Phosphate group functionalized magnetic metal–organic framework nanocomposite for highly efficient removal of U(VI) from aqueous solution

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The phosphate group functionalized metal-organic frameworks (MOFs) as the adsorbent for removal of U(VI) from aqueous solution still suffer from low adsorption efficiency, due to the low grafting rate of groups into the skeleton structure. Herein, a novel phosphate group functionalized metal–organic framework nanoparticles (denoted as Fe3O4@SiO2@UiO-66-TPP NPs) designed and prepared by the chelation between Zr and phytic acid, showing fast adsorption rate and outstanding selectivity in aqueous media including 10 coexisting ions. The Fe3O4@SiO2@UiO-66-TPP was properly characterized by TEM, FT-IR, BET, VSM and Zeta potential measurement. The removal performance of Fe3O4@SiO2@UiO-66-TPP for U(VI) was investigated systematically using batch experiments under different conditions, including solution pH, incubation time, temperature and initial U(VI) concentration. The adsorption kinetics, isotherm, selectivity studies revealed that Fe3O4@SiO2@UiO-66-TPP NPs possess fast adsorption rates (approximately 15 min to reach equilibrium), high adsorption capacities (307.8 mg/g) and outstanding selectivity ($S_u = 94.4\%$) towards U(VI), which in terms of performance are much better than most of the other magnetic adsorbents. Furthermore, the adsorbent could be reused for U(VI) removal without obvious loss of adsorption capacity after five consecutive cycles. The research work provides a novel strategy to assemble phosphate group-functionalized MOFs.

Uranium is not only a sustainable fuel source, but also a chemically toxic and radioactive pollutant for both the ecological environment and human beings1,3. Large amounts of uranium-containing waste have been released to natural water in a variety of ways, such as incorrect uranium mining, nuclear fuel fabrication and natural weathering3–5. Due to long-term radiation toxicity, uranium can not only cause carcinogenic, teratogenic or mutagenic radiation damage to human organs such as liver, kidney, skin and bone, but also result in a lasting and disastrous impact on the ecological environment6–8. Therefore, the removal and recovery of uranium from wastewater is very significant not only for ecological stability and human health, but also for nuclear sustainable development9,10.

Several strategies have been developed for radioactive wastewater treatment including coagulation11, membrane separation12,13, ion-exchange14,15, reductive precipitation16,17 and adsorption9,18,19. Among these strategies, adsorption has been proven to be the most effective treatment method owning to its low cost, simple operation and environment compatibility18–22. In the past decades, various adsorption materials such as silica nanoparticles, polymeric nanoparticles, carbon-based materials, and advanced porous materials have been extensively

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developed for U(VI) removal\textsuperscript{13–28}. Metal–organic frameworks (MOFs) are a particular class of porous materials constituted by metallic cations/clusters with organic ligands, and have superior intrinsic properties including tunability, crystallinity, stability and chemical versatility\textsuperscript{29–31}. And as a result, they have been widely applied in various fields, such as gas storage\textsuperscript{22,23}, catalysis\textsuperscript{34–38}, drug delivery\textsuperscript{39–42} and separation\textsuperscript{43–46}. At present, a variety of MOFs (i.e., ZIF-8, MIL-101, UiO-66) have been already designed and synthesized for U(VI) capture from aqueous solutions\textsuperscript{47–49}.

Since in many cases of radioactive pollution, the wastewater is a viscous, which requires adsorbents to have an adequate stability in acidic aqueous solutions. Based on this consideration, a zirconium-based MOF (UiO-66 and UiO-66-NH\textsubscript{2}) composed of a Zr\textsubscript{6}(µ\textsubscript{3}-O)\textsubscript{4}(µ\textsubscript{3}-OH)\textsubscript{4} or 12-connected Zr\textsubscript{6}(µ\textsubscript{3}-O)\textsubscript{4}(µ\textsubscript{3}-OH)\textsubscript{4}(NH\textsubscript{2}-COO)\textsubscript{12} cluster that possess strong Zr–O bonds was selected as a potential adsorbent due to its exceptional stability in acidic solutions\textsuperscript{50–55}. Hierarchical porous and functional group (–OH, –NH\textsubscript{2}, –COOH, =N–OH) post-modified UiO-66 have been prepared and studied in rapid U(VI) removal from an aqueous solution\textsuperscript{53–58}. It is also a wise strategy to modify phosphate groups on MOFs, due to strong coordination ability of phosphate groups with U(VI)\textsuperscript{59–61}. However, owning to the low grafting rate of phosphate groups into the skeleton structure, reported MOFs dotted with the phosphate group (UiO-68-P(O)(OEt)\textsubscript{2}, UiO-68-P(O)(OH)\textsubscript{2}, MIL-101-ship, Zr,P\textsubscript{3}) have low adsorption efficiency towards U(VI), which seriously affect their further application\textsuperscript{62–64}.

