Design of a renewable hydroxyapatite-biocarbon composite for the removal of uranium(VI) with high-efficiency adsorption performance

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Abstract
The hydroxyapatite-loaded swine manure derived-biocarbon was successfully prepared by pyrolysis method for the adsorption of uranium(VI). The results of the adsorption experiments displayed that the adsorption behaviors for uranium(VI) of biocarbon did almost not depend on the interfering ions except Al\(^{3+}\), Ca\(^{2+}\) and CO\(_3^{2-}\), showing the high selectivity of the composites for uranium(VI). The maximum static and dynamic removal capacity of the hydroxyapatite-biocarbon composites to uranium(VI) were 834.8 and 782.8 mg/g (pH = 3, m/V = 0.1 g/L and T = 298 K), far exceeding other reported biocarbon and hydroxyapatite materials, which indicated that the hydroxyapatite-biocarbon composites possessed an application potential in adsorption. After five cycles of adsorption–desorption processes, the removal efficiency of the hydroxyapatite-biocarbon composite for uranium(VI) was 93.2% (C\(_i\) = 5 mg/L, pH = 3, m/V = 0.1 g/L and T = 298 K), revealing that the composite had excellent stability and reusability. Moreover, the capture mechanisms of the hydroxyapatite-biocarbon composite for uranium(VI) included ion exchange and complexation, which was ascribed to the ample active adsorption sites (–OH and PO\(_4^{3-}\)). Therefore, the hydroxyapatite-loaded swine manure derived-biocarbon would be a potential material to effectively separate uranium(VI) from solution.

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Highlights

1. The recyclable high-efficiency Hap@BC was prepared for U(VI) removal.
2. The adsorption capacity for U(VI) of Hap@BC-10% achieved 834.8 mg/g.
3. The U(VI) extraction efficiency reached 99.9% in dynamic adsorption.
4. The interaction mechanism between U(VI) and Hap@BC was clearly expounded.

Keywords Hap@BC · Adsorption · Uranium(VI) · Regeneration · Interaction mechanism

1 Introduction

Uranium(VI) (U(VI)) is the most widely distributed natural radioactive metal element in the earth’s crust, which can be applied in nuclear energy engineering fields due to its efficient and economic characteristics (El-Maghrabi et al. 2019). With the rapid development of the global nuclear industry, a large amount of U(VI)-containing wastewater has been produced from several industrial activities, such as fossil fuel extraction and development of nuclear weapons, resulting in the increase of potential risks and threats to natural environment and human health (Lei et al. 2022; Tal et al. 2022). For example, the excessive exposure of U(VI)-containing wastewater will lead to serious diseases to creatures such as nephritis, neurological disorders and even cancer (Jin et al. 2021). Therefore, the removal of U(VI) from wastewater before discharge became a hot topic in many research areas. In recent years, a series of solid materials have been developed to remove U(VI) from wastewater, such as hydroxyapatite (Hap), biocarbon, metal oxides and resin (Liao et al. 2021; Yue et al. 2021; Hu et al. 2020).

Among these materials, Hap, a typical Ca-P mineral, which generally exists in hard tissues and phosphate mineral rocks, possesses a high removal capacity and efficiency for the numerous divalent cations owing to its high stability and unique crystal structure (Hassanein et al. 2021). However, the pure nano-Hap (nHap) is easy to agglomerate during use, resulting in many active sites on nHap to be coated and hidden, which will greatly inhibit its ability to remove pollutants (Zhou et al. 2021; Biedrzycka et al. 2021). Therefore, it is important to avoid the agglomeration behavior of Hap for improving its adsorption performance. It is reported that
Hap can be evenly loaded on suitable support materials, such as graphene, carbon nanotubes, MXene and polymer materials, which will effectively prevent its agglomeration behavior and improve its adsorption performance. For example, Su et al. (2021) prepared a graphene oxide material functionalized with nHap to efficiently remove uranium(VI) (U(VI)) in solution with excellent adsorption performance and the maximum removal capacity of the composite material was 373 mg/g. Wang et al. (2017) obtained a Hap-loaded carbon nanotube material through hydrothermal method, which showed a strong response to heavy metal ions. Kede et al. (2012) reported a polymer material loaded with Hap, which showed the in-situ adsorption performance of Hap to metal ions could be greatly improved by dispersing Hap on polymer. However, the application of these support materials in treating wastewater was limited owing to the high cost of graphene and carbon nanotubes and the complex synthesis process of polymers (Qin et al. 2021; Son and Park 2019; Choong et al. 2021). Therefore, it was very important to develop a support material with low cost and simple preparation process to prevent the agglomeration behavior of Hap.

