# Cellulose-Derived Nanomaterials for Affordable and Rapid Remediation of Uranium in Water

Tanmayaa Nayak, Sritama Mukherjee, Amoghavarsha Ramachandra Kini, Md Rabiul Islam, Ankit Nagar, Sonali Seth, and Thalappil Pradeep\*



necessitating ellective methods for its removal from water, although its chemical toxicity is more significant. Adsorption using advanced materials is emerging as an affordable and sustainable approach for the removal of soluble uranium, principally in the form of  $UO_2^{2+}$ , a major concern in several water sources in India and other parts of the world. This study is a comparative investigation of the adsorption capabilities of two phosphorylated cellulose-reinforced iron oxyhydroxide composites, namely, nano- and microstructures and their potential use in removing  $UO_2^{2+}$  from water. Results indicate that cellulose nanostructures exhibit superior efficiency compared to the



corresponding microstructures for  $UO_2^{2+}$  adsorption, with equilibrium achieved within 2 min of exposure. Green synthesis of the composite produces particulate media with excellent structural integrity. Furthermore, it exhibits rapid adsorption dynamics despite the presence of competing ions in water. It also exhibits high uranium extraction efficiency over a broad pH range and exhibits outstanding regeneration performance. Various analytical techniques, including XRD, SEM, HRTEM, XPS, TGA, and FT-IR, were employed to investigate the structure of the composites and their interactions with uranium. We find that  $UO_2^{2+}$  binds through oxygen and phosphorus functional groups of the material. We evaluated various sustainability metrics to assess the ecological impact of the composite and its synthesis process. We demonstrate the potential of the developed adsorbent as a highly efficient and sustainable method for uranium removal from water.

**KEYWORDS:** cellulose nanocrystal, cellulose microcrystalline, uranium, adsorption, sustainability metrics, water treatment, Langmuir isotherm

# INTRODUCTION

Downloaded via INDIAN INST OF TECH MADRAS on January 24, 2025 at 08:36:59 (UTC). See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles

Uranium (U), a dense, silvery actinide, is chemically and radiologically toxic, with chemical toxicity posing a greater health risk.<sup>1,2</sup> Naturally occurring uranium, present in the earth's crust (3 ppm) and seawater (3 ppb), consists of three isotopes: <sup>238</sup>U (99.274%), <sup>235</sup>U (0.7%), and <sup>234</sup>U (0.0055%).<sup>3,4</sup> It exhibits multiple oxidation states ranging from 2+ to 6+, but it predominantly occurs in its hexavalent (uranyl) and tetravalent (uranous) forms in nature, with the hexavalent form occurring predominantly as the uranyl ion  $(UO_2^{2+})$ .<sup>5</sup> Uranium has been mobilized into groundwater due to anthropogenic activities like nuclear power, mining, and fertilizers as well as natural processes like weathering and volcanic eruptions.<sup>6</sup> Its solubility in groundwater is influenced by pH, conductivity, redox potential, temperature, and the presence of specific ions such as carbonates, nitrates, and sulfates, with acidic, oxidizing conditions enhancing dissolution.<sup>7-10</sup> Many complexes of uranium exist at a specific pH of the solution. For example, at a pH range of 5-7, cationic

species such as  $(UO_2)_3(OH)^{5+}$  and  $UO_2OH^+$  as well as anionic species like  $UO_2(CO_3)^{4-}$  and  $(UO_2)_2CO_3(OH)^{3-}$  are present.<sup>11</sup>

Uranium can accumulate in organs, increasing the risk of cancer, blood disorders, kidney damage and affecting the neurological, reproductive, and circulatory systems.<sup>12–14</sup> According to a survey conducted by the Ministry of Jal Shakti of India in 2020, 151 districts in 18 states of India are partly affected by high concentrations (>30 ppb, which is the WHO threshold limit for uranium in drinking water) of uranium in groundwater, highlighting the critical need for efficient and cost-effective removal methods.<sup>15</sup> Chemical methods for

Received:	December 7, 2024
Revised:	January 13, 2025
Accepted:	January 14, 2025



Α

Scheme 1. Schematic Diagram of the Application of Phosphorylated Cellulose-Ferrihydrite Composite Material for Cost-Effective Removal of Uranium from Water



uranium extraction frequently implemented include ion exchange, membrane processes, precipitation, solvent extraction, adsorption, and electrochemical/photochemical techniques.<sup>16-23</sup> Among these, adsorption is the most favorable in terms of design, cost and operational flexibility, effectiveness, and efficiency.<sup>24</sup> Many adsorbents such as zeolites, biosorbents, activated carbon, carbon nanotubes, clays, metal oxides, and metal-organic frameworks (MOFs) have been reported for uranium extraction from water.  $^{25-33}$  However, carbon-based adsorbents and MOFs exhibit insufficient adsorption capacity and selectivity for uranium, while their complex synthesis, high cost, and potential ecotoxicity hinder practical water treatment applications. The development of sustainable and efficient adsorbent materials plays a vital role in addressing environmental and resource challenges. Recent advancements, such as the utilization of molten pyrolysis to synthesize high-value carbon materials from abundant sources, as reported by Zhang et al., exemplify innovative approaches that combine environmental compatibility with high performance.<sup>34</sup> Wang et al. synthesized titanium-doped zirconium-based MOFs for uranium extraction, exhibiting high sorption capacity across a broad pH range but showing reduced efficiency in the presence of competing anions such as  $CO_3^{2-}$  and  $PO_4^{3-,35}$  On the other hand, nanoscale metal oxides, like Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, MgO, Fe<sub>2</sub>O<sub>3</sub>, and ZrO<sub>21</sub> are effective adsorbents for heavy metals due to their high surface area, porosity, and stability across various pH conditions and high ionic concentrations, making them ideal for water treatment applications.<sup>36</sup> Among these, iron oxides, including forms like magnetite (Fe<sub>3</sub>O<sub>4</sub>), hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), iron oxyhydroxide (FeOOH), and metallic zerovalent iron are widely used for their low cost, easy synthesis, and efficacy in removing metals such as As, Cd, Hg, and Sb across various oxidation states.<sup>37-39</sup>

Compared with other adsorption processes, biosorption offers several advantages, including cost-effectiveness, high efficiency, reusability, and potential for metal recovery.

Chitosan, a biopolymer with hydroxyl and amine groups that exhibit a strong affinity for uranium ions, has been used for uranium adsorption.<sup>40</sup> But we cannot ignore that chitosan is environmentally less stable and expensive due to its origin from crustacean exoskeletons and degrades at 254.6 °C. In this context, cellulose, a naturally occurring polysaccharide found in plant cell walls, is more thermally stable, with degradation beginning at 312.9 °C, making it suitable for harsh conditions.41 Microcrystalline cellulose (MCC) and cellulose nanocrystals (CNCs) have been explored for pollutant removal, including uranium, with differing adsorption capabilities due to their structural properties.<sup>42,43</sup> MCC, derived via acid hydrolysis, has a crystalline structure with particle sizes of 2–50  $\mu$ m in diameter and 100–1000  $\mu$ m in length. CNCs, on the other hand, obtained through acid hydrolysis and homogenization, are smaller, with particle sizes of 5-20 nm in diameter and 100-500 nm in length, offering higher surface area and crystallinity. The phosphorus-, oxygen-, and nitrogenbased additional functional groups act as chelating agents, enhancing the binding of uranyl species. In a study, researchers synthesized phosphorylated cellulose nanofibers to improve uranium adsorption capacity.<sup>44</sup> Phosphorylated carboxy methyl cellulose and chitosan composites have also been studied for the same.<sup>45</sup> Although both the composites are showing high uptake capacity, their adsorption efficiency decreases after certain pH. To the best of our knowledge, there are no reports on the removal of U(VI) using iron oxyhydroxide-incorporated phosphorylated cellulose. This low-cost material notably overcomes the limitations of most of the previously reported adsorbents such as slow kinetics, reduced adsorption efficiency in the presence of coexisting ions, and performance across a wide pH range, making it suitable for industrial applications.

Incorporating sustainability into the synthesis of adsorbents for contaminant removal from water ensures environmental protection, cost-effectiveness, safety, and regulatory compliance and promotes resource efficiency and longevity. Here, in

**Research Article** 



Figure 1. Schematic diagrams illustrating the synthetic procedures and molecular structures of CNC/MCC and synthesized phosphorylated cellulose. Photographs of PCNC and PCNCFH are also shown. PMCC and PMCCFH are also similar to PCNC and PCNCFH, respectively, in terms of physical appearance.



