coordination environment alone, however, does not fully determine the nature or strength of actinide–ligand interactions. Comparative studies of Pu(IV) and Zr(IV) nitrate complexes with tri-*n*-butyl phosphate, for example, demonstrate that similar coordination motifs can be associated with distinct electronic structures. Differences in ionic size, electronic configuration, spin state, and metal–ligand bonding can alter metal–

oxygen distances and the distribution of electron density even when the overall coordination geometry is similar. This distinction is particularly important in the design of selective MOF adsorbents: actinide ions with comparable charge and coordination preferences may nevertheless exhibit different binding affinities toward the same functional group. [16]

Thus, actinide speciation and coordination environment should be treated as fundamental starting points in DFT studies of MOF-based adsorption. Correctly identifying the aqueous species and its likely coordination pathway allows calculated structures and interaction energies to be interpreted in the context of the actual experimental system, rather than as interactions between an isolated metal ion and an idealized framework site. [13,14]

DFT MODELLING OF MOF ADSORPTION SITES

The choice of an appropriate structural model is a critical consideration in DFT studies of actinide adsorption by metal-organic frameworks (MOFs). Because adsorption involves a chemically active local coordination site embedded within an extended porous framework, calculations can be performed using either cluster or periodic models, depending on the scientific question being addressed. [17,18]

Cluster models represent the adsorption site using the metal node, the directly coordinating linker atoms, and a suitably sized fragment of the surrounding framework. They are particularly useful for investigating the local chemistry of actinide-ligand interactions because their relatively small size permits more computationally demanding treatments of electronic structure, including hybrid functionals, relativistic methods, and detailed bonding analyses such as QTAIM and energy decomposition analysis. However, truncating the framework can alter the charge distribution, electrostatic environment, and flexibility of the adsorption site. The cluster must therefore be sufficiently large to preserve the essential coordination environment and should be terminated in a chemically consistent manner. [17,18]

Periodic DFT retains the extended crystal structure and provides a more realistic representation of the framework environment. It accounts naturally for periodic electrostatics, linker connectivity, pore geometry, and framework relaxation and is therefore particularly important when

adsorption induces significant structural changes or when neighbouring sites and long-range framework effects influence the interaction. Periodic calculations also allow different crystallographic or defect-associated adsorption sites to be compared within the same structural model. However, the computational cost increases substantially for large MOF unit cells, especially when heavy actinides, explicit solvent molecules, or multiple competing ligands are included. [17,18]

The treatment of dispersion interactions is another important consideration in MOF adsorption calculations. Although actinide binding to functionalized sites may involve direct coordination and electrostatic interactions, dispersion can contribute significantly to interactions with the organic framework and confined pore environment. Appropriate dispersion corrections should therefore be considered when selecting the DFT methodology, particularly for adsorption configurations involving substantial contact with the linker or pore surface. [6,19]

For actinide-MOF systems, cluster and periodic calculations are best regarded as complementary rather than competing approaches. Cluster models are well suited for identifying preferred coordination modes, evaluating the role of individual donor groups, and analysing the electronic origin of actinide-ligand bonding. Periodic calculations can subsequently establish whether these local interactions remain favourable within the complete framework and can quantify the effects of framework relaxation, neighbouring atoms, pore confinement, and long-range interactions. [17,18]

A practical hierarchical strategy is therefore to begin with cluster calculations to screen plausible adsorption configurations and understand their local electronic structure, followed by periodic calculations for the most relevant structures. This approach combines the chemical insight of localized cluster models with the structural realism of the extended framework, while reducing the computational cost of exploring a large number of possible adsorption configurations. [17,18]

ADSORPTION ENERGY AND ENERGY DECOMPOSITION

The calculated adsorption or interaction energy is one of the most widely used DFT descriptors for evaluating actinide binding in metal-organic frameworks (MOFs). It is generally obtained from the energy

difference between the optimized actinide–MOF complex and the corresponding separated reference species. For a defined adsorption configuration, this quantity provides a measure of the intrinsic interaction strength and can be used to compare different adsorption sites, functional groups, actinide ions, or MOF structures. However, the calculated interaction energy should not be interpreted directly as the experimental adsorption free energy, particularly for adsorption from aqueous solution. [20]

This distinction is especially important for highly charged actinide species such as U(VI), Pu(IV), and Pu(VI), which are strongly solvated and can undergo hydrolysis, protonation/deprotonation, ligand exchange, and complexation with counterions or competing solution ligands. Consequently, the energetic pathway from a solvated actinide species to an adsorbed state involves contributions from desolvation, ligand displacement, speciation, and framework binding. A rigorous thermodynamic description therefore requires an appropriate thermodynamic cycle or free-energy treatment that accounts for these processes. When such contributions are not explicitly included, DFT values are more appropriately described as binding or interaction energies rather than absolute adsorption free energies. [13,14,21]

Interaction energies alone, however, provide limited information about the physical origin of adsorption. Energy decomposition analysis (EDA) addresses this limitation by partitioning the interaction into physically interpretable components. Depending on the EDA formalism, these may include electrostatic interactions, Pauli or exchange repulsion, orbital interactions, polarization/induction, charge transfer, and dispersion. For example, the widely used Morokuma–Ziegler-type framework separates the interaction into electrostatic, Pauli repulsion, orbital interaction, and dispersion contributions, whereas ALMO-based approaches can explicitly distinguish polarization from interfragment charge transfer. Because these terms are method-dependent, the EDA scheme should always be specified when comparing results between studies. [10,11,12]

For actinide–MOF systems, EDA is particularly useful because adsorption rarely originates from a single type of interaction. Direct coordination between the actinide centre and O-, N-, S-, or P-donor

atoms may occur simultaneously with electrostatic attraction, charge redistribution, polarization, hydrogen bonding, and dispersion interactions with the surrounding framework. EDA can therefore distinguish specific coordination-driven stabilization from nonspecific host–guest interactions arising from the broader pore environment. Studies of MOF host–guest systems demonstrate that electrostatic, orbital/induction, and dispersion contributions can all make significant contributions to the overall interaction energy. [10,11,12]

The extended framework can further modify the interaction relative to an isolated metal–ligand complex. An actinide coordinated to a functionalized linker may simultaneously interact with neighbouring donor groups, metal nodes, aromatic linkers, or other surfaces within the pore. Consequently, two MOFs containing chemically similar donor functionalities may exhibit different binding energies because of differences in pore size, linker topology, framework charge, local coordination geometry, and spatial arrangement of adsorption sites. Confinement can increase the number of simultaneous host–guest contacts, while dispersion between the adsorbate and the organic framework can provide additional stabilization. Such effects highlight the importance of considering the complete local framework environment rather than interpreting adsorption solely in terms of a single actinide–donor bond. [17,18,22]

The chemical identity and protonation state of the functional group also influence the balance among these interactions. Phosphate, phosphonate, phosphinate, phosphine-oxide, carboxylate, hydroxamate, amidoxime, and related donor groups can provide different combinations of electrostatic and orbital interactions with actinide centres. Their binding strength, however, depends not only on donor-atom identity but also on protonation state, anchoring mode, orientation, electronic structure, and accessibility within the MOF. Immobilization on a rigid linker can alter the electron density and conformational freedom of a functional group and may either favour or restrict actinide coordination. [10,12,22]

EDA should therefore be interpreted together with electron-density and bonding analyses rather than used as an independent measure of selectivity. QTAIM descriptors such as the electron density at bond critical points, the Laplacian, energy

density, and delocalization indices can provide complementary information on the local nature of actinide–donor bonding, while molecular orbital and charge analyses can reveal orbital participation and charge redistribution. QTAIM has been successfully applied to metal–ligand bonding in MOFs and to actinide systems to assess differences in covalent character.[7,10]

Thus, the major strength of DFT for actinide–MOF research lies not simply in predicting which material has the most negative adsorption energy, but in dissecting the molecular origin of that preference. Combining adsorption energies with EDA, QTAIM, molecular-orbital, and charge-transfer analyses can establish whether enhanced actinide uptake arises predominantly from stronger metal–donor interactions, electrostatics, polarization, charge transfer, dispersion, or cooperative interactions involving the surrounding framework. This provides a mechanistic link between MOF structure, local electronic environment, adsorption mechanism, and selectivity, thereby enabling more rational design of MOFs for selective actinide separation. [10,12]

ELECTRONIC STRUCTURE DESCRIPTORS

Charge analysis provides a convenient first description of the electronic changes accompanying adsorption. Population schemes such as Mulliken, natural population analysis and other density-based methods can be used to quantify charge redistribution. Nevertheless, atomic charge should not be regarded as a direct measure of complexation strength. Changes in charge may be small even when dispersion or orbital interactions substantially alter the total interaction energy. [8,9]

Frontier molecular orbital analysis provides another useful descriptor. Donor orbitals associated with phosphoryl, carboxylate or other framework functionalities can interact with low-lying acceptor orbitals of the actinide-containing species. For uranyl complexes, acceptor orbitals can contain uranium 5f character together with contributions from higher-energy uranium orbitals. The strength of an interaction therefore depends on both orbital energy matching and spatial overlap. [8,9,10]

Charge-density difference maps, projected density of states and energy-decomposition analysis can be used together to obtain a more complete picture. A strong adsorption site should ideally exhibit a favourable interaction energy, an appropriate

coordination geometry and evidence of stabilizing donor–acceptor interactions. These descriptors can then be compared for different linkers, metal nodes and defect sites to establish structure–property relationships. [7,10,11]

REPRESENTATIVE DFT CASE STUDIES OF ACTINIDE ADSORPTION

Within the broader context of computational studies on actinide adsorption, recent MOF-based investigations illustrate how DFT can be integrated with experimental characterization to identify the molecular origin of selective binding. In functionalized MOF-LIC-1 systems, the metal–framework interaction was treated using simplified molecular fragments representative of the chemically active groups rather than the entire periodic framework. The functional moieties(Fig 1) were optimized using DFT to obtain lowest energy structures (Fig 2) for evaluation of their respective binding energies with U(VI).

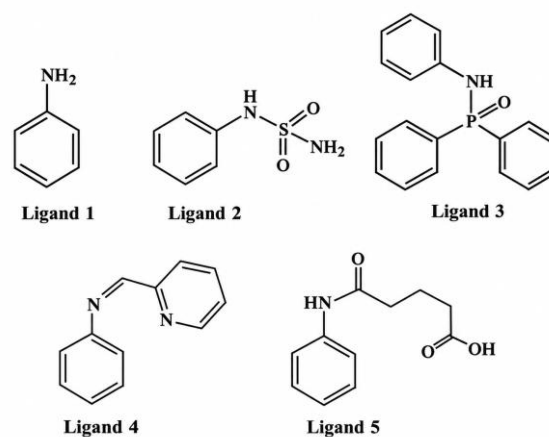


Figure 1 Functional moieties of MOF-LIC-1

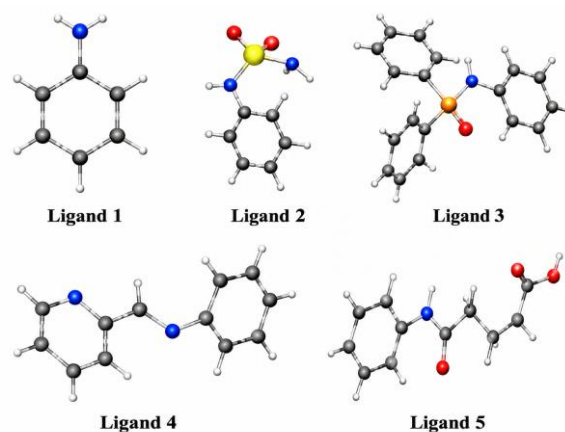


Figure 2 Lowest energy structures of functional moieties of MOF-LIC-1

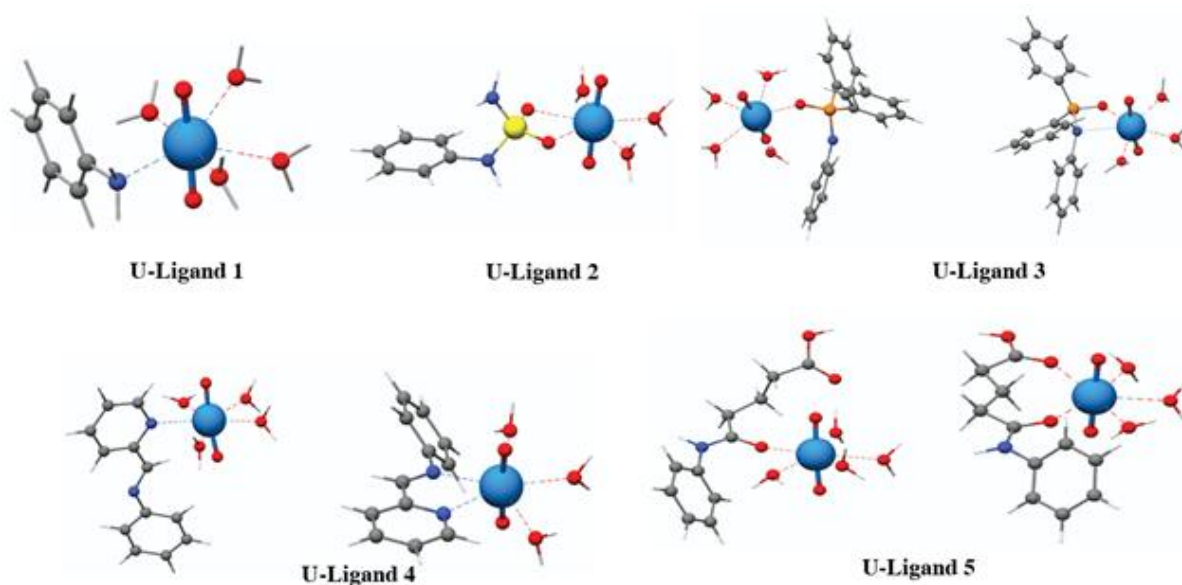


Figure 3 Lowest energy structures of U complex with functional moieties of MOF-LIC-1

This strategy enabled systematic comparison of different donor environments and coordination motifs while retaining the essential chemistry of the adsorption site. Geometry optimization, relativistic corrections, natural population analysis, and atoms-in-molecules analysis were collectively employed to assess the electronic structure of the resulting uranyl complexes (Fig. 3). Such calculations showed that adsorption cannot be understood only in terms of the formal charge of the donor atoms; instead, charge redistribution, orbital interaction, hydrogen bonding, dispersion, and the geometric compatibility of the donor group with the uranyl coordination sphere contribute collectively to the overall binding tendency. [22].

