HIGH-SPEED AND EFFICIENT REMOVAL OF URANIUM (VI) FROM AQUEOUS SOLUTION BY HYDROXYAPATITE-MODIFIED ORDERED MESOPOROUS CARBON (CMK-3)

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Abstract
In recent years, the synthesis and application of green, cost-effective, and sustainable materials for uranium (VI) removal was significant to environmental protection. The ordered mesoporous carbon (CMK-3) supported different mass of hydroxyapatite materials (HAP@CMK-3) were facilely synthesized via hydrothermal method. The resultant materials were characterized by XRD, FT-IR, BET, SEM, TEM mapping, and XPS, and implemented for immobilizing U(VI). Not only the specific surface area of HAP (7.01 m²/g) was increased by the loading on CMK-3 (818.37 m²/g), but also the adsorption capacity of CMK-3 was increased by HAP modification. Impressively, HAP@CMK-3 exhibited highly adsorption capacity of U(VI) with the increase of HAP deposition and was capable of achieving fast reaction. Therein to, the specific surface area of HAP@CMK-3(2:1) was 253.68 m²/g, as well as the adsorption capacity was up to 1072 mg/g (fitted by Langmuir isotherm, at pH=3.0, 298 K) and the adsorption process was completed in 30 min (followed by pseudo-second-order kinetic). The adsorption mechanisms of U(VI) on HAP@CMK-3 involved electrostatic forces, ionic interactions, and chemical complexation. This work offered new avenues to address the limitations of cost and less secondary pollution for the removal of U(IV) from wastewater.

Keywords Hydroxyapatite · CMK-3 · U(VI) · Adsorption

Introduction

In the future of sustainable development, it is time to develop nuclear energy to substitute for the exhausted fossil energy. With the rampant development of nuclear industry, the demand for uranium (U) as a “raw material” was gradually increasing, which was often accompanied by ecological damage and environmental pollution (Liu et al. 2016; Lu et al. 2019; Zhong et al. 2020). Uranium mainly existed in the form of soluble hexavalent U(VI) and insoluble tetravalent U(IV) in the environment. Therefore, U(VI) ions could easily migrate into Eco-environment, and health of human being and animals (Qiu et al. 2021; Zhao et al. 2021; Zhong et al. 2021a). At present, various methods had been used to remove and enrichment, including adsorption (Wang et al. 2021b; Zhong et al. 2021b), cation exchange (Taha 2021; Venkateswara Rao et al. 2021), electrochemical treatment (Potgieter et al. 2020), photocatalytic treatment (Lei et al. 2021; Li et al. 2019), and chemical precipitation (Lu et al. 2019; Zheng et al. 2020). In practical applications, adsorption became the most promising U(VI) separation and enrichment methods, attributing to its advantages of low cost, straightforward operation, fast speed, high adsorption capacity and selectivity, and wide-ranging raw materials. Nonetheless, the functional groups played a crucial role in the adsorption process. Among which, amidoxime groups (Hu et al. 2021), carboxyl groups (Zhao et al. 2021), amino groups (Kong et al. 2021), and phosphoric groups (Sun et al. 2021) had been proved have a strong affinity for U(VI). Especially, phosphoric groups not only can selectively adsorb U(VI), but also co-precipitate with U(VI), which had aroused concern about the removal and immobilization of U(VI) (Hu et al. 2020; Sun et al. 2021; Xue et al. 2017). Hydroxyapatite (HAP, Ca₁₀(PO₄)₆(OH)₂) as a typical calcium phosphate material with high environmental remediation owed to its special structure and excellent
medium adaptability features, such as the extensive resource, nontoxicity, high thermal stability, acid-base regulation, ion exchange capability, and efficient adsorption potential (Ahmed et al. 2021; Su et al. 2019). HAP had been widely researched on the immobilization of U(VI) into unstable uranyl phosphate phase (Szenknect et al. 2020). When HAP was employed as reactive material to remove U(VI) from polluted water, the synergistic mechanisms of surface complexion immobilization (U–phosphate precipitation, chernikovite, or meta-autunite), and ion exchange can occur (Foster et al. 2020; Zeng et al. 2020). However, HAP was easy to agglomerate during formation, resulting in low specific surface area and the decrease of adsorption efficiency (Ahmed et al. 2021).