In recent years, Hap is usually loaded on other economical materials to reduce cost, such as biochar (BC), g-C₃N₄ and metal oxide. Among these materials, BC is widely applied as a support material of Hap in the remediation of water environment due to its excellent physical properties (high specific surface area and good dispersion) and aplyent active functional groups related to the affinity of heavy metals (Zhou et al. 2022; Chen et al. 2021a). Besides, BC was an environment-friendly material that were usually prepared by thermochemical conversion of animal and plant residues, which not only realized the reuse of waste, but also reduced the carbon emissions (Dong et al. 2021; Huang et al. 2019; Liang et al. 2021). Especially, the animal manure-derived BC has attracted extensive attention in removing heavy metals (Idrees et al. 2018; Qiu et al. 2021). Considering the advantages of Hap and animal manure-derived BC, the combination of these two materials might obtain a novel and efficient material for the remediation of wastewater. In depth, loading Hap on the surface of BC could provide abundant functional groups for BC and Hap possessed great affinity to divalent cation, which would increase the adsorption potential of BC (Ahmed et al. 2021). However, the adsorption performance of the composite would be limited due to the agglomeration of excessive Hap particles and the loss of active sites in pyrolysis process (Li et al. 2019). Therefore, it is significance to explore the effects of the doping amount of Hap on the adsorption performance of BC. Moreover, Hap-based materials were extremely difficult to reuse, indicating that the development of a renewable Hap-based material is meaningful.

In this work, three kinds of Hap-BC composites with different content of Hap were prepared using swine manure (SM) as the biocarbon source and the adsorption properties of the composites were evaluated with U(VI) as cation source. The purpose of this paper was: (1) to provide a new idea for reasonable treatment of the SM, (2) to prepare a renewable Hap-loaded biocarbon for U(VI) adsorption, (3) to discuss the effect of the content of Hap on U(VI) adsorption behavior, and (4) to research in depth the capture mechanisms of the Hap-BC composite for U(VI).

2 Experimental

2.1 Reagents and chemicals

SM was obtained from a piggery in Sichuan Province, which was directly used after strong dispersion. Hydrochloric acid (36.0–38.0%), NaOH (98.0%), Ca(NO₃)₂ (> 97.5%), (NH₄)₂HPO₄ (98.5%), Na₂CO₃ (99.8%), NaNO₃ (99.5%), NaClO₃·H₂O (99.5%), Na₂SO₄ (99.5%), Na₃PO₄ (99.5%), NaCl (99.5%), KCl (99.5%), CaCl₂ (96.0%), MgCl₂ (99.0%), AlCl₃·6H₂O (97.0%) and ZnCl₂ (98.0%) were obtained from Chengdu Chron Chemicals. Arsenazo (III) (99.9%) and UO₂(NO₃)₂·6H₂O (> 99.5%) were purchased from Aladdin Industrial Corporation. Deionized water was used throughout the experiment.

2.2 Preparation of Hap-BC composite

2.2.1 Preparation of modified SM

The collected SM was dispersed with strong stirring in deionized water for 1 h to remove the soluble organic substance. After drying, the solid was immersed in KMnO₄ solution with a concentration of 0.1 mol/L for the surface modification of SM. Then, the modified SM was dried under natural pressure at 60 °C for 24 h.

2.2.2 Preparation of Hap@BC-5%, Hap@BC-10% and Hap@BC-15%

About 9 g of the modified SM was strongly dispersed in 50 mL of Ca(NO₃)₂ solution (0.2 mol/L) to obtain a suspension. Subsequently, 50 mL of (NH₄)₂HPO₄ solution (0.12 mol/L) was slowly dripped into the suspension under vigorously stirring to prepare the SM-Hap suspension, which was freeze-dried for about 50 h to gain the SM-Hap composite. Then, the SM-Hap composite was pyrolyzed at 500 °C under nitrogen atmosphere for 2 h to synthesize Hap-BC composite (The mass percentage of Hap was 10%), which was named Hap@BC-10%. Finally, Hap@BC-5% and Hap@BC-15% were prepared according to the same method. Moreover, the modified SM was directly calcined to prepare pure bio-carbon (BC).
2.3 Characterization and batch experiments

FT-IR spectra were recorded on a fourier transform infrared spectroscope (FT-IR, 380FT-IR, America) in the range between 4000 and 400 cm$^{-1}$. The crystallographic structures were determined via a powder X-ray diffractometer (XRD, TD3500, China) with Cu-Ka radiation over the 2θ range from 3 to 80° (10°/min). The specific surface area and pore size distribution were characterized by N$_2$ adsorption–desorption analyzer (ASAP 2460 3.01, America) and the corresponding data analysis was estimated by using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. The morphology of BC, Hap@BC-5%, Hap@BC-10% and Hap@BC-15% was characterized by scanning electron microscopy (SEM, Ultra55, Germany).

In this work, a certain amount of UO$_2$(NO$_3$)$_3$·6H$_2$O was dissolved in 100 mL of nitric acid (0.1 mol/L) and then diluted to 1 L with deionized water to obtain uranyl solution. The adsorption properties of Hap@BC-5%, Hap@BC-10% and Hap@BC-15% towards U(VI) were evaluated through batch experiments under different conditions, such as different initial pH, different initial U(VI) concentration, different interfering ions, different ionic strength and different contact time. Before adsorption, hydrochloric acid solution (pH = 1) and NaOH solution (pH = 13) were used to adjust the initial pH of U(VI) solution. After adsorption, the polyethersulfone filter (0.22 µm) was used to separate Hap@BC from solution. The U(VI) concentration in solution was assessed using a UV–vis spectrophotometry at the wavelength of 651 nm (UV, UV-1900PC) (Chen et al. 2021b; Wang et al. 2021).

