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DOPO-Modified cellulose microsphere: Preparation and Application for selective adsorption

U(VI) under acidic solutions

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ABSTRACT

Effective radioactive wastewater disposal is of great significance to the wide use of nuclear energy. In this work, 4, 4'-[1, 4-phenyl-bis (9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-yl) dimethyneimino] diphenol (t-DOPO) was used to modify microcrystalline cellulose microsphere (t-DOPOR) to further enhance its affinity toward U(VI) through radiation method. The t-DOPOR were characterized for structural, morphological, and thermal properties by FTIR, SEM and TGA, which prove that t-DOPO is successfully modified on cellulose. Combining the advantage of cellulose and t-DOPO, t-DOPOR possessed abundant functional group (-OH, -NH and P=O), and exhibited extremely strong affinity toward U(VI) with a maximum adsorption capacity of 51.51 mg/g at pH 3. Particularly, A large distribution, K_d^U , up to $2.54 \times 10^4 \text{ mL g}^{-1}$ is found, implying extremely strong affinity toward U(VI) than Ln(III) (La(III), Eu(III), Dy(III), Yb(III)) at the binary system. Dynamic column experiment confirmed that t-DOPOR could separate selectively U(VI) in column experiment. In addition, even in the simulated groundwater trace amount of U(VI) was also eliminated efficiently by t-DOPOR. Lastly, the adsorption mechanism elaborated by XPS analysis was inner-sphere surface complexation between U(VI) and -OH, -NH and P=O groups of t-DOPOR. Overall, the synthesized t-DOPOR may be utilized as a promising adsorbent for separation and remediation of U(VI) from wastewater.

Keywords: Cellulose; DOPO; U(VI); Adsorption; Chelation

Statements and Declarations

Author contributions

The first draft of the manuscript was written by Di Wen and Cong Xie and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Conflicts of Interest

The authors have no relevant financial or non-financial interests to disclose.

Introduction

With the development of nuclear technology, an increasing number of radioactive wastes have been released into the environment (Ding et al. 2015). Uranium, a major resource of nuclear fuel, is inevitably discharged with the release of radioactive wastes, which can pose serious health risks to human beings due to its biological toxicity and high radioactivity (Yuan et al. 2017). Therefore, from the standpoints of environmental protection, it is crucial to eliminate the uranium from wastewater.

Various techniques, such as ion exchange, liquid-liquid extraction, chemical precipitation, filtration, and adsorption, (Mellah et al. 2007; Beltrami et al. 2014; Shao et al. 2018; Satilmis et al. 2019) have been used to remove U(VI). Of the adopted methods, adsorption has considered as one of the more efficient methods due to its high removal efficiency, low cost, and simple operation on a large scale (Cheng et al. 2016). Recently, natural biomaterials are considered as a kind of useful matrix due to their cost-effectiveness, biodegradability, environmentally friendly, controllability (Cao et al. 2017). Among various natural bio-based materials, microcrystalline cellulose microsphere (MCC), possessing a highly crystalline structure, has attracted wide attention due to its unique mechanical and chemical properties (Hokkanen et al. 2016; Dong and Zhao 2018). In our previous work, it is evident that MCC can be used as a matrix to synthesize functionalized adsorbents and the prepared adsorbents with the spherical three-dimensional structure was favorable for the application of fixed-bed column and possessed good recyclability (Dong and Zhao 2018). However, the low adsorption capacity of MCC limited the wide application in the field of adsorption. To improve the adsorptive property of MCC, a suitable monomer with special functional group is necessary.

On the basis of Lewis acid–base theory, there are electrostatic interaction or/and chelation between the U(VI) (Lewis acids) and phosphate groups (Lewis base). Thus, the introduction of phosphate groups in cellulose is conducive to increase more active sites for U(VI) complexation, making it a potential solution for water treatment. After extensive investigations, various phosphorylating agents, for instance, tri-*n*-butylphosphate (TBP) (Zheng et al. 2018), di-1-methyl heptyl methyl phosphonate (DMHMP) (Li et al. 2017), organic phosphine (Wang et al. 2019; Yuan et al. 2020; Zhang et al. 2020) have been used to prepare phosphate-based adsorbents, which showed excellent ability in chelating metals.

