

Adsorbents for the Uranium Capture from Seawater for a Clean Energy Source and Environmental Safety: A Review

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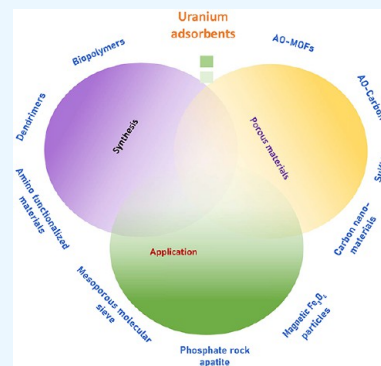
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ABSTRACT: On the global level, uranium is considered the main nuclear energy source, and its removal from terrestrial ores is enough to last until the end of the current century. Therefore, a major focus is attracted toward the capture of uranium from a sustainable source (seawater). Uranium recovery from seawater has been reported over the last few decades, and recently many efforts have been devoted to the preparation of such adsorbents with higher selectivity and adsorption capacity. The purpose of this review is to report the advancement in adsorbent preparation and modification of porous materials. It also discusses challenges such as adsorbent selectivity, low uranium concentration in seawater, contact time, biofouling, and the solution to the problems necessary to ensure a better adsorption performance of the adsorbent.



1. INTRODUCTION

Uranium extraction has gained more interest for two significant reasons: the increasing demand for uranium as a carbon-free energy source and nuclear waste management as well as its toxicity.^{1–6} Considering that uranium is limited in terrestrial ores to about 7.6 million tons, various efforts have been made toward the use of unconventional uranium sources such as seawater, which contains 4.5 billion tons of uranium, sufficient to protect nuclear development.^{7,8} On the other hand, the radioactivity and toxicity of uranium pose a lethal threat to the environment; hence there is a need to develop a sustainable technology to reduce nuclear incidents.^{9–11} However, it is not easy to extract uranium from seawater, because the uranium concentration in seawater is very low (3 ppb) as compared to other competing metal ions.^{12–15} Also, the high volume of seawater adds more challenges.^{3,4,16,17} To achieve the targeted goals, a cost-efficient adsorbent with high adsorption capacity, high durability, and fast kinetics has been reported.^{18–28}

This review aims to sum up the state of knowledge regarding the adsorbents used for the adsorption of uranium from seawater, and the articles which investigate the real application have been added and discussed with the experimental and theoretical justifications. In the last two decades, several review papers were published, and all of them provide information regarding the development and synthetic routes of adsorbent materials with numerous postmodification strategies for uranium extraction from seawater.^{7,29,30} Two review articles published by Abney et al.³¹ and Xie et al.³² reported the new synthetic routes and technological developments that have been carried out from time to time to overcome the challenges.

However, one key factor that restricts the engineering application for uranium extraction from seawater in the future is the relatively low concentration of uranium present in seawater. Uranium is found in seawater at very low concentrations, typically around 3.3 ppb. Therefore, extracting a significant amount of uranium from seawater requires significant technological advancements and engineering solutions to develop efficient and cost-effective extraction methods. This review extends the focus on the preparation of porous adsorbents and their application for uranium extraction from seawater. Seawater is a complex solution with low uranium concentration and large ionic strength and competing ions.^{30,33} The high ionic strength of carbonates and the pH command the specification of uranium, which in turn influences the adsorption property of the adsorbent. In general, adsorbents are not covered in this review; if they are not investigated, uranium extraction from aqueous solution and the influence of competing ions and low uranium concentrations complement seawater challenges. The most efficient and advanced materials such as amidoxime and amidoxime-based materials have been studied extensively for the extraction of uranium.^{34–37}

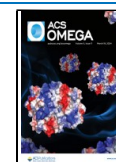
The important proceedings in this study include the new improvement in the preparation of uranium adsorbents

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including nanostructured materials,³⁸ which includes the research on porous organic polymers,^{20,21,29} porous aromatic frameworks,^{1,30–33} metal–organic frameworks,^{39–45} covalent organic frameworks, nanofibers,^{46–50} organic/inorganic nanocomposites,^{51–57} and biomaterials including cellulose,^{58–65} chitosan, etc.^{35,66–79}

Recently, the aforementioned nanomaterials and graft polymer adsorbents have been practically applied for uranium extraction from real seawater. For the advancement of the adsorption performance, the adsorption capacity of new materials was analyzed at a laboratory scale under seawater conditions. Significant advancements have been devoted to the preparation of such adsorbents (porous amidoxime materials), and to the best of our knowledge no review article summarizes their abilities to recover uranium from seawater. Such materials possess higher selectivity, adsorption capacity, and stability of adsorbents.

2. HISTORY OF URANIUM EXTRACTION FROM SEAWATER

Uranium extraction started in Japan in 1960, and many universities started different projects in 1974 for the extraction of uranium from seawater. The studies focused on different extraction techniques such as solvent evaporation, ion exchange, flotation, adsorption, and preparation of adsorbents from TiO₂ and PbS.⁸⁰ In the 1980s, inorganic materials were used for the extraction of uranium from seawater, which now is out of interest, and efforts are being made to modify them. Synthetic polymers and biopolymers are currently performing well and are deployed largely for uranium extraction. Research relating to the modification of base materials, new developments considering functionalization and tuning of physical characteristics via postsynthetic functionalization, and computer-simulated programs are used to design the ligands for uranium adsorption performance. Nonstructural adsorbents are novel ways for potential uranium adsorbents, having high surface areas and pore sizes by which one can easily tailor the properties to enhance the uranium adsorption capacity. Research fields include adsorbents such as covalent organic frameworks, metal–organic frameworks, nanofibers, mesoporous silica, and biopolymers. Overall this review article summarizes research development and the author's viewpoint on where the existing efforts should be engaged to achieve better performance.

Uranium extraction from seawater has been a hot research topic in most countries for the last seven decades. Davies et al. mentioned this research in the literature in 1964 and even cited it in recent articles.⁸¹ In the early decades efforts were devoted toward inorganic adsorbents deployed as either floating beds or fixed beds. Until 1979, 81 inorganic adsorbents were used for uranium mining, and out of them, some adsorbents including hydrous titanium oxide, lead sulfide, and lead naphthalene achieved an adsorption capacity of 1 mg/g of adsorbent.^{31,81} In 1980, the adsorption technology changed and organofunctionalized polymers came into existence with excellent adsorption performance. Egawa et al.¹²¹ first reported that an amidoxime functionalized polymer adsorbent was prepared from poly(acrylonitrile-*co*-divinylbenzene) and hydroxylamine. The uranium adsorption field test was performed in a column, and uranium adsorption was 80% from the seawater. A similar study was carried out by Witte et al., and the seawater-exposed adsorbent (130 days) showed an adsorption capacity of 450 μg/g and could recover uranium up to 10 cycles with an adsorption efficiency of 82%.⁸² In 1982, a critical overview was reported by

Schwochau et al. that articulated the significant parameters for uranium extraction from seawater, which include availability and low cost, stability under seawater, fast kinetics, high adsorption capacity, and elution efficiency. These characteristics were analyzed in more than 200 studies of organofunctionalized materials, and the results revealed that poly(acrylamidoxime) was considered a potential adsorbent for uranium.⁸³

A huge advancement resulted from the preparation of amidoxime adsorbents in Japan from 1980 to 1990, and the poor mechanical strength of poly(amidoxime) was modulated by Tamada et al. by using a radiation-induced graft polymerization method to functionalize a strong polymer backbone (polyethylene with polyacrylonitrile) and subsequently transform it into poly(amidoxime).⁸⁴ Large-scale marine experiments were performed by the Japanese for uranium extraction from seawater from 1999 to 2001.⁸⁵ To reduce the cost of uranium extraction, the adsorbent was used as a floating bed; the uranium adsorption capacity was 0.5 mg/g of adsorbent within 30 days and the elution of uranium was carried out with 0.5 M HCl.⁸⁴ For the first time in India in 2000, the emulsion polymerization method was used to prepare adsorbents for uranium adsorption from seawater including a multidentate chelating resin, hydrogels with various copolymers, and amidoxime-based polypropylene sheets.^{86–89} Since 2011, tremendous work has been carried out in the United States of America and China for the adsorption of uranium from seawater. Different approaches were applied with the highest precision, with advanced instrument characterization for materials characterization, and with developed nanoscience applied to double the adsorption performance of Japanese-reported adsorbents. The multifaceted advancements involve coordination between the uranium and the chelating sites; adsorbent characterization; computer-based ligand simulations, kinetics, and thermodynamic model fittings; and analysis of various parameters including the pH, contact time, adsorbent regeneration, elution efficiency, cost, and environmental sustainability.⁹⁰ Recently a bundle of literature emerged from China that covers special metal–organic frameworks, inorganic–organic composites, a graphene oxide/amidoxime hydrogel,^{91–94} amidoxime functionalized carbon nanofibers,^{95–98} and ultrahigh molecular weight polyethylene to enhance bulk mechanical robustness.^{99–103}

Numerous challenges have been faced during the practical extraction of uranium from seawater including very significant challenges such as the presence of a complex metal ion system, low uranium concentration availability, long pH range, etc. A big challenge is the presence of interfering ions (Na⁺, K⁺, Mg²⁺, Ca²⁺ (cations) and Br⁻, Cl⁻, S²⁻ and CO₃²⁻ (anions))¹⁰⁴ in seawater resulting in a lower selectivity adsorbent material toward the uranium extraction from seawater. To design and prepare new adsorbent materials for uranium extraction, selective functional groups are incorporated in the framework which shows affinity toward uranium, or assistant groups are inserted; for example, recently the most studied selective functional group is amidoxime, which can assist the selectivity of uranium in the presence of other functional groups such as N, P, and O in the same work.

The salty source water is largely composed of cations and ions, and the strong salinity of seawater might affect the selectivity of the adsorbent for uranium adsorption. The overall speciation of uranium was observed in both lower and higher pH ranges, such as free uranium cations UO₂²⁺ occurring at pH <4 and the formation of the polynuclear complex (UO)₂CO₃(OH)₃ seen over the range pH 6–8. The domination of UO₂²⁺ occurs at pH

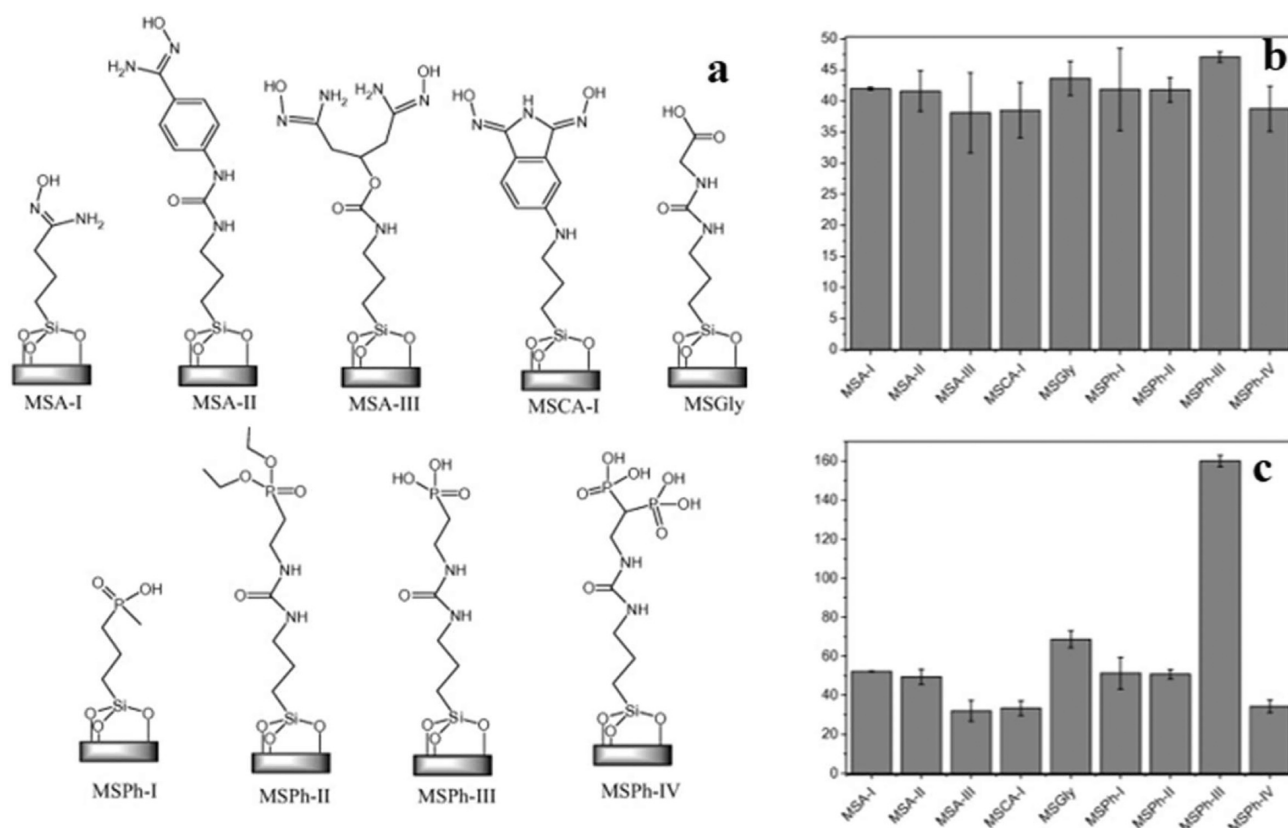


Figure 1. A series of functionalized inorganic adsorbents (a). Uranium adsorption capacity in seawater (b) and simulated solution (c). Reproduced with permission from 108. Copyright 2013 Elsevier.