The equilibrium removal percentage (RP, %) and adsorption capacity ($Q_e$, mg/g) of Hap@BC for U(VI) could be calculated according to the adsorbent mass (m, mg), liquid volume (V, mL), equilibrium concentration of U(VI) ($C_e$, mg/L) and initial concentration of U(VI) ($C_i$, mg/L) (Eqs. 1 and 2). Moreover, the structure and morphology of Hap@BC-5%, Hap@BC-10% and Hap@BC-15%-U was analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, America), scanning electron microscopy (SEM, Ultra55, Germany), Fourier-transform infrared spectrometer (FT-IR, 380FT-IR, America) and powder X-ray diffractometer (XRD, TD3500, China) to explore the removal mechanism of Hap@BC to U(VI).

\[
Q_e = \frac{C_i V - C_e V}{m} \tag{1}
\]

\[
RP = \left(\frac{C_i - C_e}{C_i}\right) \times 100\% \tag{2}
\]

3 Results and discussion

3.1 Characterization

As shown in Figure S1, the bulk SM was transformed into powder after KMnO$_4$ pretreatment. The Hap nanoparticles were in-situ formed on the surface of modified SM via precipitation method to obtain gray white solid (SM-Hap composite). Then, the SM-Hap composite was pyrolyzed at 500 °C under nitrogen atmosphere to gain the black Hap-BC composite. It was worth mentioning that the Hap-BC composite possessed fluffy structure, which could be conducive to the U(VI) adsorption in solution. Besides, the preparation of Hap-BC composite using SM as the raw material could not only solve the problem of soil damage caused by nutrient elements in SM, but also reduce the risk of water damage caused by U(VI)-containing wastewater.

The structure and morphology of Hap@BC-5%, Hap@BC-10% and Hap@BC-15% were analyzed by FT-IR spectra, XRD patterns, N$_2$ adsorption desorption curves and SEM images. As shown in Fig. 1a, the broad peak of BC at about 1053 cm$^{-1}$ was attributed to the stretching vibration of C–O bonds. After the incorporation of Hap, two new peaks were observed at 1040 and 1072 cm$^{-1}$, which were the characteristic bands of the phosphate stretching vibrations, proving that Hap was successfully incorporated into BC (Xuan et al. 2022; Han et al. 2022; Wu et al. 2019). The XRD patterns of BC, Hap@BC-5%, Hap@BC-10% and Hap@BC-15% are shown in Fig. 1b. With the increase of Hap content, the crystallization peak of BC significantly weakened and the new diffraction peaks at 31.9, 32.4 and 33.0° were observed, which corresponded to (211), (300) and (202) plane of Hap, respectively (Londoño-Restrepo et al. 2020; Ferreira et al. 2022), indicating that Hap nanoparticles were doped into BC through chemical bonding due to the altered crystallinity of the BC-based material (Li et al. 2022).

As shown in Fig. 1c, the N$_2$ adsorption–desorption isotherms of Hap@BC-5%, Hap@BC-10% and Hap@BC-15% belonged to type IV with a distinct hysteresis loop (P/P$_0$ > 0.4), indicating that Hap@BC-5%, Hap@BC-10% and Hap@BC-15% had complex and disorder pore structure (Wu et al. 2019), which were further confirmed by the BJH pore size distributions (Fig. 1d). Besides, comparing Hap@BC-5% (128.6 m$^2$/g) with Hap@BC-10% (155.2 m$^2$/g), the increase in specific surface area might be attributed to the formation of some narrow and deep pores during the precipitation of Hap nanoparticles (El-Maghrabi et al. 2019). The specific surface area of Hap@BC-15% (125.4 m$^2$/g) decreased due to the aggregation of excessive Hap nanoparticles.
The SEM images were used to analyze the morphology of the obtained BC, Hap@BC-5%, Hap@BC-10% and Hap@BC-15% (Figure S2). It was observed that the surface of BC had microporous and fluffy structure, which could provide the suitable location for the adsorption of U(VI) on the surface. After doping Hap nanoparticles, many fine particles were adhered to the surface of BC, which could raise the contact points for U(VI) in the solution. However, as the content of Hap nanoparticles increased, the carbon layers with dense structure appeared in Hap@BC-15% and the heterogeneous agglomerates were randomly attached on the carbon layers, which might cause the coating of active sites, thereby reducing its U(VI) adsorption ability.

3.2 Adsorption

3.2.1 Effect of pH

The surface charge of adsorbent and the ionization degree of U(VI) might be changed with the change of pH value, which showed that the pH value of solution was an important factor in the removal process (Verma and Kim 2022; Nezhad et al. 2021). As shown in Fig. 2a, the removal percentage of U(VI) first increased sharply and then decreased slowly with the pH of the solution increasing from 2 to 10. At the optimum pH (pH = 3), the maximum removal percentage of Hap@BC-5%, Hap@BC-10% and Hap@BC-15% reached 94.9%, 98.7% and 95.7%, respectively (Ci = 5 mg/L and m/V = 0.1 g/L). As expected, Fig. 2b shows that the change of the adsorption efficiency of Hap@BC-5%, Hap@BC-10% and Hap@BC-15% to U(VI) followed the similar trend at high concentrations (Ci = 50 mg/L). It was interesting to note that Hap@BC-10% still possessed a strong adsorption ability for U(VI) even at high U(VI) concentrations, which indicated that Hap@BC-10% has a potential to be applied to high-efficiency separation of U(VI) at large-scale level.