In addition, uniform mesoporous carbon materials were widely used as adsorbents materials (Zhou et al. 2020). As a new member of the carbonaceous material family, the ordered mesoporous carbon CMK-3 with three-dimensional network structure had been in the spotlight, on account of its interconnected nanochannels, regular mesoporous structure, narrow pore size distribution, high specific surface area, and large pore volume, as well as excellent stability (Ezzeddine et al. 2020; Liu et al. 2013). However, due to hydrophobic surface, a small amount of surface functional groups and low adsorption selectivity for U(VI) ions, CMK-3 was unsuitable for the treatment of U(VI)-containing wastewater (Wang et al. 2012; Zhang et al. 2018; Zhou et al. 2021). Thus, the adsorption capacity and selectivity of CMK-3 was usually improved by surface modification and surface functionalization. Although in situ surface functional groups CMK-3 was obtained by surface oxidation with concentrated acid treatment, this operation was easy to destroy pore structure, and the number of active functional groups attached on the surface was limited, as well as these functional groups were easy to peel off during the adsorption/desorption process (Liu et al. 2013; Zhou et al. 2021). Incorporating the active component of HAP into CMK-3 framework can not only increase the adsorption active sites but also maintain a porous structure, making a more stable adsorption process.

Herein, an environment-friendly and economically feasible HAP@CMK-3 composite was synthesized and used for U(VI) treatment. CMK-3 can not only inhibit the aggregation and growth of HAP nanoparticles, but also provided pore structure and large specific surface conducive to U(VI) transfer and adsorption. Meanwhile, the microscopic morphology and structure of the adsorption materials (HAP, CMK-3, HAP@CMK-3) were characterized by XRD, FT-IR, SEM, TEM mapping, XPS, N₂ adsorption/desorption, and so on. Additionally, the U(VI)-removing performance of HAP@CMK-3 was investigated by batch experiments, and adsorption mechanism was revealed by kinetics, thermodynamics, and XPS analysis, thereby providing reference for the application of HAP@CMK-3 in the treatment of U(VI)-containing wastewater.

Materials and methods

Materials synthesis

All chemicals used in the experiments were analytically pure or better without further purification. CaCl₂ (96%), Na₂CO₃ (99.5%), Na₂HPO₄·12H₂O (99%), UO₂(NO₃)₂·6H₂O (99.5%), and other chemical reagents were furnished by Aladdin Biochemical Technology Co., Ltd (Shanghai, China).

The mesoporous CMK-3 was prepared using SBA-15 as the template in the light of the previously reported method (Zhang et al. 2017b). HAP was synthesized by hydrothermal method (You et al. 2019). Typically, (i) 70 mL, 0.3 M CaCl₂ solution and 70 mL, 0.3 M Na₂CO₃ solution were added in a round-bottom flask, vigorous stirring for 30 min at room temperature and CaCO₃ forming (ii). The acquired CaCO₃ was weighed 2.0 g and dispersed into 50 mL deionized water, and 8.6 g Na₂HPO₄·12H₂O was added with stirring. Afterwards, the mixture was shifted to 100-mL Teflon-lined autoclave and kept at 160 °C for 60 h (iii). Lastly, the obtained HAP was cooled, filtered, and rinsed with deionized water and absolute ethanol, in a vacuum desiccation overnight at 60 °C.

The synthesis of HAP@CMK-3 was further dispersed (0.2 g, 0.4 g, 0.4 g) HAP and (0.4 g, 0.4 g, 0.2 g) CMK-3 in different proportions with ultrasonic in 50 mL ethanol, then the mixture was placed to a 100-mL Teflon-lined autoclave and heated at 120 °C for 72 h. The acquired products named as HAP@CMK-3(1:2), HAP@CMK-3(1:1), and HAP@CMK-3(2:1), respectively, which were cooled, filtered, washed with deionized water and absolute ethanol, and dried in a vacuum oven overnight at 60 °C.