Figure 2. (a) FTIR spectra of blank CNC and PCNC. (b) FTIR spectra of PCNCFH and U–PCNCFH. (c) HRTEM image: (i) PCNCFH and (ii,iii) beam-induced crystallization of PCNCFH and (iv) U–PCNCFH.

this study, we successfully synthesized phosphorylated cellulose-iron oxyhydroxide materials for uranium removal from water with a comprehensive evaluation of relevant sustainability metrics. The cellulose precursors were function-alized with phosphorus groups to enhance adsorption efficiency as uranium, a "hard" Lewis acid, preferentially forms stable complexes with "hard" Lewis bases such as phosphate, carboxyl, and amino ligands.<sup>45,46</sup> Incorporation of iron oxyhydroxide produced novel and structurally robust nanocomposites, addressing the stability and recovery limitations of phosphorylated cellulose, which exhibited a

partial water solubility. Additionally, we compared the uranium uptake performance of phosphorylated cellulose-incorporated iron oxyhydroxide nanocomposites by taking two different cellulose precursors MCC and CNC (Scheme 1). Although previous research indicated that MCC-based composites performed better than CNC-based composites for arsenic removal, our findings showed a different trend for uranium removal. Specifically, the CNC-based nanocomposite exhibited superior adsorption capacity for uranium due to its smaller particle size and higher surface area of CNC, which was confirmed from BET. In this work, the uptake capacity and



**Figure 3.** (a) XPS of PCNCFH and U–PCNCFH. High-resolution XPS spectra in the (b) O 1s, (c) P 2p, (d) Fe 2p, (e) Na 1s, and (f) U 4f regions of PCNCFH and U–PCNCFH (U-1 = U–O, U-2 = U–O–P). The structures in the inset of (f) show the possible mechanism of U(VI) adsorption on iron oxy-hydroxide and phosphorylated cellulose. Spectra in the expanded regions have been fitted using Casa XPS software.<sup>50</sup> Conditions: T = 293 K, pH = 7, initial concentration of uranium = 1000 mg/L.

comparative affinity of both composites for uranium were thoroughly investigated in the context of a variety of environmental factors, such as the pH of the solution and coexisting heavy metal ions of relevance. Both the composites exhibited rapid adsorption kinetics and maintained high performance across a broad pH range and even in the presence of coexisting ions. Further, the morphology of the composite and the mechanism of uranium uptake were thoroughly investigated by several microscopic (SEM and TEM) and spectroscopic techniques (XPS and FTIR).

# EXPERIMENTAL SECTION

The materials used, protocol of synthesis, experimental methodology adopted for characterizations, and evaluation of adsorption are presented in Supporting Information. Essentially, synthesis involved functionalizing CNC and MCC with trisodium trimetaphosphate (STMP) resulting in phosphorylated materials, which are used to create appropriate iron oxyhydroxide composites. They were characterized by XRD, SEM, HRTEM, XPS, TGA, and FT-IR techniques, and these materials were used for evaluating adsorption by established methods. Materials after adsorption were also studied using various diverse techniques. Suspended media were evaluated for toxicity characteristic leaching protocol (TCLP). Kinetics of the adsorption were fitted with various adsorption models.

# RESULTS AND DISCUSSION

The schematic diagram of material of Figure 1 represents the chemical structures of CNC, MCC, and synthesized phosphorylated cellulose and photographs of phosphorylated-cellulose nanocrystal (PCNC) and phosphorylated-cellulose

nanocrystal ferrihydrite (PCNCFH). Phosphorylated-microcrystalline cellulose (PMCC) and phosphorylated-microcrystalline cellulose ferrihydrite (PMCCFH) exhibit similar physical appearance to PCNC and PCNCFH. A green synthesis approach was used to prepare phosphorylated cellulose-ferrihydrite nanocomposites in two steps: phosphorylation of cellulose using STMP, followed by the incorporation of ferric chloride to form a stable composite. The final product, a dark brown crystalline material, was obtained through pHcontrolled reactions and thorough washing, yielding approximately 3.68 g of nanocomposite.

Characterization of PCNCFH, before and after Uranium Uptake. The FTIR spectra of CNC and phosphorylated CNC (PCNC) are compared in Figure 2a. For PCNC, there is a broad band at  $3378 \text{ cm}^{-1}$  corresponding to the -OH stretching mode in cellulose. The phosphorylation of cellulose is indicated by the disappearance of the -OH group bending vibration at 1323 cm<sup>-1</sup> and the emergence of a distinct peak at 1277 cm<sup>-1</sup>, characteristic of the free P–O stretching vibration. Additionally, the stretching vibration at 1025 cm<sup>-1</sup> corresponding to the C-O bond of cellulose disappears, while two sharp peaks emerge at 1083 cm<sup>-1</sup> and at 973 cm<sup>-1</sup> corresponding to the out-of-plane P–O–C and inplane P-O-C stretching, respectively. These spectral changes confirm the phosphorylation of hydroxyl groups in the cellulose matrix. Figure 2b represents the FTIR spectra of PCNCFH before and after uranium adsorption [samples after adsorption are labeled as (U-PCNCFH)]. The iron oxide content within the composite was confirmed using infrared

#### ACS Sustainable Chemistry & Engineering



**Figure 4.** (a) SEM image of PCNCFH and corresponding EDS elemental mapping  $(a_1-a_6)$ , and (b) SEM image of U–PCNCFH and corresponding EDS elemental mapping  $(b_1-b_6)$ .

spectroscopy, revealing Fe-O vibrations within the range of 600-700 cm<sup>-1</sup>. A prominent and intense absorption peak of the O-U-O bond overlaps with the weak P-O stretching vibration at 905 cm<sup>-1.45</sup> The peak observed at 905 cm<sup>-1</sup> corresponds to the asymmetric stretching vibration of the O-U-O bond, confirming the successful adsorption of uranyl ions onto the ferrihydrite surface.<sup>5</sup> Similar spectra were obtained for PMCC and PMCCFH [Figure S1(a,b)]. Figure 2c(i,iv) represents the high-resolution transmission electron microscopy (HRTEM) images of the PCNCFH and U-PCNCFH, respectively. From Figure 2c, it is confirmed that the iron oxyhydroxide nanoparticles were embedded within the cellulosic matrix, thereby confirming the formation of a composite.<sup>47</sup> This analysis is further supported by surface area measurements using the BET isotherm via N<sub>2</sub> adsorption. The specific surface area of the parent CNC was found to be  $3.51 \text{ m}^2/\text{g}$ , while the composite exhibited 299.89 m<sup>2</sup>/g. This substantial increase in surface area may be attributed to the incorporation of nanoscale iron oxyhydroxide particles within the cellulose matrix, which also enhances U(VI) removal efficiency of the composite. Both the structures exhibit a predominantly amorphous nature. The amorphous nature of PCNCFH was further supported by the comparative powder XRD data (Figure S2), which reveal two broad peaks characteristic of amorphous or poorly crystalline phases. Specifically, the broad peaks observed at  $25.08^{\circ}$  and  $63.4^{\circ}$ correspond to the (110) and (221) planes, respectively, of goethite ( $\alpha$ -FeOOH).<sup>48</sup> The phase remains stable under ambient conditions but progressively transforms into more stable forms of hematite and goethite upon exposure to electron beam irradiation for 25-30 min [Figure 2c(ii,iii)]. High-resolution lattice images of these phases are presented in insets  $d_1$ ,  $d_2$ ,  $d_3$ , and  $d_4$ . The phases were confirmed by the lattice planes of goethite  $(d_1, d_2)$  and hematite  $(d_3, d_4)$ .<sup>49</sup>