The importance of functional-group chemistry becomes particularly evident when comparing different post-synthetically modified MOF-LIC-1 derivatives. Phosphorus-, carboxyl/amide-, imine-, and sulfur-containing functionalities provide chemically distinct coordination environments for U(VI) and Th(IV), allowing the role of donor identity to be evaluated within a common framework architecture. The use of hard donor groups is consistent with the strong affinity of highly charged actinide ions toward oxygen- and nitrogen-containing binding sites. Importantly, these studies demonstrate that post-synthetic functionalization modifies not only the intrinsic electronic character of the

adsorption site but also the local chemical environment experienced by the incoming actinide ion. [22]

A related picture emerges from the silicon-shielded amidoxime-functionalized UiO-66 system. Here, computational modeling of the amidoxime group (Fig 4) was used to compare alternative uranyl coordination modes and to identify the most favorable donor center. The analysis indicated that the oxime nitrogen plays a dominant role in uranyl coordination and that monodentate binding can be more favorable than some nominally multidentate arrangements. (Fig 5).

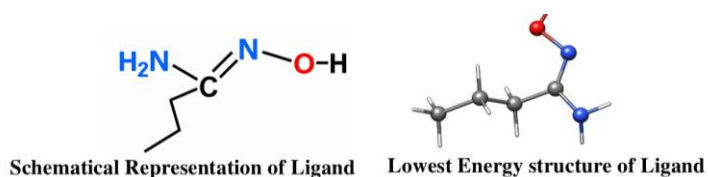


Figure 4 Functional moieties and Lowest energy structures of amidoxime-functionalized UiO-66 system

This observation is important from a materials-design perspective because it shows that increasing the number of potential donor atoms does not automatically enhance actinide binding. The spatial orientation and accessibility of the donor atoms must also be compatible with the preferred equatorial coordination environment of uranyl. [23]

The amidoxime study also highlights the importance of distinguishing intrinsic ligand

affinity from adsorption-site accessibility. Although amidoxime is intrinsically effective for uranyl binding, the silicon-containing modification reduces pore accessibility and can hinder the approach of U(VI) to some of the active groups. Thus, experimentally observed adsorption behavior reflects a balance between strong local metal-ligand interactions and framework-level factors such as pore dimensions, steric shielding, and the density of accessible functional groups. This distinction is particularly relevant when computational results are used to rationalize adsorption capacities, since a highly favorable local interaction does not necessarily imply that all such sites are experimentally accessible. [23,24]

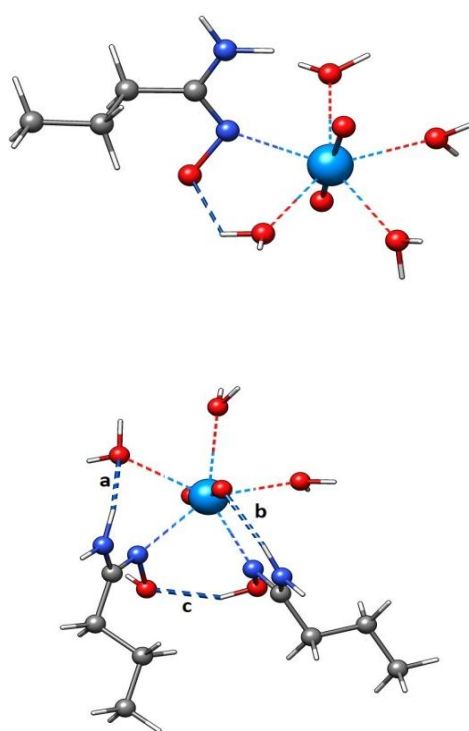


Figure 5 Structure of modeled Ligand and its optimized Uranium amidoxime complex

The thorium adsorption study on CAU-1-NH₂ extends these concepts beyond uranyl chemistry. In this case, the experimentally relevant hydrolyzed Th(IV) species was retained in the computational model, while aniline was used as a simplified representation of the amino-containing MOF binding site. Such a model preserves the first coordination environment of aqueous thorium while permitting direct assessment of ligand substitution and Th-N bond formation. (Fig 6)

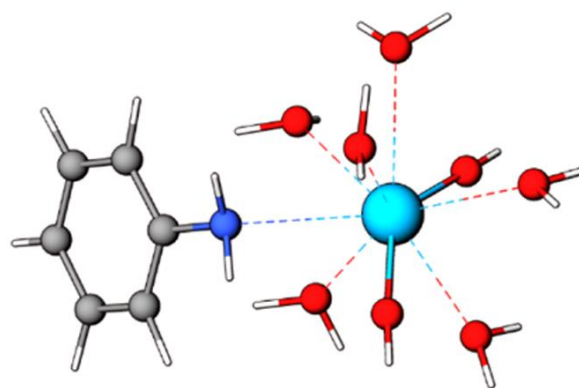


Figure 6 DFT optimized structure of Thorium ligand complex

The calculations supported ligand-to-metal electron donation and demonstrated that coordination through the amino functionality is energetically feasible. This result is consistent with the experimental spectroscopic evidence, which indicated participation of both amino and hydroxyl groups in thorium adsorption. [25]

Taken together, these studies demonstrate the value of coupling DFT with spectroscopic characterization. In the Si/UiO-66-AO system, optimized hydrated and ligand-substituted uranyl structures were compared directly with EXAFS-derived coordination environments, while XPS provided complementary evidence for changes in the chemical states of nitrogen- and oxygen-containing groups following uranium adsorption. The consistency between calculated structures and experimentally observed coordination features strongly supports direct uranyl interaction with the amidoxime functionality. Similarly, the CAU-1-NH₂ study combined XPS evidence for the involvement of amino and oxygen-containing groups with DFT calculations supporting the corresponding Th-ligand interaction. Such combined experimental-computational approaches are more informative than adsorption-energy calculations alone because they enable proposed coordination geometries to be tested against directly observable structural and electronic signatures. [23,25].

These investigations also emphasize an important methodological consideration for computational studies of actinide adsorption: the chemical form of the actinide in solution should be incorporated explicitly whenever possible. Uranyl was therefore treated using hydrated species in the amidoxime studies, while a hydrolyzed hydrated thorium species was employed for the CAU-1-NH₂ system. This approach provides a more realistic representation of

adsorption than calculations involving isolated bare ions, particularly because ligand binding generally requires displacement or rearrangement of coordinated solvent molecules. Accordingly, a meaningful theoretical description should account not only for the intrinsic donor-actinide interaction but also for the coordination environment from which adsorption occurs. [13,14,23,25].

Overall, the attached studies reveal a common mechanistic picture in which actinide adsorption by MOFs is governed by the interplay of donor-group chemistry, coordination geometry, aqueous speciation, charge redistribution, and accessibility of the active sites. DFT is therefore most useful when employed as a comparative mechanistic tool rather than simply as a means of generating complexation energies. The strongest interpretation arises when computationally predicted binding modes are supported by independent experimental evidence such as XPS, EXAFS, or vibrational spectroscopy. Such an integrated approach provides a more reliable basis for identifying the structural features that should be targeted in the rational design of MOFs for selective U(VI), Th(IV), and related actinide separations. [22,23,25]

DESIGN PRINCIPLES FOR ACTINIDE-SELECTIVE MOFs

The preceding considerations suggest that rational design of porous MOFs for actinide adsorption should begin with the coordination chemistry of the target actinide species. Hard donor atoms such as oxygen-containing functionalities can provide strong interactions with highly charged actinide centres, while the geometry and multidentate arrangement of the donor groups determine whether a stable adsorption pocket can form. ^{22,23}

Multidentate binding can provide a significant advantage because several donor atoms can coordinate the same actinide simultaneously. A MOF linker should therefore be designed not only for high donor strength but also for appropriate donor-donor distances and orientation. DFT geometry optimization is a direct way of testing whether the proposed pocket is chemically accessible. [22,23]

The electronic environment of the linker can be tuned through functional-group substitution and modification of the metal node. Such changes can alter donor orbital energies, polarization and charge distribution without necessarily changing

the overall topology. DFT calculations can identify whether a proposed modification strengthens orbital interaction or merely changes electrostatic stabilization. [22]

Finally, selectivity must be evaluated against competing ions and solution species. A framework that binds U(VI) strongly in the gas phase may not necessarily be selective in aqueous nitric acid because nitrate coordination, hydration and competing metal ions modify the thermodynamic balance. Comparative calculations using the same computational protocol are therefore more informative than absolute binding energies considered in isolation. [13,14,22,23].

CONCLUSION

DFT provides a powerful means of connecting the molecular structure of an actinide adsorption site with its observed chemical behaviour. In porous metal-organic frameworks, the adsorption process is governed by a combination of coordination, electrostatic, orbital and dispersion interactions together with solvent effects and framework relaxation. The complex electronic structure of actinides, including relativistic effects and open-shell configurations for many oxidation states, requires these factors to be treated carefully. The most useful DFT description is therefore not a single adsorption energy but a combination of structural and electronic descriptors. Optimized actinide-donor distances establish the coordination geometry; charge-density and population analyses describe electron redistribution; frontier orbitals and density-of-states calculations reveal donor-acceptor interactions; and energy decomposition identifies the physical origin of stabilization. Together, these quantities provide a basis for understanding why one MOF site can favour an actinide over another.

For future development of actinide-selective porous materials, a hierarchical strategy combining molecular cluster calculations, periodic DFT, solvent modelling and experimental validation is particularly promising. Such an approach can identify chemically meaningful adsorption motifs and translate them into framework-level design rules. DFT can consequently serve not only as a tool for explaining adsorption measurements but also as a predictive method for developing porous materials for selective actinide capture and separation.

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ASSET Bulletin on "Separations of Lanthanides, Actinides and Fission Products using Porous Materials"

Biodata



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Application of magnetic solid phase separation for metal ion separation through functionalizing metal ion-selective ligand to magnetite: Challenges and scope

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Introduction

The magnetic solid phase separation (MSPS) method has evolved into a diverse approach, replacing the metal ion separation method with magnetic force-assisted separation of the adsorbent phase from the liquid phase [1–3]. Since the method relies on cost-effective, environmentally friendly magnetite as the matrix, it is considered a sustainable approach for large-scale separation applications. The role of the paramagnetic magnetite moiety is only to consolidate the adsorbent from the liquid phase; the separation of the metal ion requires a modification of the magnetic matrix with an ion-selective ligand. Therefore, diverse magnetic materials based on ligand-modified materials, MOF/COF-modified magnetites, and porous carbon/nanocarbon-modified magnetites are widely used [4–8]. Although there are ample opportunities to utilize magnetic solid-phase adsorbents for large-scale separation applications, industrial efforts remain limited.