Materials characterization

The samples of HAP, CMK-3, and HAP@CMK-3 before and after adsorption were tested by XPS (ESCALAB 250XI) to analyze surface compositions and oxidation states. Surface functional groups were recorded on the FT-IR spectra (Thermal Fisher Nicolet 670). The morphologies and crystal structures of HAP, CMK-3, and HAP@CMK-3 were surveyed on SEM (JEOL-7800F ZEISS) and TEM (FEI Tecnai G2 F20) with EDX elemental mapping (JEOL-2100F), and XRD analysis (Bruker D8 Advance diffractometer), respectively. The specific surface area, pore size, and pore volume of adsorbents were identified by N₂ adsorption-desorption system (Quantachrome NovaWin).
Adsorption experiments

In this section, the adsorption behavior of the prepared HAP, CMK, and (HAP@CMK-3=2:1, 1:1, 1:2) composites toward U(VI) ions were determined by the static batch experiments. Typically, 5 mg adsorbent was added into 100 mL U(VI) ions solution, shaking at 120 rpm for 24 h to equilibrate. To avoid U(VI) hydrolysis, the reaction pH was adjusted to pH 3.0, which was approximated to the mining wastewater in field (Su et al. 2019). The influence of contact time, initial concentration (15~100 mg/L), and temperature (298 K, 308 K, 318 K) on the U(VI) adsorption process was investigated. The concentration of U(VI) was determined by the spectrophotometric method by Arsenazo-III at the wavelength of 650 nm. The kinetics and isotherms of U(VI) adsorption by these adsorbents were set at a pH=3.0 with different initial concentrations of U(VI) and reaction times (0 ~120 min). The amounts of U(VI) \((q_e, \text{mg/g})\) on these adsorbents were calculated according to the equation:

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]  

(1)

where \(C_0\) and \(C_e\) were the initial and equilibrium concentrations of U(VI), respectively. \(V\) was the volume of the U(VI) solution (L), and \(m\) was the mass of dry adsorbents (g).

Fig. 1 a The XRD patterns of HAP and the different proportions of HAP@CMK-3 composites; b the FT-IR spectra of HAP, CMK-3, and HAP@CMK-3 composite

Fig. 2 SEM images: a, b HAP; c, d CMK-3; e, f HAP@CMK-3(1:1); g, h TEM images of HAP@CMK-3(1:1); and i–n elements mapping images of C, O, Ca, and P
Results and discussion

Textural characterizations

As shown in Fig. 1a, the XRD patterns for HAP and the different proportions of HAP@CMK-3 composites exhibited characteristic peaks at 25.88°, 29.56°, 31.97°, 33.19°, 34.31°, 40.17°, 46.85°, and 49.51°, which separately corresponded to the (002), (210), (211), (300), (202), (310), (222), and (213) crystal planes of a typical HAP mineral (JCPDS 73-1731) (Saha et al. 2020; You et al. 2019). The XRD patterns of HAP@CMK-3 composites were completely consistent with that of HAP sample due to its containing HAP with strong crystallization. The characterization results preliminarily ascertained that the doping of the HAP in the CMK-3 was successful.

The FT-IR spectra were carried out to further investigate the structures and the surface functional groups of HAP@CMK-3 composites, shown in Fig. 1b. The vibration band at 3440 cm⁻¹ was attributed to the hydroxyl groups (–OH). The vibration bands located at 1030 cm⁻¹ (P=O), and two peaks at 605 cm⁻¹ and 565 cm⁻¹ (P–O) were the “fingerprint” of the phosphate groups (PO₄³⁻) (Wang et al. 2021a). Besides, the vibration bands located at 1629 cm⁻¹, 1462 cm⁻¹, 1411 cm⁻¹, and 875 cm⁻¹ were assigned to the carbonate group (CO₃²⁻) (Kong et al. 2020; Wang et al. 2021a), indicating CaCO₃ existed in HAP@CMK-3 composite. These results demonstrated the existence of –OH, CO₃²⁻ and PO₄³⁻ in HAP@CMK-3 composite, which can interact with U(VI) for its removal from aqueous.

