Efficient extraction of uranium (VI) from aqueous solution by Zr/Ce-UiO-66-NH2 modified by dual strategies of bimetallization and amination

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Abstract

We employed a dual strategy of bimetallization and amination to modify Zr/Ce-UiO-66-NH2 for the efficient extraction of uranium from aqueous solutions. XRD, Fourier transform infrared spectroscopy (FTIR), and XPS demonstrated the successful amination modification of the material. Furthermore, the metallic Zr in the Zr-oxo clusters of Zr/Ce-UiO-66-NH2 was partially substituted by Ce. The material exhibited commendable structural stability in both acidic and alkaline solutions. The structural integrity of Zr/Ce-UiO-66-NH2 remained unaffected when immersed in either 6 M strong acid or 0.5 M strong base solutions. Batch experiments at pH = 6.0 indicated that the uranium adsorption capacity of Zr/Ce-UiO-66-NH2 reached 376.8 mg/g and 611.33 mg/g at 298 K and 328 K, respectively. These values are significantly higher than those obtained using bimetallic Zr/Ce-UiO-66 or amine-functionalized UiO-66-NH2. After five consecutive adsorption-desorption cycles, the uranium removal efficiency of the material remained above 80%, demonstrating its excellent regenerability. The adsorption kinetic model for uranium(VI) on Zr/Ce-UiO-66-NH2 revealed that chemisorption dominated the rapid adsorption of uranium. We propose possible adsorption mechanisms involving three interactions: inner-sphere surface complexation, chemisorption, and electrostatic interaction. This study demonstrates that the dual strategy of bimetallization and amination can effectively enhance the extraction efficiency of uranium(VI) from aqueous solutions. This approach holds promise for application in the structural design of uranium adsorbents.

Full Text

Preamble

We modified Zr/Ce-UiO-66-NH2 using dual bimetallization and amination strategies to efficiently extract uranium from water resources. XRD, FTIR, and XPS characterization confirmed successful material amination and partial replacement of Zr by Ce in the Zr-oxygen clusters of Zr/Ce-UiO-66-NH2, which possessed commendable structural stability in both acidic and alkaline solutions. Irrespective of whether submerged in 6 M strong acid or 0.5 M strong base solution, the structural integrity of Zr/Ce-UiO-66-NH2 remained unaffected. Batch experiments at pH = 6.0 revealed uranium adsorption capacities of 376.8 $mg \cdot g^{-1}$ and 611.33 $mg \cdot g^{-1}$ at 298 K and 328 K, respectively—values substantially superior to those obtained using bimetallic-modified Zr/Ce-UiO-66 or amine-functionalized UiO-66-NH2 alone. After five consecutive sorption-desorption cycles, the material retained a uranium removal rate exceeding 80%, demonstrating excellent regenerative properties. Kinetic modeling of U(VI) adsorption on Zr/Ce-UiO-66-NH2 indicated that chemisorption dominated the rapid uranium sorption process. We propose potential adsorption mechanisms involving three interactions: inner-sphere surface complexation, chemisorption, and electrostatic interactions. This study demonstrates that dual strategies of bimetallization and amination can effectively enhance U(VI) extraction from water, offering a promising approach for the structural design of uranium adsorbents.

Keywords: MOF modification; Zr/Ce-UiO-66-NH2; uranium adsorption; adsorption mechanism

Introduction

Fossil fuels, currently our primary energy source, have grown progressively scarcer, while the pollution they cause and their impact on climate change are increasingly worrying []. Finding cleaner alternatives with large reserves has become necessary as fossil energy sources become insufficient to meet escalating energy demand []. Nuclear energy is energy-dense, has low environmental impact, and offers versatile applications that can replace conventional energy sources in addressing the global energy crisis []. However, the negative impacts of energy applications are also emerging.

Uranium is the primary source of nuclear energy, and its mining and usage generate significant amounts of uranium-containing wastewater that is highly toxic and radioactive. Owing to their high water solubility and very long half-life, UO_2^{2+} ions can spread throughout the environment via groundwater and surface water, potentially entering the human body and posing threats to both human health and ecosystems []. Like fossil fuels, nuclear power is a finite resource, making uranium disposal and recycling imperative from multiple standpoints [].