For further studying the removal behavior of Hap@BC-5%, Hap@BC-10% and Hap@BC-15% for U(VI) at various pH, the existing forms of U(VI) species at different pH were simulated and the surface charge of the adsorbent at different pH was studied. As displayed in Fig. 2c and d, U(VI) species in the solution with the pH in the range from 2 to 4 mainly existed in the form of free uranyl ions (UO\(_2^+\)). When the pH increased from 4 to 7, U(VI) began to form uranyl/hydroxy complexes, such as UO\(_2\)(OH\(_2\))\(^+\), UO\(_2\)(OH\(_2\))\(_2\) (aq), (UO\(_2\))\(_2\)(OH\(_7\))\(^+\) and (UO\(_2\)\(_3\))(OH\(_5\))\(^+\) (Zhu et al. 2018).
When pH exceeded 7, U(VI) species were further complexed with OH\(^-\) to form the negatively charged complexes due to the increasing concentration of OH\(^-\) in the solution (Li et al. 2018; Song et al. 2019). When UO\(_2^{2+}\) ions were transformed into uranium hydroxide complexes with stable structure, the adsorption affinity of the adsorbent to U(VI) species would decrease sharply due to the occupation of sites of U(VI) species (Liu et al. 2022; Zhu et al. 2021). Moreover, the pH value at the zero-charge point (pHzcp) was estimated via potentiometric titration. As shown in Figure S3, the pHzcp value of Hap@BC-10% was 6.23, which illustrated that the surface potential of the Hap@BC-10% showed a negative charge when pH < 6.23, while the particles showed a positive charge when pH > 6.23 (Wang et al. 2022). In other words, the binding sites on Hap@BC-10% tended to be protonated in combination with H\(^+\) at low pH (pH < 3). As the pH increased to 3, the protonation degree of Hap@BC-10% decreased, which would lead to the enhancement of the chelation with UO\(_2^{2+}\). Besides, an ionization of the Hap nanoparticles loaded on Hap@BC-10% occurred at pH = 3, supplying the adsorption system with phosphate ions which have high affinity for U(VI), precipitating and forming a new phase of H\(_2\)(UO\(_2\))\(_2\)(PO\(_4\))\(_2\)·8H\(_2\)O (Guo et al. 2020a). With the continuous rising of pH (3 < pH < 6), although the surface of Hap@BC-10% was negatively charged, the response of Hap@BC-10% to U(VI) species was decreased because –OH occupied the sites of U(VI) species. In general, Hap@BC-10% possessed excellent adsorption ability at pH = 3, which was mainly ascribed to the weakening of the protonation degree of the Hap@BC-10% and the enhancement of the adsorption affinity between Hap and UO\(_2^{2+}\).

3.2.2 Effect of the type and strength of interfering ions

The high selectivity for U(VI) is a crucial standard to assess the application value of adsorbent owing to a large number of common interfering ions in radioactive wastewater (Zhang et al. 2019; Ahmad et al. 2021). As shown in Fig. 3a
and b, it was quite clear that the influence of interfering ions on the U(VI) removal of Hap@BC-5%, Hap@BC-10% and Hap@BC-15% was comparatively weak, suggesting that the Hap@BC materials might possess a strong adsorption affinity and ability to U(VI) and it was a suitable adsorbent for separating U(VI) from multicomponent system. For

![Fig. 3](image-url)
interfering cations (C = 50 mg/L), the response of Hap@BC to high valence cations (Al³⁺ and Ca²⁺) was stronger than monovalent cations (K⁺ and Na⁺), which could be attributed to the fact that high valence cations were relatively easy to be bound caused by the excess number of electrons available for interaction comparing with monovalent cations (Huang et al. 2018). On the other hand, according to the order of hydrated radius of ions, Na⁺ (0.178 nm) < K⁺ (0.201 nm) < Mg²⁺ (0.300 nm) < Zn²⁺ (0.404 nm) < Ca²⁺ (0.412 nm) < Al³⁺ (0.480 nm) (Tansel et al. 2006; Tansel 2012). Al³⁺ ions were preferentially bound by Hap@BC due to the bigger hydrated radius. In the adsorption process, the large hydrated radius of the adsorbate compressed the double electron layer of adsorbent, resulting in the aggregation of adsorbent, which would decrease the availability of the active site (Hui et al. 2005; Zhou et al. 2021). For co-existing anions (C = 50 mg/L), the separation of U(VI) on Hap@BC was evidently inhibited by CO₃²⁻ and PO₄³⁻, which was attributed to the formation of the soluble U(VI) species caused by the strong complexation between CO₃²⁻/PO₄³⁻ and U(VI), such as UO₂CO₃, UO₂(CO₃)₂²⁻, UO₂PO₄⁻ and UO₂HPO₄ (Fig. 3c and d). In summary, the process of U(VI) removal on Hap@BC was unaffected by most of interfering ions and Hap@BC could effectively and selectively adsorb U(VI) from water, which meant that Hap@BC possessed good application potential in separating U(VI) from wastewater.