As shown in the SEM images (Fig. 2a, b), the surface of HAP nanoparticles was wrinkled with rough protrusions and had a higher tendency to agglomerate. Figure 2c and d displayed the synthesized CMK-3 was constituted with dozens of rod-like materials, which had regular structure with long one-dimensional linear channels and ordered arrangement.
and the structure remained intact after the hydrothermal process. Moreover, the morphology of HAP@CMK-3(1:1) (Fig. 2e, f) was nearly the same as the structure of CMK-3. Distinctly, as exhibited in Fig. 2g, HAP nanoparticles were evenly dispersed on the surface of CMK-3 with reducing agglomeration, which was further ascertained by TEM elements mapping (Fig. 2i–n). Meanwhile, Fig. S1 shown the peaks of EDX spectroscope for Ca, O, and P were detected in HAP@CMK-3 and the average Ca/P molar ratio was found to be 1.6, which was in agreement with the nature hydroxyapatite (Zheng et al. 2020).

To further ascertain the chemical nature and bonding configurations of HAP@CMK-3(1:1), XPS measurement was performed and the corresponding results were depicted in Fig. 3. As expected, the elements of C, Ca, O, and P coexisted in the HAP@CMK-3 composite (Fig. 3a), which was in line with the outcomes of EDX spectrum and TEM elements mapping. The coexistence of O, P, and Ca suggested that HAP was successfully deposited onto CMK-3. Additionally, the O1s spectra (Fig. 3b) located at 533.5 eV and 535 eV were separately attributed to the $\text{PO}_4^{3-}$ groups and the adsorbed H$_2$O molecule (Ahmed et al. 2021; Hu et al. 2020). The peaks of Ca 2p spectrum (Fig. 3c) observed at 353 eV and 350 eV were corresponded to Ca $2p_{1/2}$ and Ca $2p_{3/2}$, respectively (Lu et al. 2021). For the spectrum of P 2p, the peaks were exhibited at binding energies of 135.6 eV (P 2p$_{3/2}$) and 137.5 eV (P 2p$_{1/2}$) (Zhou et al. 2021).

The $\text{N}_2$ adsorption-desorption isotherms of HAP, CMK-3, and the different proportions of HAP@CMK-3 composites were displayed in Fig. 4. The samples of CMK-3 and HAP@CMK-3 composites shown the type IV isotherm curves with H1 hysteresis loops at relative pressures $(P/P_0= 0.5)$, which was the typical for mesoporous structures (Jeong et al. 2020) and also indicated that the ordered mesoporous structure of CMK-3 was well maintained. The CMK-3 material had a very high surface area of 818.37 m$^2$/g and pore volume of 1.21 cm$^3$/g and pore diameter 6.0 nm. In contrast, the specific surface area and pore volume of HAP were only 7.01 m$^2$/g and 0.032 cm$^3$/g with large pore diameter 18.2 nm, as result of the agglomeration of HAP nanoparticles. A decrease in pore volume from 1.21 cm$^3$/g (CMK-3) to 0.4 cm$^3$/g (HAP@CMK-3(2:1)) after HAP integration was related to the partial blocking of pores. Moreover, large surface areas were retained after HAP modification, even at the mass ratio of HAP@CMK-3(2:1), and specific surface area of 253.68 m$^2$/g. The order of specific surface area of five samples are as follows, CMK3$>$HAP@CMK-3(1:2)$>$HAP@CMK-3(1:1)$>$HAP@CMK-3(2:1)$>$HAP. This was the consequence of small-sized HAP nanoparticles blocking some porous sites of CMK-3. Despite the lower content of mesopores for HAP@CMK-3 series samples than
The adsorption kinetics of U(VI) onto HAP, CMK-3, HAP@CMK-3(1:2, 1:1, 2:1) ($C_0=50$ mg/L, $T=298$ K, pH 3.0, m/V=0.05 g/L): a adsorption curves; b the pseudo-second-order model; c intra-particle-diffusion model; and d the influence of ionic strength.