4.5, and accumulation of $\text{UO}_2(\text{OH})_2$ occurs at pH 6. The abundant species from pH 6.5 to 7.5 is the polynuclear complex $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ which might be replaced with species $\text{UO}_2(\text{CO}_3)_3^{4-}$ when the pH is increased from pH 7.5 to 10.³⁰ The standard salinity in seawater is another factor that affects the adsorption performance of adsorbent for the extraction of uranium, and therefore the presence of calcium, magnesium, and bicarbonate mainly retards the kinetics of the braided nano-fibers.¹⁰⁵ Recent studies showed that porous adsorbent materials showed efficient adsorption of uranium both in acidic pH (<4) and in alkaline pH (8). However, the preparation process of such materials is rare and efforts have been made for the development of porous materials which could be applied in nuclear waste and a seawater environment. In this concern, the recently developed covalent organic frameworks (COFs) could be potential candidates due to high chemical and structural stabilities under harsh conditions. In this interest, COFs could be modified with acidic functional groups such as the sulfonic group to retain resistivity in acidic and alkaline conditions, while the sulfonic groups could show higher affinity toward the uranium ions due to the hard–soft acid–base theory.¹⁰⁶

3. URANIUM ADSORBENTS

Inorganic adsorbents have been used as adsorbents for uranium extraction from seawater since 1960 due to their low cost and easy preparation, high surface areas, and tunable pore structures. Early inorganic research focused only on oxides, hydroxides, and sulfides of titanium, magnesium, and aluminum. Among all of them, hydrous titania showed promising results with a maximum adsorption capacity of 1.2 mg/g. Because of low selectivity, and durability, the inorganic adsorbents were not used longer, and

such problems were solved by functionalized polymer-based adsorbents.³¹ More recently inorganic research has emerged again with the use of silica as a base material or organosilica-based adsorbents, where silica is impregnated with organic functional groups. Mesoporous silica based adsorbent materials have been successfully tested for uranium extraction from seawater.³¹ Fryxell et al. have reported the surface functionalization of silica for the removal selective removal of uranium under acidic conditions.¹⁰⁷ Vivero-Escoto et al.¹⁰⁸ have performed comprehensive studies of various organic functional groups on mesoporous silica, and the uranium adsorption results were compared to each other. A series of silica based adsorbents modified with amidoxime, imide dioxime, phosphonate, and carboxyl groups were grafted on commercially available MSU-H mesoporous material shown in Figure 1a. The uranium adsorption performance of each function was performed in slightly basic water and artificial seawater. All the functionalized mesoporous adsorbents show high uranium adsorption capacities ranging from 40 to 50 $\mu\text{g}/\text{mg}$ of adsorbent (Figure 1b). However, in artificial seawater, the adsorption capacity was reduced 4-fold in the range 2–13 $\mu\text{g}/\text{mg}$ of adsorbent (Figure 1c).¹⁰⁸

Li et al.⁴⁶ have reported hollow hierarchically structured Mg–Co LDHs obtained by treating zeolitic imidazolate framework-67 (ZIF-67) with magnesium nitrate under a 1:1 ethanol–water ratio at 85 °C. ZIF-67 was used as a template due to its 3D topology and high surface area and can be used as a cobalt source for the preparation of special structure layered double hydroxides (LDHs). To obtain the morphology and structure of Mg–Co LDHs, SEM and TEM analyses were carried out. The SEM analysis confirmed the Mg–Co LDHs showed uniform

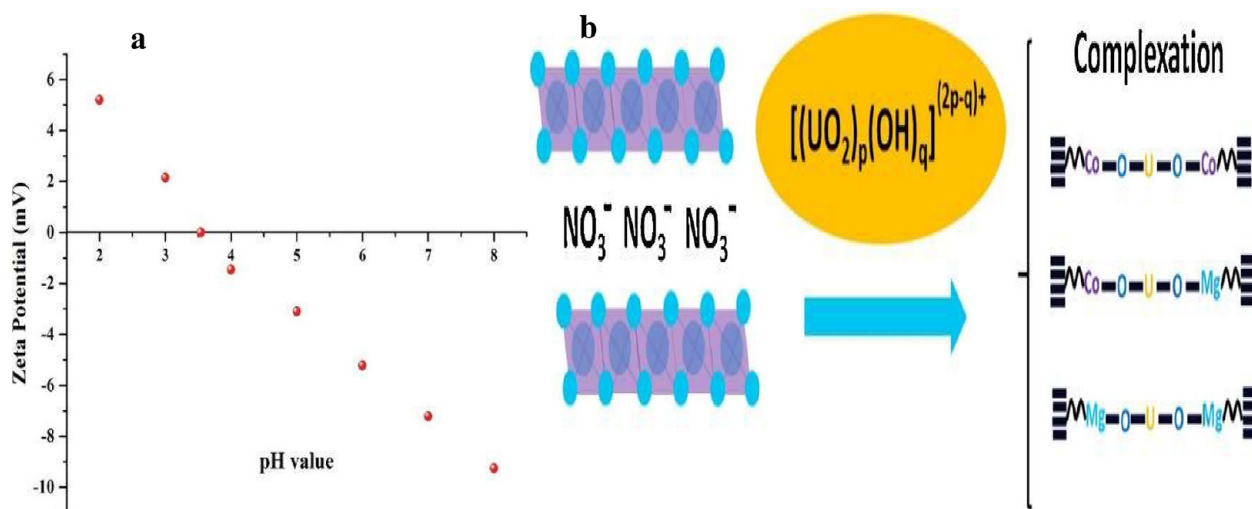


Figure 2. Zeta-potential of Mg–Co sample (0.01 mg/L) adsorbent at various pHs (a) and proposed coordination mechanism between the active sites of Mg–Co LDHs and uranium. Reproduced with permission from 46. Copyright 2017 Elsevier.

morphology with the shape of a rhombic dodecahedron, and the TEM analysis revealed a hollow structure of a rhombic dodecahedron which consists of thin nanosheets. To observe the adsorption capacity of Mg–Co LDHs, simulated seawater was used to investigate the influence of initial concentration, coexisting ions, and pH on the uranium adsorption capacity. The results show that Mg–Co LDHs retained an adsorption capacity of more than 57.3 $\mu\text{g/g}$ with a higher adsorption rate of more than 95%. Also, Mg–Co LDHs showed uranium adsorption at the extended pH range greater than point of zero charge (PZC) values (3.51) and showed limited adsorption capacity due to the predominant uranyl species attributed to the repulsion. For pH greater than 3.51, the PZC goes negative leading the Mg–Co LDHs to shift negatively charged, which is beneficial for uranium adsorption because of the electrostatic interaction mechanism (Figure 2a).

The complete uranium adsorption mechanism was analyzed using XPS before and after the uranium adsorption. The binding energy change in various peaks such as the O 1s of the pure Mg–Co LDHs showed a peak of M–OH and M–O–M produced with binding energies of 532.1, 531.2, and 530.9 eV, respectively, which indicates Mg–OH and Co–OH sites and the coordination form of Mg–O–Co. After the uranium adsorption, a new peak was observed at 529.76 eV confirming the presence of the new chemical environment around U–O. Therefore, a new uranium adsorption mechanism (Figure 2b) is proposed where the uranium first diffuses and interacts with adsorbent surfaces due to the hollow and the higher surface area and next Mg–OH and Co–OH contribute to the complexation mechanism attributes for higher selectivity and adsorption capacity. Moreover, the 3D hollow structures make easier diffusion and contact between the active sites and the uranium could be the reason for the higher uranium adsorption performance of modified Mg–Co LDHs than the LDHs.⁴⁶ Dou et al. reported a hollow Co₃S₄ obtained from the precursor ZIF-67 nanocrystals in the presence of thioacetamide via a solvothermal method for uranium extraction from a simulated solution. The adsorption capacity of Co₃S₄ was analyzed in the presence of other coexisting ions (simulated solution), and the adsorption results showed that the adsorption capacity of Co₃S₄ was 486.11 mg/g.¹⁰⁹ Lv et al. developed a MgO/carbon prepared by the hydrothermal process of MOF-74

and Mg(NO₃)₂·6H₂O and subsequent carbonization of Mg/MOF-74 under an argon atmosphere for uranium adsorption.³¹

4. POROUS MATERIALS

4.1. Amidoxime-Modified Metal–Organic Frameworks (MOFs).

Since 1990, MOFs have become quite interesting with a special structural topology obtained by self-assembled transition metal ions and the cluster of organic ligands containing hetero groups. Férey and co-workers have prepared MIL(101) Cr from chromium terephthalate based material with a high surface area and porous architecture.³⁹ The porous architectures and larger surface areas of MOFs possess several characteristics such as porosity-controlled structures, large volume spaces and surface areas, and a cluster of metal chains connected with the organic ligands.¹¹⁰ Yang and co-workers first used MOF-76¹¹¹ and UiO-68¹¹² for uranium capture from an aqueous solution. In recent years various MOF materials have been used for uranium adsorption.^{39,111–114} Amino groups have strong interaction with uranium, and its introduction to MOF structures has been studied very well.¹¹⁵ Bai et al. have reported that a series of functional groups including NH₂, ethylenediamine (ED), and DETA were grafted onto the surfaces of MOFs (MIL-101) by postsynthetic preparation, and the uranium adsorption order follows MIL(101)-DETA > MIL(101)-ED > MIL(101)-NH₂ and MIL(101).¹¹⁶ Wang et al. reported acrylamide and carboxyl modified MOFs showed ultrafast and efficient uranium adsorption from an aqueous solution.¹¹⁷ Feng et al.¹¹⁹ reported mesoporous MOFs (HKUST-1) synthesized by the solvothermal¹¹⁸ technique for the adsorption of uranium from the liquid phase. In this framework, two octahedral Cu atoms are coordinated with eight oxygen groups to form a dimeric paddle wheel structure. The adsorption of uranium in a simulated solution was analyzed using different parameters such as pH, adsorbent dosage, and contact time. In addition, study of the influence of temperature revealed that temperature has no significant impact on uranium adsorption at lower concentrations (<200 mg/L) and the temperature favors adsorption only at higher initial concentrations (>200 mg/L). The MOF HKUST-1 showed the highest uranium(VI) adsorption capacity of 840.3 mg/g in a simulated solution under a set of experimental conditions ($T = 303 \text{ K}$, pH 6, and $C_0 = 800 \text{ mg/L}$

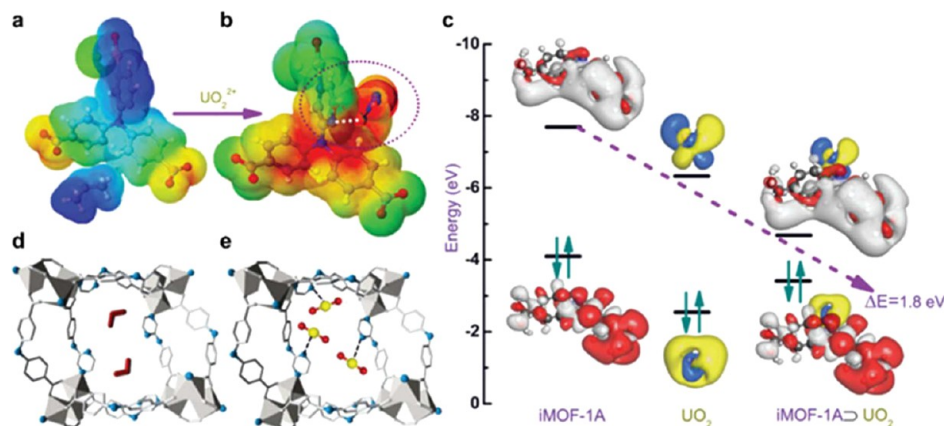


Figure 3. ESP of the asymmetric unit of iMOF-1A before and after UO_2^{2+} (a, b). Distribution of HOMO–LUMO before and after UO_2^{2+} (c). DFT optimizes host sites in iMOF-1A and DMA cations (d) and highlights the N-sites of the aromatic ring and interaction with UO_2^{2+} (e). Reproduced with permission from ref 44. Copyright 2024 John Wiley and Sons.