Phytic acid, as myoinositol hexaphosphate extracted from plants, has strong complexation ability to metal ions\textsuperscript{65–67}. In this study, we developed a group functionalized metal–organic framework nanoparticle by the chelation between Zr(IV) and phytic acid, and loaded Fe\textsubscript{3}O\textsubscript{4} nanoparticles to achieve fast magnetic separation of U(VI) from an aqueous solution (denoted as Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@[UiO-66-TPP]). The nanoparticle was synthesized by simple steps and properly characterized by transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectroscopy, Brunauer–Emmett–Teller (BET) measurements and vibrating sample magnetometer (VSM). The removal performance of Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@UiO-66-TPP for U(VI) was evaluated using batch experiments under different adsorption conditions, including solution pH, incubation time, temperature and initial U(VI) concentration. Fortunately, the nanoparticle possessed fast adsorption rates (approximately 15 min to reach equilibrium), high adsorption capacity (307.8 mg/g) and selectivity (94.4%) towards U(VI). Finally, the adsorption dynamics, isotherms and mechanism of Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@UiO-66-TPP for U(VI) were also discussed.

Experimental section

Materials. Cobaltous nitrate hexahydrate (Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O), gadolinium nitrate hexahydrate (Gd(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O), lanthanum nitrate hexahydrate (La(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O), neodymium nitrate hexahydrate (Nd(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O), ytterbium nitrate pentahydrate (Yb(NO\textsubscript{3})\textsubscript{3}·5H\textsubscript{2}O) and samarium nitrate hexahydrate (Sm(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O) were obtained from Sigma-Aldrich (USA). Nickel nitrate hexahydrate (Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O), strontium nitrate (Sr(NO\textsubscript{3})\textsubscript{2}) and zinc nitrate hexahydrate (Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O) were obtained from Damao Chemical Reagent Factory (Tianjin, China). Uranium nitrate oxide (UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}) was obtained from Chemical Reagent Purchasing and Supply Station (Shanghai, China). Zirconium chloride (ZrCl\textsubscript{4}) and 2-aminoethephosphonic acid were obtained from Heowns Biochemical Technology Co., Ltd (Tianjin, China). Phytic acid sodium salt were purchased fromSolarbio Science & Technology Co., Ltd (Beijing, China). Tetraethoxysilane (TEOS) was obtained from J&K Chemicals Ltd (China). Iron (III) chloride hexahydrate (FeCl\textsubscript{3}·6H\textsubscript{2}O), Sulfuric acid (H\textsubscript{2}SO\textsubscript{4}), nitric acid (HNO\textsubscript{3}), hydrochloric acid (HCl), ethylene glycol (EG), N, N-dimethylformamide (DMF), methanol (MeOH), ethanol (EtOH), and other reagents were obtained from Tianjin Chemical Reagent No. 6 Factory (China). High-purity deionized water (18.2 MΩ cm) was obtained from a Millipore Milli-Q direct water purification system (USA).

Preparation of silica layer coated magnetic nanoparticles (Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}). Naked Fe\textsubscript{3}O\textsubscript{4} NPs were prepared by a facile solvothermal method. Typically, 2.70 g FeCl\textsubscript{3}·6H\textsubscript{2}O, 7.71 g ammonium acetate, 0.8 g sodium citrate were dissolved in 140 mL EG solution under sonication to form a homogeneous solution. Then the mixture was heated at 200 °C for 16 h after transferring to a Teflon-lined stainless-steel autoclave (200 mL). Under an external magnetic field, the prepared Fe\textsubscript{3}O\textsubscript{4} NPs were separated from the reaction solvent, washed with water and EtOH for several times in turn, and dried in vacuum at 40 °C.

300 mg Fe\textsubscript{3}O\textsubscript{4} NPs were dispersed in the mixed solution of 0.75 mL ammonium hydroxide, 12 mL water and 46 mL EtOH under sonication, and then 0.9 mL TEOS in 3 mL EtOH was added dropwise to the above mixed solution. The mixture was stirred magnetically for 12 h at room temperature. Under an external magnetic field, the prepared Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2} NPs were separated from the reaction solvent and washed with water and EtOH for several times in turn, and dried in vacuum at 40 °C.

Preparation of magnetic Uio-66-NH\textsubscript{2} (Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@Uio-66-NH\textsubscript{2}). 200 mg Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2} NPs and 466 mg ZrCl\textsubscript{4} were dispersed in 30 mL DMF under sonication for 30 min, and then 362 mg dissolved in 30 mL DMF was added to the solution. The mixture was heated at 120 °C for 6 h. Under an external magnetic field, the prepared Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@Uio-66-NH\textsubscript{2} NPs were separated from the reaction solvent and washed with DMF and MeOH, immersed in MeOH for 3 d, and finally dried in vacuum at 40 °C.

Preparation of phosphate group functionalized magnetic metal–organic frameworks nanoparticles (Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@Uio-66-TPP). 15 mg phytic acid sodium salt was dissolved in the mixed solution of 4 mL water and 20 mL CH\textsubscript{3}COOH (2%, v/v), and then 40 mg Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@Uio-66-NH\textsubscript{2} was dispersed in the above solution under sonication. After pH value of the reaction system was adjusted to 5, the mixture was heated at 50 °C for 30 min, and then kept at 115 °C for 12 h. Under an external magnetic field, the prepared
Fe₃O₄@SiO₂@UiO₂-66-TPP NPs were separated from the reaction solvent and washed with water to neutral, and dried in vacuum at 40 °C.