Table 1 Kinetic model parameters for the U(VI) adsorption

| Adsorbents       | Pseudo-first order | Pseudo-second order | Intra-particle diffusion |
|------------------|--------------------|---------------------|--------------------------|
|                  | $k_1$ (min$^{-1}$) | $q_e$ (mg/g) | $R^2$ | $k_2$ (g/mg min) | $q_e$ (mg/g) | $R^2$ | $k_p$ (g/mg min$^{0.5}$) | $C$ | $R^2$ |
| HAP              | 0.0475             | 311.06             | 0.9166 | 2.59×10$^{-4}$ | 473.93 | 0.9983 | 4.66 | 389.58 | 0.9998 |
|                  | 78.87              | −15.07            | 0.9943 |
| CMK-3            | 0.3601             | 172.43             | 0.9352 | 1.73×10$^{-3}$ | 166.67 | 0.9808 | 2.48 | 132.08 | 0.8838 |
|                  | 83.87              | −63.97            | 0.9792 |
| HAP@CMK-3(1:2)   | 0.3574             | 170.72             | 0.9355 | 1.94×10$^{-3}$ | 194.17 | 0.9965 | 2.54 | 166.72 | 0.8977 |
|                  | 85.48              | 32.77             | 0.9873 |
| HAP@CMK-3(1:1)   | 0.0499             | 333.62             | 0.9196 | 2.66×10$^{-4}$ | 523.56 | 0.9986 | 4.65 | 439.37 | 0.9958 |
|                  | 87.53              | −5.31             | 0.9894 |
| HAP@CMK-3(2:1)   | 0.0474             | 415.72             | 0.9154 | 2.14×10$^{-4}$ | 666.67 | 0.9988 | 5.84 | 562.67 | 0.9875 |
|                  | 112.39             | −5.59             | 0.9852 |
that for pure CMK-3, this does not mean weaker uranium adsorption because the mesopores just provide area that could proceeds adsorption, but the adsorption efficiency may not beyond HAP incorporated-composites as detailed in the following adsorption performance tests (Fig. 5 and 6), which HAP@CMK-3 (2:1) (253.68 m3/g) exhibited an excellent property than CMK-3 (818.37 m3/g).

### Adsorption performance

Figure 5a displayed the influence of contact time on the performance of U(VI) removal. The uptake capacity of U(VI) improved swiftly and reached equilibrium for a relatively short time. In addition, the functionalization of CMK-3 with HAP occurred at a relatively faster rate and higher adsorption capacity with the increase of HAP loading. When HAP was loaded at low concentration, the adsorption trend was the same as that of CMK-3. On the contrary, the adsorption trend was the same as that of HAP at high concentration loading. To understand the U(VI) adsorption kinetics of HAP, CMK-3 and the different proportions of HAP@CMK-3 composites, the pseudo-first-order (Eq. S1) and the pseudo-second-order kinetics (Eq. S2) as well as the intra-particle-diffusion models (Eq. S3) were simulated, and the results obtained were tabulated in Table 1.

In contrast to Fig. 5b, Fig. S2, and Table 1, it can be speculated that the adsorption process was in line with the pseudo-second-order kinetic, manifesting that the adsorption of U(VI) by HAP, CMK-3, and HAP@CMK-3 composites was principally dominated by chemical reactions. The adsorption process (Fig. 5c and Table 1) can be interpreted into two-stages by the intra-particle diffusion model (Sun et al. 2021). Above all, the first-phase represented the prompt surface adsorption controlled by electrostatic attraction and chemical complexation. The initial pH value of 3.0 U(VI) mainly existed in the form of $\text{UO}_2^{2+}$, $\text{UO}_2(\text{OH})^+$, $\text{(UO}_2)^2(\text{OH})_2^{2+}$, and $\text{(UO}_2)^3(\text{OH})_4^{2+}$ ions, which principally interacted with a large number of active functional groups situated on the surface of absorbents, such as $-\text{OH}$, $\text{CO}_3^{2−}$, and $\text{PO}_4^{3−}$.

The second-phase was controlled by slow intra-particle diffusion, due to the combination of U(VI) and these functional groups in the pores of adsorbents. The adsorption rate of HAP@CMK-3 composites to U(VI) were faster than that of HAP and CMK-3. Besides, the adsorption capacities of U(VI) were maintained at high level even at high concentration of ionic strength (Fig. 5d), reflecting that the adsorption mechanism though complex formation (El-Maghrabi et al. 2019).