Notably, 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is a type of cyclic

phosphate with a diphenyl structure, which have received increasing attention owing to their high reactivity, good thermal properties (Bai et al. 2013; Wendels et al. 2017). In addition, DOPO contains phosphorus-bearing groups such as P=O, P-O, possessing a strong chelation ability toward U(VI) (Budnyak et al. 2016; Pan et al. 2019). Therefore, DOPO could be considered as a phosphorus-bearing monomer, and then grafted onto the solid matrix to capturing U(VI). To the best of our knowledge, few efforts are devoted to investigating material modified by DOPO and DOPO derivative for the adsorption of U(VI).

In the current work, 4, 4'-[1, 4-phenyl-bis (9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-yl) dimethyneimino] diphenol (t-DOPO) (Xie et al. 2018) was selected as functionalized monomer to enhance MCC affinity toward U(VI), owing to it not only has phosphorus-bearing groups, but also contains other functional groups such as -OH, -NH, which also shown a strong affinity toward U(VI) (Ai et al. 2018; Huang et al. 2018). Combination the advantage of cellulose and t-DOPO, t-DOPOR with high mechanical strength, chemical stability and rich functional group is expected to show synergistic effect for U(VI) removal. Therefore, a novel t-DOPO modified cellulose microspheres (t-DOPOR) was fabricated by radiation technique and used as an adsorbent for removal of U(VI) under acidic solutions. The structural, morphological, and thermal properties of t-DOPOR was investigated through various characteristic methods like FTIR, SEM and TGA, and the adsorption performance of t-DOPOR toward U(VI) were systematically investigated under different environmental factors (solution pH, contact time, ionic strength, competitive metal ions, and so on). In addition, the investigation of dynamic column experiment from simulated radioactive wastewater and the removal of the trace amount of U(VI) from contaminated groundwater was also carried out. The adsorption mechanism of U(VI) on t-DOPOR was highlighted by XPS. This work is expected to look for a powerful and high selective adsorbent for removal of U(VI) from radioactive wastewater.

Material and Experiments

Materials

Microcrystalline cellulose microspheres (MCC) (average particle size ca. 220 μm) were supplied by Asahi Kasei Chemicals Corporation (Japan). Glycidyl Methacrylate (GMA), methanol,

dimethylformamide (DMF), and dimethylsulfoxide (DMSO) were purchased from Sinopharm Chemical Reagent, China. $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, KReO_4 , $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were received from Merck (Germany). ZnCl_2 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, HNO_3 , and HCl were purchased from Sinopharm (China). All reagents were of analytical-grade and directly used.

Synthesis of the t-DOPOR

The synthetic route of modified cellulose microsphere adsorbent (t-DOPOR) is illustrated in scheme 1. Firstly, GMA was grafted onto MCC to prepare MCC-g-GMA through radiation induced graft copolymerization as reported in previous work (Dong and Zhao 2018). Secondly, certain amounts of 4, 4'-[1, 4-phenyl-bis (9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-yl) dimethyneimino] diphenol (t-DOPO) and 30% NaOH aqueous solution were added into DMF solution. And then the MCC-g-GMA was immersed in these solutions, which equilibrated at 80 °C for several hours. After that, the final product obtained was purified using deionized water. By drying in an oven at 60 °C, t-DOPO functionalized microcrystalline cellulose microspheres (t-DOPOR) was obtained.

Scheme 1 synthetic route of t-DOPOR via radiation grafting of GMA and ring opening

Characterization

The prepared t-DOPOR was characterized by FT-IR (Nicolet AVATAR 320 FT-IR spectrophotometer), TG (TGA55, TA Instruments, USA), and XPS (AXIS-Ultra instrument from Kratos Analytical). The FTIR spectra with the wavelength range ranging from 4000 – 400 cm^{-1} was recorded. The TG analysis was performed within 0-800 °C at a heating rate of 10 °C/min under air atmosphere. The XPS was conducted by using monochromatic Al K α radiation and low energy electron flooding for charge compensation. The zero potentials of t-DOPOR in the pH range of 1.0–12.0 were measured by

the immersion technique (Fiol and Villaescusa 2009).