Characterizations

The synthesized nanoparticles were systematically characterized through diverse techniques including transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR) and vibration sample magnetometer (VSM). The specific surface area, total pore volume, pore size and the Zeta potentials were also measured. Transmission electron microscopy (TEM) and composition mapping images were taken with a JEM-2100 (Japan) transmission electron microscope. Fourier transform infrared (FT-IR) spectra (4000–400 cm⁻¹) were obtained on a BRUKER TENSOR 27 (Germany) Fourier transform infrared spectrophotometer in KBr pellets. The N₂ adsorption–desorption isotherms were analyzed on a Micromeritics ASAP (USA) 2010 apparatus. The magnetic properties were characterized using a LDJ9600-1 (USA) vibrating sample magnetometer (VSM). The zeta potentials under different pH conditions were measured with a Brookhaven ZetaPALS (USA) analyzer at room temperature.

Batch experiments. To evaluate the performance of the magnetic adsorbents for the removal of U(VI) from aqueous solution, batch sorption experiments were carried out in 45 mL polyethylene tubes. Briefly, 10 mg magnetic adsorbents were dispersed in 25 mL uranium solution or multi-ion solution at a certain pH value adjusted by adding negligible volume of dilute HCl or NaOH solution. After being incubated for a given time at a certain temperature, the magnetic nanocomposites loaded with U(VI) were separated under an external magnetic field. The concentration of UO₂²⁺ in the supernatant was calculated by determining absorption of its complex with arsenazo(III) at 656 nm using an ultraviolet–visible spectrometer (SHIMADZU UV-1750). The concentration of metal ions including U(VI) was analyzed by inductively coupled plasma mass spectrometry (ICP-MS), when investigating the effect of coexisting ions and ionic strength on adsorption capacity of the magnetic adsorbent for U(VI). The adsorption capacity (qₑ, mg/g) and adsorption percentage (% adsorption) were calculated according to the following two equations:

\[
qₑ = \frac{(C₀ - Cₑ) \times V}{m} \tag{1}
\]

\[
% \text{ adsorption} = \frac{C₀ - Cₑ}{C₀} \times 100 \tag{2}
\]

where C₀ and Cₑ (mg/L) are the initial and equilibrium concentrations of UO₂²⁺ in the solution, respectively; V (L) is the volume of the solution; and m (g) is the weight of the magnetic adsorbents.

Uranium-selectivity (Sᵤ) to reflect the level of adsorption selectivity of the magnetic adsorbent towards U(VI), which was calculated according to the following equation:

\[
Sᵤ = \frac{qₑ(U)}{qₑ(tot)} \times 100 \% \tag{3}
\]

where qₑ(U) and qₑ(tot) are the U(VI) sorption capacity and all metal ions including U(VI) for the magnetic adsorbent, respectively.

For acquisition of the optimal adsorption performance of Fe₃O₄@SiO₂@UiO-66-TPP NPs towards U(VI), the influence factors, including pH (1.5–5.5), contact time (1–180 min), C₀ (20–400 mg/L), temperature (298–318 K), and ionic strength were also investigated by batch method.

The desorption study was carried out by using three kinds of acid solution (0.01 M H₂SO₄, HNO₃, and HCl). 10 mg Fe₃O₄@SiO₂@UiO-66-TPP NPs were shaken with 25 mL uranium solutions at pH 5.0 under ambient temperature (298 K) for 1 h. Under an external magnetic field, uranium loaded Fe₃O₄@SiO₂@UiO-66-TPP NPs were separated and washed with water. Finally, the U(VI) captured by Fe₃O₄@SiO₂@UiO-66-TPP NPs was released by the above-mentioned acid solutions (25 mL) at 298 K for 1 h. The nanoparticles were separated, and the U(VI) was analyzed by ICP-MS.

Results and discussions

Characterization of nanoparticles. The assembly process of phosphate group functionalized magnetic metal–organic frameworks nanoparticles (Fe₃O₄@SiO₂@UiO₂-66-TPP) is illustrated in Fig. 1. Firstly, magnetic iron oxide nanoparticles are coated with a silica layer via sol–gel emulsion method. The surface hydroxyl groups coordinate with Zr⁴⁺, which assists UiO₂-66-NH₂ to settle on the surface of the nanoparticles. Finally, the nanoparticles were dotted with phytic acid through intermolecular hydrogen bonding. To investigate whether Fe₃O₄@SiO₂@UiO₂-66-TPP shown in Fig. 1 proceed successfully and the properties of the nanoparticles, TEM and composition mapping images, FT-IR, N₂ adsorption–desorption, VSM and Zeta potential were analyzed in this work.

The size and morphology of the as-prepared nanoparticles were examined by TEM. As shown in Fig. 2a, the diameter of magnetic iron oxide was 150–270 nm, which was wrapped by a 30-nm-thick silicon layer. The SiO₂ layer was coated with MOF (UiO-66-NH₂) layer. Zr element are uniformly dispersed on the nanoparticles. After the modification of phytic acid, the phosphate group was successfully modified on the surface of the material (Fig. 2b). In addition, Fig. 2c showed that P, Zr, and U elements are evenly distributed on nanoparticles after the
sorption process, which indicated that U(VI) was successfully captured by Fe₃O₄@SiO₂@UiO-66-TPP NPs and the structure of the nanoadsorbent remained stable.