Besides the ionic strength, the coexisting ions also pay an important role for U(VI) removal. The selectivity of HAP@CMK-3 composites for $\text{UO}_2^{2+}$ was tested in the presence of common coexisting humus acid and anions containing $\text{Na}^+$, $\text{Zn}^{2+}$, $\text{Ni}^{2+}$, $\text{Sr}^{2+}$, $\text{Eu}^{3+}$, and $\text{Ce}^{4+}$, existing as typical $\text{NO}_3^−/\text{Cl}^−$ salts. It is undeniable that HAP@CMK-3 has a certain adsorption performance for other ions, which can reduce the adsorption performance of $\text{UO}_2^{2+}$ to a certain extent, when they existed at the same time (Fig. S3). However, HAP@CMK-3 still maintains the high adsorption performance for $\text{UO}_2^{2+}$, which could be affected by the surface property of HAP and CMK-3, ionic valence, mobility, pH value, existing morphology, and other factors. So, nitrogen- and oxygen-containing groups were the selective for $\text{UO}_2^{2+}$ uptake.

### Table 2 Equilibrium parameters for the U(VI) adsorption

| Adsorbents          | T(K) | $Q_{\text{max}}$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $K_F$ (mg$^{1-1/n}$g$^{-1}$L$^{-1/n}$) | $1/n$ | $R^2$ |
|---------------------|------|-------------------------|--------------|-------|--------------------------------------|-------|-------|
| HAP                 | 298  | 746.47                  | 0.025        | 0.9862| 46.53                                | 0.547 | 0.9462|
|                     | 308  | 781.81                  | 0.030        | 0.9941| 64.72                                | 0.491 | 0.9539|
|                     | 318  | 796.86                  | 0.036        | 0.9989| 91.84                                | 0.427 | 0.9709|
| CMK-3               | 298  | 290.08                  | 0.014        | 0.9976| 8.94                                 | 0.652 | 0.9858|
|                     | 308  | 313.24                  | 0.017        | 0.9954| 13.74                                | 0.586 | 0.9933|
|                     | 318  | 348.91                  | 0.022        | 0.9974| 21.98                                | 0.528 | 0.9934|
| HAP@CMK-3 (1:2)     | 298  | 304.92                  | 0.012        | 0.9930| 12.81                                | 0.629 | 0.9898|
|                     | 308  | 309.84                  | 0.013        | 0.9975| 14.44                                | 0.637 | 0.9938|
|                     | 318  | 319.93                  | 0.014        | 0.9983| 15.64                                | 0.653 | 0.9933|
| HAP@CMK-3 (1:1)     | 298  | 383.44                  | 0.016        | 0.9974| 26.05                                | 0.703 | 0.9433|
|                     | 308  | 454.78                  | 0.023        | 0.9998| 37.71                                | 0.645 | 0.9548|
|                     | 318  | 540.67                  | 0.038        | 0.9939| 51.94                                | 0.594 | 0.9543|
| HAP@CMK-3 (2:1)     | 298  | 1072.66                 | 0.020        | 0.9854| 44.70                                | 0.620 | 0.9486|
|                     | 308  | 1133.37                 | 0.021        | 0.9913| 56.83                                | 0.583 | 0.9576|
|                     | 318  | 1176.36                 | 0.024        | 0.9960| 73.70                                | 0.541 | 0.9639|
Fig. 6  a–e The Langmuir fitting curves for U(VI) adsorption onto HAP, CMK-3, HAP@CMK-3(1:2, 1:1, 2:1) ($C_0=50$ mg/L, $T=298$ K, pH 3.0, $m/V=0.05$ g/L), and f the linear plots of ln$K_0$ of U(VI) ions versus $1/T$ at three different temperatures ($T=298–318$ K).
To gain the deeper understanding on the U(VI) adsorption by HAP, CMK-3, and the different proportions of HAP@CMK-3 composites, the collated experimental data was fitted by Langmuir (Eq. S4) and Freundlich isotherms (Eq. S5), and the adsorption parameters were displayed in Table 2. According to the fitting results (shown in Fig. 6 and Fig. S4), the experimental results were consistent with the Langmuir isotherm model, which was superior to the Freundlich isotherm in the analysis of experimental data.