Scientists have devised various techniques for extracting hexavalent uranium,

including ion exchange, chemical precipitation, membrane dialysis, bioconcentration, solid-liquid separation, and adsorption []. Although these approaches have been used to treat radioactive effluents [], they suffer from limitations regarding treatment effectiveness and practical applications, including suboptimal outcomes, high costs, and regeneration difficulties. In contrast, adsorption is widely acknowledged for its extensive applications owing to its uncomplicated operation, cost-effectiveness, eco-friendliness, and superior selectivity for uranium [].

The effectiveness of adsorbent materials is defined by their pollutant removal efficiency. Previously reported adsorbent materials such as biopolymers, clays, and nanomaterials are not ideal uranium adsorbents due to limitations including high processing costs, limited adsorption properties, poor chemical and water stability, and poor reusability []. Hence, materials with better uranium removal properties are required to overcome these limitations.

Metal-organic frameworks (MOFs) are highly organized, porous structures with exceptional characteristics such as large active specific surface areas, enriched reactive sites, and manifold structural variety []. Because of these distinct properties, MOFs have the potential to overcome problems associated with traditional adsorbents and exhibit high U(VI) adsorption capabilities, successfully removing uranium from aquatic environments [].

UiO-66 is a rigid metal-organic framework material comprising metal-oxygen clusters ($Zr_6O_4(OH)_4$) and terephthalic acid (H_2BDC) []. Since its initial discovery by Cavka et al. [], UiO-66 has sparked significant research interest globally. The solvothermal and chemical stabilities of UiO-66-Zr result directly from its unique pore architecture and high coordination number []. Nevertheless, its effectiveness as a uranium adsorbent is restricted due to poor adsorption properties [].

Nitrogen atoms are soft ligands with strong affinity for light actinides []. One study revealed that amino groups can promote electrostatic interactions between MOFs and substrates while providing active sites for adsorption []. Therefore, incorporating functional amines into porous MOFs can significantly enhance uranium extraction performance. For instance, UiO-66-NH_2 exhibits excellent U(VI) sorption compared to UiO-66, along with exceptional hydrostability and adsorption performance [].

Ce(III) is an inexpensive and nontoxic rare-earth metal belonging to the same group as Zr, characterized by stability and rapid changes in its valence state []. It has applications in various disciplines including optics, catalysis, and electricity []. Its exceptional stability ensures that its properties remain unchanged even after the addition of other functional groups []. Previous studies [] have demonstrated that Ce-based UiO-66 exhibits excellent physicochemical stability and that cerium ions promote material-substrate interactions []. In particular, Ce(IV) has strong Lewis acid properties that enhance uranium adsorption, and the 4f orbital of Ce(IV) can interact with the P=O bond to facilitate reac-

tions []. Wang et al. [] presented initial evidence that incorporating Ce(III) into UiO-67 alters surface charge, sorption space and site nature and content, and electrostatic and π-π interactions, all of which affect sorption properties.

In this study, we employed a simple method to synthesize octahedrally structured nanomaterials of Zr/Ce-UiO-66-NH_2 modified by dual strategies of bimetallization and amination. Various characterization methods were applied to observe material microstructure. Batch experiments were conducted to determine U(VI) adsorption performance and explore applicability. The adsorption behavior and potential mechanisms are described. This dual-modified material shows significant potential for application in treating uranium-bearing wastewater.

II. Results and Discussion

A. Characterization

We performed XRD on the synthesized materials, as illustrated in Figure 1a [Figure 1: see original paper]. All samples exhibited satisfactory crystallinity, with Zr/Ce-UiO-66-NH_2 showing characteristic peaks at 7.6° (111), 8.6° (220), and 25.8° (442). Experiments demonstrated that the structure of the materials remained unchanged when doped with Ce, indicating that introducing other metals may not destroy the MOF structure. The images show that the material exhibits superior crystal structure and crystallinity. Notably, Zr/Ce-UiO-66 displays similar diffraction peaks, indicating that amino group inclusion did not affect material structure []. There was a decrease in peak intensity at 8.6° in materials with bimetallic central sites compared to UiO-66-NH_2 with monometallic sites. This phenomenon may result from partial Zr substitution by Ce, causing cerium-oxygen structure formation and reducing zirconium-oxygen cluster numbers, indicating that Ce doping affected sample crystallinity [].