Figure 3a presents the X-ray photoelectron spectroscopy (XPS) data of PCNCFH and U-PCNCFH. Figure 3b-f shows the deconvoluted spectra in the O 1s, P 2p, Fe 2p, Na 1s, and U 4f, regions, respectively. High-resolution C 1s spectra (Figure S3) reveal three characteristic peaks corresponding to 291.8 eV for the C-C bond, 286.1 eV for the C-OH and C-O-P bonds, and 284.7 eV for the-CH<sub>2</sub> bond. Shift can be observed in the case of the O 1s spectra (Figure 3b) of U-PCNCFH. Here, the O 1s peak of the parent PCNCFH composed of Fe-O, P-O, and C-O (C-OH, C-O-P, and O-C-O) shows peaks at 528.99, 529.98, and 534.6 eV, respectively. In U-PCNCFH, we can see a characteristic peak at 530.22 eV corresponding to the U-O bond. The P 2p spectrum of U-PCNCFH (Figure 3c) exhibits a blue shift compared to that of the pristine PCNCFH. It suggests that the phosphate groups play a crucial role in uranium removal. The Fe 2p spectra (Figure 3d) show a peak at 711.2 eV for  $2p_{3/2}$ core level and a broad satellite feature at 718.4 eV, which is characteristic of Fe (III) species in iron oxyhydroxides.<sup>51</sup> The Fe 2p spectrum of U-PCNCFH shows a slight shift toward lower binding energy. This observation could be attributed to changes in the chemical environment of the adjacent oxygen atoms due to interaction with uranium. In the case of the Na 1s spectrum (Figure 3e) of U-PCNCFH, area under the peak is less as compared to the pristine PCNCFH. This is due to the replacement of some Na<sup>+</sup> of STMP with UO<sub>2</sub><sup>2+</sup> after adsorption. The U 4f spectrum (Figure 3f) reveals two distinct interactions following adsorption: a U 4f<sub>7/2</sub> peak at 379.0 eV, corresponding to the U–O bond (U-1), and a U  $4f_{7/2}$  peak at 381.0 eV (U-2), corresponding to U-O-P. These two features appear in a 9:1 ratio, respectively. We interpret this observation in terms of two distinct kinds of interactions experienced by the hydrated uranyl species. The species  $UO_2(H_2O)_5^{2+}$  can interact with the phosphorylated cellulose, hydroxyl groups of cellulose, as well as iron-oxyhydroxide, as



**Figure 5.** Batch study comparing the uranium removal performance of the composites, PMCCFH and PCNCFH. (a) Residual uranium concentrations as a function of composite dosage. (b) Residual uranium concentrations in relation to the contact time with the composites. (c) Performance of composites made of MCC and CNC toward uranium removal over a pH window of 3–10. (d) Zeta potential as a function of pH (range 3–11) for PCNCFH particles in water (2 mg in 2 mL). Insets in a,b show magnified images in the low concentration region, for clarity.

shown in the inset of Figure 3f. Latter two types of interactions are more common as these species are available in plenty and all the hydroxyl species are electron rich. Therefore, these contribute to the lower binding energy feature at 379.0 eV. The phosphine oxide binding, in contrast, reduces the electron density slightly at uranium, making it a higher binding energy feature at 381.0 eV. From the intensity, it is apparent that the available phosphorus sites are far too few in comparison to the hydroxyl groups.

The adsorption mechanism of U(VI) on PCNCFH is attributed to inner-sphere surface complexation, where uranium forms stable bonds with oxygen and phosphorus containing functional groups. These groups generate an electron-rich environment that enhances the U(VI) binding. Recent studies have emphasized the critical role of an electrondense environment in U(VI) adsorption. For instance, Meng et al. (2024) developed an all-polymer-based 0D/2D C<sub>4</sub>N/C<sub>6</sub>N<sub>7</sub> material designed to efficiently separate charges, which helps create an electron-rich surface for better U(VI) removal. This material achieved >97% uranium removal under acidic conditions and maintained high efficiency even under radiation exposure.<sup>52</sup> Recent studies have demonstrated the role of secondary metal ions such as alkaline earth metals (e.g., Ca<sup>2+</sup> and  $Mg^{2+}$ ), transition metals (e.g.,  $Fe^{3+}$  and  $Pb^{2+}$ ), and lanthanides (e.g., Ce4+, Th4+) in stabilizing reduced uranium species during the electrochemical reduction processes, emphasizing the significance of strong binding interactions.<sup>5</sup> The combination of cellulose and Fe enhances the U(VI)sorption efficiency of PCNCFH. Cellulose provides hydroxyl and carboxyl groups for adsorption and complexation along with structural stability. Fe contributes additional active sites

through coordination and facilitates the binding of U(VI). Furthermore, the nanostructured morphology of CNCs ensures a uniform dispersion of Fe, improving the accessibility of active sites and enabling efficient uranium removal through multiple mechanisms.

The SEM images of pristine PCNCFH and U–PCNCFH are shown in Figure 4a,b, respectively. Exposure to high concentration of uranium solution did not lead to any alterations in the particle morphology, indicating that the interaction mechanism is likely to be adsorption. EDS elemental mappings of PCNCFH and U–PCNCFH are presented in  $a_1-a_6$  and  $b_1-b_6$ , respectively. From the EDS elemental mapping, it is confirmed that uranyl is evenly adsorbed and homogeneously distributed on PCNCFH. To support this, the EDS analysis of U–PCNCFH is depicted in Figure S4, with the weight percentages of each element.

**Batch Adsorption Studies of Uranium Adsorption on Cellulosic Composites.** Figure 5 shows the comparative batch adsorption performance of PCNCFH and PMCCFH toward uranium uptake from water. As illustrated in Figure 5a, it is evident that both of the composites demonstrate exceptional performance upon treating 100 mL of water spiked with 1.1 mg/L uranium using various dosages of adsorbent composites, ranging from 5 to 100 mg. For both the composites, within 2 h of exposure, uranium concentrations drop to less than 15  $\mu$ g/L upon adding just 25 mg of the composites, where the initial uranium concentration of 950  $\mu$ g/L was quickly reduced to less than 10  $\mu$ g/L within 2 min of incubation due to the abundance of available free surface sites. The residual uranium concentration decreased even further at



**Figure 6.** (a) Adsorption selectivity of PCNCFH for uranium in the presence of multiple metals, at concentrations of relevance to tap water. (b) Effect of ionic strength for the uranium adsorption capacity. (c) Regeneration performance of PCNCFH toward uranium adsorption using 0.01 M HNO<sub>3</sub>. (d) Langmuir adsorption isotherms of the composites for comparing the maximum uptake capacities of uranium.

the end of 2 h, following slower kinetics. It is clear that the PCNCFH is more effective in uranium removal.

To better understand the system, data from the kinetics study were initially evaluated using a reaction model named Ho's pseudo-second-order model (Figure S5). The plots illustrating the relationship between  $t/q_t$  [where  $q_t$  is the amount of adsorbate adsorbed at time t (mg/g)] against time (for the adsorption of uranium) followed the pseudo-secondorder model. The correlation coefficients approached unity (>0.9999), indicating that the availability of surface sites significantly impacted the adsorption process, thus playing a major role in determining the overall rate. From this, it was calculated that  $q_e$  (the amount of adsorbate adsorbed at equilibrium) is 3711.95 mg/g and  $k_2$  (the rate constant of pseudo-second-order adsorption) is 0.01939 g/mg min. This also suggests that the primary mechanism for the removal of uranium by PCNCFH could be the complexation of phosphorus and oxygen containing groups with uranium. The following complexation equations could also contribute to the overall adsorption rate.

$$\equiv FeOH + UO_2^{2+} \leftrightarrow FeOUO_2^{+} + H^{+}$$
(i)  
$$\equiv FeOH + UO_2^{2+} + H_2O \leftrightarrow FeOUO_2(OH)^{0} + 2H^{+}$$
(ii)

where  $\equiv$  denotes the reactive sites on the surface of the solid adsorbent.

In an open environment, the adsorbed species of uranium on iron oxyhydroxides consisted of  $\equiv$ FeOUO<sub>2</sub><sup>+</sup> at pH below 4.5 and  $\equiv$ FeOUO<sub>2</sub>(OH)<sup>0</sup> at pH above 4.5.<sup>54,55</sup> In contrast to the photochemical generation of studtite ((UO<sub>2</sub>)(O<sub>2</sub>).4H<sub>2</sub>O) nanodots facilitated by H<sub>2</sub>O<sub>2</sub> on imine-based covalent organic framework photocatalysts, uranium adsorption on PCNCFH

proceeds through the formation of inner-sphere surface complexes with oxygen-donating functional groups such as hydroxyl and phosphorus groups, as evidenced by XPS and FTIR analyses.<sup>36</sup> The sorption capacity of both PCNCFH and PMCCFH toward uranium was also examined under different pH conditions. As illustrated in Figure 5c, all of the composites demonstrated outstanding effectiveness within a wide pH range of pH 4-10. We find that PCNCFH performs better than PMCCFH due to its larger specific surface area, attributed to its distinctive nanostructure. The BET analysis revealed that the surface area of PCNCFH was 299.89  $m^2/g$ , whereas that of PMCCFH exhibited a surface area of 276.71 m<sup>2</sup>/g. Figure 5d represents the zeta potential of PCNCFH in aqueous solutions, which explains their pH-dependent sorption behavior. As we can see from the figure, sorption efficiency of both the composites is very high in basic pH as compared to that in acidic pH. As the pH level was changed from acidic to alkaline conditions, the zeta potential exhibited a transition from a positive value of +7.01 mV at pH 3 to a negative value of -32mV at pH 12. At a low pH level (pH 3), Fe<sup>3+</sup>-O<sup>2-</sup> (from ferrihydrite) and C-OH (from cellulose) groups of nanocomposites would undergo protonation, resulting in the formation of Fe<sup>3+</sup>- OH and C-OH<sub>2</sub><sup>+</sup> species. This would cause the composite to carry a positive charge below pH 4.0. The positively charged adsorbent would repel UO22+ electrostatically, which is the dominant species below pH 5.0. Electrostatic repulsion between the adsorbent and adsorbate led to a decreased efficiency of adsorption. As the pH increases, the sorbent becomes more negatively charged and shows a strong attraction to uranium species that are dominant in alkaline conditions, such as  $[(UO_2)_3(OH)_5^+]$  and  $[(UO_2)_2(OH)_2^{2+}]$ .<sup>57</sup> Furthermore, to gain deeper insights into the mechanism, diverse isotherm models such as