L).¹¹⁹ Zhang et al. have reported a double-shell hollow MIL-101 synthesized by a two-step process, crystal growth, and subsequent acetic acid etching. To enhance the uranium adsorption, a postsynthetic process was adopted to modify the double-shell hollow MIL-101 with diaminomaleonitrile, which possesses two nucleophiles such as $-\text{NH}_2$ and CN acting as functional sites to trap uranium with a maximum adsorption of 601 mg/g under a set of condition in simulated solutions.¹²⁰

Recently a significant piece of work was carried out by Ghosh and co-workers⁴⁴ based on ionic MOFs (i-MOFs-A; iMOF-1A) for uranium extraction with an outstanding uranium adsorption capacity of 9.42 mg/g in 30 days from natural seawater. In this study, anionic MOF based material was exploited to adsorb uranium by an ion exchange and interaction mechanism. Within chemistry MOFs are outstanding materials formed by coordination between the metal cluster and organic substrate. Ionic MOFs are potentially MOF-based host matrix demonstration structures accounting for anionic residual charges that can be exchanged with the appropriate ions and therefore instruct a desirable functional group. Recently, MOF-based adsorption and electrocatalytic extraction have gained more momentum for the capture of uranium from seawater. Tremendous efforts have been devoted to discussing the role of a chemical and structural feature that influences the adsorption process, thermodynamics, and the kinetics of the MOFs and analyte interaction. Adsorbent i-MOFs-A are the subclass of ionic MOFs which have been considered multifunctional materials with good stability in water and possess free dimethyl ammonia (DMA) cations that could be easily replaced to offer a selective application. The uranium adsorption of i-MOFs-A adsorbents is in the concentration range 20 000–24 ppb with an adsorption efficacy of 99.8% in a contact time of 120 min; the higher distribution coefficient $K_d \geq 0.97 \times 10^6$ mL/g determines the higher affinity of i-MOFs-A adsorbents toward uranium. Also, they can reduce the level of uranium lower than the level proposed by the U.S. Environmental Protection Agency (EPA); drinking water limits half of the uranium from 1.1 gal with an adsorption capacity of 9.39 mg/g in 30 days with an exception enrichment index of ~ 5754 and possesses an efficient regeneration. The uranium adsorption mechanism of i-MOFs-A was analyzed with nano-FTIR and tip force microscopy studies, and the results confirmed the extraction of uranium followed by ion exchange and supramolecular interactions throughout the single crystal of i-MOFs-A. Moreover, the experimental and

theoretical studies confirmed that the efficient uranium performance is attributed to the chelation with highly anchored basic N-sites present in the MOF backbone.

The experimental results are further supported by the theoretical calculations that were analyzed by density functional theory (DFT) calculations. The electrostatic potential (ESP) of the asymmetric unit of i-MOFs-A before and after interaction is shown in Figure 3a,b, and the results confirmed the ESP of i-MOFs-A changes drastically after interacting with UO_2^{2+} and the coordination of the DMA with i-MOFs-A disappears. The results were further analyzed by investigating the HOMO–LUMO in the interaction of i-MOFs-A and UO_2^{2+} to determine the change in the energy levels (Figure 3c). The levels of HOMO and LUMO are responsible for the electron donation and electron acceptance of the molecule, and therefore the active sites of the molecule are responsible for physicochemical attraction. Figure 3c depicts the HOMO–LUMO electron distribution of i-MOFs-A before and after the interaction with UO_2^{2+} . The results revealed that before the interaction of UO_2^{2+} with i-MOFs-A the HOMO–LUMO energy gap of i-MOFs-A was ~ 4 eV and after the interaction of UO_2^{2+} with i-MOFs-A the separation of HOMO–LUMO was ~ 1.8 eV. This allowed the LUMO of UO_2^{2+} to fall in between the valence and conduction bands of i-MOFs-A; that allowed the transfer of electron from the i-MOFs-A to UO_2^{2+} .

To gain the theoretical mechanism between the i-MOFs-A and the uranium, a single subunit of i-MOFs-A which bears two DMA cations and the cationic exchange process render the framework interaction that allows two DMA cations to be selectively replaced by UO_2^{2+} ; thereby UO_2^{2+} further combines with the aromatic ring of the i-MOFs-A to achieve stability in the i-MOFs-A framework (Figure 3d,e).⁴⁴

4.2. Amidoxime-Modified Carbon Materials. The construction of adsorbents for uranium adsorption from seawater was started using inorganic adsorbents including hydroxides, oxides, and carboxyls of titanium, magnesium, and aluminum. In early 1980, uranium adsorption changed dramatically due to the existence of polymeric adsorbents.³¹ At the end of the preceding decade, after the screening of various organofunctional groups, a chemical structure (amidoxime) was analyzed and the results confirmed amidoxime as a potential chelating site for uranium.⁸³ Simultaneously, Egawa¹²¹ and Astheimer⁸³ developed cyano-functionalized beads, and the cyano groups were converted into amidoxime groups. However,

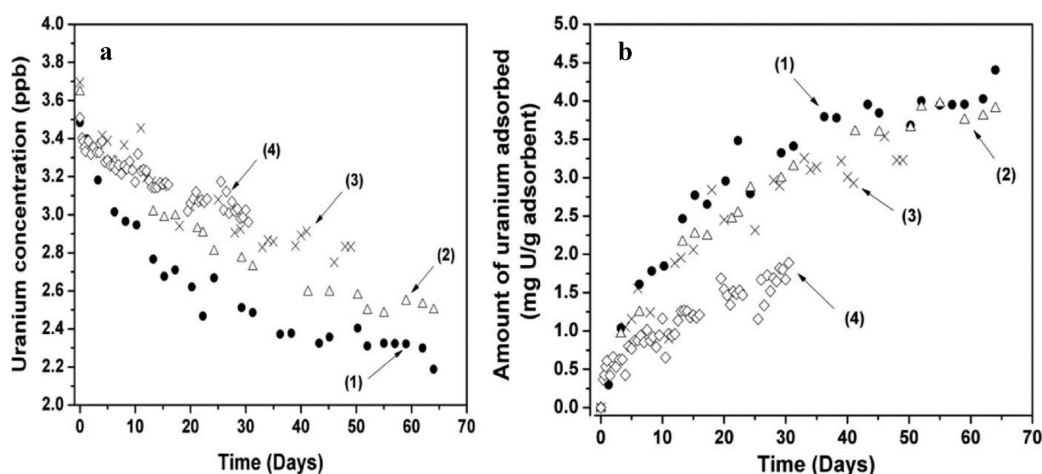


Figure 4. Uranium adsorption experimental results from seawater in batch method. Various adsorbents (a) and JAEA adsorbent (b). Reproduced from ref 129. Copyright 2016 American Chemical Society.

Table 1. Uranium Adsorption Capacity of Various Amidoxime Adsorbents from Seawater

adsorbent	adsorption capacity (mg of U/g)	contact time; source of solution; conditions; method of preparations; advantages/disadvantages	ref
amidoxime chelating resins	3.2	180 days; seawater	124
amidoxime–silica composite fiber	0.2	1 day; seawater	125
amidoxime resin	0.97	30 days; RIGP	126
amidoxime beads	1.32	34.5 days	127
amidoxime polyethylene/polypropylene nonwoven fabric	2.85	240 days; seawater	85
amidoxime polypropylene fibers	1.5	30 days; seawater	137
amidoxime adsorbents (ORNL)	3.3	56 days; seawater; RIFF	129
ORNL's AI (amidoxime–vinylphosphonic acid)	3.5	56 days; 3 h KOH; seawater; RIGF	131
AF (amidoxime–itaconic acid copolymer)	3.9	56 days; 1 h KOH; seawater; RIGF	138
amidoxime polymer adsorbent (ORNL)	6.56	56 days; KOH/NaOH; seawater; ATRP	133
hydrous titanium oxide	1.1	seawater	139, 140
lead sulfide	0.6	seawater	139, 141
dithiocarbamate chelating resin	0.05	1 day; seawater	142
dithiocarbamate chelating resin	5.1	seawater	142
cyclic imide dioxime (CID) modified nanofibers	11.39	87 days; seawater; RIGP and CIGP	136
Mg–Co LDHs	0.057	simulated seawater	46
hollow cobalt sulfide	486.11	simulated solution; solvothermal	109

the beads require the package to hold the adsorbent to make easy contact between the uranium in seawater and the active sites with the loss of materials. From the perspective of the practical application of adsorbents, the National Institute of Advanced Science and Technology has prepared amidoxime-modified fibers from acrylonitrile fibers with hydroxylamine.⁸⁴ The amidoxime fibers were deployed directly to the waves and currents of the ocean when they were placed in the sea.¹²² In Japan, during the 1980s and 1990s major progress was made in the preparation of amidoxime fibers. After successful preparation, poly(amidoxime) exhibits poor mechanical strength. Tamada and co-workers¹²³ have used radiation-induced graft polymerization (RIGP) (Figure 4) to functionalize the strong polymer polyethylene with acrylonitrile, and subsequently nitrile groups were transformed into amidoxime groups. The polyethylene trunk provides strength to the poly(amidoxime) groups and is easily accessible to uranium ions. Also, electron beam radiation under an inert atmosphere produces radicals and is

placed in an acrylonitrile solution to graft polyacrylonitrile on the radical sites formed.¹²³ In some studies, a comonomer such as methacrylic acid was added to enhance the hydrophilicity, which in turn increases the probability of contact between the active sites of adsorbent and uranium ions. As a final point, the treatment of adsorbent with KOH prompts swelling of the amidoxime fibers for interaction with the seawater.^{84,123} Marine practical analysis of amidoxime was started in the early 1980s. Among all the studies Sugasaki and co-workers synthesized amidoxime grafted resin prepared by different copolymers and cross-linking agents with a maximum uranium adsorption capacity of 3.2 mg/g of adsorbent with 180 days of contact time (Table 1).¹²⁴ Later, Kobuke and co-workers developed amidoxime-modified silica composite fiber where the functionalized powder was supported with polyethylene or copolymer of ethylene-vinyl acid with an adsorption capacity of 0.2 mg/g of adsorbent within 1 day of seawater exposure.¹²⁵

The marine testing of amidoxime resin was started in the early 1990s by Takeda and co-workers using a fixed-bed column of amidoxime fibers prepared by RIGP with an adsorption capacity of 0.97 mg/g of adsorbent placed in seawater on the sea coast Table 1.¹²⁶ Egawa and co-workers have analyzed amidoxime beads obtained from a copolymer of acrylonitrile and divinylbenzene with the adsorption capacity of 1.32 mg/g of adsorbent exposed for 34.5 days in seawater in an affixed column manner.¹²⁷ Seko and co-workers performed a similar experiment using a polyethylene/polypropylene nonwoven resin modified with amidoxime suspended in a cage to hold the adsorbent in the sea in the cage with a higher uranium adsorption capacity of 2.85 mg/g of adsorbent in 240 days of contact time in seawater.⁸⁵ The amidoxime polypropylene fibers were attached to the bottom of the sea at Okinawa, and after 30 days of exposure, the uranium adsorption capacity was 1.5 mg/g of adsorbent.¹²⁸

Recently, efforts have been continued to modify the amidoxime materials founded by the Japanese (2000s) under the instructions of the Department of Energy, Oak Ridge National Laboratory (ORNL).¹²⁹ This research group prepared an amidoxime group containing adsorbent which follows three steps: irradiation, grafting, and conditioning. Polyethylene fibers were irradiated to obtain free radicals and next were grafted with acrylonitrile and methyl acrylic acid, and the grafted fibers were subsequently treated with hydroxylamine to provide amidoxime polyethylene fibers. The ORNL materials were first analyzed by batch and column methods in seawater. The practical application was performed with a real 5 gal of seawater with three adsorbents as shown in Figure 4. The uranium concentration was decreased with time, and adsorbent 1 showed a higher adsorption performance than adsorbents 2 and 3. The results demonstrated that adsorbent 1 showed a higher adsorption capacity within 30 days than the adsorbent used by JAEA adsorbent under similar conditions. The uranium adsorption capacity of adsorbent 1 was 3.2 mg/g higher than the adsorbent used by JAEA for 180 days of contact time for uranium adsorption.¹²⁹

With the same material (ORNL), a follow-up study performed at Pacific Northwest National Laboratory showed similar results under the same set of conditions at Sequim Bay.¹³⁰ Das and co-workers report the polymer composition and conditions under new materials formulation. Two adsorbents of ORNL AI and AF were prepared from poly(amidoxime–vinyl phosphonic acid) copolymer¹³¹ and amidoxime–itaconic acid copolymer,¹³² respectively, to produce hollow-shaped fibers, and both of them were treated with KOH (0.44 M) for 1–3 h. AF with an amidoxime–itaconic acid ratio = 10:14 with 1 h of KOH treatment achieved the highest uranium adsorption capacity of 3.9 mg/g within 56 days, and the highest recovery uranium of AI (amidoxime–vinyl phosphonic acid, ratio = 3:52, 3 h KOH treatment) was 3.35 mg/g. The ORNL modification to the adsorbent preparation was the substitution of the RIGP method with the atom-transfer radical polymerization (ATRP) method to the grafting polymer as a support material. The ATRP method has numerous advantages as compared to the RIGP method including the control of polymer morphology and composition, reduction of the homopolymerization allowing ready manipulation of the molecular weight of the polymers, improved synthesis of polymer, and weight distribution.