As shown in Figure 1b, the FT-IR image was comparable to that of UiO-66-NH_2, indicating that Ce(III) inclusion does not disrupt the metal-organic material skeleton, which agrees with existing evidence []. The image shows distinct absorption peaks at approximately 1585 cm^{-1}, 1431 cm^{-1}, and 1396 cm^{-1}, likely due to asymmetric and symmetric stretching vibrations of carboxyl groups in ligands of synthesized materials []. Additionally, absorption peaks at 1450–1580 cm^{-1} are strongly connected to C=C vibrations of H_2BDC ligands []. For both materials, a spectral range of 600–800 cm^{-1} was observed, coinciding with the spectral range of Ce-O and Zr-O bonds. Researchers have identified asymmetric stretching vibrations of O–Zr–O near 661 cm^{-1} []. Previous reports indicated that interaction between elemental Ce and the ligand leads to Ce-O and Ce-C bond formation, with the absorption peak at 1502 cm^{-1} in Figure 1b reinforcing this viewpoint and verifying successful Ce metal doping in the MOFs []. The spectrum of Zr/Ce-UiO-66-NH_2 exhibited moderate double peaks within the 3500–3300 cm^{-1} range, with peaks at 3453 cm^{-1} and 1258 cm^{-1} aligning with stretching vibrations of N-H and C-N, respectively. These results confirmed successful -NH_2 integration into the Zr/Ce-UiO-66 structure [].

The SEM plots presented in Figure 2a [Figure 2: see original paper] and Figures S1(a, b, c) illustrate that regular structures of both modified MOF materials remained intact. The structure of Zr/Ce-UiO-66-NH_2 was ortho-octahedral, similar to typical UiO-66-NH_2 structures containing single-metal sites. Ce metal introduction led to nanoparticle adhesion and binding, whereas MOF particles exhibited strong aggregation. TEM analysis of modified MOF morphologies (Figures 2b, S1d, and 2(b, c)) shows typical octahedral structures of Zr/Ce-UiO-66 and Zr/Ce-UiO-66-NH_2 corresponding to their SEM images. Comparing Figures 2(b,c) reveals that amino group introduction increases material dip-sticking ability and causes agglomeration. However, owing to low material crystallinities, these images did not show distinct lattice streaks [].

The EDS patterns shown in Figure 2d and Figure S1e indicate Ce(III) doping. The composites in the MOFs consist of C, N, O, Zr, and Ce, with their presence in the test area agreeing with material morphology. The SEM, TEM, and EDS results indicated that the solvothermal technique effectively produced bimetallic MOFs.

XPS analysis determined elemental species and valence states of prepared samples. The complete spectrum scan (Figure 3e [Figure 3: see original paper]) shows clear peaks corresponding to five elements, agreeing with EDS elemental identification (Figures 2e and S1e) and further confirming successful synthesis of bimetallic Zr/Ce-UiO-66 and dual-strategy-modified Zr/Ce-UiO-66-NH_2. Figures 3a and 4 show high-resolution XPS C 1s spectra. Figure 4a [Figure 4: see original paper] shows three distinct peaks at 284.80 eV, 286.10 eV, and 288.80 eV corresponding to binding energies of C-C, C=C, and O-C=O bonds reported in literature []. These characteristic peaks are similar to those observed for UiO-66 []. Zr 3d spectra shown in Figure 3c (at 183.15 eV and 185.50 eV) and Figure 4d (at 183.10 eV and 185.50 eV) correspond to Zr $3d_5/_2$ and Zr $3d_3/_2$ binding energies []. The characteristic N 1s spectrum at 399.16 eV is consistent with amino peak manifestation in MOFs [] and agrees with FTIR characterization. O 1s spectra in both materials (Figure 3b at 532.85 eV, 531.80 eV, and 530.50 eV; Figure 4b at 533.28 eV, 531.80 eV, and 530.40 eV) reveal characteristic peaks generated by C-O, C=O, and Zr-O bonds []. A characteristic peak similar to that of UiO-66 was identified for Ce metal, which can replace Zr, leading to Ce-O presence with peak location equivalent to Zr-O [].