The FT-IR spectra of obtained nanoparticles (Fe₃O₄@SiO₂, Fe₃O₄@SiO₂@UiO-66-NH₂ and Fe₃O₄@SiO₂@UiO-66-TPP) were shown in Fig. 3a. In the spectrum of Fe₃O₄@SiO₂, the peak located at 590 cm⁻¹ was assigned to the stretching vibration of Fe–O bond, the peak at 1086 cm⁻¹ was ascribed to the Si–O–Si vibration, and the peak at 1628 cm⁻¹ and the broad peak centered at 3431 cm⁻¹ were ascribed to the stretching vibration of C=O bond and the stretching vibration of O–H and/or N–H bond, respectively. Compared to the above spectrum, there are some new peaks in the spectrum of Fe₃O₄@SiO₂@UiO-66-NH₂. The additional peak at 1428 cm⁻¹ was assigned to the symmetrical stretching vibration of C–O bond, the peaked at 1506 cm⁻¹ was assigned to the stretching vibration of C=C bond, and the peak at 1572 cm⁻¹ was assigned to the deformation vibration of N–H bond. These bonds all come from the organic monomer (2-aminoterephthalic acid) that constructed the MOF layer. In the spectrum of Fe₃O₄@SiO₂@UiO-66-TPP, the peak at 1055 cm⁻¹ was ascribed to the stretching vibration of P=O bond.

The powder XRD pattern of Fe₃O₄@SiO₂@UiO-66-TPP NPs is given in Fig. 3b. UiO-66-NH₂ was assembled successfully on the surface of Fe₃O₄@SiO₂ with characteristic peaks of UiO-66-NH₂ (2θ = 7.48, 8.62 and 25.81). The crystal size of the lattice calculated from the XRD pattern by Debye–Scherrer equation was about 39.59 nm.

The N₂ adsorption–desorption isotherms were employed to characterize the specific surface areas of Fe₃O₄@SiO₂@UiO-66-NH₂ and Fe₃O₄@SiO₂@UiO-66-TPP (Fig. 3c). The N₂ sorption isotherms showed typical type I curves, suggesting a mesoporous structure. The BET surface areas of the as-synthesized nanoparticles were calculated to be 515.3 and 600.9 m²/g, respectively. On account of the presence of the Fe₃O₄@SiO₂ core, the BET surface areas of the as-synthesized nanoparticles is lower than that for UiO-66-NH₂. The high specific area of Fe₃O₄@SiO₂@UiO-66-TPP NPs was beneficial for the effective removal of U(VI) from solution.

The magnetic property of Fe₃O₄@SiO₂@UiO-66-TPP NPs was characterized by VSM. As shown in Fig. 3d, the nanoparticles were superparamagnetic, the saturation magnetization (Mₛ) value was 10.15 emu g⁻¹, and the magnetic coercivity (Hc) value was 3.67 Oe (Fig. 3 inset). The Fe₃O₄@SiO₂@UiO-66-TPP NPs can be separated and redispersed effectively in aqueous solution with/without an external magnetic field, which is beneficial to its application in U(VI) removal from aqueous solution.

The surface charge properties of Fe₃O₄@SiO₂@UiO-66-TPP NPs were evaluated through the measurement of Zeta potentials over pH range 1.5–5.5. As shown in Fig. 4, the surface charges of Fe₃O₄@SiO₂@UiO-66-NH₂ and Fe₃O₄@SiO₂@UiO-66-TPP NPs changed greatly, which is due to the decoration of phosphate groups on the nanoparticles. The isoelectric point for Fe₃O₄@SiO₂@UiO-66-TPP NPs was about 3.1. When the pH value was higher than 3.1, the surface of the nanoparticles was negative, and the Zeta potential was −23.3 mV at the pH 5.0. The high negative charge is beneficial for dispersion of Fe₃O₄@SiO₂@UiO-66-TPP NPs, and diffusion of U(VI) ions towards the surface of the magnetic adsorbents.

**Effect of solution pH.** The solution pH is an important parameter that affects the adsorption performance of adsorbents towards U(VI), because it closely related to the speciation of U(VI), the surface charges and binding sites of adsorbents. Herein, the sorption studies of U(VI) on magnetic adsorbents (Fe₃O₄@SiO₂@UiO-66-NH₂, Fe₃O₄@SiO₂@UiO-66-TPP) were carried out over pH range 1.5–5.5. As shown in Fig. 5a, the adsorption capacity of Fe₃O₄@SiO₂@UiO-66-TPP NPs increased rapidly with increasing pH value up to 5.0 for U(VI), followed by a decline at pH 5.5. The Fe₃O₄@SiO₂@UiO-66-TPP NPs reached maximum adsorption capacity at pH 5.0, and the qₑ values was 247.7 mg/g. Meanwhile, the adsorption capacity of Fe₃O₄@SiO₂@UiO-66-NH₂ for U(VI) had no obvious change with the increase of pH, and the maximum adsorption capacity was 32.51 mg/g at pH 5.0.