Freundlich and Langmuir were assessed.<sup>58,59</sup> The Freundlich isotherm yielded a correlation coefficient ( $R^2$ ) of 0.949, which is inferior to the  $R^2 = 0.994$  value acquired from the Langmuir fit (Figures S6 and 6d). This indicates a prevalent chemisorption pathway for the UO<sub>2</sub><sup>2+</sup> species.

Since natural groundwater typically contains a variety of other ions, it is crucial to assess the impact of these coexisting ions on the adsorption of  $UO_2^{2+}$  by PCNCFH. Figure 6a represents the uranium uptake performance of PCNCFH in the presence of ions such as  $Mg^{2+}$ ,  $SO_4^{2-}$ ,  $F^-$ ,  $Ca^{2+}$ ,  $CO_3^{2-}$ ,  $HCO_3^{--}$ ,  $K^+$ ,  $PO_4^{3-}$ ,  $SiO_3^{2-}$ ,  $CI^-$ ,  $Na^+$ , and  $NO_3^-$  with concentrations relevant to tap water. PCNCFH maintains a uranium removal effectiveness of >98% in the presence of all other anions, except for sodium. It may be due to increase of ionic strength of the solution due to high concentration of sodium, in agreement with the Na<sup>+</sup> release mentioned in the section on XPS. To further understand the influence of ionic strength on uranium adsorption by PCNCFH in detail, we have conducted ionic strength experiment by varying the concentration of NaCl from 0.001 to 0.008 M, representing the maximum TDS levels permissible in groundwater or drinking water. As shown in Figure 6b, uranium removal efficiency remains consistently above 99% even at 0.008 M NaCl, indicating no significant reduction in performance compared with a pristine U(VI) solution. This observation suggests that uranium uptake capacity of PCNCFH in groundwater level is unaffected by ionic strength, affirming that the adsorption process predominantly involves inner-sphere surface complexation rather than outer-sphere interactions.<sup>60</sup> We evaluated the uranium uptake performance of PCNCFH in a multi-ion solution containing major heavy metals such as Cu(II), Cd(II), Al(III), Zn(II), Mn(II), Mg(II), Cr(III), Li(I), Co(II), and Ni(II) with concentrations up to 1 ppm (Figure S7). Metal ion removal percentage is calculated using the equation mentioned (Supporting Information, eq i). Despite the existence of several interfering cations, PCNCFH shows a uranium removal efficiency of >88%. Al(III) and Cr(III) are two main competitors for adsorption. Notably, it has the added advantage of simultaneously removing uranium with toxic contaminants such as chromium, highlighting its versatile remediation potential. The concurrent removal of chromium and aluminum, alongside uranium by iron oxide-based materials can be attributed to the speciation of these ions at specific pH. In the pH range of 5-7, Cr(III) and Al(III) predominantly exist as hydroxylated species such as  $Cr(OH)^{2+}$ ,  $Cr(OH)_2^+$  and  $Al(OH)_2^+$ ,  $Al(OH)_3$ , which exhibit stronger affinities for oxygen-donating functional groups (e.g., hydroxyl, phosphate).<sup>61-63</sup> Conversely, the adsorption of Zn(II), Mn(II), Li(I), Co(II), and Ni(II) is significantly lower, likely due to their lower charge density compared to those of Cr(III), Al(III), and U(VI). This result demonstrates that PCNCFH adsorbent possesses good selectivity for uranium in water with a significant number of relevant ions. Considering that V(V)and U(VI) have similar properties for binding to oxygencontaining functional groups, U(VI) adsorption experiments were carried out in the presence of V(V), with concentrations of both the metals being nearly equal (Figure S8). The results indicate that the presence of V(V) does not adversely affect the U(VI) removal efficiency of PCNCFH, but it can also remove V(V) up to 85%. However, it is worth noting that V(V)concentrations are negligible in uranium-contaminated groundwater regions of India.<sup>64</sup> Figure 6c shows the regeneration of PCNCFH up to four cycles toward uranium

adsorption. The reusability of sorbents is a crucial characteristic that impacts their environmental sustainability and economic viability.<sup>65</sup> Here, 0.01 M HNO<sub>3</sub> was used as the eluent, and the continuous adsorption-desorption cycle revealed that regeneration efficiency of the sorbent is above 99% even after four continuous cycles. HNO<sub>3</sub> is a good eluting agent as regeneration happens within 90 min of the reaction. This can be attributed to the protonation of the negatively charged surface groups such as hydroxyl groups on PCNCFH in acidic solutions. This reduces the electrostatic attraction between the surface and adsorbed uranium species (often in the form of uranyl ions,  $UO_2^{2+}$ ).<sup>54</sup> Adsorbed uranyl cations on the adsorbent can form water-soluble uranyl nitrate complexes such as  $UO_2(NO_3)_2$ . Formation of these soluble complexes facilitates the desorption of uranium from the adsorbent surface into the solution. The adsorption isotherm of both the composites (PCNCFH and PMCCFH) at neutral pH and room temperature was examined using the Langmuir equation to obtain a better understanding of the adsorption mechanism and efficiency. The plots of  $C_{\rm e}/q_{\rm e}$  against  $C_{\rm e}$  exhibit linear relationships when utilizing the linearized form of the Langmuir eq (Supporting Information, eqs S3 and S4) for both the composites, as illustrated in Figure 6d. A linear relationship observed in the plot of  $C_e/q_e$  against  $C_e$ , coupled with a high correlation coefficient value exceeding 0.99 in each instance, suggests that the mechanism was monolayer adsorption. PCNCFH exhibited a higher adsorption capacity compared to PMCCFH.

The differences in U(VI) sorption performance between PMCCFH and PCNCFH, as seen in Figure 5 and Table 1, can

# Table 1. Comparison of the Adsorption Capacity ofPCNCFH with Other Reported Cellulose-Based Adsorbentsfrom the Literature

adsorbents	$q_{\rm max}~({\rm mg/g})$	pH and temperature	refs
amidoximated cellulose	52.88	5.0	66
cellulose microspheres modified by $n$ -aminotrizole, $n = 3$ $n = 4$	98.90 $(n = 3)$ and 72.20 $(n = 4)$	5.0	67
plasma-light-amidoxime-cellulose	101.15	6 and 303 K	68
PGTDC-COOH	99.4	6	69
Poly(B2MEP)-g-cellulose	79.9		70
PCNCFH	100	neutral	this work
РМССҒН	25	neutral	this work
cellulose p-toluidine	80	10.5	71
Fe <sub>2</sub> O <sub>3</sub> -impregnated cellulose beads	7.6	7	72
phosphate-functionalized bacterial cellulose	50.65	4.0-8.0	73
graphene oxide-cellulose (GOC)	101.01		74

be attributed to the experimental conditions and material structure. In Figure 5, adsorption studies were performed with an initial uranium concentration of 1 ppm, consistent with typical uranium levels in Indian groundwater, showing minimal differences in U(VI) removal efficiency at this lower concentration. However, the maximum adsorption capacity, calculated from the Langmuir isotherms in Table 1 with uranium concentrations up to 150 ppm, shows a substantially higher sorption capacity for PCNCFH. This is due to the nanostructure of PCNCFH, which provides a larger surface

area and more accessible active sites compared to the microstructure of PMCCFH. At higher concentrations, these features enable PCNCFH to achieve much greater uranium removal efficiency. This highlights the critical role of nanostructure in enhancing sorption performance.

The thermal stability of PCNCFH was assessed through thermogravimetric analysis (TGA) conducted under both nitrogen and air atmospheres (Figure S8). The composite experiences weight losses of 25.66% and 28.61% as it was heated from room temperature to 1000 °C in nitrogen and air atmospheres, respectively. The composite initially releases loosely bound water from both its interior and exterior surfaces up to 100 °C, accounting for the initial weight loss. Subsequently, significant thermal degradation of the cellulosic framework occurs as the temperature reaches 250–300 °C.