Additionally, peaks at 884.90 eV and 904.40 eV in Figure 3d and at 883.38 eV and 902.90 eV in Figure 4e indicate Ce^{3+} presence in both materials, while 907.65 eV and 908.10 eV peaks were identified as Ce^{4+} []. However, the elemental peak at 917 eV is absent in Figure 4e, indicating absence or very small amounts of Ce^{4+} in this material, implying that while Ce is abundant, it mainly exists as Ce^{3+} [].

TGA analyzed material thermostability from 20–800 °C. During initial thermal treatment, Zr/Ce-UiO-66 and Zr/Ce-UiO-66-NH_2 underwent mass losses of approximately 9.53% and 7.33%, respectively, mainly due to thermal volatilization of water polymer in pore channels up to 200 °C. Subsequent slower pyrolysis

occurred from 200–800 °C, with mass loss primarily explained by MOF organic skeleton collapse and degradation. Notably, approximately 31.62% and 38.84% mass remained, implying thermal stability (Figure 1d).

Porosity is an important quality indicator for synthesized materials. N_2 adsorption-desorption experiments at 77 K investigated BET surface area and apertures. Figure 1d shows calculated surface areas of 974.67 $m^2 \cdot g^{-1}$ and 642.06 $m^2 \cdot g^{-1}$, indicating substantial specific surface areas. The microporous structure exhibited pore sizes concentrated at 3.28 nm for Zr/Ce-UiO-66 and 1.67 nm for Zr/Ce-UiO-66-NH_2. Data from Figures 1d and 1f demonstrate that amino functionalization modification resulted in decreasing trends for both indicators, though Zr/Ce-UiO-66-NH_2 still exhibits relatively high specific surface area, enabling excellent U(VI) adsorption through increased active sites.

B. Adsorption Experiments

Effect of pH. The pH of the reaction system significantly affects uranium distribution in water and material surface nature []. Uranium solutions (10 $mg \cdot L^{-1}$) were allowed to adsorb onto Zr/Ce-UiO-66-NH_2 at pH 2–10 for 6 h. Figure 5a [Figure 5: see original paper] shows that adsorption capacity was low at pH 2–4, increased rapidly at pH 5–8, peaked at pH 8, then declined at pH 8–10. The Zr/Ce-UiO-66 material with bimetallic central sites demonstrated significantly superior U(VI) removal compared to UiO-66 with single metallic sites. Additionally, dual-strategy-modified Zr/Ce-UiO-66-NH_2 exhibited higher U(VI) removal than bimetallic-modified Zr/Ce-UiO-66 or purely aminated UiO-66-NH_2, indicating promising potential for practical applications. The superior capacity of bimetallic materials may be attributed to the high Lewis-acid properties of Ce and 4f orbital interaction with the P=O bond facilitating reaction [], while cerium ions promote material-substrate interactions []. The superior performance of Zr/Ce-UiO-66-NH_2 over Zr/Ce-UiO-66 may be attributed to amino group introduction increasing binding site numbers.