Batch adsorption experiments

The batch experiments of U(VI) removal were carried out with 0.01 g t-DOPOR adding into 10 mL polyethylene tubes at 313 K. That is, the ratio of solid (adsorbent dosage) and liquid (solution Volume) (m/v) was 1 L·g⁻¹. The pH of the testing solution was adjusted by 0.1M HCl or NaOH. After a certain time (t), the solutions were collected by filtered with a syringe filter (0.45 µm).

The adsorption amount of U(VI) (q_e , mg/g) and removal efficiency (E, %) by t-DOPOR were calculated by the initial (C_0 , mg/L) and equilibrium concentration of U(VI) (C_e , mg/L) as following Eq. (1-3):

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

$$E = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

Where V and m was the volume of U(VI) solution and the weight of t-DOPOR, respectively.

The distribution coefficient (K_d , mL/g) and separation factor (SF) for the adsorbent were calculated by Eq. (3-4):

$$K_d = \frac{q_e}{C_e} \quad (3)$$

$$\beta_{Re/M} = \frac{K_{d(U)}}{K_{d(M)}} \quad (4)$$

Where $K_{d(U)}$ and $K_{d(M)}$ represented the distribution coefficient of U(VI) and other representative lanthanides ions (La(III), Eu(III), Dy(III), and Yb(III)). The concentration of metal ions was measured by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES-5110, Agilent, American) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS, 147 PE, USA). The ICP data were the average of three parallel measurement.

Dynamic column experiment

To further explore the feasibility of t-DOPOR toward U(VI) in practical application, column adsorption experiments were performed in plastic column (φ5 x 60 mm), and the column was filled with t-DOPOR (0.4 g). Simulated radioactive wastewater containing U(VI), La(III), Co(II), Ni(II), Zn(II) and

Nd(III)) was prepared and used as feed solution. The velocity of space (SV) was regulated at 19.32 h⁻¹. The effluent sample was collected at regular intervals and analyzed for metal ions using ICP.

U(VI) uptake at trace amount of concentration

The contaminated pure water was prepared by injecting U(VI) into pure water. The composition of simulated groundwater (Chen et al. 2019) includes 0.32 mM NaNO₃, 0.78 mM Na₂SO₄, 0.054 mM K₂SO₄, 0.41 mM MgSO₄, 0.17 mM NaHCO₃, and the uranium concentration was 24.3 ug/L. The simulated groundwater was used. 0.01 g t-DOPOR were added into 10 mL of contaminated pure water (6.37 ppb), simulated groundwater (24.3 ppb). After shaking for 48 h in 313 K, the residual trace amount of U(VI) was detected by ICP-MS.

Results and discussion

Characterization

FTIR and SEM analysis

The conversion rate of t-DOPO introduced into cellulose was calculated to be 30% in term of weight method. The FTIR spectra of MCC, MCC-g-GMA, t-DOPOR are given in Fig. 1a. It's seen that after the ring-opening reaction, the peak of the epoxy group (~904 cm⁻¹, ~843 cm⁻¹) disappeared significantly. By contrast, the new adsorption peak of P=O (~1243 cm⁻¹) (Chen et al. 2012), P-O-C (~1115 cm⁻¹, 888 cm⁻¹) (Yuan et al. 2020) were appeared in t-DOPOR. Also, the appearance of new peak at 2922 cm⁻¹, 2851 cm⁻¹ could be ascribed to =CH and -CH stretching of benzene ring (Guo et al. 2019). The band at ~3425 cm⁻¹ are assigned to -NH overlapping with the stretching vibration of the -OH group (Zhu et al. 2018). Thus, the above results proved that the successful introduction of t-DOPO to the microcrystalline cellulose microsphere (MCC)..

Fig. 1b-d showed the SEM images of MCC, MCC-GMA and t-DOPOR. MCC exhibited a spherical shape with smooth surface, while the surfaces of MCC-GMA and t-DOPOR appear rougher with some fracture surfaces. Among the sample, t-DOPOR exhibited largest spherical shape with a diameter ranging from 150-200 μm. These changes were attributed to addition of functional groups (confirmed by FTIR), which directly affected the surface morphology of t-DOPOR.