**Preliminary Sustainability Evaluation.** Water treatment processes often require substantial energy consumption and have numerous economic, environmental, and social implications. Consequently, for a technology to be sustainable, it must address the three core aspects of sustainability: environmental, economic, and societal.<sup>75</sup> To evaluate these parameters, it is essential to first determine the extent of its "greenness" by assessing some relevant sustainability parameters.<sup>76–78</sup> The formulas used to compute the sustainability metrics are detailed as eqs 4–8 in Supporting Information

**Resource Efficiency.** One of the primary raw materials is cellulose, which is both biodegradable and renewable. CNCs are derived from cellulose and are abundantly available from renewable sources such as wood pulp, waste materials, and agricultural residues. This makes CNCs a sustainable alternative to nonrenewable materials. Alkali and iron salts were utilized in minimal amounts, both of which are not considered toxic. Additionally, water was used as the solvent in the process. The mass intensity (excluding water) was determined to be 3.11, while the water intensity was measured as 22.28. The reaction mass efficiency was calculated to be 32.08%. Enhancing the reaction mass efficiency can be accomplished by further optimizing the quantities of reactants and minimizing the use of surplus reagents.

**Energy Use.** Electricity was employed for the purposes of stirring, vacuum filtration, and drying. There will be no consumption of energy in the operation of the technology. The energy intensity, determined through the lab-scale synthesis setup, was 2.63 kW·h/kg of the composite. Mukherjee et al. reported the energy use of 2.3 kW h/kg for cellulose-ferrihydrite composite, which is comparable with the above-mentioned value.<sup>59</sup>

**Emission.** No deleterious solvents or fumes or secondary products were emitted during the synthesis of the composite. The E-factor was 0.11, signifying minimal release of harmful byproducts.

Similar calculations were also performed for PCNC (Table S2).

**Toxicity potential of the reagents** In toxicology analysis,  $LD_{50}$  (Lethal Dose 50) values are important because they provide a standardized measure of the acute toxicity of a substance.  $LD_{50}$  represents the dose of a substance required to cause death in 50% of a population of test animals (typically rodents) within a specified time period. The lower the value of  $LD_{50}$ , the more toxic the substance is. The  $LD_{50}$  values for some common phosphorylated reagents are presented in Table 2. Here, STMP is used as the phosphorylating agent for cellulose. STMP is less toxic than other phosphorylating agents

pubs.acs.org/journal/ascecg

phosphorylating agent	route	organism	dose (mg/kg)
STMP	oral	rat	3650
phosphoric acid	oral	rat	1530
phosphorous acid	oral	rat	1560-1580
diphosphorus pentoxide	oral	rat	200

such as phosphoric acid, phosphorus acid, and diphosphorus pentoxide.

Furthermore, according to the European Chemicals Agency (ECHA),  $FeCl_3$  (ferric chloride) has been categorized as a skin irritant, while NaOH (sodium hydroxide) has been classified as corrosive. Despite these classifications, both substances exhibit nonflammable properties and remain stable at ambient temperature.

**Waste Management.** Uranium-loaded composites underwent repeated regeneration processes through acidic treatments to facilitate subsequent adsorption cycles. They can be disposed of by methods such as encapsulation in cementitious materials, incorporation into ceramic waste forms, deep geological disposal, and incineration followed by immobilization.

**Societal Approval.** The social acceptability of a technology based on adsorption depends on various factors, including its perceived benefits, potential risks, and alignment with societal values and norms. The PCNCFH-based technology is environmentally sustainable, straightforward, and economically efficient and does not entail excessive operational expenses. Therefore, it is anticipated that the project will garner significant acceptance from the impacted communities.

The TCLP studies, following the USEPA standard SW-846 Test Method 1311, were performed on saturated composite PCNCFH to evaluate the potential leaching of adsorbed uranium. The analysis indicated a leaching concentration of 2.41 mg/L, which is below the permissible limits. We have taken the limit of leaching as that of arsenic as no limit for TCLP is mentioned for uranium.<sup>79</sup> Note that limit of arsenic in drinking water (10 ppb) is below that of uranium (30 ppb), and so, using the arsenic limit in TCLP is justified.

By considering the maximum adsorption capacity of PCNCFH as 100 mg/g, we have theoretically assessed the cost of this technology, including both material and electricity expenses. It is estimated that this method can deliver uranium-free water at a cost of less than rupee 14.60 per 1000 L of clean water (0.17 per 1000 L).

# CONCLUSIONS

We employed a sustainable and cost-effective method to synthesize a phosphorylated cellulose ferrihydrite composite for uranium removal from water. The composite, PCNCFH, exhibited superior performance over PMCCFH in adsorbing uranium. Both the oxygen and phosphorus groups on the composite surface serve as the binding sites for uranium adsorption. The enhanced capacity of PCNCFH is found to be due to the enhanced specific surface area of the adsorbent. Equilibrium was reached within 2 min of the reaction (at  $C_o = 1$  ppm, adsorbent dose, 25 mg). Utilizing the Langmuir model, the highest adsorption capacity of PCNCFH for uranium was determined to be 100 mg/g at room temperature and neutral pH. Furthermore, the composite demonstrated effectiveness across a wide pH range and in the presence of various

interfering ions. SEM, HRTEM, XPS, and IR analyses confirmed that the surface morphology of both the composites remained unchanged even after saturation with uranium, while TCLP results indicated negligible leaching of uranium from PCNCFH. PCNCFH displayed efficient reusability for up to 4 cycles with a minimal decrease in adsorption efficiency. Assessing the sustainability metrics further offered deeper insights into the socioeconomic benefits and environmental impact of the manufacturing process of nanocomposites. Due to its high uranium extraction capacity, affordability, and rapid adsorption rate, PCNCFH emerged as a promising bioadsorbent for uranium extraction from water.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.4c10246.

Instrumentation; materials, synthesis, and batch adsorption studies; comparative FTIR spectra of phosphorylated MCC and blank MCC; powder XRD patterns of blank cellulose nanocrystal (CNC), phosphorylated CNC, and PCNCFH; deconvoluted XPS spectra of C 1s of PCNCFH before and after U(VI) adsorption; SEM-EDS of PCNCFH after U(VI) adsorption with weight percentage of elements; pseudo-second-order reaction kinetics plot for the adsorption of uranium on PCNCFH; Freundlich adsorption isotherm model showing the correlation coefficient for uranium adsorption on PCNCFH; selectivity of adsorption of PCNCFH for multiple metals; effect of V(V) on U(VI)adsorption on PCNCFH; thermogravimetric analysis (TGA) of PCNCFH at air and nitrogen atmospheres from room temperature to 900 °C with 10 min scan rates; equations used in the main text; composition of synthetic tap water; and sustainability metrics evaluation for the synthesis of PCNC (PDF)

# AUTHOR INFORMATION

# **Corresponding Author**

Thalappil Pradeep – DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India; orcid.org/0000-0003-3174-534X; Email: pradeep@iitm.ac.in

#### Authors

- Tanmayaa Nayak DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India
- Sritama Mukherjee DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India; orcid.org/0000-0002-3204-3043
- Amoghavarsha Ramachandra Kini DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India; orcid.org/ 0009-0003-6863-7729
- Md Rabiul Islam DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE), Department of

Chemistry, Indian Institute of Technology Madras, Chennai 600036, India; orcid.org/0000-0001-6454-4013

- Ankit Nagar DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India
- Sonali Seth DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

Complete contact information is available at: https://pubs.acs.org/10.1021/acssuschemeng.4c10246

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

Authors thank B. K. Spoorthi and S. Banupriya for TEM measurements. The authors also thank the Common facility, Department of Chemistry, IIT Madras, and Sophisticated Analytical Instrument Facility at IIT Madras for XRD and TGA measurements, respectively. T.P. acknowledges financial support of SERB SUPRA (Grant SPR/2021/000439) and funding from the Centre of Excellence on Molecular Materials and Functions under the Institution of Eminence scheme of IIT Madras. T.N. thanks the Ministry of Human Resource Development, Government of India, for a senior research fellowship. A.R.K. thanks CSIR for his research fellowship. The authors also acknowledge the Department of Science and Technology, Government of India, for supporting our research program on nanomaterials.

#### REFERENCES

(1) Liddle, S. T. The Renaissance of Non-Aqueous Uranium Chemistry. *AngewandteReviews* **2015**, *54* (30), 8604–8641.