Uranium exists in various ionic forms at different pH values. Fig. S2 shows the proportional occurrence of uranium species in aqueous solutions at different pH levels. In acidic environments, UO_2^{2+} is typically the dominant positively charged species []. As pH increases, chemical precipitation occurs in uranyl solutions. Figure 1c shows that at pH 6, the material surface carries a negative charge while uranium exists in its positively charged hexavalent form, generating electrostatic attraction that enhances U(VI) adsorption. At high pH (pH > 8), the primary U(VI) species are $UO_2(CO_3)_3^{4-}$ or $UO_2(OH)_3^-$, which are water-insoluble []. Under these conditions, uranium was eliminated via material adsorption and physical precipitation. Zeta potential data in Figure 1c further substantiate this sorption behavior. At lower pH (2–5), both materials showed positive zeta values, indicating favorable surface charge. Under these conditions, uranium predominantly exists as positively charged UO_2^{2+}, and electrostatic repulsion leads to significantly lower adsorption capacity. Nevertheless, at pH

6, both material surfaces possessed negative charge, and hexavalent uranium existed primarily as UO_2^{2+} polymers, generating more electrostatic attraction and enhanced adsorption capacity.

Although both materials performed more efficiently under alkaline conditions, higher pH levels in the studied uranium concentration range caused precipitation [], implying that experimental results only partially reflect adsorption characteristics. This study focused on treatment of weakly acidic nuclear wastewater, and both substances displayed satisfactory adsorption capabilities at pH 6. Considering all factors, adsorption experiments were conducted at pH 6.

Ionic Strength Effects. Ionic strength dependence is a valuable tool for identifying inner- and outer-surface complexes. In less dependent scenarios, inner-surface complexes are believed to form through adsorption []. This study examined U(VI) adsorbability on Zr/Ce-UiO-66 and Zr/Ce-UiO-66-NH_2 at different $NaNO_3$ concentrations. Various $NaNO_3$ amounts were added to 10 ppm uranium aqueous solutions and incubated for 6 h. Figures 6e and 6f show that adsorption curve alterations are nearly imperceptible even with $NaNO_3$ concentration changes, indicating that ionic strength does not interfere with uranium ion sorption. Changes in ionic strength did not significantly affect uranium ion sorption behavior, confirming our hypothesis that uranium ions adsorb onto the material by chemically binding to active sites and creating internal surface complexes.

Effect of Coexisting Ions. Nuclear industry wastewater contains numerous ions besides U(VI) that may significantly interfere with U(VI) removal efficiency. Therefore, investigating the impact of different electrolyte ions (including anions NO_3^-, Cl^-, CO_3^{2-}, SO_4^{2-} and cations K^+, Co^{2+}, Ni^{2+}, Mg^{2+}, Sr^{2+}, Zn^{2+}, and Ca^{2+}) on uranium elimination is imperative.

Adsorbent removal effects are shown in Figures 6a and 6b. Zr/Ce-UiO-66 and Zr/Ce-UiO-66-NH_2 achieved hexavalent uranium removal efficiencies of 62.4% and 69.6% in the presence of Ca^{2+}, and 69.6% and 63.6% in the presence of Sr^{2+}, respectively. Ternary Ca^{2+}–uranyl complex formation affects hexavalent uranium migration in water, potentially resulting in lower solubility and mobility []. Sr(II) presence in aqueous solution partially overlapped with U(VI) adsorption sites, including oxygen-containing functional groups (–OH, -C-O-C, and –COOH), resulting in competitive adsorption that affects U(VI) adsorption []. CO_3^{2-} and SO_4^{2-} anions significantly affected material adsorption performance, resulting in hexavalent uranium removal efficiencies of only 56.3% and 3.37% for Zr/Ce-UiO-66, and 58.8% and 2.17% for Zr/Ce-UiO-66-NH_2, respectively. SO_4^{2-} forms new, highly stable complexes with uranyl ions that diminish material adsorption properties []. Carbonates readily form negatively charged U(VI)–carbonate complexes that are not easily adsorbed on most materials []. Although ion effect magnitudes varied between the two materials, overall they were comparable, with effects on Zr/Ce-UiO-66-NH_2 slightly smaller than on Zr/Ce-UiO-66, attributable to amino group introduction increasing binding site numbers.

Histograms in Figures 6a and 6b show that ions other than the four mentioned previously have minimal influence on U(VI) adsorption. Therefore, when considering Zr/Ce-UiO-66-NH_2 effects on U(VI) adsorption, the focus should be on internal surface complexation.