Fig. 1 FTIR spectra of MCC, MCC-g-GMA, t-DOPOR (a), SEM mages of MCC (b), MCC-GMA (c) and t-DOPOR (d)

TG analysis

The excellent thermal stability of adsorbent is important from the view of practical application. The thermos-stability of MCC, MCC-g-GMA, t-DOPOR was evaluated by TG analysis. The results of TG curves and DTGA (Derivative thermogravimetric analysis) were exhibits as Fig. 2, the thermal stability of t-DOPOR was improved in compared with MCC. As shown in Fig. 2(a), the three peak were represent as volatilization of physically adsorbed water, pyrolysis of the grafted GMA and MCC, and the grafted phosphorus-containing t-DOPO, respectively (Misra et al. 2016). t-DOPOR exhibited higher char yields (22.77%) than MCC and MCC-g-GMA at 800 °C due to the introduction to phosphorus-containing groups of t-DOPO. The TG curve of t-DOPOR indicated three distinct stages corresponding to the three peaks in the DTGA curve (as shown in Fig. 2(b)). Generally, the temperature of radioactive wastewater would elevate with the fission of radionuclides therein (Cai et al. 2017). Thus, the great thermal stability of the t-DOPOR is conducive to the remediation of radionuclide effluents.

Fig. 2 TGA (a) and the corresponding differential thermal gravimetric analysis (DTG) (b) curves of MCC, MCC-g-GMA, t-DOPOR under nitrogen atmosphere

pH studies

Solution pH is an important parameter that affects both adsorbent surfaces and uranium species. In view of this, the adsorption efficiency of U(VI) by t-DOPOR was investigated at pH ranging from 1 to 10. As shown in Fig. 3a, the adsorption efficiency of U(VI) increased dramatically from 12.7 mg/g to a maximum value of 20.18 mg/g with the solution pH increased from 1 to 3. Afterward, the adsorption efficiency gradually decreased with the increasing pH, while maintained stable at ~11 mg/g as the pH ranging from 4.5–10.0. To explain the segmented sorption behavior, pH_{pzc} analysis of t-DOPOR was determined as shown in Fig. S1, which revealed the surface charge of t-DOPOR is positive at $pH < 7$ (pH_{pzc}). The predominant species of U(VI) at solution $pH < 5$ (as shown in Fig. S2), namely UO_2^{2+} , are hardly attached to the positively charged t-DOPOR surfaces due to electrostatic repulsion. The maximum adsorption efficiency of t-DOPOR toward U(VI) was found at $pH=3$, which indicated that the adsorption of U(VI) onto t-DOPOR was attributed to surface complexation. The chelating groups such as amino, hydroxyl, and phosphate shown various formation at a series of pH due to their protonation or deprotonation behavior (Chang and Chen 2006; Dartiguelongue et al. 2016). At low pH values, the hydroxyl, phosphate, and amino group on t-DOPOR will be highly protonated, thus the affinity of t-DOPOR towards U(VI) decreases and correspondingly affect the U(VI) adsorption efficiency. With the increasing pH, the chelation groups become more deprotonated, which exposes more lone pair electrons, thus increase the complexation ability of t-DOPOR toward U(VI). However, $UO_2(OH)_2^-$, $UO_2(OH)_3^-$, $(UO_2)_3(OH)_7^-$ is the main species at $pH > 4.5$ (Fig. S3). These huge molecules hardly approach to the

surface of t-DOPOR owing to the steric hindrance, thus the adsorption capability decreased at alkaline media.

Fig. 3 (a) Effect of pH on U(VI) sorption ($m/v = 1$ g/L, $C_{0(U(VI))} = 20$ mg/L, $t = 24$ h); (b) The effect of contact time on U(VI) sorption ($m/v = 1$ g/L, $pH = 3$, $C_{0(U(VI))} = 20$ mg/L); (c) Effect of the initial U(VI) concentration ($m/v = 1$ g/L, $pH = 3$); (d) The effect of temperature; (e) the effect of ionic strength ($m/v = 1$ g/L, $pH = 3$, $C_{0(U(VI))} = 0.1$ mmol/L); (f) adsorptive capacity on t-DOPOR as function of the consecutive adsorption-desorption cycles ($C_{0(U(VI))} = 20$ mg/L, $m/v = 1$ g/L)