Generally, the concentration of interfering ions in actual wastewater was high (Yin et al. 2019; Huang et al. 2020). In this study, the removal behavior of Hap@BC to U(VI) under different ionic strength (5, 50, 500 mg/L) was studied. For NaNO₃ (Fig. 3e), even if the concentration of NaNO₃ increased to 500 mg/L, the removal efficiency of Hap@BC remained constant, indicating that the adsorption of U(VI) on Hap@BC was mainly controlled by inner-sphere surface complexation process and the chemical bonds were formed between U(VI) and active functional groups on Hap@BC (Han et al. 2018). For Ca(NO₃)₂ and Al(NO₃)₃ (Fig. 3f and Figure S4), as the concentration of Al³⁺ and Ca²⁺ increased, the adsorption percentage for U(VI) on Hap@BC significantly decreased. Comparing with Ca²⁺, Al³⁺ had obvious inhibition on the removal ability of Hap@BC, which further indicated that the adsorbent preferentially adsorbed the ions with large hydration radius. It was worth mentioning that Hap@BC-10% still had a certain removal efficiency for U(VI) at high ionic strength, which revealed that there were enough active sites on Hap@BC-10% for its application potential in separating U(VI).

### 3.2.3 Effect of contact time and initial concentration

The influence of contact time on U(VI) adsorption by Hap@BC-5%, Hap@BC-10% and Hap@BC-15% is displayed in Fig. 4a. Hap@BC-5%, Hap@BC-10% and Hap@BC-15% responded strongly to U(VI) within the first 2 min and reached adsorption equilibrium within 5 min. It was encouraging that Hap@BC-10% displayed a favorable adsorption process and the removal percentage was close to 100% (98.7%), indicating that Hap@BC-10% possessed excellent removal ability for U(VI). The high efficiency of Hap@BC-10% for U(VI) removal was probably traceable in the abundant surface functional groups, which could offer sufficient binding sites for U(VI).

The relationship between equilibrium concentration of adsorbate in solution and adsorption capacity was very central for understanding the removal behavior and optimizing the removal process (Song et al. 2019; Zhang et al. 2018). Figure 4b shows the effect of initial U(VI) concentration on the adsorption behavior of Hap@BC. The loading of U(VI) on the adsorbent increased significantly with the increase of initial concentration. At relatively high U(VI) concentration, the adsorption capacity reached equilibrium, indicating that the available binding sites on Hap@BC-5%, Hap@BC-10% and Hap@BC-15% reached saturation (Sureshkumar et al. 2010). Comparing with Hap@BC-5% and Hap@BC-15%, the experimental value of Q_m of Hap@BC-10% was 772.8 mg/g, exceeding that of Hap@BC-5% (567.6 mg/g) and Hap@BC-15% (667.6 mg/g). This might be because Hap was evenly loaded on biocarbon in Hap@BC-10% and Hap did not agglomerate due to the appropriate addition amount, while the agglomeration of Hap particles occurred in Hap@BC-15%. For Hap@BC-5%, its effective active sites were relatively less, which resulted in a lower adsorption capacity than Hap@BC-10%. In a word, Hap@BC-10% was a more efficient adsorbent for U(VI) due to its relatively high adsorption capacity.

### 3.2.4 Effect of adsorbent dosage

The dosage of Hap@BC-5%, Hap@BC-10% and Hap@BC-15% would lead to the change of removal percentage (Zhang et al. 2017). As shown in Figure S5, the adsorption percentage of U(VI) on Hap@BC-5%, Hap@BC-10% and Hap@BC-15% increased to 99% when the dosage increased to a certain amount, which might be partly explained by the fact that the high dosage of Hap@BC-5%, Hap@BC-10% and Hap@BC-15% supplied enough effective active sites. It was worth mentioning that the adsorption efficiency for U(VI) on Hap@BC-10% exceeded 99.8% and the concentration of residual U(VI) in solution was less than 10 μg/L (C_i = 5 mg/L, pH = 3 and m/V > 0.3 g/L), reaching the limit value of the World Health Organization (30 μg/L). The result revealed that Hap@BC-10% possessed great prospects in removing U(VI) from wastewater.
3.2.5 Dynamic adsorption

The U(VI) removal capacity and efficiency of Hap@BC-10% were higher than those of Hap@BC-5% and Hap@BC-15%. Therefore, a self-made filter (Figure S6) was applied to further research the dynamic removal behavior of Hap@BC-10% for U(VI). In dynamic adsorption process, the flow rate of the liquid remained constant and it was not affected by the external conditions. 1.0 L U(VI)-containing liquid repeatedly flowed through the filter with 100 mg Hap@BC-10% for 5 times to complete the dynamic adsorption process. As shown in Fig. 4c, the U(VI) was completely removed in the solution with Cᵢ = 3 mg/L after the solution was circulated once. For the U(VI) solution with Cᵢ = 50 mg/L, the adsorption efficiency was 90.4% after the solution was circulated once and the adsorption efficiency increased to 99.1% with the increase of cycle times (4 times). Figure 4d shows the relationship between adsorption capacity/efficiency and initial U(VI) concentration. The separation efficiencies of Hap@BC-10% for U(VI) were above 99.0% at low concentrations (Cᵢ < 50 mg/L). In other words, Hap@BC-10% could nearly completely separate U(VI) from water at low concentrations, further proving that Hap@BC-10% was a potential material to separate U(VI) for large-scale application. As the initial U(VI) concentration rose to 75 and 100 mg/L, the removal capacity of Hap@BC-10% for U(VI) achieved 735.2 and 782.8 mg/g and the removal efficiency was only 98.0% and 78.3%, which might be attributed to the fact that the active sites on Hap@BC-10% were almost completely occupied by U(VI). Therefore, it could be considered that Hap@BC-10% would be an ideal adsorbent for separating U(VI) owing to its high dynamic removal capacity and efficiency.