Brown and co-workers¹³³ first applied the ATRP method for the synthesis of uranium adsorbent from seawater using amidoxime acrylic acid with poly(vinyl chloride)-*co*-chlorinated poly(vinyl chloride) (PVC-*co*-CPVC) fibers. ATRP was used for

acrylonitrile (AN) and *tert*-butyl acrylate (tBA) for surface graft polymerization of precursor groups for developing the interacting groups for the adsorption of uranium from seawater. The ratio between the tBA and AN was varied to identify the optimum ratio between the hydrophilic groups and the binding groups. The best uranium adsorption performance and the ratio between tBA and AN with the grafting percentage of 1390% represent the uranium adsorption capacity which is higher than that of the JAEA fiber adsorbent with the adsorption capacity of 2.42–3.24 g/kg in contact for 42 days and 5.22 g/kg in 49 days in seawater, versus 1.66 g/kg in 42 days in seawater and 1.71 g/kg in 49 days of seawater exposure for JAEA. The adsorption of the uranium and the corresponding kinetics were also studied in real seawater. To determine the reproducibility, the best adsorbent was selected and the three-batch process was carried out by repeating the same experimentation. From the kinetics plot (onsite ligand saturation model) Figure 5 was used to

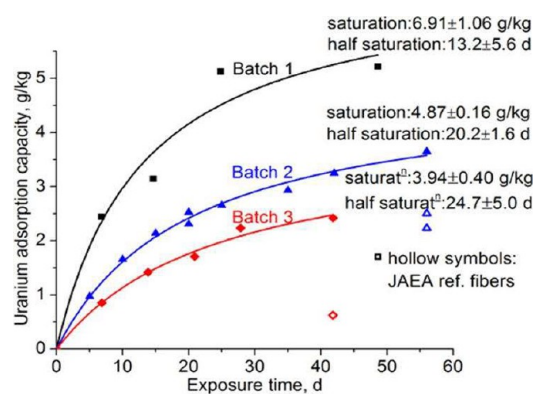


Figure 5. Kinetic plot of fiber with back-to-back three batches at Sequim Bay, WA, by applying one site ligand saturation model in comparison to JAEA reference fibers. Reproduced from ref 133. Copyright 2016 American Chemical Society.

determine the back-to-back kinetics of the fiber, and the uranium performance ranged from 3.94 ± 0.40 to 6.91 ± 1.06 g/kg, which is much higher than that of the fibers used by JAEA up to 2.50 g/kg after 56 days of exposure. The half-saturation time ranged from 13.2 ± 5.6 to 24.7 ± 5.0 days.¹³³ The flow-column field analysis shows the highest adsorption capacity of 6.56 mg/g within 56 days of contact time.¹³⁴ The investigation of NaOH treatment to adsorbent performed by Das and co-workers revealed the adsorbent treatment with KOH or NaOH showed similar adsorption capacities.¹³⁵

Recently in China (2022), efforts have been devoted toward the amidoxime nanofibers for effective uranium extraction. Huang and co-workers have prepared cyclic imide dioxime (CID) modified nanofibers from polyvinylidene fluoride (PVDF) NFs with the loading of acrylonitrile (AN) nanoparticles to obtain CID NFs.¹³⁶ The flexibility and strength of PVDF-NFs combine with the selectivity of CID toward the utilization of amidoxime groups for the uranium adsorption capacity. In addition, the thinner diameter fibers also expose more chelating sites and the mechanism of functionalization reduced the free holes and fabricated the CID in a three-dimensional array to trap uranium ions readily. The preparation process includes the two methods of radiation-induced graft polymerization (RIGP) and chemical-induced graft polymerization (CIGP). First, the NFs from PVDF were prepared by an electrospinning process, and next, grafting of 2-hydroxyethyl

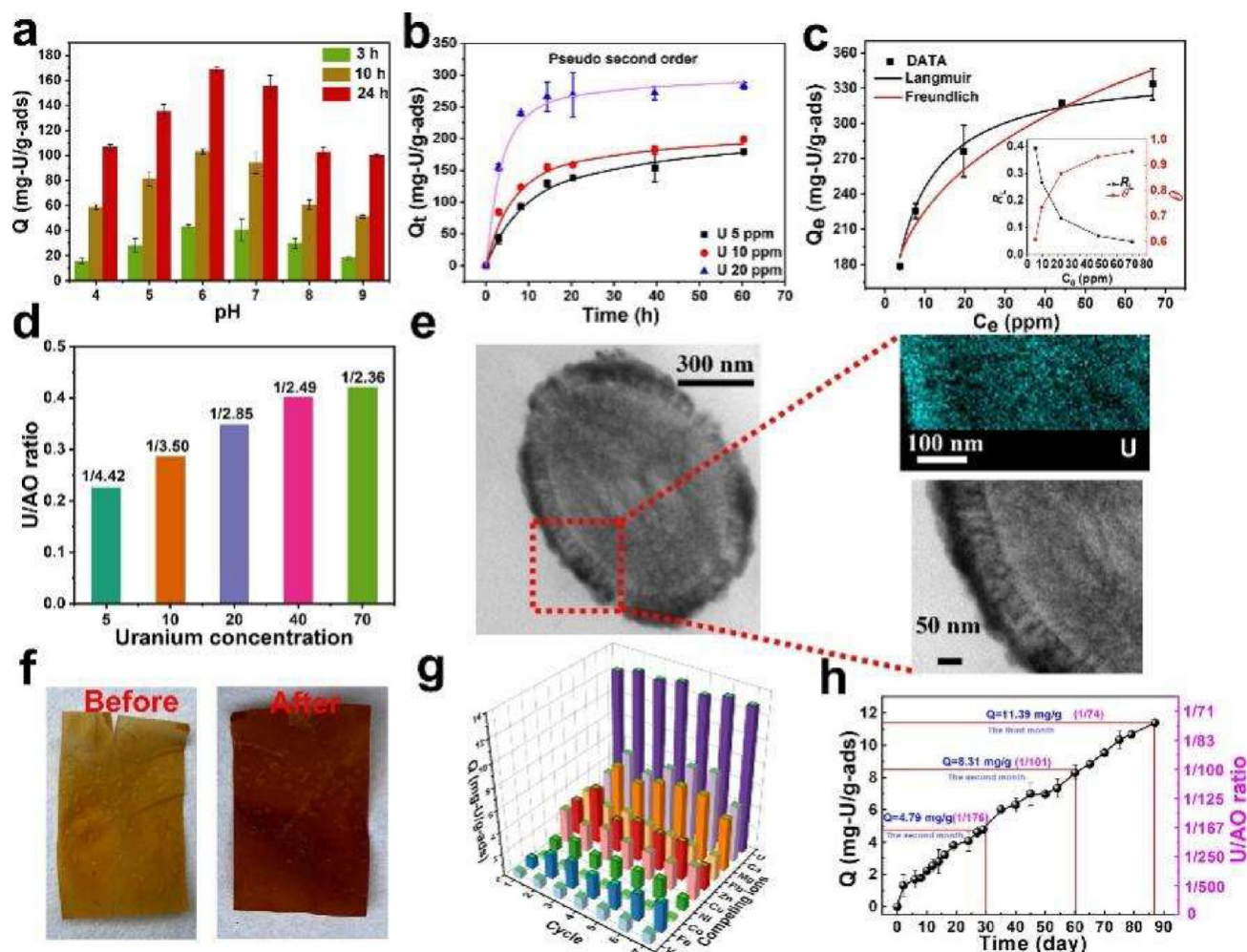


Figure 6. Uranium adsorption performance of CID NFs. (a) U adsorption capacity at various pHs, (b) adsorption kinetics at various concentrations (5, 10, 20 ppm), (c) adsorption isotherm model at various concentrations (Langmuir isotherm inset), (d) AO utilization ratio of CID NFs from U adsorption isotherm, (e) TEM images of CID NFs after adsorption of U, (f) color changes of CID NFs before and after uranium adsorption, (g) adsorption–desorption cycles of CID at a concentration of 330 ppb and existing ions, and (h) uranium adsorption of CID NFs in seawater at different contact times. Reproduced with permission from ref 136. Copyright 2022 Elsevier.

acrylate (HEA) was performed by RIGP. The CIGP method was used to axially grow AN nanoparticles, and finally, nitrile groups were converted into amidoxime groups by the amidoximation reaction. The adsorption capacity was performed by batch methods. The adsorption capacity after the exposure of 87 days was 11.39 mg of U/g of adsorbent, which is the highest uranium adsorption from seawater (Table 1).^{94,136} The reason for the higher adsorption capacity may be that the high amidoxime (AO) utilization resulted in a higher uranium adsorption capacity even with a low degree of grafting, resulting in the reduction of the cost for the preparation of adsorbent material. The optimum degree of grafting of 20% was selected for CID nanofibers.

The pH of the solution significantly influences the adsorption capacity due to a change in the proton binding ability of the CID nanofibers and the chelating activity of the uranyl species. The results in Figure 6 represent that the adsorption capacity increased with the increase in pH up to pH 6 and further increases in pH decreased the adsorption capacity. The optimal pH was 6, and the lower pH increased the H^+ and H_3O^+ which resulted in the repulsion between the uranyl species which is dominant at lower pH; therefore the adsorption capacity was reduced at lower pH. The adsorption kinetics was analyzed at

different concentrations, and with the increase in the uranium initial concentration from 5 to 20 ppm, the adsorption efficiency increased from 76 to 93% in a contact time of 14 h; furthermore, the adsorption time was extended from 14 to 60 h to achieve equilibrium with the uranium adsorption capacity at 177.77, 191.81, and 288.28 mg/g for the uranium initial concentrations of 5, 10, and 20 ppm, respectively. The adsorption mechanism was investigated by the use of adsorption isotherm models. The experiment results confirmed the adsorption data were best fitted with the Langmuir adsorption isotherm with $R^2 = 0.999$ and $q_{max} = 342.47$ mg/g. The TEM images in Figure 6 show the grafted PAN possesses a porous structure that improves the diffusion attributed to the higher adsorption capacity. The higher adsorption is visually observed with the color change in Figure 6; the color changed to brown after the uranium adsorption. The adsorption–desorption of the CID nanofibers was performed in the presence of the various competing ions. The results showed the CID nanofibers achieved an uranium adsorption capacity of 12.29 mg/g in the first cycle of the adsorption–desorption. The results also confirmed the least adsorption capacity drop with the seven cycles confirmed that CID nanofibers act as a potential adsorbent for uranium extraction (Figure 6).¹³⁶

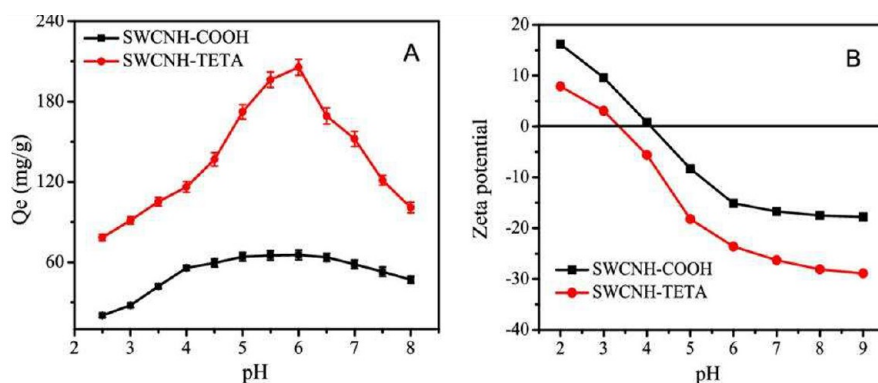


Figure 7. Influence of pH (A) and zeta potential at various pHs (B). Reproduced from ref 153. Copyright 2020 American Chemical Society.