(2) Chen, L.; Liu, J.; Zhang, W.; Zhou, J.; Luo, D.; Li, Z. Uranium (U) Source, Speciation, Uptake, Toxicity and Bioremediation Strategies in Soil-Plant System: A Review. *J. Hazard. Mater.* **2021**, *413*, 125319.

(3) Skierszkan, E. K.; Schoepfer, V. A.; Fellwock, M.; Lindsay, M. B. J. Uranium Speciation and Mobilization in Thawing Permafrost. *Environ. Sci. Technol.* **2024**, *58*, 17058.

(4) Zhang, D.; Fang, L.; Liu, L.; Zhao, B.; Hu, B.; Yu, S.; Wang, X. Uranium Extraction from Seawater by Novel Materials: A Review. *Sep. Purif. Technol.* **2023**, 320, 124204.

(5) Lu, G.; Haes, A. J.; Forbes, T. Z. Detection and Identification of Solids, Surfaces, and Solutions of Uranium Using Vibrational Spectroscopy. *Coord. Chem. Rev.* **2018**, *374*, 314–344.

(6) Rani, N.; Singh, P.; Kumar, S.; Kumar, P.; Bhankar, V.; Kamra, N.; Kumar, K. Recent Advancement in Nanomaterials for the Detection and Removal of Uranium: A Review. *Environ. Res.* **2023**, 234, 116536.

(7) Chaudhari, U.; Mehta, M.; Sahoo, P. K.; Mittal, S.; Tiwari, R. P. Co-Occurrence of Geogenic Uranium and Fluoride in a Semiarid Belt of the Punjab Plains, India. *Groundw. Sustain. Dev.* 2023, 23, 101019.
(8) Nolan, J.; Weber, K. A. Natural Uranium Contamination in Major U.S. Aquifers Linked to Nitrate. *Environ. Sci. Technol. Lett.* 2015, 2 (8), 215–220.

(9) Coyte, R. M.; Jain, R. C.; Srivastava, S. K.; Sharma, K. C.; Khalil, A.; Ma, L.; Vengosh, A. Large-Scale Uranium Contamination of Groundwater Resources in India. *Environ. Sci. Technol. Lett.* **2018**, 5 (6), 341–347.

(10) Coyte, R. M.; Vengosh, A. Factors Controlling the Risks of Co-Occurrence of the Redox-Sensitive Elements of Arsenic, Chromium, Vanadium, and Uranium in Groundwater from the Eastern United States. *Environ. Sci. Technol.* **2020**, *54* (7), 4367–4375.

(11) Hassan, A.; Mollah, M. M. R.; Jayashree, R.; Jain, A.; Das, S.; Das, N. Ultrafast Removal of Thorium and Uranium from Radioactive Waste and Groundwater Using Highly Efficient and Radiation-Resistant Functionalized Triptycene-Based Porous Organic Polymers. *ACS Appl. Mater. Interfaces* **2024**, *16* (19), 24547–24561.

(12) Orloff, K. G.; Mistry, K.; Charp, P.; Metcalf, S.; Marino, R.; Shelly, T.; Melaro, E.; Donohoe, A. M.; Jones, R. L. Human Exposure to Uranium in Groundwater. *Environ. Res.* **2004**, *94* (3), 319–326.

(13) Kurttio, P.; Komulainen, H.; Leino, A.; Salonen, L.; Auvinen, A.; Saha, H. Bone as a Possible Target of Chemical Toxicity of Natural Uranium in Drinking Water. *Environ. Health Perspect.* **2005**, *113* (1), 68–72.

(14) Canu, I. G.; Ellis, E. D.; Tirmarche, M. Cancer Risk In Nuclear Workers Occupationally Exposed To Uranium—Emphasis On Internal Exposure. *Health Phys.* **2008**, *94* (1), 1–17.

(15) Uranium Occurrence In Shallow Aquifer In India, 2020. https:// www.cgwb.gov.in/old\_website/WQ/URANIUM\_REPORT\_2019-20.pdf (accessed 2024–07–27).

(16) Meng, C.; Du, M.; Zhang, Z.; Liu, Q.; Yan, C.; Li, Z.; Dong, Z.; Luo, J.; Ma, J.; Liu, Y.; Wang, X. Open-Framework Vanadate as Efficient Ion Exchanger for Uranyl Removal. *Environ. Sci. Technol.* **2024**, 58 (21), 9456–9465.

(17) Liu, T.; Li, Z.; Zhang, X.; Tan, H.; Chen, Z.; Wu, J.; Chen, J.; Qiu, H. Metal–Organic Framework-Intercalated Graphene Oxide Membranes for Selective Separation of Uranium. *Anal. Chem.* **2021**, 93 (48), 16175–16183.

(18) Zarrougui, R.; Ferhi, N.; Raouafi, N.; Hamzaoui, A. H.; Messaoudi, S. Advanced Uranium Removal with Pure, Nonfluorinated Ionic Liquids: Fine-Tuning Hydrophilic and Hydrophobic Properties for Enhanced Selectivity. *Inorg. Chem.* **2024**, *63* (18), 8059–8069.

(19) Wang, S.; Yang, X.; Xu, L.; Miao, Y.; Yang, X.; Xiao, C. Selective Extraction of Uranium(VI) from Thorium(IV) Using New Unsymmetrical Acidic Phenanthroline Carboxamide Ligands. *Ind. Eng. Chem. Res.* **2023**, *62* (38), 15613–15624.

(20) Lin, T.; Chen, T.; Jiao, C.; Zhang, H.; Hou, K.; Jin, H.; Liu, Y.; Zhu, W.; He, R. Ion Pair Sites for Efficient Electrochemical Extraction of Uranium in Real Nuclear Wastewater. *Nat. Commun.* **2024**, *15* (1), 4149.

(21) Li, Y.; Wang, S.; Wang, X. Highly Selective Removal of U(VI) from Aqueous Solutions by Porous Nanomaterials. *EcoEnergy* 2024, 2 (2), 205–219.

(22) Ma, X.; Meihaus, K. R.; Yang, Y.; Zheng, Y.; Cui, F.; Li, J.; Zhao, Y.; Jiang, B.; Yuan, Y.; Long, J. R.; Zhu, G. Photocatalytic Extraction of Uranium from Seawater Using Covalent Organic Framework Nanowires. J. Am. Chem. Soc. **2024**, 146 (33), 23566– 23573.

(23) Balakrishnan, A.; Kunnel, E. S.; Sasidharan, R.; Chinthala, M.; Kumar, A. Tailored Citric Acid-Functionalized Carbon Nitride Homojunction-Immobilized Carboxymethyl Cellulose 3D Photocatalytic Hydrogels: A Multifaceted Approach toward Environmental Remediation. ACS Sustain. Chem. Eng. 2024, 12 (13), 5169–5185.

(24) Bolisetty, S.; Peydayesh, M.; Mezzenga, R. Sustainable Technologies for Water Purification from Heavy Metals: Review and Analysis. *Chem. Soc. Rev.* **2019**, *48* (2), 463–487.

(25) Tuo, K.; Li, J.; Li, Y.; Liang, C.; Shao, C.; Hou, W.; Li, Z.; Pu, S.; Deng, C. Construction of Hierarchical Porous and Polydopamine/ Salicylaldoxime Functionalized Zeolitic Imidazolate Framework-8 *via* Controlled Etching for Uranium Adsorption. *Mater. Horiz.* 2024, 11 (14), 3364–3374.

(26) Zhang, N.; Li, J.; Tian, B.; Li, T.; Zhang, J.; Wang, Q.; Zhao, H. RIGP-Induced Surface Modification of Cellulose for the Preparation of Amidoxime-Modified Cellulose/Graphite Oxide Composites with Enhanced Uranium Adsorption. *Ind. Eng. Chem. Res.* **2024**, 63 (5), 2337–2346.

(27) Liao, J.; Ding, C.; Shi, J.; Jiang, L.; Wang, Q.; Wang, L. Efficient Separation of Uranium(VI) by CaCO<sub>3</sub>-Doped Chitosan with  $PO_4^{-3}$ -

Modification: Adsorption Behaviors and Mechanism Study. ACS Appl. Polym. Mater. 2024, 6, 4885–4895.

(28) Ji, D.; Wang, Y.; Liu, Y.; Hao, S.; Yang, J.; Yan, Y.; Lu, C.; Guan, S.; Gao, Q.; Wu, H. Efficient Capture of Uranium by a Hydroxyapatite-Modified Polyethyleneimine@carbon Nanotube Composite from Radioactive Nuclear Waste. *Dalton Trans.* **2023**, *52* (29), 10136–10144.