MSPS offers several advantages for the treatment of nuclear waste compared with conventional solid-phase extraction. Since this method uses an external magnetic field, the adsorbent particle size can be reduced to the nanometer range, enabling efficient and rapid extraction of metal ions from waste solutions. Higher surface area and smaller particle size facilitate efficient particle coalescence in aqueous solutions. Since agitation of particles in aqueous solutions can be achieved with external agitators, adsorption can be controlled than in a conventional column-based separation process. The use of magnetite-based separation techniques also offers several advantages, including high selectivity, reusability, and the potential for low environmental impact. Adsorbent replacement can also be performed online, another advantage of MSPS. In addition,

there is no need to pack MPs in a column, as it is usually operated in batch mode, and phase separation is quickly achieved by an external magnetic field. From a waste management perspective, the spent adsorbent can be either vitrified or converted into an unleachable ceramic waste form for the final disposal of the spent contaminated iron oxide particles. Since the organo-modified material contains only 10% of organics on the inorganic solid matrix, the swelling and radiolytic degradation usually encountered with organic solid supports or resins during the treatment of radioactive waste is negligible with the use of MSPS.

What is magnetic-assisted solid-phase separation?

In the MSPS technique, the magnetic particles (MPs) are added to the aqueous solution to adsorb the target metal ion. The MPs are then separated from the solution using an external magnetic field [6]. The major difference between magnetic solid phase separation and conventional column-based separation lies in the use of an external magnetic field to concentrate the magnetic materials (adsorbents in the present context) from the aqueous phase. The heart of a magnetic solid phase separation system is a paramagnetic (or superparamagnetic) material, in which the material exhibits magnetic properties in response to an external magnetic field. A brief outline of the operational methodology of magnetic solid-phase separation can be tacitly represented figuratively as in Fig. 1. The actual separation system may vary depending on the separation methodology. For the separation of metal ions, the feed solution can be introduced into a stirred-tank reactor, wherein effective particle-particle interaction (mass transfer) and thus separation can be achieved using agitators (impellers). Subsequently, the magnetic particles can be separated by applying an external magnetic field [9–11]. Another

practical demonstration of MSPS is magnetic-in-tube microextraction (MTME). MTME is more appropriate for analytical purification [12–14]. In this method, a fused silica tube is impregnated with the magnetic material (adsorbent). The fused silica tube is wrapped with a magnetic coil. Therefore, magnetic separation can be achieved by applying a magnetic field. Few efforts to utilize MTME have been demonstrated by some researchers. The separation efficiency depends on the surface area, coating thickness, magnetic field strength etc. MTME utilizes the magnetic field to improve separation efficiency. Unlike the previous case of MSPS, which used a stirred-tank reactor-type separator for bulk separation, MTME uses adsorption in capillary tubes with simultaneous application of a magnetic field.

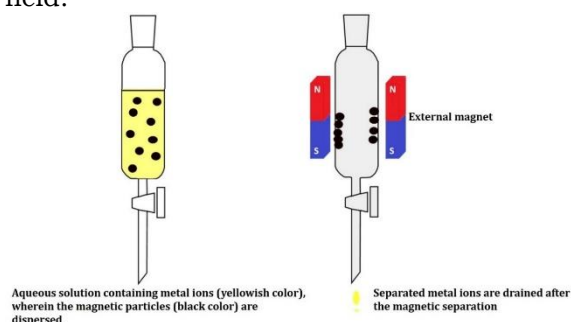


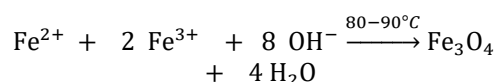
Fig.1. A pictorial representation of magnetic solid phase separation of metal ions.

Magnetite: The core matrix of MSPS

MSPE is an unconventional type of solid-phase extraction that relies on the superparamagnetic property of the adsorbent matrix to enhance the separation of the adsorbent from the aqueous phase. Needless to mention that the metal ion is indeed separated from the aqueous phase by the ligand anchored to the magnetic matrix. The essential benefit of using a magnetic adsorbent over a nonmagnetic one is that it can be readily dispersed in aqueous solutions, thereby increasing interfacial area and improving separation. A magnetic adsorbent should exhibit high paramagnetism, high surface area and porosity, superior chemical stability, and fast kinetics. The magnetic adsorbents possess a magnetic matrix to facilitate magnetic separation. Therefore, the dispersed adsorbent is separated using an external magnetic field. However, the adsorbent's magnetic property had no significant effect on adsorption. Although several materials, such as Fe_2O_3 (maghemite), NiFe_2O_4 , and CoFe_2O_3 , can be

used, Fe_3O_4 (magnetite) has been widely used to prepare magnetic adsorbents because of its superior magnetic properties.

Fe_3O_4 is prepared by the alkaline hydrolysis under inert conditions at temperatures between 80 and 90°C (using ammonia or sodium hydroxide) of Fe^{3+} and Fe^{2+} salts in the mole ratios of 2:1, as interpreted by the following chemical reaction.



Fe_3O_4 is a crystalline material, having a $Fd\bar{3}m$ cubic inverse spinel group structure in which Fe^{3+} and Fe^{2+} ions are in 2:1 ratios [15–19]. O^{2-} occupies an fcc site. Half of the Fe^{3+} ions occupy octahedral sites, and the remaining half occupy tetrahedral sites along with Fe^{2+} ions. Both Fe^{2+} and Fe^{3+} contain unpaired 3d electrons. The unpaired 3d electrons' magnetic spins on octahedral sites cancel each other, whereas the magnetic spins due to 3d electrons (Fe^{2+}) present on the tetrahedral sites show a residual magnetic moment. Therefore, Fe_3O_4 behaves as a ferrimagnet. The magnetic property of Fe_3O_4 is also size dependent. Very small particles or, under certain conditions, surface disorder, oxidation, defects, and finite-size effects can strongly modify the magnetic behavior.

Fe_3O_4 possesses a layered structure. The phase composition of Fe_3O_4 can be seen from the XRD pattern (Fig. 2). The indices (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) are typical features of Fe_3O_4 , reported by the JCPDS card no. 3-863.

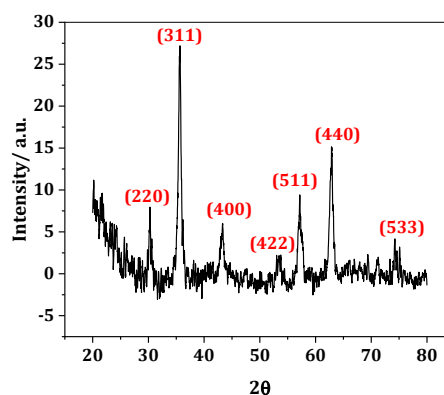


Fig.2. The X-ray diffraction pattern on of the Fe_3O_4 nanoparticles.

The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio is critical for controlling the magnetic properties of iron oxides.

Several researchers conducted XPS analyses to detect the presence of Fe^{2+} and Fe^{3+} ions. Several previous reports showed evidence of the presence of Fe^{2+} and Fe^{3+} ions by XPS, based on peaks around 711.09 eV ($2p\ 3/2$) and 729.25 eV ($2p\ 1/2$), characteristic of Fe_3O_4 [20].

Surface modification of Fe_3O_4

Since Fe_3O_4 does not exhibit any selectivity towards a particular metal ion, and moreover, it cannot be used as such for adsorption applications, the adsorption capability of Fe_3O_4 can be improved by incorporating other moieties that exhibit metal ion selectivity. These moieties can be (i) other ligands (organic functional groups/inorganic ion exchangers), (ii) porous materials like MOF, COF, (iii) nano carbon or nano silica materials.

A composite adsorbent of Fe_3O_4 with other inorganic materials, such as titania, magnesia, calcium oxide, and so on, exhibited selectivity in uranium adsorption. Another difficulty with using Fe_3O_4 for adsorption is that exposed Fe_3O_4 can undergo chemical reactions with acidic or alkaline media. A prudent approach to overcome the above is to provide a silica protective coating that prevents Fe_3O_4 from exposure to the acidic/alkaline medium without compromising the paramagnetic properties of the adsorbent. The silica modification also facilitates a subsequent modification of the adsorbent with other materials.

The introduction of the silica protective layer into Fe_3O_4 is carried out by the Stobbers' process. A typical preparative method can be illustrated in Fig. 3. Briefly, the Fe_3O_4 particles (1 g) were initially soaked in 0.5 M HCl (10 mL), then sonicated and washed extensively with deionized water. The separated magnetic particles were further soaked in 40 mL of ethanol, approximately 15 mL of deionized water (10 mL), and 2 mL of aqueous ammonia solution (28 wt %). TEOS (2 mL) was added to the above solution, and the entire reaction vessel was subjected to agitation (stirring) for 16 hours. The silylated iron oxide (Fe-Si) collected and washed with ethanol, water, and acetone to remove any residual starting materials or impurities.

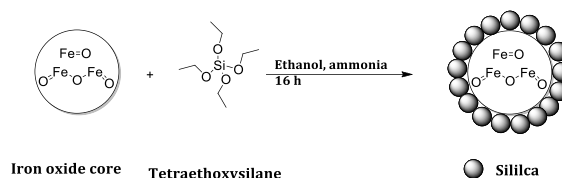


Fig.3 Silylation of magnetic particles.

Recovery of metal ions using magnetite functionalized with metal-ion-selective organic ligands is a pioneering approach that combines the magnetic properties of magnetite (Fe_3O_4) with the selective complexing capabilities of organic ligands. Magnetite nanoparticles are functionalized with organic ligands aimed to selectively complex metal ions from a mixture of other metal ions. Ligand functionalization of magnetite enhances the specificity and efficiency of metal ion separation through tailored chemical interactions between metal ions and ligands. Once the metal ion is complexed to the functionalized magnetite, the magnetic properties of magnetite enable easy recovery of the metal ion-loaded nanoparticles with an external magnetic field, thereby facilitating a more straightforward separation process than traditional methods. Organic ligands can be designed to exhibit high affinity and selectivity for metal ions, even in the presence of competing ions. This reduces the need for extensive purification steps and minimizes the generation of hazardous waste. Moreover, the magnetic separation technique is less energy-intensive and can be performed under milder conditions than other separation methods. The functionalized nanoparticles can be regenerated and reused, making the process cost-effective and sustainable. This technology holds promise for applications in nuclear waste management, uranium mining, uranium recovery from seawater, and environmental remediation of uranium-contaminated sites.

As mentioned before, the introduction of a silica protective layer to Fe_3O_4 further facilitates surface modification with different ligands. The silica layer further facilitates the introduction of organosilane functional groups, which can be further modified with the desired organic ligands.

Magnetic adsorbents modified with diverse ligands such as diglycolamic acid, succinic acid, ionic liquids, etc., have been studied for the separation of americium, uranium, etc. These adsorbents find applications in

bulk separation-cum-purification from a waste management perspective, as well as in analytical separation. While preparing the ligand incorporated Fe_3O_4 , silylating (silicate-functionalized) reagents (also known as silica coupling agents or otherwise known as organosilanes) such as 3-amino (or 3-chloro) triethoxy (or trimethoxy) silanes, tetraethoxy (or tetramethoxy) silanes, vinylsilanes, epoxysilanes facilitate linking of an organic moiety with the silica-coated Fe_3O_4 . These organosilanes not only protect Fe_3O_4 from reacting with other chemicals but also facilitate the incorporation of diverse functional groups onto Fe_3O_4 .

The mutual separation of lanthanides (Ln) and actinides (An) is a critical step in advanced nuclear waste management because of their similar ionic radii, oxidation states, and coordination chemistry. Conventional solvent extraction and ion-exchange processes can achieve separation but often require multiple stages and generate secondary liquid waste. Magnetic adsorbents offer an attractive alternative by combining selective metal-ion binding with rapid magnetic solid-liquid separation. For the mutual separation of Lns and Ans by adopting a protocol similar to the TALSPEAK process (Trivalent Actinide-Lanthanide Separation by Phosphorus-reagent Extraction from Aqueous Complexes), therefore, functionalized Fe_3O_4 can be tailored with lanthanide-selective hard donor ligands such as phosphates, phosphonates, amides, amidoximes, carboxylates, and nitrogen-containing ligands. These functionalities can exploit subtle differences in the complexation chemistry of An(III/IV/VI) and Ln(III), enabling selective uptake and subsequent elution using DTPA.