Kinetic studies

The effect of the contact time on t-DOPOR toward adsorption U(VI) at pH 5.0 is depicted in Fig. 3b. The adsorption efficiency of U(VI) increased rapidly at 6 h and then gradually reached the maximum at 10 h. To investigate the controlling mechanism of the adsorption process, pseudo-first-order and pseudo-second-order were used to evaluate the experimental data. As shown in table S1, the highest correlation coefficient value ($R^2 > 0.999$) of pseudo-second-order model and the closest $q_{e, cal}$ to $q_{e, exp}$ indicated the adsorption kinetic data of U(VI) on t-DOPOR was well fitted by the pseudo-second-order kinetics model, indicating the occurrence of chemisorption in the adsorption process.

Sorption isotherm

Adsorption isotherms are crucial to evaluate the amount of U(VI) adsorbed by adsorbents and the adsorption behavior. The adsorption isotherms were investigated using different initial concentrations of U(VI) from 20 mg/L to 200 mg/L. As shown in Fig.3c, the adsorption capacity increased with the uranium concentration. To evaluate the adsorption behavior of t-DOPOR, Langmuir and Freundlich models were applied to fit the experimental data (Lv et al. 2018), the corresponding parameters were summarized in Table S2. The correlation coefficient ($R^2=0.99$) of the Langmuir model was larger than that of the Freundlich models ($R^2=0.98$). Furthermore, the maximum adsorption capacity based on the Langmuir model was calculated as 69.49 mg/g, which agrees with the experimental adsorption data. The results indicated that the Langmuir model described the adsorption well, suggesting the adsorption of U(VI) on t-DOPOR is monolayer coverage.

Thermodynamic studies

The thermodynamic parameters are conducive to evaluate the ease of the adsorption process (Xiao et al. 2019). Fig. 3d showed that the adsorption capacity of t-DOPOR toward U(VI) was increased with the increasing of temperature. Based on the temperature-dependent sorption data, the thermodynamic parameters (i.e., the changes of Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS)) were determined with the following Eq.(5, 6) (Wang et al. 2012):

$$RT\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (5)$$

$$\Delta G = \Delta H - T \Delta S \quad (6)$$

As shown in table S3, the positive ΔH values and the negative ΔG indicated the sorption process is endothermic and spontaneous. The phenomenon can be attributed to the following two reasons: 1) the deprotonation of surface phosphate group would occur with the increasing temperature, which enhances the affinity of t-DOPOR toward U(VI); 2) higher temperature is conducive to U(VI) ion migrated to the surface of t-DOPOR in solution (Malamis and Katsou 2013). Besides, the ΔG value become more negative with the increasing temperature, implying the sorption easily occurs in high temperature.

The effect of ionic strength

The adsorption trend at various ionic strengths can be used to identify the potential adsorption mechanisms (Wang et al. 2016). The adsorption behavior of U(VI) by t-DOPOR was investigated at various ionic strengths (*i.e.*, 0.1, 1, 10, 100, 1000 mmol/L). With the ionic strength increasing from 0.1 to 1000 mmol/L, there were no distinct change of adsorption efficiency observed in Fig. 1d. As demonstrated by previous study, the adsorption trend is very sensitive to ionic strength when U(VI) adsorbed by cation exchange and/or outer-sphere complexation, conversely, the adsorption trend is not affecting when U(VI) adsorbed by the inner-sphere complexation (Sun et al. 2017). Herein, the ignorable effect of ionic strength implied that the interaction of U(VI) and t-DOPOR can be elucidated as an inner-sphere complexation. In addition, the results revealed that t-DOPOR could remove U(VI) from highly saline low level radioactive effluents (Yin et al. 2021).