Adsorption Kinetics. Practical MOF applicability derives from adsorption kinetics. U(VI) adsorption rates onto Zr/Ce-UiO-66-NH_2 were examined by maintaining substrate concentration at 50 $mg \cdot L^{-1}$ and measuring U(VI) concentrations at different time intervals. Figure 5b shows that Zr/Ce-UiO-66 adsorption kinetics were relatively slow, requiring almost two hours to reach equilibrium. Meanwhile, U(VI) adsorption onto Zr/Ce-UiO-66-NH_2 occurred quickly in the first forty minutes, followed by gradual equalization, requiring approximately one hour to reach equilibrium. This increased rate may be caused by actinide soft-donor amino groups, increased uranium ion affinity, and multiple uptake sites [].

Initially, the material offers abundant uranium-binding sites to absorb considerable U(VI) quantities. Upon U(VI) contact, adsorptive ability increases dramatically due to transient sorption or outer surface adsorption. As adsorption progresses, most surface sites become occupied, and resulting U(VI) diffuses inward to adhere to internal active sites for further adsorption, resulting in broader U(VI) diffusion range and decreased adsorption rate [].

As shown in Table 1 , to gain insights into U(VI) adsorption dynamics on both materials, we applied pseudo-first-order and pseudo-second-order kinetic models to experimental data (Equations (5) and (6) in Supporting Information). Figure 5b shows Zr/Ce-UiO-66-NH_2 reaching kinetic equilibrium within 50 min. Under identical conditions, dual-strategy-modified Zr/Ce-UiO-66-NH_2 reached adsorption equilibrium significantly earlier than single-strategy-modified Zr/Ce-UiO-66. U(VI) adsorption onto Zr/Ce-UiO-66-NH_2 is well-described by pseudo-second-order kinetics, as demonstrated by an R^2 value of 0.999 and q value of 216.16 $mg \cdot g^{-1}$, indicating that chemisorption primarily controls the uranyl adsorption rate [].

Adsorption Isotherms. Temperature significantly influences chemisorption. We studied uranium sorption on Zr/Ce-UiO-66-NH_2 to determine adsorption reaction type through batch experiments using substrate concentrations of 10–200 $mg \cdot L^{-1}$ at temperatures of 298 K, 313 K, and 328 K and pH 6. Maximum sorption ability was determined by studying adsorption isotherms, which showed increasing adsorption capacity across the entire concentration range studied. The previously reported optimal sorption capacity of UiO-66-NH_2 was approximately 114.4 $mg \cdot g^{-1}$ under equivalent pH conditions []. We synthesized Zr /Ce-UiO-66-NH_2 (x = 2, 1, 0.5) with different Zr:Ce ratios (2:1, 1:1, 1:2) and conducted adsorption experiments at pH 6 and 298 K. XRD plots in Figure S4 show that all three materials were well crystallized, with results in Figure S5 indicating optimal Zr/Ce-UiO-66-NH_2 adsorption performance at a Zr:Ce ratio of 1:1.

Figures 5c and 5d illustrate Zr/Ce-UiO-66-NH_2 adsorption effects at 298 K, 313 K, and 328 K and pH 6. At pH = 6.0 and 298 K, the dual-strategy-modified Zr/Ce-UiO-66-NH_2 achieved 376.8 $mg \cdot g^{-1}$ adsorptive capacity, compared to 293.8 $mg \cdot g^{-1}$ for bimetallic-modified Zr/Ce-UiO-66 and 114.4 $mg \cdot g^{-1}$ for aminated UiO-66-NH_2 [], revealing significantly better dual-strategy-modified material performance. At 313 K and 328 K, the material exhibited U(VI) extraction capacities of 433.84 $mg \cdot g^{-1}$ and 611.33 $mg \cdot g^{-1}$, respectively. Both isotherms show ascending gradients with increasing temperature, indicating that high temperatures promote adsorption. These experiments demonstrate that bimetallization and amination modification conferred Zr/Ce-UiO-66-NH_2 with superior U(VI) adsorption ability.