(29) Wall, N. A.; Maulden, E.; Gager, E. J.; Ta, A. T.; Ullberg, R. S.; Zeng, G.; Nava-Farias, L.; Sims, A. P.; Nino, J. C.; Phillpot, S. R.; Szecsody, J. E.; Pearce, C. I. Functionalized Clays for Radionuclide Sequestration: A Review. *ACS Earth Space Chem.* **2022**, *6* (11), 2552–2574.

(30) Zhao, M.; Cui, Z.; Pan, D.; Fan, F.; Tang, J.; Hu, Y.; Xu, Y.; Zhang, P.; Li, P.; Kong, X.-Y.; Wu, W. An Efficient Uranium Adsorption Magnetic Platform Based on Amidoxime-Functionalized Flower-like Fe <sub>3</sub> O <sub>4</sub> @TiO <sub>2</sub> Core–Shell Microspheres. *ACS Appl. Mater. Interfaces* **2021**, *13* (15), 17931–17939.

(31) Gandhi, T. P.; Sampath, P. V.; Maliyekkal, S. M. A Critical Review of Uranium Contamination in Groundwater: Treatment and Sludge Disposal. *Sci. Total Environ.* **2022**, *825*, 153947.

(32) Xie, Y.; Yu, L.; Chen, L.; Chen, C.; Wang, L.; Liu, F.; Liao, Y.; Zhang, P.; Chen, T.; Yuan, Y.; Lu, Y.; Huang, B.; Yang, H.; Wang, S.; Wang, S.; Ma, L.; Luo, F.; Liu, Y.; Hu, B.; Wang, H.; Pan, D.; Zhu, W.; Wang, N.; Wang, Z.; Mao, L.; Ma, S.; Wang, X. Recent Progress of Radionuclides Separation by Porous Materials. *Sci. China Chem.* **2024**, 67 (11), 3515–3577.

(33) Hao, M.; Liu, Y.; Wu, W.; Wang, S.; Yang, X.; Chen, Z.; Tang, Z.; Huang, Q.; Wang, S.; Yang, H.; Wang, X. Advanced Porous Adsorbents for Radionuclides Elimination. *EnergyChem.* **2023**, *5* (4), 100101.

(34) Zhang, K. H.; Huang, Z.; Yang, M.; Liu, M.; Zhou, Y.; Zhan, J.; Zhou, Y. Recent Progress in Melt Pyrolysis: Fabrication and Applications of High-Value Carbon Materials from Abundant Sources. *Susmat* **2023**, *3* (5), 558–580.

(35) Wang, X.; Xiao, C.; Qi, J.; Guo, X.; Qi, L.; Zhou, Y.; Zhu, Z.; Yang, Y.; Li, J. Enhancing Uranium Removal with a Titanium-Incorporated Zirconium-Based Metal–Organic Framework. *Langmuir* **2023**, 39 (48), 17366–17377.

(36) Wang, L.; Shi, C.; Wang, L.; Pan, L.; Zhang, X.; Zou, J.-J. Rational Design, Synthesis, Adsorption Principles and Applications of Metal Oxide Adsorbents: A Review. *Nanoscale* **2020**, *12* (8), 4790–4815.

(37) Aragaw, T. A.; Bogale, F. M.; Aragaw, B. A. Iron-Based Nanoparticles in Wastewater Treatment: A Review on Synthesis Methods, Applications, and Removal Mechanisms. *J. Saudi Chem. Soc.* **2021**, 25 (8), 101280.

(38) Li, Q.; Li, R.; Ma, X.; Sarkar, B.; Sun, X.; Bolan, N. Comparative Removal of As(V) and Sb(V) from Aqueous Solution by Sulfide-Modified  $\alpha$ -FeOOH. *Environ. Pollut.* **2020**, *267*, 115658.

(39) Mohamed, A.; Atta, R. R.; Kotp, A. A.; Abo El-Ela, F. I.; Abd El-Raheem, H.; Farghali, A.; Alkhalifah, D. H. M.; Hozzein, W. N.; Mahmoud, R. Green Synthesis and Characterization of Iron Oxide Nanoparticles for the Removal of Heavy Metals (Cd2+ and Ni2+) from Aqueous Solutions with Antimicrobial Investigation. *Sci. Rep.* **2023**, *13* (1), 7227.

(40) Jabbar, A. A.; Hussain, D. H.; Latif, K. H.; Jasim, A. K.; Al-aqbi, Z. T.; Alghannami, H. S.; Albishri, A. High-Efficiency Adsorption of Uranium from Wastewater Using Graphene Oxide/Graphene Oxide Nanoribbons/Chitosan Nanocomposite Aerogels. *ACS Omega* **2024**, *9* (25), 27260–27268.

(41) Arora, S.; Lal, S.; Kumar, S.; Kumar, M.; Kumar, M. Comparative Degradation Kinetic Studies of Three Biopolymers: Chitin, Chitosan and Cellulose. *Arch. Appl. Sci. Res.* **2011**, *3* (3), 188–201.

(42) Garba, Z. N.; Lawan, I.; Zhou, W.; Zhang, M.; Wang, L.; Yuan, Z. Microcrystalline Cellulose (MCC) Based Materials as Emerging Adsorbents for the Removal of Dyes and Heavy Metals – A Review. *Sci. Total Environ.* **2020**, *717*, 135070.

(43) Kurniawan, T. W.; Sulistyarti, H.; Rumhayati, B.; Sabarudin, A. Cellulose Nanocrystals (CNCs) and Cellulose Nanofibers (CNFs) as Adsorbents of Heavy Metal Ions. *J. Chem.* **2023**, 2023, 1–36.

(44) Lehtonen, J.; Hassinen, J.; Kumar, A. A.; Johansson, L.-S.; Mäenpää, R.; Pahimanolis, N.; Pradeep, T.; Ikkala, O.; Rojas, O. J. Phosphorylated Cellulose Nanofibers Exhibit Exceptional Capacity for Uranium Capture. *Cellulose* **2020**, *27* (18), 10719–10732.

(45) Cai, Y.; Chen, L.; Yang, S.; Xu, L.; Qin, H.; Liu, Z.; Chen, L.; Wang, X.; Wang, S. Rational Synthesis of Novel Phosphorylated Chitosan-Carboxymethyl Cellulose Composite for Highly Effective Decontamination of U(VI). ACS Sustain. Chem. Eng. 2019, 7 (5), 5393–5403.

(46) Wang, C.-Z.; Lan, J.-H.; Wu, Q.-Y.; Luo, Q.; Zhao, Y.-L.; Wang, X.-K.; Chai, Z.-F.; Shi, W.-Q. Theoretical Insights on the Interaction of Uranium with Amidoxime and Carboxyl Groups. *Inorg. Chem.* **2014**, 53 (18), 9466–9476.

(47) Mukherjee, S.; Ramireddy, H.; Baidya, A.; Amala, A. K.; Sudhakar, C.; Mondal, B.; Philip, L.; Pradeep, T. Nanocellulose-Reinforced Organo-Inorganic Nanocomposite for Synergistic and Affordable Defluoridation of Water and an Evaluation of Its Sustainability Metrics. ACS Sustain. Chem. Eng. **2020**, *8* (1), 139–147.

(48) Ghosh, M. K.; Poinern, G. E. J.; Issa, T. B.; Singh, P. Arsenic Adsorption on Goethite Nanoparticles Produced through Hydrazine Sulfate Assisted Synthesis Method. *Korean J. Chem. Eng.* **2012**, *29* (1), 95–102.

(49) Chernova, E.; Botvin, V.; Galstenkova, M.; Mukhortova, Y.; Wagner, D.; Gerasimov, E.; Surmeneva, M.; Kholkin, A.; Surmenev, R. A Comprehensive Study of Synthesis and Analysis of Anisotropic Iron Oxide and Oxyhydroxide Nanoparticles. *Nanomaterials* **2022**, *12* (23), 4321.

(50) Fairley, N.; Fernandez, V.; Richard-Plouet, M.; Guillot-Deudon, C.; Walton, J.; Smith, E.; Flahaut, D.; Greiner, M.; Biesinger, M.; Tougaard, S.; Morgan, D.; Baltrusaitis, J. Systematic and Collaborative Approach to Problem Solving Using X-Ray Photoelectron Spectroscopy. *Appl. Surf. Sci. Adv.* **2021**, *5*, 100112.

(51) Mallet, M.; Barthélémy, K.; Ruby, C.; Renard, A.; Naille, S. Investigation of Phosphate Adsorption onto Ferrihydrite by X-Ray Photoelectron Spectroscopy. *J. Colloid Interface Sci.* **2013**, 407, 95–101.