Treatments of simulated radioactive wastewater

Fig. 4 Effect of co-existing metal ions on the adsorption of U(VI) by t-DOPOR ($C_0 = 0.5 \text{ mmol L}^{-1}$, pH=3, $m/v=1 \text{ g/L}$), (a) K_d and q_e of metal ions

The synthesized adsorbent should have satisfying selectivity toward capturing U(VI) from competing ions in practical application. To evaluated the selectivity of t-DOPOR toward U(VI) from the practical point of view, simulated radioactive wastewater containing a range of metal ions, such as Ce(III), Zn(II), Co(II), Ni(II), Yb(III), Nd(III), Eu(III) and La(III), was prepared. As shown in Fig. 4, the adsorption capacity of U(VI) in the presence of competitive ions was 51.51 mg/g. Also noteworthy is that the remarkable high value of K_d^U of t-DOPOR was around 1200 than the value of K_d of other co-existing ions, indicating t-DOPOR holds an excellent affinity for U(VI). This performance is superior to those of reported GO-CS (Huang et al. 2017), PEI- rGO/MoS₂CAs-3 (Guo et al. 2020) and FH/GO (Li et al. 2018). Clearly, t-DOPOR enable highly selective U(VI) adsorption over multi-component system that major content in radioactive wastewater.

Separation experiments in the binary system

The effect of pH

Fig. 5 (a) Distribution coefficient (K_d) for uranium and other metals on t-DOPOR in U-La, U-Eu, U-Dy, U-Yb binary system in pH 1-3 ($C_0 = 0.1 \text{ mmol L}^{-1}$ for all metal ions, $m/v=1 \text{ g/L}$); (b) Effect of different ratio of composition vs % removal efficiencies in U-La, U-Eu, U-Dy, U-Yb binary system (pH 3, $m/v=1 \text{ g/L}$)

The separation of actinides from lanthanides is an important challenge for the processing of radioactive water. Herein, the effect of lanthanides ions on t-DOPOR for U(VI) adsorption in the binary

system was investigated at various pH. Among the experiment, La^{3+} was the representative of light lanthanides, Eu^{3+} , Dy^{3+} were the representatives of middle lanthanides, and Yb^{3+} was the representatives of heavy lanthanides. As shown in Fig. 5, t-DOPOR could efficiently adsorb U(VI) ions and rarely adsorb other lanthanide ions (La(III) , Eu(III) , Dy(III) , Yb(III)) when $\text{pH} < 3$. As shown in Fig. 5a, at $\text{pH}=3$, a large distribution coefficient, K_d^{U} , exceed 1.4×10^4 mg/g and even up to 2.54×10^4 , while the corresponding values for other earth elements were below 205 mg/g. Consequently, the values of $\text{SF}_{\text{U/La}}$, $\text{SF}_{\text{U/Eu}}$, $\text{SF}_{\text{U/Dy}}$, and $\text{SF}_{\text{U/Yb}}$, are 192.30, 86.04, 161.17, and 73.42, respectively (see Table 1).

Table1 Separation factors (SF) of U(VI) and other metal ions (M) at different pH

pH	$\text{SF}_{\text{U/M}}$			
	U/La	U/Eu	U/Dy	U/Yb
1	25.71	172.40	297.65	408.66
2	180.39	1543.93	154.06	261.31
3	192.30	86.04	161.17	73.42

The effect of different ratio of composition

The concentration of ions is variable in the practical industrial. Thus, the effect of different ratio of composition in binary system was studied at pH 3 on adsorption of U(VI). As shown in Fig. 5b, when the U(VI) concentration was lower (0.1 mmol L^{-1} in 10:1 ratio), the K_d of U(VI) exceeded 4.0×10^3 mg/g, while the K_d of other lanthanides ions (La(III) , Eu(III) , Dy(III) , Yb(III)) were below 100 mg/g. In the high U(VI) concentration (1 mmol L^{-1} in 1:10 ratio), the K_d^{U} exceeded 450 mg/g, while the K_d^{Ln} were below 55 mg/g. Thus, t-DOPOR exhibited attractive U/Ln separation factors of $\text{SF}_{\text{U/Ln}}$ (Table 2).

In summary, t-DOPOR can yield good separation of U(VI) from other lanthanides ions, suggesting that t-DOPOR could be used as potential adsorbent in separation of actinides ions from lanthanides ions in the practical industrial.