Experimental data were fitted to Langmuir and Freundlich models to determine agreement with theoretical data and explain the adsorptive process. Data in Table 2 align more closely with the Langmuir model, as indicated by R^2 values, illustrating that active sorption sites were uniformly distributed across the adsorbent, forming a monolayer on the surface. The results indicate Zr/Ce-UiO-66 and Zr/Ce-UiO-66-NH_2 adsorbed 293.8 $mg \cdot g^{-1}$ and 376.8 $mg \cdot g^{-1}$ of U(VI), respectively, at 298 K, consistent with recorded data. Moreover, both nanomaterials exhibited superior adsorption performance compared to many other MOFs. Ce incorporation enhances material-U(VI) interactions [], while amino group integration increases available binding sites []. Both materials exhibited exceptional adsorption properties, making them ideal adsorbents for radionuclide eradication (Table 3).

Recyclability. To evaluate absorbent application potential, reusability must be considered. Each material (10 mg) was dissolved in 100 mL of 10 ppm uranium solution at pH 6.0, and the reaction progressed for 12 h on a shaker. After centrifugal solid-liquid separation, supernatant uranium content was tested. The solid phase was submerged in 0.5 M Na_2CO_3 solution for 6 h to facilitate desorption, then washed with ultrapure water to neutrality and vacuum-dried for subsequent cycles. This process was repeated five times, with uranium removal efficiency determined for each trial. Figures 6c and 6d show that more than 80% of initial uranium was recovered from Zr/Ce-UiO-66 and Zr/Ce-UiO-66-NH_2 after five cycles, indicating that sorption efficiencies remained unaffected. Both materials exhibit excellent recyclability and can be used continuously for long-term wastewater treatment.

Both MOFs were submerged in acidic, alkaline, and neutral solutions with varying pH values for 24 h, then washed to neutral pH. The resulting precipitate was dried by centrifugation and analyzed using XRD. As illustrated in Figures 5e and 5f, MOF structural integrity remained unaffected after submersion in 6 M HCl or 0.5 M NaOH aqueous solutions, showing high structural stability in acidic and alkaline solutions, exceptional acid and chemical resistance, and potential for effective practical applications.

III. Possible Adsorption Mechanism

Chemisorption and physisorption are widely accepted methods for separating heavy metal ions from powdered materials. We conducted numerous experiments to ascertain potential U(VI) adsorption mechanisms on Zr/Ce-UiO-66 and Zr/Ce-UiO-66-NH_2, including FTIR, XRD, zeta potential, and XPS analyses. Under different pH conditions, Zr/Ce-UiO-66-NH_2 with bimetallic central sites exhibited superior uranium removal performance compared to Zr/Ce-UiO-66 or UiO-66-NH_2. Notably, Zr/Ce-UiO-66-NH_2 modified by dual bimetallization and amination strategies showed further improved uranium sorption properties compared to Zr/Ce-UiO-66, indicating better application potential for the newly produced substance.

The increased uranium absorption ability of Zr/Ce-UiO-66-NH_2 might result from Ce addition to UiO-66 during synthesis, which may lead to isomorphic substitutions generating defects that reveal more acidic locations. Enhanced uranium adsorption may be attributed to several factors: Ce(IV) has strong Lewis-acid properties, the 4f orbital of Ce(IV) can facilitate reactions, and Ce enhances substance-U(VI) interactions []. The high uranium sorption performance of Zr/Ce-UiO-66-NH_2 could also be linked to amino groups increasing available binding sites []. Zeta potential testing indicated Zr/Ce-UiO-66-NH_2 was negatively charged at pH 6, suggesting higher electrostatic interaction between the surface adsorbent and UO_2^{2+} ions (Figure 1c).

XRD analysis determined changes in Zr/Ce-UiO-66 and Zr/Ce-UiO-66-NH_2 before and after uranium adsorption to investigate chemical stability, as shown in Figure 5f. XRD patterns of native and uranium-loaded samples showed no noticeable discrepancies, indicating that Zr/Ce-UiO-66-NH_2 crystal structure remained unchanged after U(VI) adsorption. XPS scrutinized Zr/Ce-UiO-66-NH_2 changes after uranium absorption, as illustrated in Figures 7 and 8. Comparing the two substances' spectra and high-resolution U 4f XPS spectra indicates that U $4f_5/_2$ and U $4f_7/_2$ peaks correspond to 392.80 eV and 382.10 eV in Figure 7e [Figure 7: see original paper] and 392.55 eV and 382.70 eV in Figure 8e [Figure 8: see original paper], confirming reliable uranium adsorption.