![Figure 1. Schematic illustration of the fabrication of Fe₃O₄@SiO₂@UiO-66-TPP NPs.](image-url)
Uranium mainly exists in the form of $^{\text{UO}_2}{}^{2+}$ in aqueous solution at or below pH 4.0\textsuperscript{65}. When pH < 3.1, the phosphate groups of Fe$_3$O$_4$@SiO$_2$@UiO-66-TPP NPs were positive, and intense competition between H$^+$ and $^{\text{UO}_2}{}^{2+}$ for binding sites resulted in lower adsorption capacity of the adsorbent. As pH increased, the deprotonation of phosphate groups was promoted, and U(VI) still existed in the form of positive ions, therefore the high and rapid adsorption efficiency could be attributed to the strong electrostatic interaction and chelation between phosphate groups and U(VI). At pH 5.5, the pH environment of solution is not conducive to the chelation between phosphate groups and U(VI), which resulted in the decrease of the adsorption efficiency of the adsorbent for U(VI). When pH is 6, schoepite precipitation ($^{\text{UO}_3}{}^2\cdot2\text{H}_2\text{O}$) appeared in the solution, so further adsorption experiments were conducted at pH 5.0.

Figure 2. TEM and composition mapping images of Fe$_3$O$_4$@SiO$_2$@UiO-66-NH$_2$ (a), Fe$_3$O$_4$@SiO$_2$@UiO-66-TPP (b) NPs before and after (c) U(VI) sorption.
Figure 3. (a) FT-IR spectra of Fe3O4@SiO2 (blue line), Fe3O4@SiO2@UiO-66 (green line) and Fe3O4@SiO2@UiO-66-TPP (pink line) NPs. (b) XRD pattern of Fe3O4@SiO2@UiO-66-TPP NPs. (c) N2 adsorption/desorption isotherms of Fe3O4@SiO2@UiO-66-NH2 and Fe3O4@SiO2@UiO-66-TPP NPs. (d) Magnetization curve of Fe3O4@SiO2@UiO-66-TPP NPs.
**Effect of contact time and kinetic studies.** Figure 5b showed the influence of contact time on the sorption of U(VI) onto magnetic adsorbents (Fe₃O₄@SiO₂@UiO-66, Fe₃O₄@SiO₂@UiO-66-TPP). The adsorption of Fe₃O₄@SiO₂@UiO-66-TPP towards U(VI) quickly reached equilibrium within 15 min, which is due to the strong complexation of phosphate group on the Fe₃O₄@SiO₂@UiO-66-TPP with U(VI).

The pseudo-first-order, pseudo-second-order, mixed 1 2 order, intraparticle diffusion and Avrami kinetic models were used to further explore the interaction mechanism (Fig. 6).

Pseudo-first-order equation:
Pseudo-second-order equation:

\[
q_t = q_e \left(1 - e^{-k_1 t}\right)
\]  
(4)

Pseudo-second-order equation:

\[
q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}
\]  
(5)

Mixed 1,2 order equation:

\[
q_t = q_e \frac{1 - \exp(-kt)}{1 - f_2 \exp(-kt)}
\]  
(6)

Intraparticle diffusion equation:

\[
q_t = k_{ip} \sqrt{t} + c_{ip}
\]  
(7)

Avrami equation:

\[
q_t = q_e \left[1 - \exp(-k_{av} t)^{n_{av}}\right]
\]  
(8)

where \(q_e\) and \(q_t\) (mg/g) are the sorption amounts of U(VI) on \(\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{UIO-66-TPP}\) at equilibrium and at time \(t\) (min), respectively; \(k_1\) (1/min) and \(k_2\) (1/min) represent the rate constants of the pseudo-first-order model.
and pseudo-second-order model, respectively; \( k \) (mg/(g min)) is the adsorption rate constant, \( f_2 \) (dimensionless) and \( K_{ip} \) (mg/(g min\(^{0.5}\))) are the coefficient of mixed 1,2 order and intraparticle diffusion, respectively; \( c_{ip} \) (mg/g) is the intraparticle diffusion constant; \( k_{av} \) (1/min) is the Avrami rate constant; \( n_v \) (dimensionless) is the Avrami component.

Table 1 listed the fitting parameters calculated from these kinetic models (Fig. 6). The pseudo-first order, pseudo-second order, mixed 1, 2-order and Avrami models with a high correlation coefficient \((R^2 > 0.98)\) described the adsorption process of U(VI) better than the intraparticle diffusion kinetic model \((R^2 = 0.44)\).