3.2.6 Adsorption kinetics and isotherms

For analyzing the control steps of adsorption process, intra-particle diffusion, Elovich, pseudo-second-order (PSO)
and pseudo-first-order (PFO) kinetic models were used to match the experimental data (Equations S1 ~ S6) (Zhang et al. 2020; Yuan et al. 2020). The PFO can well describe the physical adsorption behavior, the PSO presumes that the rate-limiting step is essentially chemisorption, the Elovich kinetic model considers that the rate-controlling step is the diffusion of the target ions and the intraparticle diffusion kinetic model assumes that the internal diffusion is a velocity-controlled step (Liao et al. 2020). As shown in Fig. 5, Figure S7 and Table 1, the $Q_e$ of PSO was close to the experimental value and the correlation coefficient ($R^2$) was relatively high comparing with PFO and PSO model also displayed that the adsorption rate was proportional to the square of unoccupied active sites. In other words, PSO model could be relatively well to describe the removal for U(VI) by Hap@BC, clarifying that chemical adsorption dominated the U(VI) removal process (Zhao et al. 2019; Abdelwahab et al. 2015). As shown in Fig. 5c, the adsorption process of U(VI) on Hap@BC contained two stages.

![Fig. 5 Adsorption kinetic models: a Nonlinear PFO model, b Nonlinear PSO model, c Intraparticle diffusion model and d Elovich model](image)

| Table 1 Kinetic parameters of U(VI) adsorption on Hap@BC-5%, Hap@BC-10% and Hap@BC-15% |
|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| Models | Parameters | Samples |
|--------|------------|---------|
| PFO    | $K_1$ (min⁻¹) | Hap@BC-5% | Hap@BC-10% | Hap@BC-15% |
|        | $Q_e$ (mg·g⁻¹) | 1.879 | 2.511 | 2.195 |
|        | $R^2$ | 0.995 | 0.998 | 0.998 |
| PSO    | $K_2$ (g·min⁻¹·mg⁻¹) | 0.107 | 0.204 | 0.153 |
|        | $Q_e$ (mg·g⁻¹) | 47.5 | 49.6 | 48.0 |
|        | $R^2$ | 0.999 | 0.999 | 0.999 |
| Elovich | $\alpha$ (4.03 * $10^8$ | 7.48 * $10^{16}$ | 2.80 * $10^{12}$ |
|         | $\beta$ | 0.464 | 0.840 | 0.650 |
|         | $R^2$ | 0.997 | 0.998 | 0.997 |
The first stage was the dispersion of U(VI) species to the surface of Hap@BC and the second stage occurred inside of them (Yang et al. 2021). It was noteworthy that the curves did not pass through the origin, showing that the intraparticle diffusion was not the only speed-control factor (Ren et al. 2016). For Elovich kinetic model (Fig. 5d), the value of $\beta$ was much smaller than $\alpha$, showing that the equilibrium time of the adsorption process was relatively short. All in all, the speeding-control factor of adsorption process include chemical bonding and intraparticle diffusion.

The isotherm models were used to study the removal behavior for U(VI) (Equations S7 ~ S12) (Kushwaha et al. 2020; Zhang et al. 2021), including Langmuir, Freundlich, Sips and Redlich–Peterson (R–P) isotherm models. The Langmuir model assumes that monolayer adsorption takes place on the homogenous surfaces, and the Freundlich isotherm is applied to represent the multilayer adsorption on heterogamous surfaces. The Sips and R–P models are hybrid model combining the Langmuir and Freundlich models and they are the most applicable 3-parameter isotherm models for monolayer adsorption (Liao and Zhang 2020). The related parameters are listed in Table 2 and the fitted curves are displayed in Fig. 6. The results illustrated that the correlation coefficient ($R^2$) of the Langmuir model approached 1, which was higher than the other models, showing that the Langmuir model was suitable for fitting the removal behavior of Hap@BC to U(VI). Besides, the experimental value of $Q_e$ was near to the fitting value from Langmuir. These results revealed that the U(VI) removal process by Hap@BC was controlled by a homogeneous monolayer adsorption. Moreover, the adsorption capacity of Hap@BC-5%, Hap@BC-10% and Hap@BC-15% reached 606.6, 834.8, 711.9 mg/g, respectively, which were much higher comparing with other materials (Table S1).