(52) Meng, Q.; Wu, L.; Chen, T.; Xiong, Y.; Duan, T.; Wang, X. Constructing the Electron-Rich Microenvironment of an All-Polymer-Based S-Scheme Homostructure for Accelerating Uranium Capture from Nuclear Wastewater. *Environ. Sci. Technol.* **2024**, *58*, 15333.

(53) Liu, X.; Xie, Y.; Hao, M.; Li, Y.; Chen, Z.; Yang, H.; Waterhouse, G. I. N.; Wang, X.; Ma, S. Secondary Metal Ion-Induced Electrochemical Reduction of U(VI) to U(IV) Solids. *Nat. Commun.* **2024**, *15* (1), 7736.

(54) Ping, L.; Zhuoxin, Y.; Jianfeng, L.; Qiang, J.; Yaofang, D.; Qiaohui, F.; Wangsuo, W. The Immobilization of U(vi) on Iron Oxyhydroxides under Various Physicochemical Conditions. *Env. Sci. Process. Impacts* **2014**, *16* (10), 2278–2287.

(55) Wang, Y.; Wang, J.; Li, P.; Qin, H.; Liang, J.; Fan, Q. The Adsorption of U(VI) on Magnetite, Ferrihydrite and Goethite. *Environ. Technol. Innov.* **2021**, 23, 101615.

(56) Gao, P.; Hu, Y.; Shen, Z.; Zhao, G.; Cai, R.; Chu, F.; Ji, Z.; Wang, X.; Huang, X. Ultra-Highly Efficient Enrichment of Uranium from Seawater via Studite Nanodots Growth-Elution Cycle. *Nat. Commun.* **2024**, *15* (1), 6700.

(57) Lu, G.; Forbes, T. Z.; Haes, A. J. Evaluating Best Practices in Raman Spectral Analysis for Uranium Speciation and Relative Abundance in Aqueous Solutions. *Anal. Chem.* **2016**, *88* (1), 773–780.

(58) Manjunath, S. V.; Kumar, M. Evaluation of Single-Component and Multi-Component Adsorption of Metronidazole, Phosphate and Nitrate on Activated Carbon from Prosopis Juliflora. *Chem. Eng. J.* **2018**, 346, 525–534.

(59) Mukherjee, S.; Kumar, A. A.; Sudhakar, C.; Kumar, R.; Ahuja, T.; Mondal, B.; Srikrishnarka, P.; Philip, L.; Pradeep, T. Sustainable and Affordable Composites Built Using Microstructures Performing

Better than Nanostructures for Arsenic Removal. ACS Sustain. Chem. Eng. 2019, 7 (3), 3222–3233.

(60) Mei, D.; Li, H.; Liu, L.; Jiang, L.; Zhang, C.; Wu, X.; Dong, H.; Ma, F. Efficient Uranium Adsorbent with Antimicrobial Function: Oxime Functionalized ZIF-90. *Chem. Eng. J.* **2021**, *425*, 130468.

(61) Gupta, V. K.; Agarwal, S.; Saleh, T. A. Chromium Removal by Combining the Magnetic Properties of Iron Oxide with Adsorption Properties of Carbon Nanotubes. *Water Res.* **2011**, 45 (6), 2207– 2212.

(62) Botté, A.; Zaidi, M.; Guery, J.; Fichet, D.; Leignel, V. Aluminium in Aquatic Environments: Abundance and Ecotoxicological Impacts. *Aquat. Ecol.* **2022**, *56* (3), 751–773.

(63) Asrarian, R.; Jadidian, R.; Parham, H.; Haghtalab, S. Removal of Aluminum from Water and Wastewater Using Magnetic Iron Oxide Nanoparticles. *Adv. Mater. Res.* **2013**, *829*, 752–756.

(64) Mouttoucomarassamy, S.; Virk, H. S.; Dharmalingam, S. N. Evaluation and Health Risk Assessment of Arsenic and Potentially Toxic Elements Pollution in Groundwater of Majha Belt, Punjab, India. *Environ. Geochem. Health* **2024**, *46* (6), 208.

(65) Xu, M.; Zhou, L.; Zhang, L.; Zhang, S.; Chen, F.; Zhou, R.; Hua, D. Two-Dimensional Imprinting Strategy to Create Specific Nanotrap for Selective Uranium Adsorption with Ultrahigh Capacity. *ACS Appl. Mater. Interfaces* **2022**, *14* (7), 9408–9417.

(66) Wang, Y.; Zhang, Y.; Li, Q.; Li, Y.; Cao, L.; Li, W. Amidoximated Cellulose Fiber Membrane for Uranium Extraction from Simulated Seawater. *Carbohydr. Polym.* **2020**, *245*, 116627.

(67) Wen, D.; Dong, Z.; Ao, Y.; Xie, K.; Zhai, M.; Zhao, L. Aminotriazole Isomers Modified Cellulose Microspheres for Selective Adsorption of U(VI): Performance and Mechanism Investigation. *Carbohydr. Polym.* **2021**, *257*, 117666.

(68) Yu, S.; Sun, C.; Fang, S.; Wang, C.; Alharbi, N. S.; Chen, C. Preparation of Cellulose@amidoxime by Plasma-Induced Grafting Technology and Its Potential Application for Uranium Extraction. *Appl. Surf. Sci.* **2023**, *637*, 157883.

(69) Anirudhan, T. S.; Sreekumari, S. S. Synthesis and Characterization of a Functionalized Graft Copolymer of Densified Cellulose for the Extraction of Uranium(VI) from Aqueous Solutions. *Colloids Surf. Physicochem. Eng. Asp.* **2010**, *361* (1–3), 180–186.

(70) Misra, N.; Rawat, S.; Kumar Goel, N.; Shelkar, S. A.; Mallavarapu, A.; Tiwari, M.; Kumar, V. C.U. S. CellUSorb: A high-performance, radiation functionalized cellulose based adsorbent for Uranium (VI) remediation in ground water. *Sep. Purif. Technol.* **2023**, 322, 124215.

(71) Dacrory, S.; Haggag, E. S. A.; Masoud, A. M.; Abdo, S. M.; Eliwa, A. A.; Kamel, S. Innovative Synthesis of Modified Cellulose Derivative as a Uranium Adsorbent from Carbonate Solutions of Radioactive Deposits. *Cellulose* **2020**, *27* (12), 7093–7108.

(72) Rule, P.; K, B.; Gonte, R. R. Uranium(VI) Remediation from Aqueous Environment Using Impregnated Cellulose Beads. J. Environ. Radioact. 2014, 136, 22–29.

(73) Zhuang, S.; Wang, J. Removal of U(VI) from Aqueous Solution Using Phosphate Functionalized Bacterial Cellulose as Efficient Adsorbent. *Radiochim. Acta* **2019**, *107* (6), 459–467.

(74) Yang, A.; Wu, J.; Huang, C. P. Graphene Oxide-Cellulose Composite for the Adsorption of Uranium(VI) from Dilute Aqueous Solutions. J. Hazard. Toxic Radioact. Waste 2018, 22 (2), 04017029. (75) Mukherjee, S.; Nayak, T.; Pradeep Chapter 17 - Evaluating Sustainability for Water and Wastewater Treatment Technologies. In Technological Solutions for Water Sustainability: Challenges and Prospects; Philip, L., Pradeep, T., Bhallamudi, S. M., Eds.; IWA Publishing, 2023; pp 191–199..

(76) Curzons, A. D.; Mortimer, D. N.; Constable, D. J. C.; Cunningham, V. L. So You Think Your Process Is Green, How Do You Know?–Using Principles of Sustainability to Determine What Is Green – a Corporate Perspective. *Green Chem.* **2001**, *3* (1), 1–6.

(77) Jiménez-González, C.; Constable, D. J. C.; Ponder, C. S. Evaluating the "Greenness" of Chemical Processes and Products in the Pharmaceutical Industry—a Green Metrics Primer. *Chem. Soc. Rev.* 2012, 41 (4), 1485–1498.

(78) Sheldon, R. A. Metrics of Green Chemistry and Sustainability: Past, Present, and Future. *ACS Sustain. Chem. Eng.* **2018**, *6* (1), 32–48.

(79) Toxicity Characteristic Leaching Procedure (TCLP) for VOCs, SVOCs, Chlorinated Pesticides and Herbicides, and Metals by SW-846 Method 1311 and Analysis. 2017. https://19january2017snapshot.epa.gov/sites/production/files/2015-06/documents/tclp.pdf (accessed 2024-09-16).