**Effect of initial U(VI) concentration and isotherm studies.** The adsorption behavior of U(VI) on Fe\(_3\)O\(_4@\)SiO\(_2@\)UiO-66-TPP NPs was investigated by changing the initial U(VI) concentration from 1.6 to 280 mg/L. As shown in Fig. 7a, the adsorption amounts increased quickly with the enhancement of the initial U(VI) concentration from 1.6 to 78.5 mg/L. Then the adsorption reached the maximum capacity when the initial U(VI) concentration was above 200 mg/L, which is ascribed to the saturation of phosphate group binding sites embellished on Fe\(_3\)O\(_4@\)SiO\(_2@\)UiO-66-TPP NPs. The most widespread isotherm models (Langmuir, Freundlich, Temkin, Sips, Toth and Langmuir–Freundlich,) were applied to describe the adsorption behavior (Fig. 7a).

Langmuir isotherm equation:

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{9}
\]

Freundlich isotherm equation:

\[
q_e = K_F C_e^{1/n} \tag{10}
\]

Temkin isotherm equation:

\[
q_e = \frac{RT}{b_T} \ln(A_T C_e) \tag{11}
\]

Toth isotherm equation:
Langmuir–Freundlich isotherm equation:

\[ q_e = \frac{K_{LF}C_e}{1 + (K_{LF}C_e)^{n_{MLF}}} \]  

where \( q_e \) (mg/g) is the equilibrium adsorption capacity (mg/g), \( q_m \) and \( q_{MLF} \) (mg/g) are the maximum adsorption capacities, \( K_{LF} \) is the adsorption equilibrium constant (L/mg), \( K_{LF} \) (mg/g)/(mg/L) is the Freundlich parameter, \( n_{MLF} \) is the Freundlich intensity parameter, \( C_e \) (mg/L) is the equilibrium concentration, \( b_T \) and \( A_T \) (L/g) represent the constant and equilibrium constant of Temkin isotherm model, respectively, \( R \) (8.314 J/(mol K)) is the universal gas constant, \( T \) is the absolute temperature at 298 K, \( n \) and \( K_{LF} \) are the isotherm constants, MLF represent the heterogeneous parameter.

The Langmuir and Freundlich isotherm models describes a monolayer and multilayer adsorption of targeted molecules on adsorbent surfaces. Temkin model incorporates a linear variation of the adsorption enthalpy, which is an extension of Langmuir model. Toth model is also an extension of traditional Langmuir model, which takes into account of heterogeneity and non-uniformity of the binding sites on the adsorbent surface. Langmuir–Freundlich model represents a combination of Langmuir and Freundlich isotherm models, at low concentration it reduces to Freundlich isotherm, it predicts a Langmuir monolayer adsorption. The model isotherm parameters obtained from fitting curves (Fig. 7a) were summarized in Table 2. Obviously, the adsorption process followed Langmuir–Freundlich and Langmuir isotherm models due to high correlation coefficients (R²). The maximum adsorption capacities calculated from Langmuir–Freundlich and Langmuir isotherm models were very close (310.1 and 308.9 mg/g, respectively) to practical adsorption amount (307.8 mg/g).

To investigate the effect of temperature on the U(VI) adsorption capacity of the Fe₃O₄@SiO₂@UiO-66-TPP NPs, the adsorption isotherms of U(VI) on Fe₃O₄@SiO₂@UiO-66-TPP NPs were conducted at three temperatures (298, 313, 328 K) at pH 5.0 (Fig. 7b). The thermodynamic parameters, including \( \Delta S^0 \) (entropy change), \( \Delta H^0 \) (enthalpy change) and \( \Delta G^0 \) (Gibbs free energy change), were calculated by Van't Hoff equation and Gibb's free energy function, to reveal whether the adsorption process was endothermic and exothermic, spontaneous or nonspontaneous.

Van't Hoff equation:

\[ \ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \]  

Gibb's free energy function:

\[ \Delta G^0 = \Delta H^0 - T\Delta S^0 \]  

where \( K_d \) is the equilibrium constant at different temperature, \( R \) is the gas constant (8.314 J/(mol K)), \( \Delta S^0 \) (J (mol K)), \( \Delta H^0 \) (kJ/mol), \( \Delta G^0 \) (kJ/mol) are the entropy, enthalpy and Gibb's free energy change, respectively.

### Table 2. Adsorption isotherm model constants derived from Langmuir and Freundlich isotherms.

| Isotherm models          | Parameters | Fe₃O₄@SiO₂@UiO-66-TPP |
|--------------------------|------------|------------------------|
| Langmuir                 | \( q_m \)  | 308.9                  |
|                          | \( K_L \)  | 0.118                  |
|                          | \( R_L \)  | 0.0782                 |
|                          | R²         | 0.899                  |
| Freundlich               | \( K_f \)  | 99.036                 |
|                          | \( 1/n \)  | 4.522                  |
|                          | R²         | 0.776                  |
| Temkin                   | \( b_T \)  | 47.010                 |
|                          | \( A_T \)  | 2.356                  |
|                          | R²         | 0.895                  |
| Toth                     | \( K_e \)  | 308.0                  |
|                          | \( K_e \)  | 0.731                  |
|                          | \( n \)    | 0.414                  |
|                          | R²         | 0.909                  |
| Langmuir–Freundlich      | \( q_{MLF} \) | 310.1                 |
|                          | \( K_{LF} \) | 0.136                 |
|                          | MLF        | 1.265                  |
|                          | R²         | 0.996                  |