4.3. Sulfide Composite. Since the 1950s, uranium extraction has been studied with a variety of materials such as ion exchangers and adsorbents including tannic acid, lead sulfide,^{141,143} zinc carbonate,¹³⁹ activated carbon, and oxides of titanium, iron, magnesium, and aluminum.^{139,140} Among all of these, titanium oxide and lead sulfide were considered promising adsorbent materials with higher adsorption capacities of 1.1 and 0.6 mg/g of adsorbent, respectively. Despite the higher adsorption capacity of lead sulfide, it was not easy to keep its surfaces fresh, which resulted in the loss of adsorption capacity.⁸⁰ Therefore, titanium oxide was selected as a promising adsorbent for uranium adsorption until the existence of amidoxime-modified adsorbents.^{7,80} Ion exchange resins for uranium adsorption from seawater include materials such as Zeo-Karb 226, 8-hydroxyquinoline, and resorcinol arsenic acid; however, such kinds of adsorbents show lower stability or degrade rapidly and or show low uranium adsorption performance.^{25,144,145}

In the syntheses of ion exchangers under controlled conditions, some of them posed higher thermal stability or radiation resistance. A few of these are zirconium phosphate gels and zeolites that were prepared and framed for atomic energy applications.¹⁴⁶ The adsorption of the metal ion by ion exchange is not easily clogged in comparison with the adsorption of metal ions by precipitation.¹⁴⁷ Uranyl is present in the form of uranium as a Lewis acid, and a strong attraction was reported between S^{2-} and the uranyl cation. Sulfide is considered as an efficient adsorbent for the adsorption of uranium by the reduction process and precipitation of U_3O_8 , and the narrow pH range (4–7) is also a limitation for the adsorption of uranium.¹⁴⁸ This work was carried out by Manos and co-workers to sort out the above-mentioned problems. They successfully prepared the three-dimensional layered sulfide $K_{2x}Mn_xSn_{3-x}S_6$ ($x = 0.5–0.95$) and proved it to be an adsorbent for the selective adsorption of uranium from natural seawater.^{149,150} Dithiocarbamate chelating resin as a promising ion exchange material exhibited an adsorption capacity for 1 day of 0.05 mg/g, and the overall adsorption capacity was 5.1 mg/g of adsorbent; it was further evaluated and developed to improve the adsorption performance of the adsorbent.¹⁴²

4.4. Carbon Nanomaterials. Carbon nanomaterials include carbon nanotubes or activated carbon and or carbon composites that have been used for the extraction of uranium. The existence of carbon materials has opened ways to adhere organic/inorganic functional groups onto the surface of carbon materials. At first carbon nanotubes were considered contaminants, as they are not dispersed easily.¹⁵¹ Carbon nanotubes are

hydrophobic and show poor dispersion in aqueous solutions due to their van der Waals interactions. The dispersibility of carbon materials was increased by grafting/functionalization of hetero groups which modulate their rapid dispersion in an aqueous medium.¹⁵² Carbon materials have been functionalized using concentrated HNO_3/H_2SO_4 for uranium adsorption. In this study, multiwalled carbon nanotubes were functionalized with COOH groups and subsequent grafting with triethylenetetramine (TETA). The results were analyzed using the contact time, pH influence, temperature, and uranium initial concentrations, and the uranium adsorption was analyzed using XPS analysis before and after the adsorption.

The pH values play a significant role in effecting the uranium adsorption; therefore, the pH influences were analyzed in the range 2.8–8 (Figure 7A).¹⁵³ Two adsorbents made with single-walled carbon nanohorns were selected (SWCNH–COOH and SWCNH–TETA) with similar tendencies for uranium adsorption in a neutral pH or weak basic medium; however, the uranium adsorption depends on the distribution of uranium species of the solution that depends on the pH of the solution. At pHs below 4.0, the dominant species was only UO_2^{2+} ions that compete with H_3O^+ , and accumulation of H_3O^+ in the solution weakens the electrostatic interaction between the uranyl and the adsorbent active sites. The adsorption capacity increased from 116.35 to 205.6 mg/g with the pH change from 4.0 to 6.0, and the maximum adsorptions of SWCNH–COOH and SWCNH–TETA were 65.5 and 205.6 mg/g, respectively. The higher adsorption with the pH increases the negative charge on the adsorbent surface and improves the electrostatic interaction mechanism. When the pH is higher than 6, the uranium gets hydrolyzed with the other species to form complexes causing electrostatic repulsion and the results show a decrease in the uranium adsorption. Besides, the adsorption capacity of SWCNH–TETA showed higher within the pH range 2.5–8. The higher adsorption could be accounted for by the presence of the amino group, which has a stronger electronegativity and coordination ability with U(VI). To better understand, the influence of the pH on uranium adsorption of SWCNH–COOH and SWCNH–TETA was analyzed by zeta potential by varying the pH as shown in Figure 7B. With the pH increase the zeta potentials of SWCNH–COOH and SWCNH–TETA were decreased and the corresponding values of the pH at zero charge were 4.05 and 3.32. At pH lower than the point of zero charge (pH_{PZC}) the surface of the adsorbent is positively charged and produces a repulsive force on the uranium.

The influence of time on the uranium adsorption of SWCNH–COOH and SWCNH–TETA is shown in Figure 8.

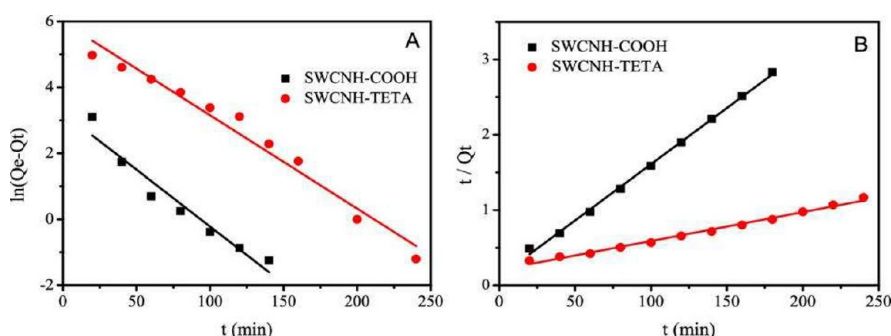


Figure 8. Uranium adsorption kinetics; pseudo-first-order kinetics (A) and pseudo-second-order kinetics (B). Reproduced from ref 153. Copyright 2020 American Chemical Society

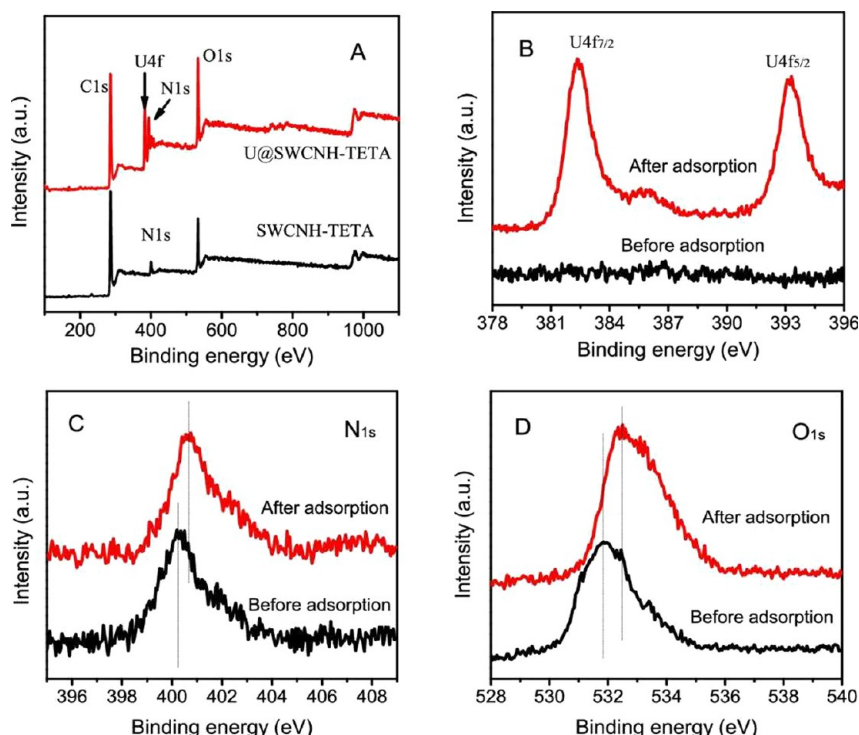


Figure 9. Uranium adsorption mechanism before and after adsorption. Wide scan survey (A) and high-resolution XPS spectra of U 4f (B), N 1s (C), and O 1s (D). Reproduced from ref 153. Copyright 2020 American Chemical Society.

Initially, the adsorption rate was quick due to the availability of a lot of vacant sites. Afterward, the vacant sites were occupied slowly by the uranium ions, which made the rate of adsorption gradually slow in comparison to the initial stage and the equilibrium after 60 and 240 min. The dynamics of the adsorption were analyzed using a kinetics equation, and the presentation is shown in Figure 8. The results from $\ln(Q_e - Q_t)$ versus t and t/Q_t versus t are shown for the two models. The results revealed the higher correlation coefficients of pseudo-second-order kinetics, $R^2 = 0.997$ and $R^2 = 0.990$, than those of pseudo-first-order kinetics. Moreover, the calculated adsorption capacities of SWCNH-COOH and SWCNH-TETA (71.43 and 333.33) were close to the experimental adsorption capacity values of 65.5 and 205.6 mg/g, confirming the better fit with the pseudo-second-order kinetics.¹⁵³

The stability depends on the cationic stability of carbon nanotubes, and the functionalization by $\text{HNO}_3/\text{H}_2\text{SO}_4$ was confirmed by using FTIR analysis which confirmed frequencies at 1212 and 1735 cm^{-1} , indicating the presence of carboxyl groups on the surface of the carbon nanotubes.^{25,154} Activated

carbon plays a vital role in uranium adsorption from aqueous solution due to its larger surface area,¹⁵⁵ and its chemical activation makes large-scale application costly.¹⁵⁶ To reduce the cost, agricultural wastes are used for the preparation of activated carbon¹⁵⁷ such as fruit peels, edible waste, and shells of nuts. Reportedly bioadsorbents play a major role in the adsorption.¹⁵⁸ For example, corncob is an agro-waste obtained from maize crop waste; about 16% corncob is present in maize plants.¹⁵⁹ Activated carbon was prepared from corncob using a chemical activation process, and is efficient for the adsorption of uranium and other metal ion.¹⁶⁰ Corncobs mainly consist of 40–45% silica by mass,¹⁶¹ and a silica-carbon nanocomposite from corncobs was reported by Dutta and co-workers for uranium extraction.¹⁶²

The uranium adsorption mechanism onto the carbon nanotube (SWCNH-TETA) before and after the uranium adsorption was analyzed by an XPS investigation (Figure 9). Wide scan XPS spectra are shown in Figure 9A with the visible peaks of U 4f, N 1s, and O 1s. The high-resolution XPS spectrum of U 4f shows two peaks at 382.3 and 393.2 eV assigned to U

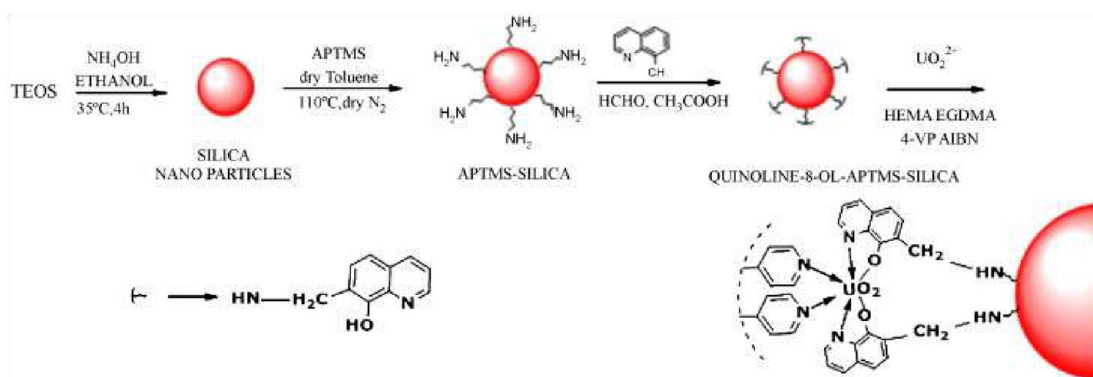


Figure 10. Systematic preparation of uranyl ion nanosurface imprinting method. Reproduced with permission from ref 163. Copyright 2011 Elsevier.