In this context, an Ln-selective ligand, diglycolamic acid, was tethered to Fe_3O_4 . In this context, several ligand-modified Fe_3O_4 were developed. One such attempt was an ionic liquid-modified diglycolic acid-anchored Fe_3O_4 , in which an ionic moiety was stitched onto the Fe_3O_4 framework via a multi-step approach. The ionic nature of the ligand ensured effective Ln-An separation, and the magnetic component ensured effective interfacial activity due to its fine size. 1-butyl-3-methylimidazolium bis(2-ethylhexyl)diglycolamate (Fe-Si-MeIm-DEHDGA) [21]. Fe_3O_4 was initially modified with silica to protect its surface. Subsequently, 3-(3-methylimidazolium)

propyltrimethoxysilane chloride (Si-MeIm), prepared by reacting 1-methylimidazole (5 g, 60 mmol) with 3-chloropropyltriethoxysilane (13 g, 62 mmol), was reacted with the above silica-modified Fe_3O_4 in the presence of acetonitrile at 350 K. The product obtained (Si-MeIm, 10 g) was then refluxed with Fe-Si (5 g) in chloroform at 380 K, yielding 1-butyl-3-methylimidazolium chloride anchored on Fe-Si. The above product was further converted to the hydroxide (OH^-) form by treating Fe-Si-MeIm-Cl with excess 1 M sodium hydroxide (50 mL). The product Fe-Si-MeIm-OH thus obtained was then refluxed with bis(2-ethylhexyl) diglycolamide (HDEHDGA) to yield the imidazolium diglycolamate-anchored adsorbent (Fe-Si-MeIm-DEHDGA). Synthetic scheme is shown in Fig. 4.

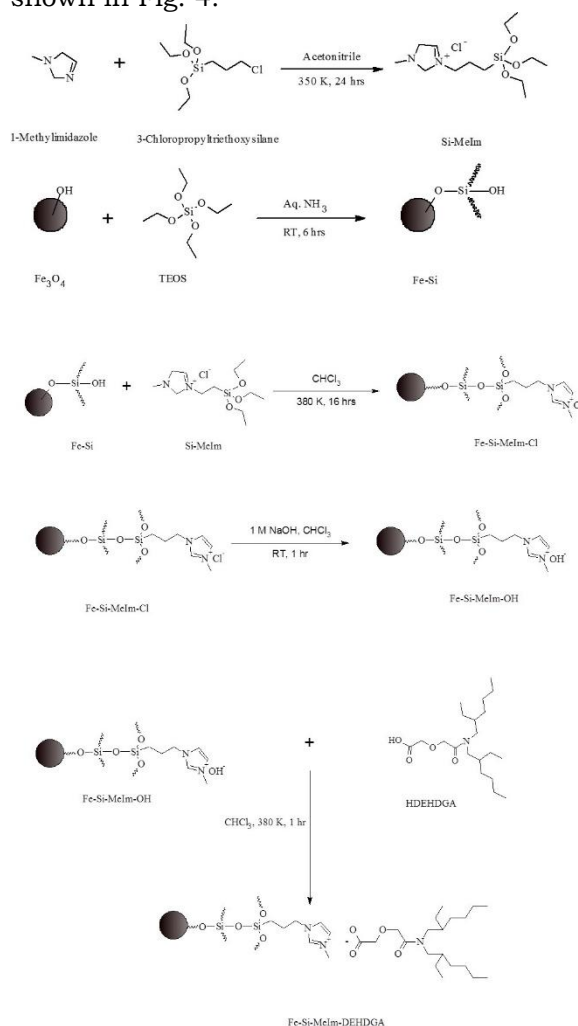


Fig. 4 Synthetic scheme for the preparation of ionic liquid incorporated magnetite (Fe-Si-MeIm-DEHDGA)

It can be seen that the extraction of both Eu(III) and Am(III) decreases as nitric acid

concentration increases, with higher adsorption at pH 3 (Fig. 5). The K_d of Eu(III) decreases from ~28000 to 90 and K_d of Am(III) decreases from 2586 mL/g to 18 mL/g with the increase in the concentration of nitric acid from 0.001 M to 0.1 M. Negligible adsorption of Am(III) and Eu(III) was observed with the precursors Fe-Si-MeIm-DEHDGA, namely Fe₃O₄, Fe-Si, Fe-Si-MeIm-Cl, Fe-Si-MeIm-OH at all nitric acid concentrations confirms that the adsorption can occur only due to the presence of diglycolamate moiety present in Fe-MeIm-DEHDGA. Fig. 4 also shows the variation in the distribution coefficient of Am(III) and Eu(III) as a function of DTPA concentration. It can be seen that the separation factor of Eu(III) over Am(III) increases with increasing DTPA concentration. At 0.01M nitric acid, the separation factor increases from ~5 in the absence of DTPA to the value of ~60 at 0.005 M DTPA concentration. Further increasing the DTPA concentration to 0.05 M enhances the separation factor to ~110.

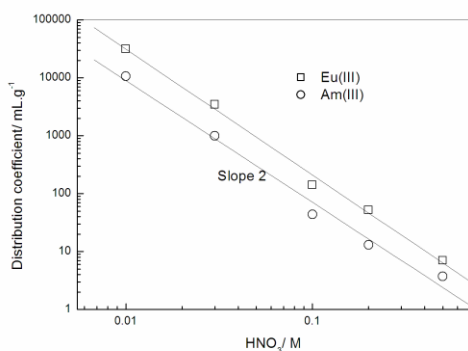
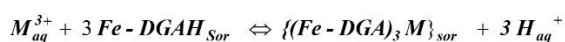


Fig. 5 Adsorption behavior of Am and Eu by Fe-Si-MeIm-DEHDGA.

Another magnetic adsorbent, diglycolamic acid (Fe-DGAH), was prepared by refluxing (80-90°C) the silylated iron oxide (Fe-Si) and Si-DGAH in toluene medium for 6 h, wherein Si-DGAH was prepared by reacting 3-aminopropyltriethoxysilane [21]. During this reaction, the surface silanol groups on Fe-Si react with Si-DGAH to form diglycolamic acid-functionalized iron oxide, as shown in the reaction scheme in Fig. 6.

The sorption of trivalent metal ions in Fe-DGAH could be represented by the equilibrium reaction shown in equation 5.



where Fe-DGAH_{sor} is the sorbent phase, and Fe-DGA is the proton dissociated form of the sorbent.

Subsequently, a TALSKPEAK-type process utilizing DTPA was employed for the mutual separation of Eu and Am, which showed a dramatic improvement in the separation of Eu over Am. In the absence of DTPA, the separation factor (quotient of K_d of Eu(III) and K_d of Am(III)) achieved for the extraction of these metal ions is very small (~1-3), as shown in Fig. 7. Since DTPA forms a complex with Am(III) in preference to Eu(III), the extractions carried out in the presence of DTPA facilitates the retention of Am(III) in the aqueous phase and thus enhances the separation factor of Eu(III) over Am(III) with the increase in the concentration of DTPA. At pH 2, the separation factor increases from ~1 in the absence of DTPA to the value of 150 at 0.05 M DTPA concentration.

The nanoparticles showed a fine morphology, as evidenced by the SEM images. Both Fe-Si-MeIm-DEHDGA and Fe-DGAH showed superior adsorption of trivalent lanthanides and have been studied for the mutual separation of Eu(III) from Am(III). The diglycolamic acid -based magnetic adsorbents provide a promising platform for the mutual separation of trivalent lanthanides and actinides by integrating selective coordination chemistry of diglycolamic acid with facile magnetic assisted separation, utilizing the TALSPEAK-inspired approach. The DGA moiety provides the chemical selectivity, while the magnetite support offers high surface accessibility and rapid magnetic recovery of the loaded sorbent. Such multifunctional magnetic systems could ultimately contribute to compact, selective and potentially recyclable processes for lanthanide-actinide partitioning.

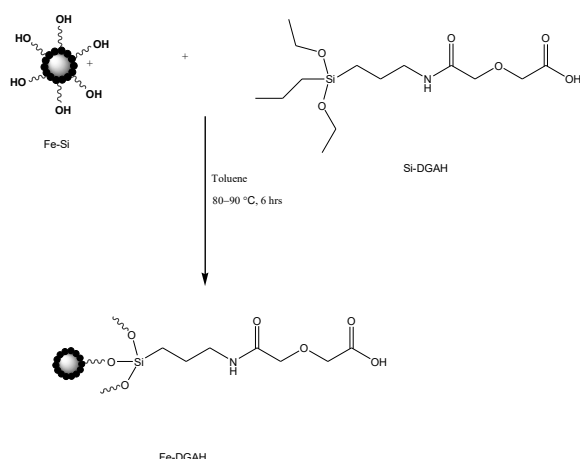


Fig.6 Synthetic scheme for the preparation of Fe-DGAH

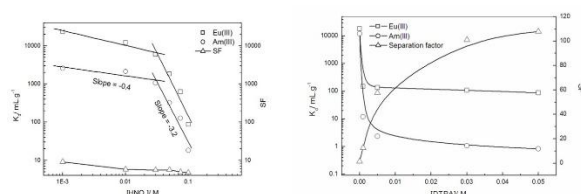


Fig. 7 Variation in the distribution coefficient of Am(III) and Eu(III) as a function of nitric acid concentration (left), and as a function of DTPA concentration (right).

Magnetic adsorbents are also highly useful for the recovery of uranium recovery from natural water considering its wide scope in reactor requirement. Uranium is a naturally occurring radioactive element that is widely distributed in the environment with seawater being an attractive option for its recovery. Although the uranium concentration in seawater is very low, typically around $3.3 \mu\text{g L}^{-1}$, the enormous volume of the oceans results in a substantial overall uranium inventory, estimated to be on the order of billions of tonnes. However, its recovery is difficult because uranium occurs at trace levels and must be selectively separated from a large excess of competing ions such as Na^+ , Mg^{2+} , Ca^{2+} , and other dissolved species.

In this context, magnetic adsorbents offer considerable scope for uranium removal and recovery. Magnetic nanoparticles and magnetic composites can offer high adsorption capacity while enabling rapid separation from treated water with an external magnetic field. Their surfaces can be further modified with suitable ligands to improve uranium selectivity. Amine-

containing ligands can provide nitrogen donor sites for interaction with uranyl species, whereas weakly acidic ligands such as carboxylic acids ($-\text{COOH}$) can enhance binding through deprotonated oxygen donor groups. Tuning particle size, surface area, and ligands is equally important for optimizing recovery efficiency. Incorporation of magnetic particles into mesoporous frameworks, such as mesoporous silica, carbon, or metal-organic frameworks, can provide high surface area, interconnected pores, and improved mass transfer. Tailoring pore size, pore volume, surface functionality, and magnetic content can therefore enhance uranium accessibility and adsorption kinetics. Therefore, in this context, a magnetic adsorbent (see Fig. 8 for the synthetic scheme), based on an amine functional group tethered to Fe_3O_4 , showed superior uranium selectivity in near-neutral aqueous solutions [22]. The amine moiety anchored on the magnetite surface preferentially complexed with uranium which helped for its recovery.

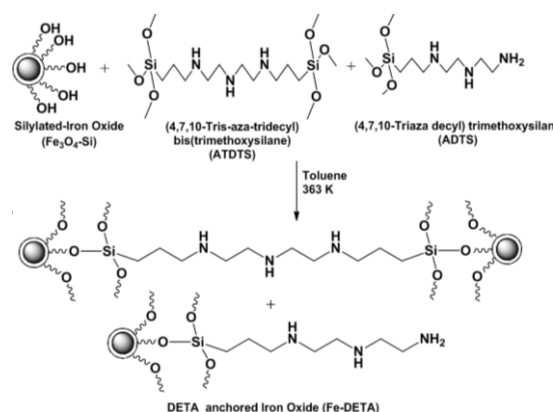


Fig. 8 Synthesis scheme for the preparation of Fe-DETA

The adsorbent exhibited uranium adsorption via a cation-exchange mechanism with good recyclability. The ability to remove uranium from a carbonate medium, with high sorption capacity, indicates that the material can be considered for uranium removal from seawater or uranium-contaminated mine solutions [7]. Likewise, another magnetic adsorbent based on succinic acid-anchored Fe_3O_4 showed superior uranium removal capability (see Fig. 8 for the synthetic scheme), with negligible interference from other ions in seawater-like solutions, indicating good sorption behavior. Another recent study also showed the prospect of using magnetite in a mesoporous framework, wherein silicate growth at the

meso-scale, employing CTAB (cetyltrimethylammonium bromide) as a template on silica-coated Fe_3O_4 , resulted in Fe_3O_4 in a mesoporous architecture with a very high surface area. CTAB is a soft template, particularly useful for preparing mesoporous Fe_3O_4 because it can simultaneously control particle growth, prevent aggregation, and generate nanoscale pore channels. CTAP, which possesses a hydrophobic C16 tail and a positively charged quaternary ammonium head, undergoes self-assembly above its critical micelle concentration (CMC). CTAB molecules self-assemble, with hydrophobic tails pointing inward and the charged ammonium groups remaining exposed to the surrounding solution, thereby forming mesoporous structures. The above mesoporous magnetite was further reacted with a succinic acid functionalized silane (by reacting 3-aminopropyltriethoxysilane with succinic anhydride) to form a carboxylic acid functionalized mesoporous magnetite material. In this material, the mesoporous structure has increased the surface area, and the particle size could be reduced to a few nanometers, which also showed a positive effect on magnetic strength. It was further observed that, compared to the organofunctionalized Fe_3O_4 , the mesoporous Fe_3O_4 exhibited a very high uranium adsorption capacity on the order of 430 mg/g. The mesoscopic channels created by the surfactant (CTAB) aided the formation of adsorbent having larger surface area compared to the regular magnetites.