### 3.2.7 Desorption and regeneration of Hap@BC-10%

The reusability of Hap@BC-10% was important to reduce the use-cost in application. For exploring the regeneration of Hap@BC-10%, different CaCl$_2$ solutions were used as the desorption reagents. As shown in Fig. 7a and b, the pH and concentration of the CaCl$_2$ solution were the important factors affecting the desorption process. With the increase of CaCl$_2$ concentration, the desorption efficiency for U(VI) in solution became higher, which might reveal that ion exchange was the main interaction mechanism in the adsorption process. In other words, the chemical reaction proceeded towards the direction of generating adsorbent in the desorption process due to the large amount of Ca$^{2+}$ in the solution. In addition, U(VI) species were relatively easy to be released in acidic solution, which was attributed to the intense competition of Ca$^{2+}$ for the binding sites in the solution with high Ca$^{2+}$ concentration, resulting in high desorption efficiency for U(VI) in acidic CaCl$_2$ solution. About 99.1% of the captured U(VI) was leached in the CaCl$_2$ solution with the concentration of 0.1 mol/L and pH = 1, which would be beneficial to the recovery of U(VI). The adsorption and desorption efficiency of Hap@BC-10% for U(VI) removal remained above 93.2% and 94.6%, respectively, even after five regeneration processes (Fig. 7c and d), which

| Models  | Adsorbents | Parameters | $Q_m$ (mg·g$^{-1}$) | $K_L$ (L·g$^{-1}$) | $n_F$ | $R^2$ |
|---------|------------|------------|---------------------|-------------------|------|-------|
| Langmuir | Hap@BC-5%  | $Q_m$  | 606.6              | 0.337             |      | 0.969 |
|         |            | $K_L$    |                     |                   |      |       |
|         | Hap@BC-10% | $Q_m$  | 834.8              | 0.505             |      | 0.980 |
|         |            | $K_L$    |                     |                   |      |       |
|         | Hap@BC-15% | $Q_m$  | 711.9              | 0.410             |      | 0.980 |
|         |            | $K_L$    |                     |                   |      |       |
| Freundlich | Hap@BC-5%  | $K_F$ ((mg·g$^{-1}$)(L·mg$^{-1}$)$^{n_F}$) | 189.9             | 3.149             |      | 0.885 |
|          | Hap@BC-10% | $K_F$  |                     |                   |      |       |
|          | Hap@BC-15% | $K_F$  |                     |                   |      |       |
| Sips    | Hap@BC-5%  | $Q_m$  | 593.2              | 0.357             | 0.933| 0.992 |
|         | Hap@BC-10% | $Q_m$  | 1055.1             | 0.226             | 1.370| 0.997 |
|         | Hap@BC-15% | $Q_m$  | 665.7              | 0.497             | 0.835| 0.997 |
| R–P     | Hap@BC-5%  | $K_R$  | 181.0              | 0.249             | 1.050| 0.991 |
|         | Hap@BC-10% | $K_R$  | 972.9              | 2.698             | 0.716| 0.955 |
|         | Hap@BC-15% | $K_R$  | 228.8              | 0.202             | 1.138| 0.990 |
overcame the problem of poor reusability of Hap materials, showing that Hap@BC-10% had strong stability and excellent regeneration. In brief, Hap@BC-10% would be a truly valuable material for adsorbing U(VI) in water environment due to its excellent reusability, which has practical significance for the development and application of Hap materials.

3.3 Mechanism

3.3.1 SEM

The SEM image of Hap@BC-10% is shown in Fig. 8a. Obviously, the nHap nanoparticles (about 100 nm) with rice-like morphology were uniformly loaded on the surface of the biocarbon, providing many active adsorption sites. After adsorbing U(VI) (Fig. 8b), the rice-like morphology of nHap nanoparticles transformed into spherical morphology and the surface of the nanoparticles became rough, which was ascribed to the generation of complexes between U(VI) and the active sites on the surface of nHap nanoparticles. After desorption, the nHap nanoparticles loaded on the biocarbon recovered to rice-like morphology and the nanoparticles were relatively smooth (Fig. 8c), which indicated that U(VI) species were resolved from the nHap nanoparticles into the solution. Moreover, the U(VI) species on Hap@BC-10%-U could be completely separated from Hap@BC-10% in the mixture of CaCl₂ (0.1 mol/L) and HCl (0.1 mol/L), which was attributed to the fact that Ca²⁺ would recapture the active sites occupied by U(VI) species and Hap@BC-10%-U would be completely restored to Hap@BC-10% in acidic solution, demonstrating that the ion exchange process was the main adsorption mechanism.

3.3.2 FT-IR and XRD

The FT-IR spectra of UO₂(NO₃)₂·6H₂O, Hap@BC-10% and Hap@BC-10%-U are shown in Fig. 8d. A new peak at 940 cm⁻¹ corresponded to the antisymmetric stretching vibration of O=U=O after U(VI) capture, indicating that U(VI) was successfully immobilized onto Hap@BC-10%. The broad peak from 480 to 700 cm⁻¹ was attributed to the bending vibrations of PO₄³⁻ (Beh et al. 2021; Kong et al. 2021).