$4f_{7/2}$ and $U 4f_{5/2}$. The high-resolution spectra of N 1s and O 1s before and after uranium adsorption are shown in Figure 9C,D. The peak shifts from 400.2 to 400.7 eV in N 1s and from 531.9 to 532.5 eV in O 1s after uranium adsorption confirm the decreased electron density due to the coordination of valence electrons of N and O of SWCNH–TETA taking part in the coordination with the uranium.¹⁵³

4.5. Magnetic Fe_3O_4 Particles. The advent of nanotechnology boosts modern science in several industrial applications. Nanoparticles from different sources are interesting due to their larger surface areas and the adherence of functional groups on their surfaces to boost the adsorption performance of uranium extraction. Milja and co-workers have prepared 8-hydroxyquinoline functionalized 3-aminopropyltrimethoxysilane modified silica nanoparticles for uranium adsorption, and the synthetic process followed self-imprinting with a functional monomer of 4-VP (4-vinylpyridine) and HEMA (2-hydroxyethyl methacrylate) and cross-linking agent EGDMA (ethylene glycol dimethacrylate) with the use of initiator AIBN (2,2'-azo-bis-isobutyronitrile) and 2-methoxyethanol as the porogen (Figure 10).¹⁶³ However, such materials are economically less worthy due to poor separation or need further processing, and therefore, at an industrial scale, such techniques are economically costlier. Reducing the separation and regeneration cost of adsorbent, magnetic nanoparticles come into existence which can be ready as separate and considered an effective technique for recovering the nanomaterial from the aqueous media.¹⁶⁴ Tan and co-workers have developed oxime-functionalized surface-coated Fe_3O_4 nanoparticles for the adsorption of uranium with an adsorption capacity of 125 mg/g. The adsorption capacity by magnetic oxime nanoparticles¹⁶⁵ showed higher results in comparison to other adsorbents such as polymer-coated silica gel, oxime-grafted CMK-5, amine-coated silica gel, and amidoxime-modified $Fe_3O_4@SiO_2$.^{166–168}

4.6. Phosphate Rock Apatite. Recently, ore adsorbents have been used for the treatment of toxic metal pollution. Phosphate ore possesses several substances like calcium phosphate and impurities such as potassium, iron, and aluminum oxides, silica, organic matter, carbonates, and other clayey substances. Phosphate rock apatite is a calcium phosphate material with a percentage of P_2O_5 less than 15%. Most phosphate rock apatite was used for fertilizer production; however, the cost of phosphate rock apatite was high for fertilizers while phosphate rock apatite was used as a low-cost adsorbent for metal ion adsorption.¹⁶⁹ Phosphate rock is efficient for the adsorption of metal ions as well as an organic

pollutant, which revealed that phosphate ore can be used as a low-cost adsorbent.^{169–173} Over a wide range of circumstances, uranium phosphate possesses low solubility.¹⁷⁴ The low solubility of uranium phosphate proposed that hydroxyapatite was successfully used for the adsorption of uranium, forming uranyl phosphate followed by oxidation of uranium in ore deposits.¹⁷⁵ Uranium adsorption onto the phosphate surface was done after the amendments of phosphate present in the aqueous media. Large-level adsorption of uranium was carried out by synthetic hydroxyapatite, and the adsorption efficiency was evaluated under laboratory conditions.¹⁷⁶ Synthetic hydroxyapatite was replaced with a low-cost phosphate rock apatite with larger stabilization, and effective uranium adsorption was performed by Chen et al.¹⁷⁷

4.7. Mesoporous Molecular Sieve. Kresge et al. and Beck et al. have discovered molecular mesoporous sieve materials (M41S).^{178,179} In this family, the core structures are hexagonal stage MCM-41, cubic stages MCM-48 and MCM-48, or a nonstable lamellar stage.¹⁸⁰ MCM-41 stands for Mobil Composition of Matter No. 41, which shows a single-direction pore array with narrow pore distribution.¹⁸¹ The high surface area, large pore volume, and fast kinetics attracted researchers to use it as an adsorbent for the detoxification of radioactive elements. Stamberg et al. have investigated various parameters of uranium adsorption of MCM-41 from an aqueous solution including the influences of pH, contact time, initial concentration, and CO_3^{2-} .¹⁸² In subsequent studies, MCM-41 was modified with salicylaldehyde for the separation and detection of uranium in natural seawater.¹⁸³ Sert et al.¹¹⁵ have modified MCM-41 by grafting aminopropyl functionality on its surface to enhance the adsorption capacity of uranium. In all these studies the amino-functionalized MCM-41 showed the highest adsorption capacity of 625 mg/g (pH 4.2 and $T = 60^\circ C$).

4.8. Amino Functionalized Materials. Glycine is a simple amino acid consisting of an asymmetric carbon which can act as a zwitterion that carries both acidic and basic groups and work simultaneously existing in an ionized state. The zwitterion region ranges from pH 3 to 9, and out of this pH range glycine exists as an anion or cation.¹⁸⁴ The amino and carboxylic groups of glycine take part in uranium adsorption.¹⁸⁵ Tesfay Reda et al.¹⁸⁴ have prepared an amine-functionalized europium hydroxide composite to increase the kinetics and uranium adsorption capacity. The pH of the solution plays a vital role in uranium adsorption. With the increases in pH from 1.70 to 2.41 the adsorption of the uranium was higher (100%), and with the further increase up to pH 5.8 the adsorption performance was similar. With a further increase in pH >5.8, the adsorption

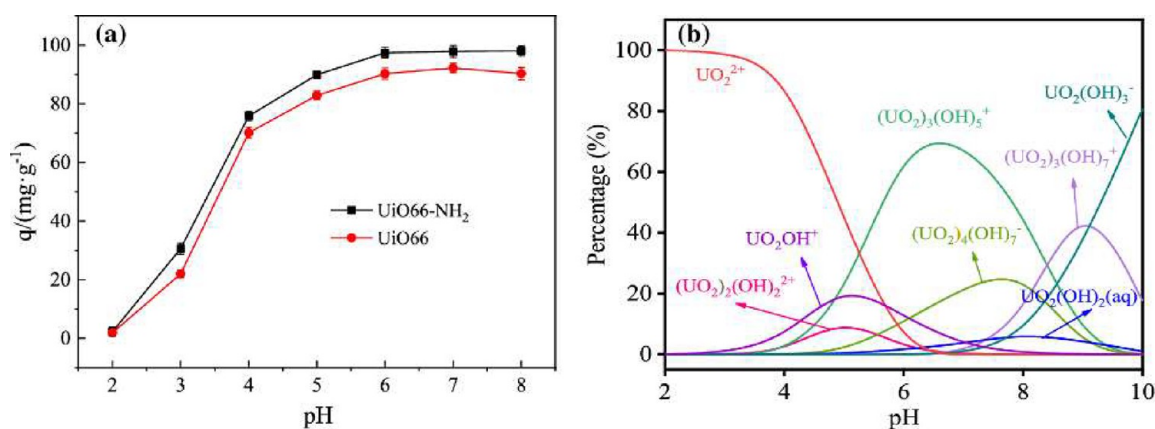


Figure 11. Influence of pH uranium adsorption (a) and relative proportion of uranium species at various pHs (b). Reproduced with permission from ref 193. Copyright 2021 Springer Nature.

efficiency was decreased by 99.58% at pH 6. Here two factors played a role in decreasing the adsorption: (i) protonation of amino groups in glycine which increases the competition between the uranium and H ions; (ii) at low pH the possibility of a small dissolution of the surface layer prevailing, resulting in limited exposure of active sites for the adsorption.¹⁸⁶ The role of the amino group in the adsorption of uranium is significant, while the carboxyl groups combine with the europium hydroxide.¹⁸⁷ This is because the glycine oxide forms a bond with Eu³⁺ to form a single layer to adsorb the uranium by dipole–dipole interaction of the amino groups and also the surface oxides.¹⁸⁸

4.8.1. Amino Functionalized MOFs. MOFs are special structures with a crystalline nature containing metal centers connected with organic bridging ligands that have received attention for various applications due to characteristics such as higher stability in harsh conditions and large surface areas.¹⁸⁹ Recently, MOFs have been widely used for the extraction of uranium from seawater and have shown tremendous performances at the laboratory scale. Among MOFs, Zr-based UiO-66 MOFs showed excellent stability in water due to the high affinity of oxygen for Zr⁴⁺ and the strong coordination of secondary building units.¹⁹⁰ However, UiO-66 MOFs are synthesized at high-pressure conditions which utilize a substantial amount of energy. To reduce the cost of the uranium adsorption from seawater, it is necessary to use UiO-66 MOFs. It has been found that the introduction of functional groups on the adsorbent would increase the adsorption capacity according to the requirement of the selectivity and size of the adsorbate.¹⁹¹ Several studies report the introduction of an amine group enhances the uranium adsorption capacity. Several amine-containing groups such as amino-modified hydroxyapatite showed a uranium adsorption capacity of 96 mg/g. In another study diaminomaleonitrile-functionalized double-shelled hollow MIL-101(Cr) showed a uranium adsorption capacity of 601 mg/g.¹⁹²

Li and co-workers¹⁹³ have successfully prepared MOFs and amine-functionalized MOFs (UiO-66 and UiO-66-NH₂) by a simple solvothermal method. The as-synthesized MOFs (UiO-66-NH₂) were used for uranium adsorption with an adsorption capacity of 384.6 mg/g at pH 6. A better understanding of the introduction of amine to improve the adsorption performance was given by FTIR and XPS analyses. The adsorption data followed pseudo-second-order kinetics, and the thermodynamic investigation proved the uranium adsorption on the amine-

modified MOFs was an endothermic and spontaneous adsorption process. Regarding the influence of the pH on the uranium adsorption of UiO-66 and UiO-66-NH₂, the pH of the solution not only affects the surface charge of the adsorbent and the proton change on the functional groups but also controls the uranium species present in a particular pH range. Therefore, the adsorption of uranium by MOF-based adsorbent is strongly dependent on the pH of the solution. The adsorption performances of UiO-66-NH₂ and UiO-66 indicated the introduction of amine groups onto the MOFs improves the uranium adsorption capacity. As can be seen from the results in Figure 11, as the pH increased from 2 to 6, the adsorption increased sharply (Figure 11a). At the lower pH the functional groups get protonated and the repulsive force between the positive functional group and UO₂²⁺ leads to a decrease of the uranium adsorption capacity. As the pH of the solution increased, the functional groups started to deprotonate, and the surface got negative changes, and the electrostatic interaction between the negative surface and the uranium species enhanced. In the pH range 2–8 the adsorption capacity remained unchanged with UiO-66-NH₂. When the pH exceeded 7, the uranium hydrolyzed and the uranium carbonate species existed, as shown in Figure 11b.

The adsorption mechanism of uranium onto UiO-66 and UiO-66-NH₂ was analyzed with XPS in Figure 12. The wide scan spectra before and after uranium adsorption show clear distant peaks for O 1s, N 1s, C 1s, Zr 3d, and U 4f. The peak shifts in the high resolution spectra (Figure 12b–f) after adsorption represent the coordination between the functional group and the uranium due to decreases in the electron density of the functional group. Notably, the bridge O atoms in Zr–O–Zr most likely attach to the uranium through the covalent bond resulting in the binding energy of the O. On the basis of that analysis, Figure 13 represents the proposed uranium adsorption mechanism onto UiO-66-NH₂.¹⁹³

4.8.2. Amino Functionalized Carbon Materials. Adsorption attracts attention due to its low cost, easy operation, and high efficiency in adsorbing uranium from seawater. Selecting the adsorbent materials for uranium adsorption is a key parameter in controlling the cost of uranium adsorption.¹⁹⁴ High surface area, porous structure, and chemical stability played a crucial role in the selection of mesoporous carbon (MC) as a novel adsorbent material.¹⁹⁵ The introduction of functional groups in MC results in a new adsorbent with higher uranium performance.¹⁹⁶ As a nucleophile, the amino group (NH₂) gets protonated and