(12) \[ q_e = \frac{K_{e}C_e}{1 + (K_{e}C_e)^{n}} \]  

(13) \[ q_e = \frac{q_{MLF}(K_{LF}C_e)^{MLF}}{1 + (K_{LF}C_e)^{MLF}} \]  

(14) \[ \ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \]  

(15) \[ \Delta G^0 = \Delta H^0 - T\Delta S^0 \]
The thermodynamic parameters were listed in Table 3. The positive $\Delta H^0$ value proved that the adsorption of U(VI) on Fe$_3$O$_4$@SiO$_2$@Uio-66-TPP was endothermic. The positive $\Delta S^0$ value revealed an increase in the randomness at the solid–liquid interface during the adsorption process. The negative $\Delta G^0$ value indicated that the adsorption process was spontaneous and Fe$_3$O$_4$@SiO$_2$@UiO-66-TPP owned high affinity toward U(VI) in aqueous solution. $\Delta G^0$ values decreased with temperature increasing, indicating that higher temperature, the higher the spontaneous trend of spontaneous adsorption of U(VI) on Fe$_3$O$_4$@SiO$_2$@UiO-66-TPP.

Effect of ionic strength and coexisting ions. Nuclear industrial wastewater and seawater contain many kinds of ions, which may affect the mutual interaction between Fe$_3$O$_4$@SiO$_2$@UiO-66-TPP and U(VI). Therefore, the effects of ionic strength and coexisting ions on the adsorption selectivity and capacity of Fe$_3$O$_4$@SiO$_2$@UiO-66-TPP for U(VI) should be further investigated. Figure 8 shows the influence of ionic strength on the adsorption capacity of Fe$_3$O$_4$@SiO$_2$@UiO-66-TPP. As shown in Fig. 8a, the adsorption capacity decreased

| $\Delta H^0$ (kJ/mol) | $\Delta S^0$ [J/(mol K)] | $\Delta G^0$ (kJ/mol) |
|-------------------------|--------------------------|-----------------------|
|                         |                          | 298 K | 308 K | 313 K |
| 35.64                   | 172.89                   | $-15.87$ | $-17.61$ | $-19.33$ |

Table 3. Thermodynamic parameters for the U(VI) adsorption onto Fe$_3$O$_4$@SiO$_2$@UiO-66-TPP NPs.

![Figure 8](https://example.com/fig8.png)

Figure 8. (a) Effect of ionic strength on removal of U(VI) by Fe$_3$O$_4$@SiO$_2$@Uio-66-TPP NPs ($C_0 = 100$ mg/L, $m/V = 0.4$ g/L, $pH = 5.0 \pm 0.1$, and $T = 298$ K). (b) Effect of competitive ions on the selective sorption of U(VI) onto the sorbent ($C_0 = 0.5$ mmol/L for all ions, $pH = 5.0 \pm 0.1$, $T = 298$ K, $V = 25$ mL, $t = 60$ min, and $m = 10$ mg).
slightly by about 18% in the NaCl concentration range of 0.1–0.5 mol/L, which may be attributed to the decrease of ion transfer rate and the interference of electrostatic interaction caused by higher NaCl concentration.

As shown in Fig. 8b, the adsorption capacity of Fe₃O₄@SiO₂@UiO-66-TPP for U(VI) is significantly higher than that of other coexisting ions. The uranium-selectivity (Sₚ) of Fe₃O₄@SiO₂@UiO-66-TPP was 94.4% calculated according to the Eq. (3), exhibiting an excellent selectivity of the magnetic adsorbent for U(VI). The mutual interaction of Fe₃O₄@SiO₂@UiO-66-TPP and U(VI) depends on the chelation of U(VI) with phosphate groups grafted on the magnetic adsorbent. Phosphate group is more inclined to coordinate with actinides than other metal ions in aqueous solutions, leading to the excellent selectivity of Fe₃O₄@SiO₂@UiO-66-TPP for U(VI). Meanwhile, the phosphate group endowed Fe₃O₄@SiO₂@UiO-66-TPP with high adsorption capacity (320.3 mg/g) and fast adsorption rate (15 min). The adsorption selectivity, capacity and rate of Fe₃O₄@SiO₂@UiO-66-TPP are higher than other magnetic adsorbents listed in Table 4.

Desorption analysis. The selection of suitable eluent for desorption of U(VI) from the uranium-loaded Fe₃O₄@SiO₂@UiO-66-TPP NPs may provide better recovery of U(VI). The desorption of U(VI) from Fe₃O₄@SiO₂@UiO-66-TPP NPs was studied in a batch mode using different eluents (HCl, H₂SO₄, HNO₃) at a concentration of 0.01 M. As shown in Fig. 9a, H₂SO₄ was the best eluent with a elution rate of 86.0% due to the extensive protonation on the adsorbent surface, which was further used for five successive adsorption–desorption cycles under identical experimental conditions. As shown in Fig. 9b, the adsorption capacity of U(VI) on Fe₃O₄@SiO₂@UiO-66-TPP NPs decreased from 248.5 to 217.5 mg/g after five regeneration, which was approximately 12.5% reduction. Moreover, the XRD analysis result indicated that the utilized Fe₃O₄@SiO₂@UiO-66-TPP NPs retained the crystal structure stability after 5 cycles (Fig. 9c). These results indicate the potential reusability of Fe₃O₄@SiO₂@UiO-66-TPP NPs for U(VI) removal from aqueous medium.