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which shifted to low wavenumber after adsorption, indicating that PO₄³⁻ played an important role in the adsorption for U(VI) (Guo et al. 2020b). The XRD patterns of Hap@BC-10% and Hap@BC-10%-U are shown in Fig. 8e. After adsorption, the weak peaks at 8.8° and 10.8° were observed, which were attributed to the immobilization of U(VI) by the adsorption sites on Hap@BC-10%, showing that new substances were formed on the surface of Hap@BC-10% after adsorption (Ma et al. 2019).

### 3.3.3 XPS

The XPS spectra of Hap@BC-10% and Hap@BC-10%-U are shown in Fig. 9a to quest the removal mechanism. After U(VI) capture, a new peak emerged at near 390 eV, which was attributed to the capture of U(VI) through chemical bonding, confirming that U(VI) was successfully immobilized on Hap@BC-10%. Besides, the high-resolution of U⁴f could be fitted in the form of U⁶⁺ with binding energies of 393.0 eV (U⁴f⁵/₂) and 382.2 eV (U⁴f⁷/₂) (Eb > 382.0 eV) (Fig. 9b), proving no presence of redox reaction from U(VI) to U(IV) in the process of uranium adsorption (Guo et al. 2020b). The O₁s could be separated into three peaks, corresponding to the C = O/P = O at 532.4 eV, the –OH at 530.9 eV and the bound water at 530.3 eV, respectively (Liao et al. 2022a). After U(VI) removal, the position and relative ratio of the binding energy of these O donors changed and the binding energies of –OH and C = O/P = O were moved to relatively high values owing to the decrease of electron cloud density surrounding O atoms (Fig. 9c), illustrating that the oxygen-containing groups were the essential active sites for removing U(VI) (Liu et al. 2021; Zheng et al. 2020). The binding energy of P₂p shifted from 132.8 to 133.1 eV (Fig. 9d), indicating that Ca in Hap particles might be replaced in-situ by UO₂²⁺ to form the P–U bonds, which resulted in the increase of the extranuclear electron cloud density around P atoms (Ma et al. 2021). This conclusion was confirmed by the shift of the binding energy.
of Ca2p. The intensity of binding energy of Ca2p reduced by about 7% after adsorption and the binding energies of Ca2p1/2 and Ca2p3/2 increased from 346.9 and 350.5 eV to 347.1 and 350.7 eV, respectively (Xiong et al. 2022), which further proved that Ca2+ in Hap was substituted in-situ by U(VI), revealing that the ion exchange occupied a crucial position in the adsorption of U(VI) on Hap@BC-10%.

In summary, Hap@BC-10% possessed an excellent adsorption property for U(VI) in solution, which could be attributed to the following reasons: (1) The surface of Hap@BC-10% was rich in acidic functional groups. (2) The strong response between Hap nanoparticles and U(VI) species. (3) Hap@BC-10% possessed the characteristics of fluffy, porous and high specific surface area, as displayed in Fig. 9f. At pH = 3, due to the various active sites, U(VI) species could be immobilized on Hap@BC-10% in many ways, including electrostatic attraction, complexation (Eq. 3), ionization-precipitation (Eqs. 4 and 5) and ion exchange (Eqs. 6 and 7) (Liao et al. 2022b; Liang et al. 2017).

$$2R - OH + UO_2^{2+} = (R - O -)_2UO_2^2 + 2H^+ \quad (3)$$

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 10Ca + 6PO_4^2+2OH \quad (4)$$

$$2H^+ + 2UO_2^{2+} + 2PO_4^{3-} + H_2O \rightarrow H_2(UO_2)_2(PO_4)_2 \cdot 8H_2O \quad (5)$$

$$Ca_{10}(PO_4)_6(OH)_2 + xUO_2^{2+} \rightarrow (Ca_{10-x})(UO_2)_x(PO_4)_6(OH)_2 + xCa^{2+} \quad (6)$$

$$\equiv Ca^{2+}(s) + UO_2^{2+}(l) \rightarrow \equiv UO_2^{2+}(s) + Ca^{2+}(l) \quad (7)$$

4 Conclusion

In conclusion, Hap@BC was successfully obtained via a simple pyrolysis technology for efficiently removing U(VI). Hap@BC showed noticeable advantages in adsorption, including good selectivity, fast adsorption rate, high removal percentage and high adsorption capacity for U(VI). The static state adsorption behavior of Hap@BC-10% to U(VI) reached the equilibrium within 5 min with the removal percentage of 98.7% (C_0 = 5 mg/L, pH = 3, m/V = 0.1 g/L and T = 298 K) and the maximum adsorption capacity of 834.8 mg/g (pH = 3, m/V = 0.1 g/L and T = 298 K), which
were similar to the results of dynamic adsorption experiments. These experimental results far exceeded other reported Hap materials. Besides, Hap@BC-10% possessed excellent recyclability. After 5 times of adsorption–desorption processes with the mixture of HCl (0.1 mol/L) and CaCl$_2$ (0.1 mol/L), the adsorption efficiency was still over

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**Fig. 9**  
(a) XPS spectra of Hap@BC-10% and Hap@BC-10%-U,  
(b) High-resolution XPS spectra of U4f,  
(c) High-resolution XPS spectra of O1s,  
(d) High-resolution XPS spectra of P2p,  
e High-resolution XPS spectra of Ca2p and  
f Adsorption mechanism
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