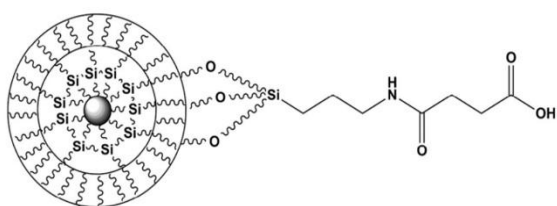


Fig. 9 Magnetic mesoporous adsorbent

Challenges in Using Ligand-Grafted Magnetic Nanoparticles for Metal-Ion Separation

Magnetic nanoparticles modified with diverse ligands have emerged as attractive materials for the separation and recovery of metal ions from aqueous systems. The superior surface area of the particles, which facilitates the incorporation of large amounts of ligands and thereby improves adsorption capacity, is the major advantage

of this type of separation system. Additionally, their ability to rapidly recover the adsorbent from a treated solution using an external magnetic field eliminates or reduces the need for conventional filtration and centrifugation steps. Improvements in separation efficiency by adopting an automated separation system incorporating an electromagnetic field, wherein the application of a magnetic field is driven by an external electrical supply, and by using agitators to promote effective coalescence of particles in aqueous solutions to improve mass transfer, are major attractive features of MSPS. The porous matrix provided by the magnetic moiety facilitates the functionalization of MNPs with selective ligands and selectivity toward specific metal ions. However, translating ligand-grafted magnetic nanoparticles from laboratory-scale studies to practical separation systems presents several significant challenges.

Whilst adsorption capacity usually depends on the amounts of ligands present on the surface of magnetite matrix, because of the stronger magnetic dipole-dipole interactions, magnetic nanoparticles can undergo self-aggregation, which reduces the effective surface area available for ligand-metal interactions and can consequently decrease adsorption of metal ions. The ligand loading should be optimized using computational approaches or batch studies to avoid excessive loading.

The magnetite matrix modified with ligands is stable under near-neutral pH conditions. The silica coating provides additional stability by protecting the magnetite matrix from exposure to aqueous solutions. Protecting the magnetite matrix from acidic or highly alkaline conditions is a major concern. Under such conditions, oxidative or reductive reactions, protonation, or degradation of the ligands may occur. Leaching of the ligand can result in a gradual loss of separation performance and may introduce secondary contaminants into the treated solution. These effects can be minimized by making magnetite composites with polymers, wherein the polymer coating prevents magnetite from exposure to highly acidic or alkaline media.

The magnetic strength of magnetic adsorbents decreases in the presence of a protective coating (such as silica or polymers) and of ligands. Therefore, in addition to adsorption capacity, the ligand

loading should also be optimized with respect to the external magnetic field strength to achieve effective magnetic-assisted separation.

Effective magnetic-assisted separation requires particles with a smaller size and greater surface area. Therefore, optimizing the surface area and particle size plays a crucial role in dictating the particle properties. Therefore, the synthesis protocols should be optimized to yield magnetic particles having a larger surface area and a smaller size. Very small nanoparticles with high superparamagnetic behavior and excellent dispersion are an attractive choice for MSPS applications.

A large-scale separation system relies on the effective use of magnetic materials for multiple regeneration cycles, without significant loss of capacity. Chemical compatibility with the reagents used for recycling and retention of structural and chemical integrity is an important challenge. The magnetic adsorbents are attractive for converting the waste-loaded adsorbent form into a permanent waste form. The chemical processing steps for transforming them to a stable waste form also require the destruction of organics (ligands) and the optimization of concentrations of glass-forming additives to convert the adsorbent to a permanent waste form.

Scope of magnetic nano adsorbents for metal ion separation

The tunable surface properties and high surface area facilitate the engineering of the magnetic nanoparticles for the large-scale separation of metal ions. From the nuclear elements recovery perspective, magnetic adsorbents with burnable C, N, and O-based moieties are attractive as organic components, as the organic moiety of the adsorbent can be completely incinerated, thereby converting the adsorbent matrix to a permanent waste form. The silica and iron oxide components of the adsorbent can be easily modified into a permanent, unleachable waste form by vitrification. MSPS can also be considered for the permanent geological isolation of selective metal ions having longer half-lives. However, the equipment and process systems development required to deploy the process at an industrial scale must progress from simple batch magnetic recovery toward continuous, automated, high-throughput separation equipment.

MSPS can be effectively applied to various process streams in nuclear fuel cycles, including waste management, selective separation of metal ions, purification of heavy water, and decontamination of uranium mine water tailings.

Composite adsorbents comprising magnetite with other nanomaterials, such as polymers, graphene oxides, nanosilica, covalent organic frameworks, and metal-organic frameworks, could also offer promising directions for employing MSPS, particularly under acidic and alkaline conditions. The above-suggested porous frameworks can increase surface area, improve mechanical and chemical stability, and provide more accessible binding sites. The incorporation of multiple ligands could also allow simultaneous removal of several metal ions or sequential separation of different species.

The development of magnetic nanocomposites for continuous-flow and column-based separation represents an important step toward practical application. Immobilizing ligand-functionalized nanoparticles within porous matrices or magnetic membranes could overcome difficulties associated with handling free nanoparticles while retaining magnetic separation capability.

The next stage of equipment development involves magnetically assisted contactors. These systems are designed to provide controlled contact between the magnetic sorbent and the process solution while preventing excessive nanoparticle aggregation. Mechanically stirred tanks, static mixers, fluidized beds, and recirculating contactors can potentially be adapted for this purpose. The equipment should provide sufficient mixing to maximize mass transfer while avoiding conditions that cause irreversible aggregation or degradation of the functionalized magnetic material.

The principal gap is no longer simply demonstrating that a ligand-functionalized magnetic nanoparticle can capture a metal ion. Instead, the challenge is to develop an integrated system that can operate reliably for long periods at high flow rates, high recovery efficiency, low pressure drop, minimal sorbent loss, repeated regeneration, and consistent separation performance.

Ultimately, the major opportunity lies in moving from high-capacity laboratory

sorbents toward selective, regenerable, robust, and scalable separation platforms. Integration with magnetic separation, membrane technology, flow systems, and automated process control could enable rapid and selective recovery of valuable metals while minimizing secondary waste. Such developments could have applications in nuclear waste management, hydrometallurgy, resource recovery, environmental remediation, and advanced chemical processing.

Conclusions

Magnetic solid-phase separation, a next-generation separation technique that promises an adsorbent with superior surface chemistry, thereby enabling the incorporation of a large number of metal-ion-selective ligands. The inherent ferromagnetic nature of the adsorbent material facilitates the faster disengagement of the solid adsorbent particles from the aqueous phase when an external magnetic field is applied. The tunable properties of the magnetic particles enable the incorporation of diverse ligands via surface chemical modification using silica-coupling agents, making them an ideal choice for metal ion removal from a waste management perspective. The composite magnetic adsorbents utilizing a mesoporous silica matrix are the latest development in this direction, wherein the larger surface area and smaller particle size provide effective dispersion and mass-transfer interactions. Although not yet mature from a commercial perspective, MSPS offers advantages over conventional methods in efficiency, environmental friendliness, selectivity, and faster separation. From the point of view of nuclear waste management, magnetic adsorbents can be easily converted to a vitrified waste form, as the residues leave only oxides of iron and silica.

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ASSET Bulletin on "Separations of Lanthanides, Actinides and Fission Products using Porous Materials"

Biodata



Dr. A. S. Suneesh joined Materials Chemistry and Metal Fuel Cycle Group (MC&MFCG) at the Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam in 2008 after completing a one-year orientation course from 51st batch of BARC Training School. He earned his Ph.D. in Chemistry from HBNI, and he is also an Assistant Professor at the Homi Bhabha National Institute (HBNI). He was awarded DAE Group achievement award in the year 2011. His research centers on composite materials, including graphene oxide hybrid adsorbents, polymer and magnetic nanocomposites, with applications in metal ion separation, catalysis, sodium-ion batteries, and molecular dynamics simulations. He has published over 65 publications in peer reviewed international journals.



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Engineered graphene oxides for the separation of fission products and actinides: Surface chemical modification and its application to metal ion separation

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Introduction

Advanced solid-phase separation systems involving functionalized graphene oxides and their composites have been explored for separating U and various fission products such as Zr, Pd, Cs, Sr, etc. from aqueous solutions, thereby reusing valuable resources and recycling precious metals [1–3]. These advanced separation systems are proposed to achieve desired purity levels and to overcome the drawbacks associated with conventional separation techniques, owing to inherent complexities such as poor selectivity, secondary waste generation, and poor performance at trace concentrations. In this context, advanced separation systems utilizing solid-phase adsorbents with high surface area, such as Graphene Oxide (GO), have emerged as promising next-generation adsorbents.

Graphene is a 2-D allotrope of carbon fabricated with sp^2 hybridized carbon atoms, whilst its oxidized sibling GO is also a 2-D allotrope having both sp^2 and sp^3 hybridized carbon atoms characterized with the presence of abundant oxygenated functional groups, such as hydroxyl, epoxy, carbonyl, and carboxyl groups [4–6]. The popular chemical synthesis method for GO is the oxidative exfoliation of graphite, popularly known as the Hummers' method. Graphite is another allotrope of carbon, with stacked layers of sp^2 -hybridized carbon atoms [7–10]. The Hummers' oxidation method utilizes $KMnO_4$ and sulfuric acid as oxidizing agents, which introduce defects and the oxygenated functional groups. These functional groups provide hydrophilicity and thus facilitate pristine GO's strong interaction with diverse metal ions through surface complexation, electrostatic attraction, and ion-exchange mechanisms.

GO has also been identified as a suitable ion exchanger due to the presence of functional moieties such as hydroxyl, epoxy, carbonyl, and carboxyl groups [1,11]. Furthermore,

the selectivity and surface chemistry of GO can be tailored through covalent functionalization with metal-ion-selective ligands. In nuclear applications, GO-based materials offer opportunities for the selective removal of radionuclides and fission products from contaminated aqueous streams and high-level liquid waste. As mentioned before, GO can be tailored for preferential interaction with ions such as Cs^+ , Sr^{2+} , Eu^{3+} and other lanthanide/fission-product species. Modification with crown ethers, phosphonates, amidoximes, amines, amides, carboxylates, or other donor groups can provide enhanced selectivity.

The tenability of surface functionalization and large surface area is particularly relevant for radioisotope separation from the perspective of nuclear waste management. This is because many fission products and actinides can be present in chemically complex matrices containing high concentrations of competing ions in nuclear waste.

Apart from the advantage that smaller GO sheets generally provide a higher specific surface area and a greater number of accessible functional groups, potentially improving metal-ion uptake and mass-transfer kinetics, the smaller particle size is also a critical parameter governing the practical performance of graphene oxide-based separation materials. This is because very small sheets can remain highly dispersed in aqueous media, making their recovery after adsorption difficult. This is particularly problematic for radioactive waste treatment, where release of nanoscale material must be strictly avoided.

To overcome this difficulty, composite adsorbents of GO are developed by combining the advantages of GO with magnetic nanoparticles, silica, polymers, or porous frameworks to overcome limitations associated with free GO. For example, the magnetic GO composites, though again very

small in size, could enable rapid recovery of the adsorbent from aqueous solution by applying an external magnetic field. Polymer or silica composites with GO can further improve their porosity and provide structural, chemical, and mechanical integrity with improvements in particle size, thereby improving the pressure drop and improving mass transfer kinetics, an attractive route toward regenerable and reusable separation media.

Conversely, larger GO aggregates or composite particles are easier to separate and handle but may exhibit reduced accessible surface area, slower intraparticle mass transfer, and incomplete utilization of functional groups. Aggregation can become particularly pronounced at high ionic strength or in concentrated acid media because electrostatic stabilization is suppressed. Therefore, an optimum particle or aggregate size must balance adsorption kinetics, accessible surface area, and suspension stability and separation efficiency. Designing GO as larger, mechanically stable porous composites provides a promising strategy for retaining nanoscale functionality while enabling efficient solid-liquid separation and safe process operation.

GO also offers scope for selective pre-concentration of radionuclides prior to analytical determination. Functionalized GO could concentrate trace radionuclides from large volumes of aqueous media, thereby improving detection sensitivity and facilitating radiochemical analysis.