Application in adsorption of uranium from pre-treated seawater. From the experimental results obtained, it can be seen that Fe₃O₄@SiO₂@UiO-66-TPP NPs has a high adsorption rate and a high adsorption capacity for U(VI) and the adsorption can reach equilibrium in a very short time. Furthermore, the adsorbent exhibits a very good selectivity for uranium ions in the presence of coexisting ions. In order to evaluate the potential application of Fe₃O₄@SiO₂@UiO-66-TPP NPs for U(VI) removal from seawater, we carried out the experiments on adsorption of U(VI) from the uranium-doped seawater. The natural seawater used in the adsorption experiments came from near-surface seawater from Tianjin, China. The concentrations of uranium ions in the uranium-doped seawater is 100 mg/L, and the pH of the solution was adjusted to 5.0. The adsorption capacity of U(VI) on Fe₃O₄@SiO₂@UiO-66-TPP NPs from the pre-treated seawater was 228.6 mg/g, and the adsorption rates reached 91.4%, which were only a little bit lower than the adsorption capacity (249.3 mg/g) and adsorption efficiency (99.7%) from ultrapure water (Fig. 10). This demonstrates that Fe₃O₄@SiO₂@UiO-66-TPP NPs have great potential application in the removal of U(VI) from radionuclide-polluted seawater.

Conclusions

In summary, a novel phosphate group functionalized magnetic metal–organic framework nanocomposite composed of magnetic Fe₃O₄ NPs and UiO-66-NH₂ was successfully prepared and characterized by various techniques. The magnetic nanocomposite was used to remove U(VI) from aqueous solution. The nanocomposite was interspersed with phosphate group that forms a stable chelate with U(VI), and the adsorption of Fe₃O₄@SiO₂@UiO-66-TPP NPs for U(VI) reached equilibrium in 15 min, the maximum adsorption capacity is 307.8 mg/g, and the selectivity (Sₚ) is 94.4% in aqueous media including 10 coexisting ions. Fe₃O₄@SiO₂@UiO-66-TPP NPs possess high adsorption capacities, outstanding selectivity and excellent recyclability towards U(VI), which were

| Adsorbents | qmax (mg/g) | time | Sₚ (%) | pH | References |
|------------|-------------|------|--------|----|------------|
| Uio-66     | 109.9       | 4 h  | Not analyzed | 5.5 | 75         |
| Uio-66-NH₂ | 114.9       | 4 h  | Not analyzed | 5.5 | 75         |
| Fe₃O₄/UiO-66-TPP | < 200 | Not analyzed | 37   | 4.5 | 75         |
| M/SiO₂-Si-SBC | 114.7 | 10 h | Not analyzed | 5.0 | 75         |
| SβCD-APTES@Fe₃O₄ | 286 | 3 h  | Not analyzed | 6.0 | 75         |
| MNHA       | 310         | 2 h  | Not analyzed | 5.0 | 75         |
| Fe₃O₄@C@Ni-Al LDH | 227 | 3 h  | Not analyzed | 6.0 | 75         |
| AO-Fe₃O₄/UiO-66-TPP | 255.0 | 30 min | 57   | 4.5 | 75         |
| Fe₃O₄/P(AA-MMA-DVF) | 413.2 | 45 min | 95.8 | 4.5 | 75         |
| Fe₃O₄/P(GMA-AA-MMA) | 274.7 | 20 min | 77   | 4.5 | 82         |
| Fe₃O₄@AMCA-MIL53(AI) | 227.3 | 1.5 h | Not analyzed | 5.5 | 81         |
| Fe₃O₄@MnO₂ | 106.7       | 120 min | Not analyzed | 5.0 | 84         |
| Fe₃O₄@SiO₂@Uio-66-NH₂ | 27.7 | 130 min | Not analyzed | 5.0 | 84         |
| Fe₃O₄@SiO₂@Uio-66-TPP | 307.8 | 15 min | 94.4 | 5.0 | This work |
Figure 9. Desorption (a) and recyclability (b) studies of Fe₃O₄@SiO₂@UiO₂-66-TPP NPs. (c) XRD pattern of the utilized Fe₃O₄@SiO₂@UiO₂-66-TPP NPs after 5 cycles.
endowed with magnetic separation performance by Fe₃O₄ cores, but the low adsorption efficiency at pH < 3.1 under anoxic condition limited its practical applications. Nevertheless, the research work provides a novel strategy to assemble phosphate group-functionalized MOFs.

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Author contributions
C.B. conceived the experiments; C.B. and Y.Y. synthesized and characterized phosphorus group functionalized magnetic metal–organic framework nanocomposites, and analysed the results. H.N., W.G. and J.G. conducted literature research. The manuscript was prepared by C.B., L.C., W.H. and Y.L. All authors edited the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
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