The UiO-66 framework cell contained two Zr-O bond variants: the Zr-O-Zr bond and the Zr-H_2BDC connection (specifically Zr-O interconnection). Figures 7c and 8c show two Zr-O bonds at 183.20 eV and 185.50 eV, with the 185.50 eV peak corresponding to Zr-O-Zr bonds and the 183.15 eV peak representing the second Zr-O bond type, consistent with prior research []. Figure 7c also shows Zr-O binding energy decreasing from 183.15 eV to 182.53 eV after uranium adsorption, implying that Zr-O plays a significant role in uranium adsorption []. Comparison of O 1s spectra before and after uranium sorption (Figures 7b and 8b) reveals shifts and peak changes, with C-O and C=O peak intensities and areas decreasing while Zr-O peaks increased. These findings suggest that oxygen-containing functional groups facilitate U(VI) pre-enrichment throughout the reaction process, with surface complexes formed between U(VI) and

various functional groups (specifically C-O and C=O containing groups) significantly controlling removal. Meanwhile, N 1s peak intensity (Figures 4c and reffig:3f) corresponding to -NH_2 groups decreases significantly after U(VI) adsorption, suggesting amino groups play a significant role in uranium adsorption, contributing to increased uranium-adsorption capacity of Zr/Ce-UiO-66-NH_2.

After analyzing characterization, kinetic, and isothermal experimental results, we assessed potential causes and mechanisms underlying Zr/Ce-UiO-66-NH_2's remarkable sorption performance. Sorption was almost unaffected by ionic strength changes, and combined with pH effects, functional groups such as N-H, C=O, C-O, Ce-O, and Zr-O were present on the material surface where uranyl ions formed inner-sphere surface complexes by direct binding. Additionally, at pH 6.0, UO_2^{2+} interacted with the negatively charged adsorbent via electrostatic attraction, resulting in prompt removal. The remarkable acid-base and chemical stability, exceptional adsorption capacity, and recyclability of dual-strategy-modified Zr/Ce-UiO-66-NH_2 suggest promising potential for wastewater treatment. An adsorption mechanism diagram is shown in Figure 9 [Figure 9: see original paper].

IV. Conclusion

This study employed a simple method to synthesize octahedral-structured Zr/Ce-UiO-66-NH_2 nanomaterial using dual bimetallization and amination strategies to extract uranium from aqueous solutions. Batch experiments demonstrated that at pH 6.0, Zr/Ce-UiO-66-NH_2 achieved uranium sorption capacities of 376.8 $mg \cdot g^{-1}$ and 611.33 $mg \cdot g^{-1}$ at 298 K and 328 K, respectively—significantly better than bimetallic-modified Zr/Ce-UiO-66 or amine-functionalized UiO-66-NH_2. Kinetic and isotherm studies indicated that Zr/Ce-UiO-66-NH_2 undergoes spontaneous single-molecule chemisorption, with uranium ions predominantly preserved through chemical bonding to active sites, forming internal surface complexes. Cycling experiments demonstrated good recovery performance and structural stability. Ce introduction exposes more active sites and increases substance-U(VI) interaction, while amino group incorporation increases binding site numbers, facilitating uranium binding to Zr/Ce-UiO-66-NH_2. Possible adsorption mechanisms include internal surface complexation, chemisorption, and electrostatic interactions.

In brief, this study demonstrated the benefits of dual strategies for modifying Zr/Ce-UiO-66-NH_2 to remove hexavalent uranium, suggesting promising applications for treating uranium-containing wastewater.

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Conflicts of Interest. The authors declare no competing interests.

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Note: Figure translations are in progress. See original paper for figures.