Preparation of GO: Chemical exfoliation of graphite

The starting material for GO preparation is graphite powder. A typical preparative method (Hummers' method) of GO involves oxidation of graphite using KMnO_4 , sulphuric acid, and phosphoric acid. The properties of GO, particularly with respect to the functional groups (preferentially carboxylic acid group, epoxy group, and minor contributions of sulfonic acid and hydroxyl group), are dictated by the method of oxidation (use of sodium/potassium nitrate, use of phosphoric acid along with KMnO_4 and sulfuric acid), and duration of oxidation [2,11]. A typical preparative method aimed at having higher concentrations of carboxylic acid functionalities on GO is by utilizing KMnO_4 , sulfuric acid and phosphoric acid is depicted

in Fig. 1. Briefly, the preparation involves treating graphite powder (5 g) with an oxidizing mixture composed of concentrated sulphuric acid (450 mL), phosphoric acid (50 mL) and KMnO_4 (15 g) at 50°C . After stirring for 10 hours, ice-cold water was added to the above reaction mixture, followed by 5 mL of hydrogen peroxide. The resulting GO particles were filtered from the aqueous phase and washed four times with dilute hydrochloric acid (0.2 M, 250mL), then with water to neutralize the product. The GO particles were then dried by vacuum drying at 60°C . Approximately 4 g of GO was obtained by this method. The original chemical exfoliation method was attributed to Hummer and Offeman, who used KMnO_4 , sulfuric acid, and NaNO_3 to oxidize graphite powder [3]. Later, several modifications to the method, including replacing NaNO_3 with KNO_3 and using phosphoric acid, were devised.

In preparation, a higher proportion of sulphuric acid, with a typical sulphuric acid-orthophosphoric acid ratio of 9:1, was reported to yield higher amounts of carboxylic acid. The amount of carboxylic acid also increased with contact duration. The typical Hummers' oxidation results in the formation of a few-layered GO (graphitic oxide). Preparation of monolayered GO may require several steps sonication-cum-dialysis. However, upon functionalization, the material approaches a monolayer geometry.

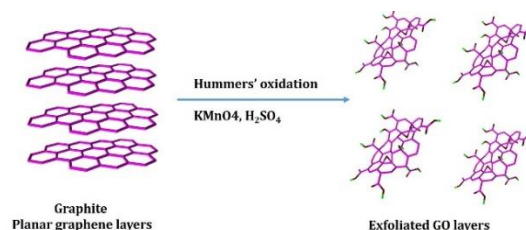


Fig. 1. Synthesis scheme of GO.

Fig. 2 shows the XRD pattern of graphite and the exfoliated GO. It can be seen that graphite has a characteristic diffraction peak at $2\theta = 26.3^\circ$ corresponding to the (002) plane which shows an interlayer distance (calculated based on the Sherrer's formula) of approximately 3.3 Å. The exfoliated GO shows a characteristic diffraction peak corresponding to (001) plan located at $2\theta = 11.42^\circ$. The interlayer distance of GO appears to be 7.5 Å. As discussed, the formation of functional groups (carboxyl, epoxy, etc.) causes the graphene layers to

lose their planarity and thus disrupts the π -electron cloud interactions that keep the layers together. Therefore, in addition to the above, the repulsive interaction between adjacent oxygen-bearing functional groups helps maintain the exfoliated state of the graphene layers.

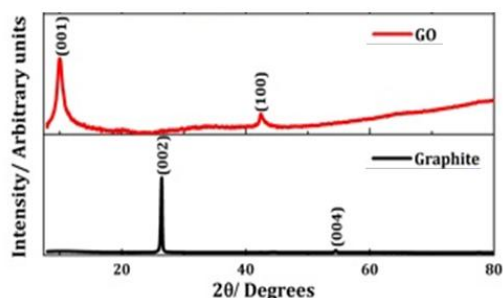


Fig. 2. XRD pattern of graphite and GO.

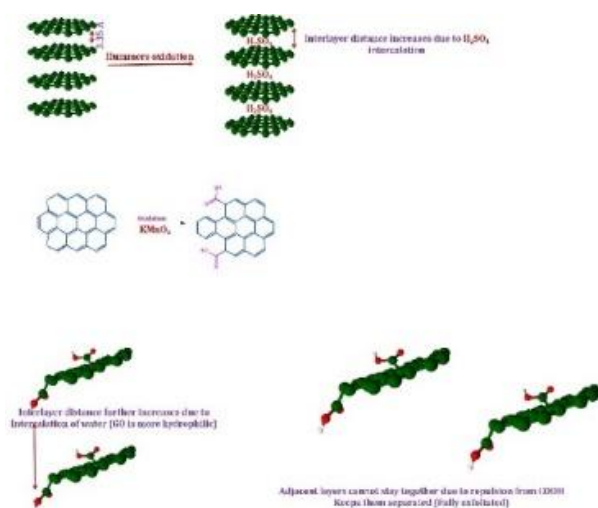


Fig. 3. Exfoliation mechanism of Graphene oxide

In graphite, the graphene layers associate with each other because of the π - π interaction between two adjacent graphene layers. Because of the interaction between two π electrons of the same graphene layer, they behave as a polarizable electron cloud. Therefore, the graphene layers are considered non-bonded, separated by an interlayer distance of 3.35 Å. At this distance, the graphene layers of graphite are at an optimal distance to overcome the interlayer repulsive forces between the perpendicularly oriented π electron cloud. Under normal circumstances, the layers tend to remain together due to the cumulative attractive interactions between adjacent π -electron clouds, making exfoliation of the graphene layers difficult.

During the Hummers' oxidation process, H_2SO_4 initially intercalates into the graphite layers, which are originally separated by an interlayer distance of 3.35 Å. Due to the influence of KMnO_4 , some of the carbon atoms of graphene layers are oxidized to COOH , as depicted in Fig. 3 (pictorially).

On the other hand, SO_3H and even OH groups can also form in the presence of sulfuric acid. Since the majority of functional groups formed are COOH , which can exist as their anionic conjugate base at higher pH values, the GO layers tend to remain unassociated. This leads to the complete exfoliation of graphene oxide layers [12,13]. The GO surface, further modified with functional groups, stays unassociated. This is because of the enhanced repulsion caused by bulky functional groups on the layers, which prevents them from associating.

Composite adsorbents of GO

The enhanced surface area, tunable surface properties, and resilience towards acidic and alkaline environments make functionalized GO an attractive choice for metal ion separation. However, the fine particle size limits their use in column mode of operation, where it can impede mass transfer. Therefore, the composite adsorbents incorporating the GO would be a viable choice. Among the different matrices chosen for making the composite, the polymeric matrix could be a better option, as it can be modified with functionalized GO for the desired application. Additionally, other silica-, titania-, and porous carbon-based composites can be considered. In this article, we discuss the scope of polymeric-functionalized GO composites for the recovery of Zr from acidic solutions and U from pH solutions.

For the preparation of the GO-polymer composite, Pickering emulsion polymerization was the most recognized method considered. See Fig. 4 for a pictorial representation of Pickering emulsion polymerization. In this process, porous polymer microspheres of GO-polymer can be formed from the polymer monomer (eg, styrene), using GO dispersed in water instead of a surfactant used in conventional polymerization [14–16]. During the polymerization of the monomer (with the addition of a free radical initiator), the GO (or functionalized GO) dispersed in water acts as a hydrophilic emulsifier/stabilizer,

wherein the polymer network will grow around GO, which forms a GO-incorporated polymer network.

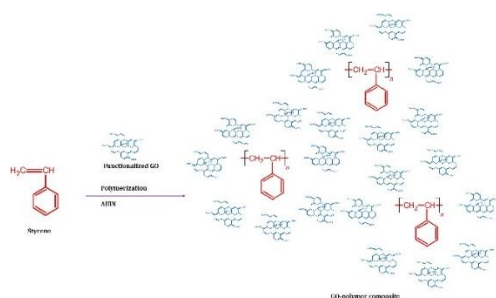


Fig. 4. Pickering emulsion polymerization of functionalized GO with polystyrene.

During polymerization, because GO acts as a surface stabilizer (emulsifier/surfactant), its contact angle also matters. Usually, the high wettability makes GO highly unsuitable for Pickering emulsion polymerization. However, the functionalized GO with amine, amides, etc. enhances the contact angle of GO making them amenable for Pickering emulsion polymerization. A pictorial representation of the process is depicted in Fig. 4.

Additionally, a hybrid composite adsorbent based on magnetite-supported GO was considered, in which pristine GO was used for U separation.

Amine-modified GO polystyrene composite adsorbent for U removal from neutral medium.

Composite adsorbents with a polymeric backbone and functionalized GOs could play a vital role in the selective separation of U from natural media such as seawater and contaminated mine water. Substantially lower abundance of U in seawater ($3 \mu\text{g/L}$), along with several other interfering ions that could reduce U separation efficiency and high salinity, pose challenges for U recovery from seawater, and a commercially viable separation process has yet to be established [17]. The low abundance of U poses a significant challenge, despite seawater being the largest reservoir of U in terms of overall availability relative to terrestrial sources. The adaptability of GO to engage with diverse functional groups makes it an ideal adsorbent for metal ion recovery from solutions dominated by competitive chemical environments and the challenges posed by low abundance. In this context, an amine-modified GO incorporated in a

polystyrene matrix has been employed for U removal from aqueous solutions (near neutral).

The composite adsorbent, amine-functionalized GO-polystyrene, was prepared by in situ polymerization of styrene in the presence of amine-functionalized GO [2]. The amine-functionalized GO was prepared by dispersing 6.5 g of GO in ethanol via sonication for 15 minutes, followed by the addition of ~40 mL of diethylenetriamine (DETA). The mixture was then heated at 80°C for 2 hours.

For the Pickering emulsion polymerization, 0.5 g of GO-DETA in 100 mL of distilled water (5 mg mL^{-1}), with 25 mL of styrene in the presence of 2,2'-azobis(isobutyronitrile), AIBN (10 mg), was reacted to initiate polymerization [2]. The reaction was left to continue for 6 hours at 70°C . The obtained product was filtered and washed with acetone multiple times to remove styrene monomers. The reaction scheme for preparing the adsorbent is summarized in Fig. 5. The resulting amine-functionalized GO-polystyrene composite was subsequently evaluated for its U removal efficiency in aqueous solutions. The hybrid properties of these two materials are expected to exhibit superior U uptake compared to previously reported adsorbents of a similar nature. Furthermore, the micrometer-sized polystyrene beads observed in the SEM images (Fig. 6) suggest the potential for employing these materials in large-scale column studies.

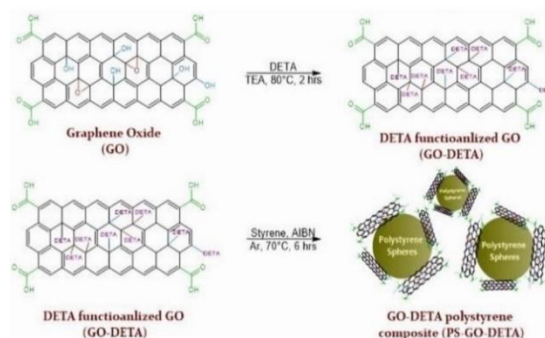


Fig. 5 Synthesis scheme adopted for the preparation of PS-GO-DETA composite.

The FTIR signature of the amine modified GO incorporated polystyrene is shown in Fig. 7. Compared to the FTIR of GO, wherein the signature peaks appeared at 3400 , 1710 , 1622 , 1226 and 1053 cm^{-1} corresponding to O-H, C=O, C=C, C-O (hydroxyl) and C-O-C (epoxide) stretching frequencies respectively

amine functionalized GO with DETA introduced new peak at 1562 cm^{-1} which is ascribed to C-N. The disappearance of 1710 cm^{-1} peak denotes the reduction of carbonyl groups by amine. PS-GO-DETA shows the same features as GO-DETA, along with additional peaks at 2922 cm^{-1} (C-H stretching), 747 cm^{-1} (-C-H rocking), and 694 cm^{-1} (C-H rocking) corresponding to polystyrene vibrations. This shows that GO-DETA's functionality is unaffected by its structural upgrade to polystyrene [2]. The XPS spectrum (shown in Fig. 8) of GO showed the presence of C 1s at 284 eV and O 1s at 532 eV . The presence of 'oxygen' is due to the formation of carboxylic acid groups, which are produced due to the Hummers' oxidation. The XPS of amine-functionalized GO also showed the above peaks, with the additional appearance of N 1s at 402 eV , confirming the incorporation of an amine moiety on the GO surface [2].

The composite adsorbent showed high U uptake capacity even when U was adsorbed from an acetate buffer and a carbonate medium. The adsorption behavior was even higher than that of pristine GO, possibly because the amine functionalities played a positive role in enhancing U uptake.