As illustrated in Fig.6f, the linear fitting $\ln K_0$ and $1/T$, thus the enthalpy ($\Delta H^0$) and entropy ($\Delta S^0$) can be read from the slope and intercept, respectively. Afterwards, the entropy ($\Delta S^0$) was estimated from Eq. S6–Eq. S8, and all the thermodynamic parameters were listed in Table 3. As shown in Table 3, $\Delta G^0$ values were negative and decreased with temperature, specifying that the adsorption was carried out spontaneously, and the higher temperature, the more beneficial to the adsorption process. Furthermore, $\Delta H^0$ and $\Delta S^0$ values were positive, indicating that the adsorption was an endothermic process, and the degree of disorder increased at the contact interface, which was consistent with the above research results.

In addition to possessing the excellent performance towards U(VI) adsorption, the HAP@CMK-3 also presented a superior stability after four cycles of reusability tests. As shown in Fig. S5, the equilibrium adsorption capacity barely decreased after using four times, indicating an excellent reusable potential as a novel adsorbent.

### Adsorption mechanism

The aforementioned results indicate that the immobilization of U(VI) by chemical complexation was mainly contributed by the surface reactive sites. Consequently, the analysis of the surface composition after U(VI) adsorption allowed more profound insight into their adsorption mechanisms. Notably, the presence of U(VI) element in the samples of HAP, CMK-3, and HAP@CMK-3(2:1) after adsorption was shown in XPS spectra Fig. 7a and d and Fig. S6a. Meanwhile, the high-intensity double peaking concerned with the antisymmetric vibration of $\text{[O=U(VI)=O]}^{2+}$ can be observed in the XPS spectra after U(VI) adsorption. Through deconvolution of U(VI) peaks, the fitting results of U 4f$_{7/2}$ and U 4f$_{5/2}$ appeared at approximately 381.9 eV and 392.8 eV for HAP after U(VI) adsorption, indicating no existence of oxidation and reduction during the adsorption process (Ahmed et al. 2021; Guo et al. 2020). Contrarily, the U 4f spectra of HAP@CMK-3 after adsorption can be resolved into U 4f$_{7/2}$ ($E_B = 394.8$ eV) and U 4f$_{5/2}$ ($E_B = 383.9$ eV), suggesting a certain degree of redox activity during the adsorption process.

In Fig. 7e and f, compared with the P 2p spectra of HAP@CMK-3 at 135.6 eV and 137.5 eV before adsorption, the binding energies of PO$_4^{3–}$ migrated to the lower-energy region after adsorption at 135 eV and 136.3 eV, attributing to the PO$_4^{3–}$ in Ca(UO$_2$)$_2$(PO$_4$)$_2$·3H$_2$O (Shi et al. 2020; Zheng et al. 2020). Hence, U(VI) was immobilized by HAP@CMK-3 composite, which indicated that PO$_4^{3–}$ was involved in the surface complexation reactions. In addition, the area of the Ca peak (almost disappeared in Fig. 7b) and the proportion of Ca/P in the HAP and HAP@CMK-3 decreased drastically from 1.6 (before reaction) to 0.53 and 0.16 after the reaction, respectively. Uranium (UO$_2^{2+}$) was typically the predominant specie in natural water systems at pH < 5.0, ascribing to the substitution of Ca$^{2+}$ by UO$_2^{2+}$ in the HAP and HAP@CMK-3. Meanwhile, the binding energy value of Ca 2p on HAP (Fig. S5b) shifted from 350 to 347.6 eV upon U(VI) adsorption, identifying the obvious interactions between U(VI) and Ca (Chen et al. 2016).

As shown in Fig. 7g and h, the O 1s spectra of HAP@CMK-3 can be deconvoluted into the PO$_4^{3–}$ groups and the adsorbed H$_2$O molecule at 533.5 eV and 535 eV. Inevitably, the area of adsorbed H$_2$O molecule peaks decreased after U(VI) adsorption, representing the surface water containing hydrophilic oxygen provided active sites for binding U(VI). It can be observed in Fig. S6d that the high resolution C 1s of HAP@CMK-3 deconvoluted into three peaks at 284.8 eV, 285.6 eV, and 289.6 eV before adsorption, which were corresponded to the binding energies of the carbon atoms of C–C, C–O and O–C=O groups, respectively (Zhang et al. 2017a). After U(VI) adsorption, the O–C=O peak and the