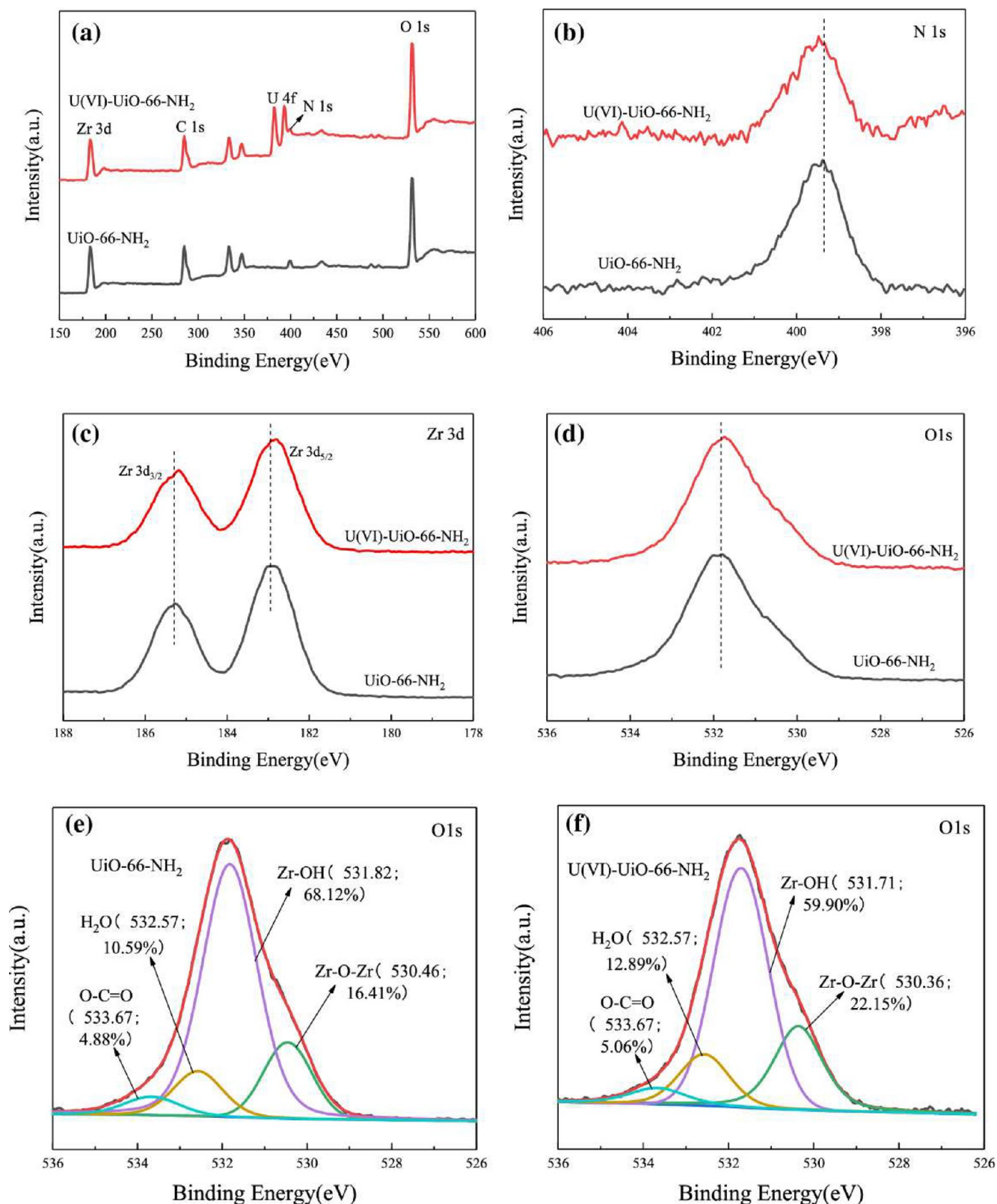


Figure 12. XPS spectra of UiO-66 and UiO-66-NH₂ before and after uranium adsorption; (a) wide scan XPS spectra and high-resolution XPS spectra of (b) N 1s, (c) Zr 3d, and O 1s (d–f). Reproduced with permission from ref 193. Copyright 2021 Springer Nature.

selectively adsorbs the uranium species in a higher pH medium and also improves the dispersibility of materials in aqueous solution.^{197,198} Existing compounds such as chitosan, amino-functionalized graphite, and silica showed efficient uranium

adsorption.¹⁹⁹ Amino-functionalized silica showed a 118 mg/g uranium adsorption capacity.²⁰⁰ A quick strategy for the amino preparation is the reduction of nitrogen, which is a simple way to introduce an amine group in carbon materials such as carbon

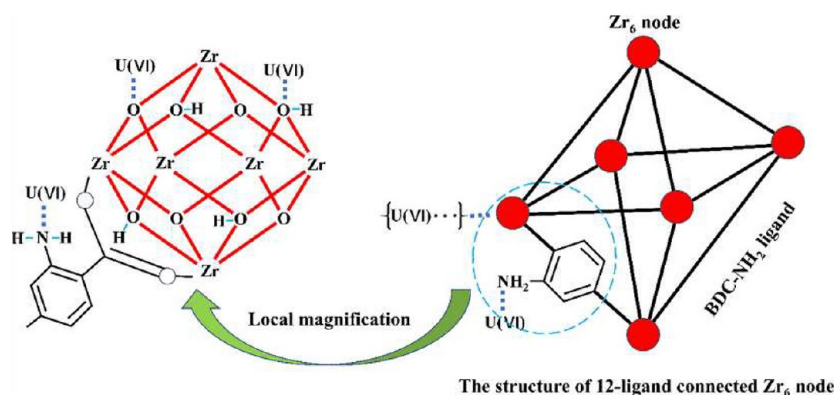


Figure 13. Proposed uranium adsorption mechanism onto Zr-based MOFs. Reproduced with permission from ref 193. Copyright 2021 Springer Nature.

nanotubes and activated carbon.²⁰¹ The process involves nitration and reduction steps, but before the functionalization, the tough step is the template removal using concentrated acids which might destroy the porous structure of the MC. Recently, Wang and co-workers²⁰² introduced the amino group in MC without template-removing methods for the adsorption of uranium from seawater. Characterization was employed to check the adsorbent functionalization, and various studies were performed to analyze the uranium adsorption performance. The two materials before and after amine functionalization (MC and MC-NH₂) were designed for various batch methods such as the influence of the pH, adsorbent dosage, initial concentration, and temperature. The pH of the solution plays a vital role in designing the uranium adsorption of MC and MC-NH₂. The pH not only influences the activity of MC-NH₂ but also influences the speciation of the uranium. The solution was organized using dilute NaOH and HNO₃ to raise or lower the pH of the solution. From the results, it was observed that with the increase in the pH the adsorption capacity of MC-NH₂ reaches the uranium adsorption capacity of 219 mg/g of MC-NH₂, which is 2.1 times higher than that of the unmodified MC (91 mg/g) and indicating the introduction of amine groups improves the uranium adsorption of MC (MC-NH₂). The selectivity of the adsorbent is another significant parameter. The selectivity of MC-NH₂ in the presence of other competing ions (Mg²⁺, Zn²⁺, Mn²⁺, Cu²⁺, Ni²⁺, Sr²⁺, and Hg²⁺) was analyzed, and the results in Figure 14 show higher uranium adsorption and that other metal ion adsorption was negligible.²⁰²

4.9. Dendrimers. Dendrimers are long-chain polymer-type materials with narrow molecular weight distributions, high degrees of uniformity of the functional groups, loosely packed internal pockets, and highly functional terminals. Hence dendrimers play a role in various applications such as catalysis, photonics, biomedicine, and metal chelators.^{203,204} Large efforts are made toward dendrimers, and attention is paid to their coordination behavior in aqueous solution.²⁰⁵ Particularly poly(amine dioxime) has a huge number of heteroatoms such as oxygen and nitrogen of amide and amine groups on the chains of dendrimers which show strong chelation.²⁰⁶ It was reported that poly(amine dioxime) was commonly used for uranium adsorption by the ultrafiltration method from aqueous media.^{207,208} However, the operation of ultrafiltration was restricted due to its high cost, high pressure, and membrane fouling and to the preparation of symmetrical poly(amine dioxime) and its purification. Polymer chelating resin was prepared from styrene–divinylbenzene modified with poly-

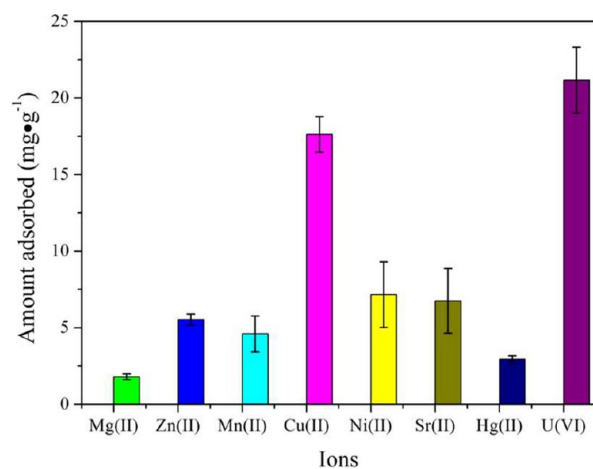


Figure 14. Influence of competing ions on uranium adsorption of NH₂-MC. Reproduced with permission from ref 202. Copyright 2021 Springer Nature.

(amine dioxime) dendrimers as a chelating functionality for enhancing the uranium adsorption on the surface of divinylbenzene-modified poly(amine dioxime) dendrimers. The results from various studies such as the influences of pH, concentration, dose amount, and the regeneration of the dendrimers demonstrate the high adsorption capacity was 130.5 mg/g with 99% desorption under acidic conditions.²⁰⁹

4.10. Biopolymers. Biopolymers are polymers obtained from biobased materials, and they are readily biodegradable and nontoxic materials. Cellulose-based materials anchored with amine groups were used for the adsorption of uranium from phosphate ore. The prepared material was tested with two solutions: one was synthetic and the other was a phosphate ore solution. The synthetic solution (35% P₂O₅ and 100 ppm uranium) was used for the loading of the uranium. The second solution was the phosphate ore solution (35% P₂O₅ and 100 ppm uranium) used in the case study for the adsorption. The overall adsorption capacity of amine-impregnated cellulose was found to be 56.5 mg/g.²¹⁰ Anirudhan et al.²¹¹ have prepared a lignocellulosic material based cationic exchange resin for the adsorption of uranium. A cation exchanger (PGTFS-COOH) was developed with –COOH groups at the end of the chains by graft polymerization of hydroxyethyl methacrylate on tamarind fruit shell (lignocellulosic material) in the presence of *N,N'*-methylenebis(acrylamide) as a cross-linking reagent followed by functionalization of –COOH groups used for the adsorption of

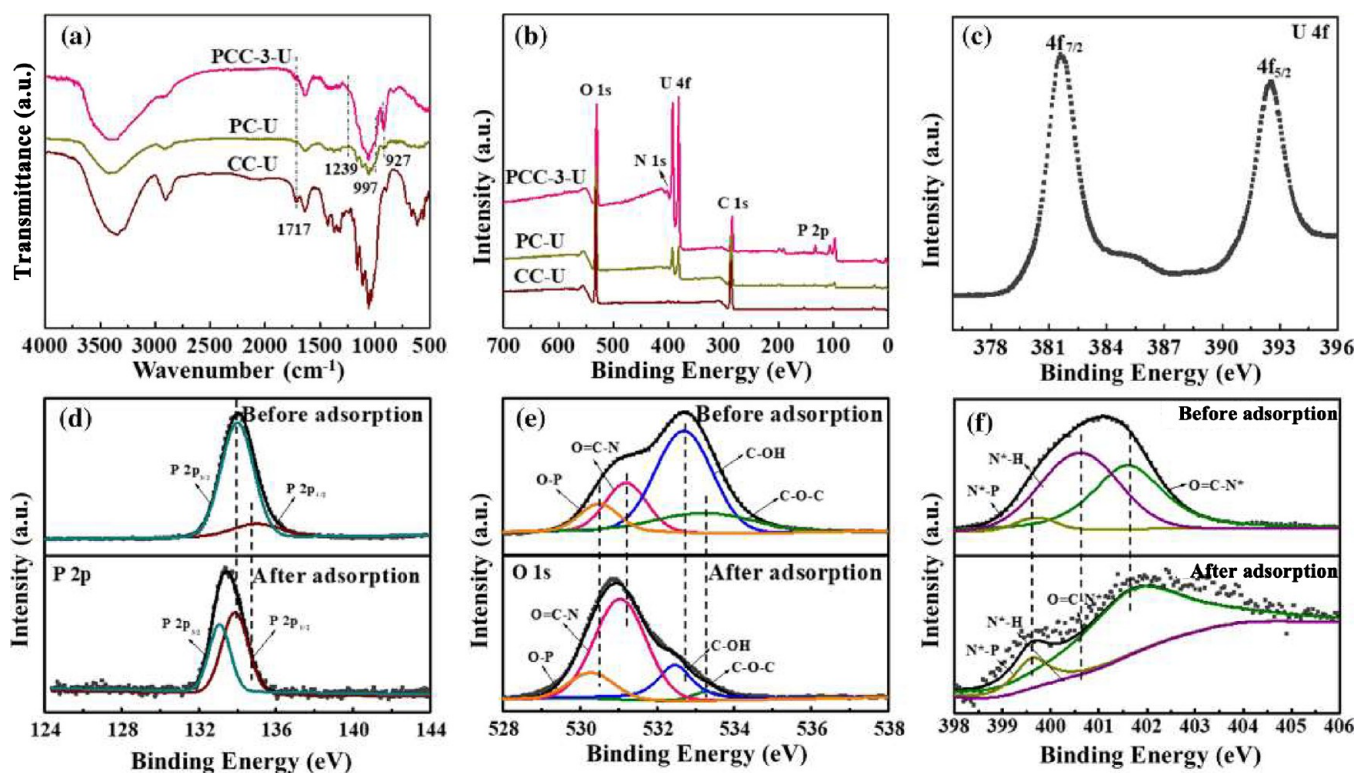


Figure 15. FTIR and XPS spectra before and after uranium adsorption. Reproduced with permission from ref 228. Copyright 2023 Springer Nature.