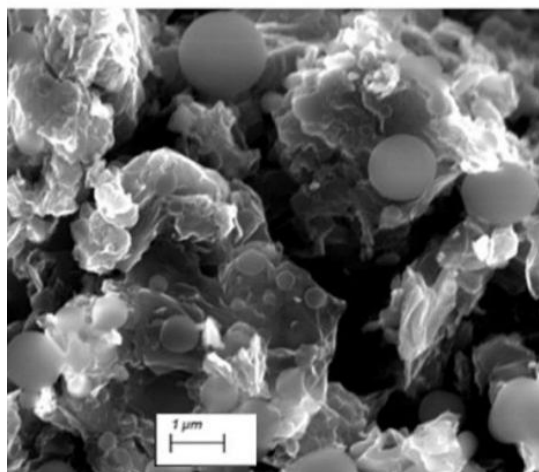


Fig. 6. SEM images of Polymer-amine GO composite.

An increase in U uptake up to pH 5 was observed, followed by a reduction. The increased adsorption of U from pH 2 to 5 is attributed to the presence of anionic species of U. The subsequent reduction of U adsorption is likely due to the role of other anionic species, which tend to exhibit competitive adsorption with U. The duration of contact and metal ion concentration, pH

and salt effects also play a crucial role in metal ion adsorption. The uptake behavior of U from uranyl acetate buffer (which consists of acetic acid and sodium acetate) was analogous to that of U carbonate solutions. It has been known that U tends to hydrolyze and precipitate as its hydroxides (eg, $[\text{UO}_2\text{OH}]^+$, $[(\text{UO}_2)_3(\text{OH})]^{5+}$ or $[(\text{UO}_2)_2(\text{OH})_2]^{2+}$) at higher pH. However, the present study was conducted in acetate and carbonate media, where at pH 4 and 5, neutral $\text{UO}_2\text{-(Acetate)}_2$, UO_2CO_3 , cationic $[\text{UO}_2\text{-Acetate}]^+$ species were dominant according to the theoretical speciation results [17]. Also, as the concentration of H^+ was comparatively lower, DETA and other functional groups on both adsorbents were hardly protonated and were available for interaction, resulting in maximum extraction. At pH beyond 5, $[\text{UO}_2\text{-(Acetate)}_2]^-$ and $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ being the major species, do not have any affinity towards the adsorbents, as higher pH makes the adsorbent's surface negatively charged as well. This explains the decrease in the q_e at pH beyond 5. The reduction in U extraction beyond pH 5 was gradual in the acetate medium but drastic in the carbonate medium. This can be attributed to the magnitude of the charge in U species.

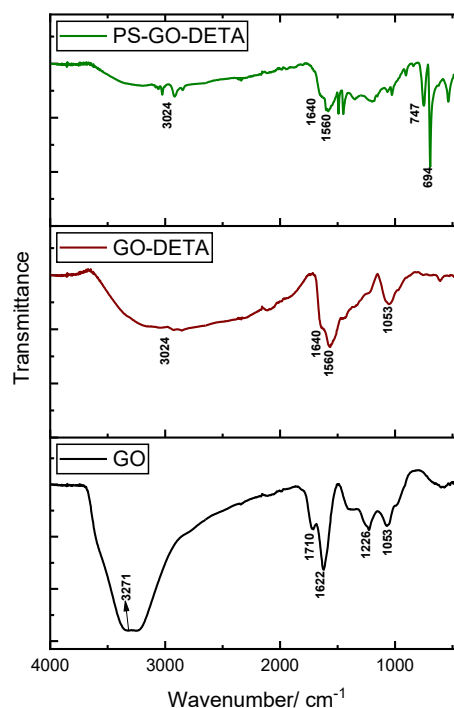


Fig. 7. FTIR of Polymer-amine GO composite.

The prevalent U species in the carbonate medium, $\text{UO}_2(\text{CO}_3)_3^{4-}$, with an intense

negative charge, is less attracted to the adsorbent than $[\text{UO}_2(\text{Acetate})_2]^-$ in the acetate medium, which has only a unit negative charge. The result can be inferred as follows: the electrostatic repulsion mitigates the extraction by altering the charge on the U species and adsorbent surface in opposite ways, and the extraction of U proceeds with its neutral species complexing with the functional groups present in the adsorbent. Speciation behavior of uranyl ion in carbonate medium as a function of pH generated by MintEQ is given in Fig. 10.

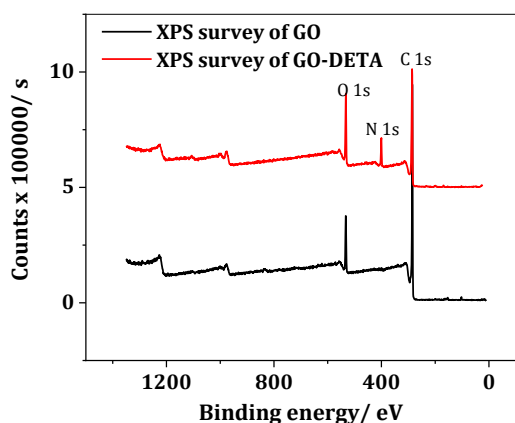


Fig. 8 XPS GO and GO-DETA.

The U adsorptive features of the above adsorbent in the presence of metal ions that are present in sea water condition have been tested, and the data is shown in Fig. 9. It was observed that V, Mg, Si and Sr were extracted to a lesser extent (less than 5 %), whereas Ni, Cu, Co, Na and Ca were adsorbed to less than 30 %. U adsorption to the resin was more than 90 %. Therefore, it can be expected that PS-GO-DETA can remove U from seawater-like solutions with minimal interference from other ions.

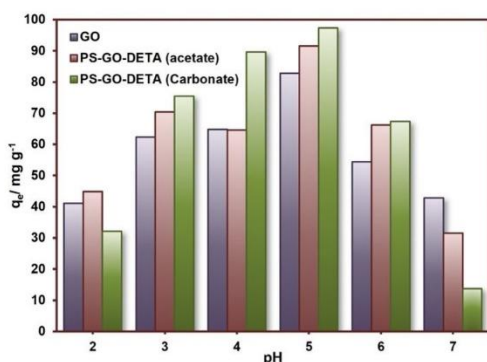


Fig. 9 Adsorption behavior of the adsorbent in the presence of acetate buffer medium

and in carbonate medium, as a function of pH of the aqueous phase

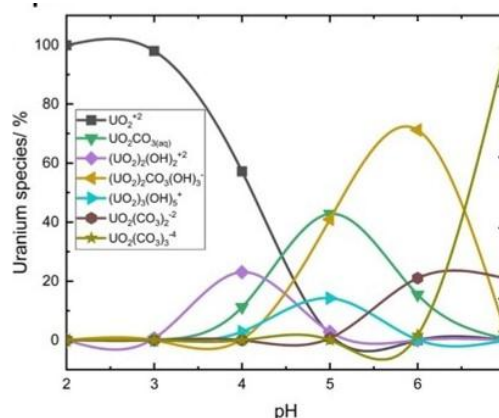


Fig. 10 Speciation behavior of uranyl ion in carbonate medium as a function of pH generated by MintEQ.

One critical challenge with the majority of solid-phase adsorbents is their poor chemical stability in acidic environments. Another polymeric-GO composite adsorbent with an amide functional group on the GO matrix was prepared for the separation of Zr from PUREX-derived acidic waste that could arise during the reprocessing of U-Pu-Zr-based fuel through an aqueous reprocessing route [3]. One of the critical issues with respect to Zr during the processing of U-Pu-Zr-based fuel through aqueous reprocessing is the elevated Zr concentrations, which can significantly affect subsequent processing steps, particularly during PUREX raffinate management. Here, the high concentrations of Zr could interfere with the subsequent minor actinide portioning process steps. Therefore, to minimize the threat posed by the presence of Zr, it is planned to remove Zr prior to the minor actinide portioning process. Compared to a solvent extraction-based process, which adds one more liquid-based processing step, a solid-phase adsorbent using a Zr-selective material could address the above issue, thereby minimizing the volume of liquid waste. Studies using amide-group-functionalized GO-polystyrene composites showed Zr removal from highly acidic aqueous solutions.

Unlike the functionalization of typical organic molecules or polymers, functionalizing graphene oxide is not straightforward. The original functional groups present in GO, such as carboxylic acids, need to be modified to different functional groups. In this context, to

introduce amide functionality onto GO, the GO was first converted to a chlorocarboxylate derivative by reaction with SOCl_2 [3]. Briefly, the synthetic protocol involved the chemical reaction of GO (3 g) with thionyl chloride (3 mL) in the presence of chloroform (50 mL) to generate GO-COCl, and then reacting the resultant GO-COCl (1.5 g) with diethylenetriamine (DETA, 4.5 mL) in the presence of triethylamine (TEA). The produced amide was purified by washing it with ethanol, and the GOA particles were dried under vacuum (at 50 °C) for solvent evaporation (30 min) before use. Quantitative conversion of GO to GO-CONHR was achieved during this step, yielding approximately 3.2 g of the product (GO-CONHR). A detailed synthetic scheme for the preparation of GOA is shown in Fig. 11.

Subsequently, the amide-anchored GO was introduced into the polystyrene matrix to prepare the composite adsorbent via pickering emulsion polymerization, using a similar approach as discussed earlier [3].

Upon characterization, this adsorbent also exhibited signatures of an amide functional group, in addition to GO features (similar to those of the previously discussed adsorbent) [3].

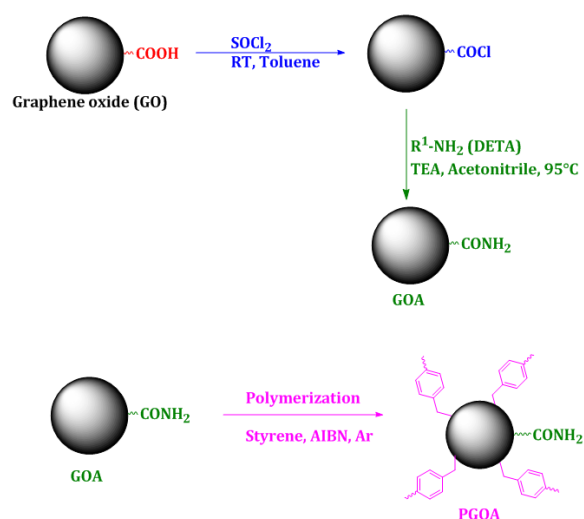


Fig. 11 Synthesis scheme for the preparation of amide GO-polymer composite.

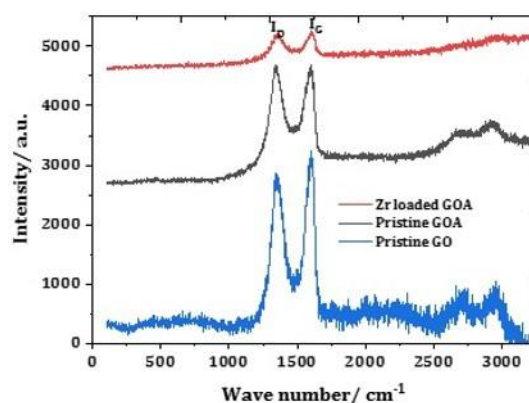


Fig. 12 Laser Raman spectra of amide modified GO, compared to GO, and after Zr loading.

The Raman spectroscopic studies also revealed interesting aspects of the defects-activated breathing vibration introduced by the oxidative exfoliation of GO (Fig. 12). The above Raman identification, noted popularly as 'G' band, appears around 1585 cm^{-1} . In addition to the above, the typical sp^2 -hybridized vibrational bands of graphite are retained in graphene oxide.

For the Zr separation studies, the feed solution considered was acidic and could be derived from reprocessing of U-Pu-Zr or U-Zr-generated PUREX raffinate, in which Zr may limit the efficacy of trivalent removal by TRUEX. In this connection, the ability of PGOA to adsorb Zr from aqueous phase was examined in a variety of acidic solutions ranging from 1 to 7 M nitric acid. At all nitric acid concentrations from 1 to 6 M, Zr adsorption was high and then partially decreased above 6 M.

The amide group in PGOA is the one responsible for Zr adsorption. The amides are expected to form a neutral, solvating-type complex with the metal ions under acidic conditions. The carbonyl group of the amide is expected to be polarized during this reaction.

Based on various findings from neutral ligand complexation techniques, it is presumed that Zr complexation with PSGOA may be referred to merely as follows [3].



The 'n' denotes the total amount of amide ligands accessible for complexation with the Zr.