### Table 3 Thermodynamic parameters for the U(VI) adsorption.

| Adsorbents   | $T$ (K) | $\Delta G^0$ (kJ/mol) | $\Delta S^0$ (J/(mol·K)) | $\Delta H^0$ (kJ/mol) |
|--------------|---------|-----------------------|--------------------------|-----------------------|
| HAP          | 298     | −8.24                 | 76.07                    | 14.43                 |
|              | 308     | −8.99                 |                         |                       |
|              | 318     | −9.76                 |                         |                       |
| CMK-3        | 298     | −9.48                 | 91.95                    | 17.92                 |
|              | 308     | −10.40                |                         |                       |
|              | 318     | −11.32                |                         |                       |
| HAP@CMK-3(1:2) | 298   | −10.58                | 55.95                    | 6.09                  |
|              | 308     | −11.14                |                         |                       |
|              | 318     | −11.70                |                         |                       |
| HAP@CMK-3(1:1) | 298 | −8.19                 | 142.59                   | 34.30                 |
|              | 308     | −9.62                 |                         |                       |
|              | 318     | −11.04                |                         |                       |
| HAP@CMK-3(2:1) | 298 | −9.28                 | 55.54                    | 7.27                  |
|              | 308     | −9.84                 |                         |                       |
|              | 318     | −10.39                |                         |                       |
C–O peak of CMK-3 and HAP@CMK-3 shifted to higher binding energy (Fig. S6e, f), implying that the oxygenated functional groups also took part in the coordination with U(VI) (Liu et al. 2021; Yin et al. 2019).

The immobilization of U(VI) on the HAP@CMK-3 was controlled by the mechanisms of electrostatic interactions, ion exchange, and chemical complexation, amongst HAP as both chelating and capping agents. The negative charge P−O− group within phosphate groups interacted with UO$_2^{2+}$ through electrostatic forces, and the chemical complexation of U(VI) with O–C=O, C–O, P–O, and P=O oxygen atoms on the surface ($\equiv$O−UO$_2^{2+}$, $\equiv$O$_3$P−O−UO$_2^{2+}$), bonding with the donation of lone pairs of electrons to unoccupied molecular orbitals of UO$_2^{2+}$. Moreover, UO$_2^{2+}$ displaced the Ca$^{2+}$ though ion exchange ($\equiv$Ca$^{2+}$ + UO$_2^{2+}$ = $\equiv$UO$_2^{2+}$ + Ca$^{2+}$). Therefore, the possible synergistic mechanism of U(VI) adsorption by HAP@CMK-3 was illustrated in Fig. 8.

**Conclusion**

In conclusion, we synthetized the HAP@CMK-3 composite as a novel, green, and stable absorbent in a simple hydrothermal way for the fast and efficient removal of U(VI). HAP@CMK-3 composites were characterized by XRD, FT-IR, BET, SEM, and TEM mapping, XPS before adsorption and after adsorption. Therein to, HAP nanoparticles provided sufficient active sites as both chelating and capping agents for highly efficient removal of U(VI) from solution. With the increase of HAP loading, HAP@CMK-3(2:1) has shown the excellent kinetic attributes, and the adsorption process was completed in 30 min as well as the adsorption capacity was up to 1072 mg/g. Therefore, HAP loading aggrandized the immobilization function of CMK-3. Adsorption mechanism was essentially accomplished by different interactions, including electrostatic forces (P−O− group), ionic interactions (Ca$^{2+}$), and chemical complexation (O−C=O, P−O, and P=O oxygen atoms). HAP can not only modified materials to reduce costs, but also can be used as an emergency material for the remediation of nuclear leakage accident.

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**Author contribution** Ming Ma: writing-original draft; formal analysis; validation; investigation; resource; funding acquisition. Hao Deng: formal analysis; validation; investigation; resources. Zhenyu Ren: validation; investigation; resources. Xin Zhong: conceptualization; methodology; supervision; visualization.

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**Data availability** Yes.

**Declarations**

**Ethical statement and consent to participate** Not applicable.

**Consent for publication** Yes.
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