uranium. The optimum pH of 6 was used for analyzing the kinetic and equilibrium data, which followed pseudo-second-order kinetics and the Sips model, respectively.²¹¹

Chitosan is a natural biopolymer with glucosamine-repeating units present in its polymer backbone. It has been deployed as one of the potential materials for the adsorption of uranium from seawater.^{212,213} The lesser solubility of chitosan in acid solution and its poor performance in mechanical properties make it of limited use for treatment under acidic conditions.²¹⁴ Different approaches have been applied to improve the characteristics and properties of chitosan to increase the maximum adsorption capacity,²¹⁵ and such approaches include chemical modification or composite formation. A typical composite was successfully prepared by adding a phosphate rock to the chitosan matrix to enhance uranium adsorption under a set of experimental conditions (pH 2.5 and contact time 5 h).¹⁹⁹ The addition of phosphorus to the chitosan surface was carried out to adhere to the functionality of the surface of the chitosan, which in turn enhances the uranium adsorption performance of the adsorbent material. Westerback et al. have reported that phosphorus-containing agents are more complex reagents than the COOH groups.²¹⁶ The well-known alkaline phosphonic ligands ($-\text{NH}_2-\text{CH}_2-\text{PO}_2^{3-}$) have enough capability for the chelation of metal ions by amino donation and the monodentate ligand present, PO_2^{3-} .²¹⁷ P-Chitosan showed an adsorption capacity of 54.6 mg/g by two ligand donations for uranium adsorption.²¹⁸ Recently Pu et al.²¹⁹ used biomass-based aerogel (Fk-AO) prepared from feather keratin (Fk) for sustainable extraction of uranium from seawater with a high adsorption capacity of 990.10 mg/g due to a high surface area. In addition, Fk-AO adsorbent is prepared on a large scale and could be used for practical application in large amounts of seawater. The preparation of the biomass-based aerogel involves a direct reaction of the Fk with the acrylonitrile for the grafting of

cyanide groups, and next the cyanide groups are converted into amidoxime groups. This preparation method not only prepares the material for uranium extraction adsorbent but also decreases the garbage impact of feathers in the environment. More interesting, Fk-AO represents a higher selectivity ion presence of the other interfering ions and the salinity is 35 g/L.²¹⁹

With the advancement in technology, extensive studies on amidoxime-based adsorbents concluded the amidoximation process involves hydroxylamine hydrochloride and postalkali treatment makes the overall process difficult. Recently, phosphate-based polymers gained interest in uranium extraction due to low toxicity and environmental friendliness. In natural uranium ore deposits, it has been observed that uranium is available in the form of phosphate complexes, and therefore the available phosphate monomers could be considered as new ligands for the complexation of uranium selectively from seawater. Al-Sheikhly et al. have reported bis(2-methacryloxyethyl) phosphonate (B2MEP) as a potential ligand for the extraction of uranium from seawater.²²⁰ Different preparation techniques such as chemical grafting, UV-mediated grafting, radiation-induced graft polymerization (RIGP), and free radical copolymerization have been used for the preparation of phosphate-possessing polymers. Among all of these RIGP has been considered the effective preparation technique for the development of uranium adsorbent.^{62,221} Phosphorated cellulose has been considered a potential adsorbent for uranium extraction due to its low cost, its biodegradability, its high abundance, and the renewable features of cellulose.²²² Cai et al. reported phosphate-decorated carboxymethyl cellulose for the extraction of uranium, and the highest adsorption of uranium was due to the inner-sphere surface complexation between the phosphate and uranium ions.²²³ It was confirmed that the presence of the phosphate group is not only responsible for the higher affinity to uranium, but also the higher surface area and

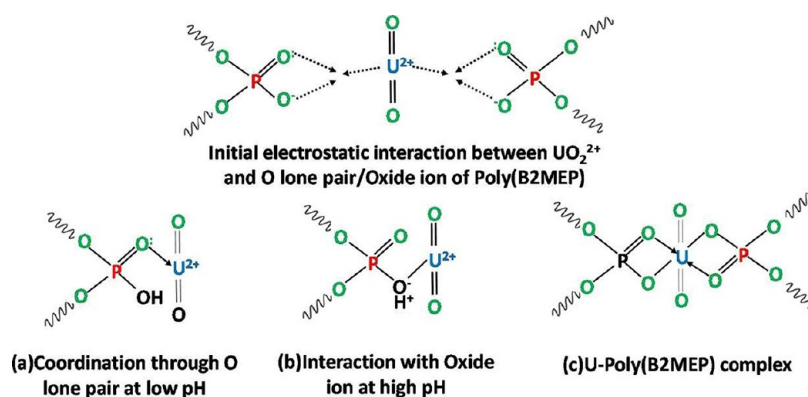


Figure 16. Graphic representation of adsorption mechanism between uranium and poly(B2MEP)-g-cellulose adsorbent, CellUSorb. Reproduced with permission from ref 62. Copyright 2023 Elsevier.

anionic charge facilitate the uranium extraction. Overall, phosphorylation is mainly endorsed by the substitution of the hydroxyls of the side chains of the cellulose.^{224–227} Recent studies reported the higher phosphorylation of the amino sites than of the hydroxyls; however, the phosphorylation on the amino sites has not been used for uranium extraction until now.

Zhang et al.²²⁸ developed phosphorylated cellulose carbamate by reaction of H_3PO_4 /urea/DMF for efficient uranium extraction. It was found that the urea takes part in the reaction and converts cellulose into cellulose carbamate and that the amount of urea has a significant effect on the degree of phosphorylation. The cellulose-based phosphate functionalized adsorbent showed good adsorption performance with an adsorption capacity of 1006.9 mg/g under the optimal pH 5 at a temperature of 298 K. The adsorption equilibrium was achieved in 100 min under the experimental conditions ($m/V = 0.1$ g/L and $C_0 = 100$ mg/L) with better selectivity and regeneration capability than other cellulose-based adsorbents reported. The adsorption mechanism study was confirmed by XPS and FTIR analyses. In FTIR various cellulose-based phosphate functionalized derivatives have been analyzed, and the results in Figure 15 show the PCC-U derivative shows a peak at 927 cm^{-1} which corresponds to $\text{O}=\text{U}=\text{O}$; that such a peak is not seen in CC-U confirmed the lesser contribution of the amino groups toward uranium. In addition, the peak at 930 cm^{-1} shifts to 997 cm^{-1} , suggesting the involvement of the phosphonate group in the chelation of uranium ions. In the case of PCC-3-U, the peak is greater than that for PC-U, and the peak shift of $\text{P}-\text{O}$; the decreased intensity of $\text{C}=\text{O}$ and $\text{P}=\text{O}$ confirmed that after phosphorylation of cellulose both $\text{C}=\text{O}$ and $\text{P}=\text{O}$ are involved in the chemical coordination with uranium. The results of the adsorption mechanism were further supported by the XPS analysis with additional peaks at 381.6 and 392.5 eV corresponding to $\text{U } 4f_{7/2}$ and $\text{U } 4f_{5/2}$. The high-resolution XPS spectra of CC-U, PC-U, and PCC-3-U further show the detailed mechanism. The XPS spectra of P 2p before uranium adsorption showed two deconvolution peaks at 133.5 and 132.7 eV corresponding to $\text{P } 2p_{1/2}$ and $\text{P } 2p_{3/2}$; after uranium adsorption peak shifts to 135.0 and 134.0 eV confirmed the contribution of the phosphate group in uranium adsorption. The high resolution N 1s spectra of PCC-3 and PCC-3-U were split into three peaks for N^*-P , N^*-H , and $\text{O}=\text{C}-\text{N}^*$ without any remarkable changes before or after uranium adsorption. The O 1s spectra before adsorption showed peaks at 530.5, 531.2, and 532.7 eV corresponding to $\text{C}=\text{O}$, $\text{P}=\text{O}$, and $\text{P}-\text{O}$, and after uranium adsorption the peaks shifted to 530.3, 531.0, and

532.4 eV, confirming the involvement of the oxygen-containing functional group of cellulose carbamate in uranium adsorption.²²⁸

Recently Misra et al. developed a cellulose-based phosphate-containing adsorbent originally obtained by modification of B2MEP onto the cellulose backbone (poly(B2MEP)-g-cellulose adsorbent; CellUSorb) by RIGP for cost-effective extraction of uranium. Uranium in an aqueous solution existing as UO_2^{2+} showed a tendency to form complexes with hard ligands. The uranium adsorption mechanism of CellUSorb is based on the coordination between phosphate functional groups of uranium ions as well as electrostatic interactions at certain pH ranges. The presence of $\text{O}=\text{P}-\text{OH}$ in B2MEP is oriented to facilitate the ring structure containing a metal ion in the center of the complex. A graphic representation of the possible adsorption mechanism between the active functional groups of B2MEP UO_2^{2+} is shown in Figure 16.⁶²

5. CURRENT CHALLENGES AND FUTURE DIRECTION OF URANIUM CAPTURE

The low uranium concentration ($3.3\text{ }\mu\text{g/L}$) requires extremely large amounts of seawater, i.e., 3000 L of seawater, to achieve an adsorption capacity of 3 mg/g of adsorbent when the adsorption efficacy of the adsorbent is 100%, which is not possible to date. To address these challenges, efforts are made to prepare an adsorbent material with a higher adsorption performance at a lower adsorbent amount. The addition of uranium in the spiked solution makes it easy to detect uranium in active sites of the adsorbent which is not the actual concentration of seawater. Simulated seawater could be used as a substitute to analyze the reproducibility of the adsorbent for uranium extraction; however, at low concentrations, the same problems will be encountered in the seawater. There are other challenges such as the pH, organic content, competing ions, and biofouling.³¹ “Biofouling” means the accumulation of microorganisms on the adsorbent surface, and it is another big challenge faced by adsorbent materials used in practical fields.^{229,230}

Biofouling of the adsorbent surface occurs in four stages: the first stage is the accumulation of organisms in the form of a thin film starting quickly after the immersion of the adsorbent in the seawater. The second stage starts after the settling and formation of bacterial colonization, and other diatoms form a microbial layer that constitutes the third stage. The fourth stage starts after the beginning of the growth of the microorganism on the adsorbent surface. Recently, various studies have been carried out to stop biofouling using antimicrobial agents anchored in

nanotexture adsorbent materials.^{29,49,231} However, the design of the nanotexture adsorbents is advantageous for the promotion of the biofouling of the adsorbent surface. The development of a macroporous texture adsorbent with antibacterial functional groups would help to stop the biofouling of the adsorbent surface in practical application.

In conclusion, the research on uranium adsorption from seawater has developed with the recent advancements in the methods and technology. However, additional breakthroughs are essential to overcome the recent challenges and the affinity of the adsorbents toward the other precious metal ions at the same platform. In practice, the uranium adsorption capacity and selectivity of the adsorbent could be presented with the highest K_d value which could be achieved by improving the physicochemical characteristics such as surface area, pore size, pore volume, functional group density, and the alignment of the functional groups. The functional group alignment and the density of the designed adsorbent before the preparation could be checked by theoretical calculations, and the simulated results will save time to provide the efficacy of the adsorbent. Improving the uranium adsorption rate, the optimum contact between the adsorbent and the uranium could be analyzed theoretically. The effective and nondestructive regeneration process of the adsorbent could reduce the cost of uranium adsorption. Evaluation and optimization of used reagents and other functionalized materials could be checked along the way to find sustainability and environmental friendliness. All of these research directions could be carried out with proper adsorption techniques combined with the latest advancements in preparation and application.

6. CONCLUSION

Uranium as a carbon-free energy source has attracted attention toward uranium extraction from seawater. Several adsorbents based on graft polymers, functionalized nanostructures, and biomass-based adsorbents have been used for uranium extraction. Among all of these adsorbents, amidoxime grafted polymer-based adsorbents showed promising results and were extensively used for uranium capture from seawater (Table 1). These materials have a strong affinity toward uranium ions, better stability, and rigid porous structures, and their high mechanical strength offers considerable advantages. This review article includes the various aspects of uranium adsorbents, including the preparation and characterization of adsorbents, influencing parameters, and applicable technology for practical application. In short, the selection of the adsorbent depends on the performance of the adsorbent, and the key to improving the adsorption performance depends on recognition of high dispersion of adsorbent and exposure of chelating sites as much as possible. In addition, the development of new adsorbents would be demand-oriented and need to meet the requirements. It is important to use advanced techniques and theoretical analysis to study the binding mechanism between the chelating sites and the uranyl ions to analyze the relationship between the material and structural properties, which helps in designing a new generation of adsorbents. Therefore, this paper helps to design new adsorbents and acts as a guide to face every challenge related to uranium adsorbents and solve the problems in the field testing of uranium extraction from seawater.

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Notes

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