Establishing a neutral Zr-amide complex is responsible for the absorption of Zr by PGOA. Thus, in PGOA, Zr uptake increases with increasing Zr content in the aqueous phase, reaches a maximum near 100 mg g^{-1} , and then remains constant. 0.1 M nitric acid + 0.5 M citric acid could remove Zr from the loaded GO-phase, though the removal efficiency was only 12 %. Therefore, for the quantitative removal of the loaded Zr, approximately 11 stages of contacting the Zr adsorbed PGOA with the citric acid-containing aqueous phase (0.1 M nitric acid + 0.5 M citric acid) were required. The Zr-uptake capability of PGOA in the presence of other elements present in the proposed feed (High-Level Liquid Waste; HLLW generated from U-Pu-Zr fuel) has been studied using a simulated waste composition corresponding to 80 GWd/Te [5]. The amount of metal ions adsorbed was calculated as the difference between the metal ion concentrations before and after contact with PGOA. It can be concluded that even in the presence of other elements, a significant portion of Zr ($\sim 40 \text{ mg g}^{-1}$) was loaded to PGOA. Approximately 5 mg g^{-1} each of Fe, Ba, Nd, and Ce were loaded to PGOA, whereas loading of other elements was quite insignificant. Results of the study pointed towards the feasibility of employing PGOA for the separation of Zr from the PUREX raffinate (HLLW) of U-Pu-Zr derived fuel waste, so that the possible complications in TRUEX anticipated due to the presence of Zr can be averted. Overall, PGOA can be endorsed as an efficient solid-state adsorbent for the bulk removal of Zr from the PUREX raffinate generated from U-Pu-Zr metallic fuel.

Magnetic graphene oxides

Magnetic solid phase separation is a novel concept in solid-phase adsorption techniques, wherein, instead of a column-type adsorption technique, a stirred-tank-type reactor can be employed for the adsorption process. Briefly, the process involves agitating the adsorbent with the feed solution, then physically separating it by applying an external magnetic field. The advantage of incorporating GO in a magnetic matrix is that the size restriction in carrying out bulk separation of metal ions with GO can be conveniently overcome by having a composite matrix with Fe_3O_4 . The magnetic matrix facilitates magnetic-assisted solid-phase separation. The metal ion separation can be optimized by optimizing the ligand component. Separation of U from seawater-

like solutions was attempted using a hybrid adsorbent based on GO and Fe_3O_4 . Unlike previous attempts, pristine GO was investigated as such for ion-exchange-based U separation.

In this composite material, the carboxylic acid present in the GO was explored for U separation. As discussed earlier, the Hummers' chemical exfoliation reaction produces several functional groups (viz., COOH , SO_3H , OH , etc.) on GO, which can be exploited for metal-ion separation. Optimizing the surface functional groups on GO is a key aspect when employing it for adsorption applications. The duration of oxidative exfoliation increases the production of COOH groups on GO, which can further improve the ion-exchange property. By providing a longer oxidation duration, GO predominantly consisting of carboxylic acid groups can be prepared. Further, MGO was prepared by co-precipitation via alkaline hydrolysis (using 800 mL of ammonia) of a mixture of FeCl_3 (0.8 M, 10 g) and FeSO_4 (0.4 M, 7.3 g) in Millipore water (250 mL), in the presence of GO. For this purpose, GO powder was dispersed in the alkaline solution during co-precipitation by refluxing at 85°C for 2 hours. The MGO particles formed were separated from the mixture and washed several times with de-ionized water, isopropanol and acetone. The MGO particles were dried in air overnight before use. A permanent magnet (1 tesla, cylindrically shaped, of 100 mm length and 15 mm diameter) was used for the physical separation of magnetic particles from the liquid phase. Fig. 13 shows the images of the magnetic-GO hybrid adsorbent, its dispersed form in aqueous phase, and the consolidation of the adsorbent when an external magnet is kept close by.



Dispersed MGO in aqueous medium



Faster magnetic separation of MGO

Fig. 13. Images of magnetic-GO composite (MGO) dispersed in aqueous medium, and their consolidation in the presence of external magnetic field.

When GO and Fe_3O_4 are both present in a single material, wherein they individually also exhibit a layered framework, the combined hybrid material should exist as interlayers of GO and Fe_3O_4 [6]. The SEM and TEM images (shown in Fig. 14) confirm this by showing the interwoven layers of GO and Fe_3O_4 . The SEM images indicate that the samples are powder agglomerates, and the high-resolution image of MGO shows the particles as flat agglomerates. TEM show Fe_3O_4 nanoparticles dispersed in the GO layer. The particles are spherical, with a mean diameter of ~ 50 nm.

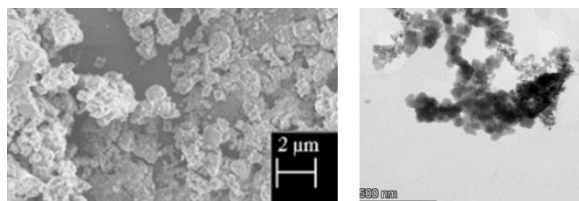


Fig. 14 SEM (left) and TEM (right) images of MGO.

Raman spectra of the samples are shown in Fig. 15. The Raman spectrum of GO shows peaks at ~ 1350 and ~ 1601 cm^{-1} , designated as the defect (D) and graphitic (G) peaks, respectively. Monolayer, defect-free graphene has a high-intensity G' peak, whereas the corresponding G peak is low-intensity. Raman spectrum of GO samples shows the G' peak at ~ 2700 cm^{-1} , which is typical of a few-layered graphene-like structures. Hence, Raman spectral studies substantiate the layered structure of GO. Iron oxide shows Raman peaks corresponding to magnetic iron oxide (Fe_3O_4) and maghemite (γ -phase). The Raman spectrum of MGO shows bands corresponding to both Fe_3O_4 and GO. The Fe_3O_4 peaks of MGO are blue-shifted, and certain peak intensities have increased or decreased relative to the pristine sample (Fig. 15). This indicates that its surroundings influence the corresponding vibrational modes of Fe_3O_4 . This is possibly due to the intercalation of Fe_3O_4 in GO. The presence of Fe_3O_4 also influences the defect in the GO. The ID/IG ratio (the intensity ratio of the D and G peaks) of MGO is 1.7, whereas for GO it is 0.94. This shows that the iron oxide reduces the graphitic ($\text{C}=\text{C}$) configuration and linear vibrations, contributing to an increase in defect density.

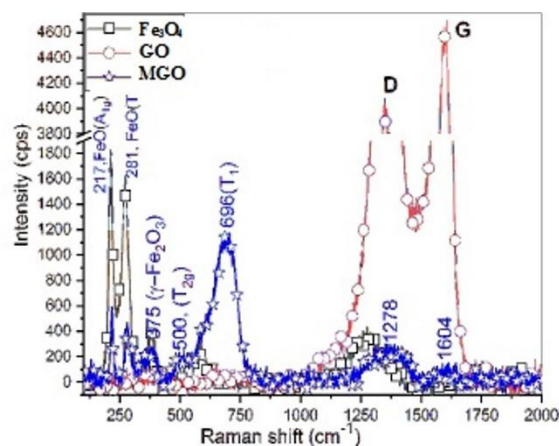


Fig. 15 Raman spectra of Fe_3O_4 GO and MGO.

XRD pattern (Fig. 16) of GO indicates the signature of a typical GO peak around 12° , which corresponds to the (001) plane, evidencing the formation of GO. It also showed the presence of graphite at 25° (corresponding to the (002) plane). The XRD peaks of Fe_3O_4 have the same positions as those reported in the literature. The XRD pattern of MGO also shows peaks corresponding to the (311) planes of Fe_3O_4 and the (511) (002) planes of graphite. The XRD peaks corresponding to the (001) plane are less pronounced in MGO, as they may have merged with other peaks due to Fe_3O_4 . As indicated by SEM, the XRD of MGO also suggests the formation of a layered GO (due to the presence of a graphitic signature). Moreover, the presence of Fe_3O_4 could have facilitated the formation of GO layers in MGO, as reported earlier. It is interesting to note that the (002) peak in MGO is shifted to lower 2θ values. The shift in 2θ toward lower values indicates increased d-spacing, providing direct evidence of increased intercalation of Fe_3O_4 between the graphitic planes of GO. It is worth recalling that the TEM images also provided direct evidence of Fe_3O_4 intercalation between two GO layers.

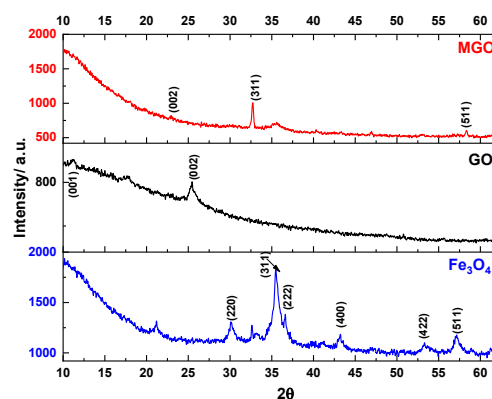


Fig. 16. Powder XRD pattern of Fe_3O_4 , GO and MGO showing the crystallographic planes.

Fe_3O_4 is known to form an inverse spinel structure and is paramagnetic. Because of its paramagnetic nature, Fe_3O_4 facilitates faster disengagement of MGO from aqueous solutions. In the MGO, the spherical Fe_3O_4 particles are embedded in the interlayers of GO. The graphene wrapping around Fe_3O_4 enhances stability in MGO-based adsorbents. Unlike the usual Fe_3O_4 , wherein the Fe_3O_4 is protected with silica coverage, the Fe_3O_4 in MGO is covered by the GO sheets. Besides facilitating the physical separation of the adsorbent from the aqueous phase (rapid separation using a magnetic field), Fe_3O_4 plays no role in the adsorption process.

Adsorption of U to MGO is shown in Fig. 17. The adsorbent exhibited higher adsorption of U above pH 5, with an adsorption capacity of above 120 mg g^{-1} . The adsorbent was also tested for its suitability for U removal under sea-water-like conditions. The amount of U adsorbed onto MGO was determined in the presence of some of the interfering cations, such as Fe, V, Zn, Cu, Ni, Co, Cs and Mg and the results of which are shown in Fig. 17. It can be that except in the presence of V, the reduced U adsorption in the presence of other interfering ions was only 25 % in case of Fe. The reduction in U adsorption in the presence of other elements such as Zn, Cu, Ni, Co, Cs, and Mg was within 5%. U adsorption was reduced from 120 mg g^{-1} to 65 mg g^{-1} when $200 \mu\text{g/mL}$ of V was present alongside 100 mg/mL of U. The reduction in the adsorption of U in the presence of V could be due to the presence of the pentavalent oxidation state of V, exhibiting significant competition to U^{6+} . Moreover, the actual concentration of V in seawater is 5 to 6 times lower than that of U, while in the present study concentration of V was twice that of U. Overall, efficiency of MGO in selectively separating U even in the presence of interfering cations is highly superior.

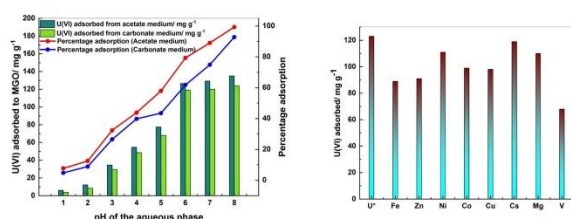


Fig. 17 Adsorption of U to MGO in the presence of interfering from acetate buffer and carbonate buffer as a function of pH of aqueous medium (left), and adsorption of U with reference to interfering ions such as Fe, Zn, Ni, Co, Cu, Cs, Mg, V. (right).

Conclusions

GOs are next-generation solid-phase adsorbents with superior surface features, demonstrating extraordinary chemical stability in acidic and alkaline environments, and facilitating surface chemical modification by incorporating metal ion-selective functional groups, making them an attractive candidate for metal ion separation in nuclear waste management and reprocessing-related applications. The scope of composite adsorbents comprising GO with a polymeric matrix or magnetite makes them versatile for the above application, wherein the unique features of GO can be explored. GO, being a cost-effective option, could be further expanded for diverse applications, including metal-ion purification, radiopharmaceutical purification, waste management, and decontamination.

GO's surface properties can be tuned with the reagents used for surface modification and by incorporating task-specific functional groups, enabling exploration of GO's application to achieve highly selective metal-ion separation with minimal interference from coexisting ions.

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ASSET Bulletin on "Separations of Lanthanides, Actinides and Fission Products using Porous Materials"

Biodata



Dr. A. S. Suneesh joined Materials Chemistry and Metal Fuel Cycle Group (MC&MFCG) at the Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam in 2008 after completing a one-year orientation course from 51st batch of BARC Training School. He earned his Ph.D. in Chemistry from HBNI, and he is also an Assistant Professor at the Homi Bhabha National Institute (HBNI). He was awarded DAE Group achievement award in the year 2011. His research centers on composite materials, including graphene oxide hybrid adsorbents, polymer and magnetic nanocomposites, with applications in metal ion separation, catalysis, sodium-ion batteries, and molecular dynamics simulations. He has published over 65 publications in peer reviewed international journals.



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