Table 2 Separation factors (Sf) of U(VI) and other metal ions (M) at different concentrations

C(U): C(Ln)	$\text{SF}_{\text{U/M}}$			
	U/La	U/Eu	U/Dy	U/Yb
1: 1	192.30	86.04	161.17	73.42

10: 1	497.28	123.52	168.20	231.30
1: 10	64.48	36.27	8.35	74.55

Regeneration study

The service life of adsorbent is important as it greatly affected the treatment cost from the practical point of view. The consecutive adsorption-desorption cycles were repeated five times using 0.1 M HCl used as eluting reagent. As presented in Fig. 1e, the adsorption efficiency slightly decreased from ~97% to ~80% after five desorption-desorption cycles. It was noted that the adsorption efficiency of t-DOPOR was almost constant from the second adsorption-desorption cycle to the five one. The results reveal that t-DOPOR possesses good stability and reusability.

Dynamic column and the trace amount of U(VI) experiment

Fig. 6 The process of fixed-bed column experiments and (b) breakthrough curves of U(VI) selective adsorption on t-DOPOR at pH=3, T=293 K, m(t-DOPOR) = 0.4 g, $C_{0(M)}=1$ mmol/L, $C_{0(U)}=0.1$ mmol/L, $V= 19.32$ mL/h.

The dynamic column experiment of U(VI) and other competing ions (Zn(II), Co(II), Ni(II), Nd(III), La(III)) was explored, which can give theoretical and technical advice to increase the usage of t-DOPOR on the large-scale application. As shown in Fig. 6, the breakthrough point (defined as $C_i/C_0 \leq 5\%$) of Zn(II), Co(II), Ni(II), Nd(III), La(III) took place at the beginning and reached complete saturation at around 15 BV. It can be seen that the value of C_i/C_0 of U(VI) on t-DOPOR remained below 5% at BV <

251 mL/mL, which was significantly higher than that of competing metal ions, which suggests the considerable selectivity of t-DOPOR for U(VI) in the presence of competing metal ions.

In addition, given the uranium contamination in groundwater caused by the improper treatment of uranium tailings is a serious problem, the simulated groundwater was prepared to check the removal performance of t-DOPOR under the environmentally relevant conditions. As shown in table S4, t-DOPOR could remove ~98.5% of the 6.37 ug/L U(VI) from contaminated pure water, and remove ~99.8% of the 24.3 ug/L U(VI) from simulated groundwater. This result demonstrated t-DOPOR is capable of effectively removing U(VI) from the contaminated groundwater at trace levels.

FTIR analysis

After adsorption U(VI), as shown in Fig. S1, a new peak appeared at 925 cm^{-1} which was assigned to the antisymmetric vibration of the UO_2^{2+} (Szlachta et al. 2020). The peak of $-\text{NH}$ (~1577 cm^{-1}), the N-H deformation vibration at 1569 cm^{-1} in t-DOPOR is replaced by two absorption peaks at 1544 and 1572 cm^{-1} , which related to the protonation and hydration of amino group on the surface of t-DOPOR (Cai et al. 2020). Besides, the peak of P=O shifted from 1243 cm^{-1} to 1253 cm^{-1} . Accordingly, the P=O and N-H group were contributed to the adsorption of U(VI).

XPS analysis

The XPS analysis was adopted to further investigate the adsorption mechanism between t-DOPOR and U(VI). After the adsorption of U(VI), a strong double U 4f peaks was appeared in the spectrum of t-DOPOR (Fig. 7a), indicating the U(VI) adsorbed by t-DOPOR. The U 4f peak could be resolved into two peaks at 392.82 eV (U 4f_{5/2}) and 381.93 eV (U 4f_{7/2}) (Fig. S3).

The fitting of P 2p and O 1s, N 1s spectra could deduce the specific functional group that coordinated with U(VI). The high-resolution P 2p spectrum (Fig. 7b) was decomposed into two peaks at 133.04, 132.20 eV, which are assigned to P 2p_{1/2} and P 2p_{3/2}, respectively. The peaks of P 2p_{1/2} and P 2p_{3/2} were shifted to a higher energy after U(VI) uptake, suggesting that the P-related functional group plays a crucial role in the capture of U(VI). The concrete phosphorus group involved can be deduced by O 1s spectra. As shown in Fig 7c, the high-resolution O 1s spectrum was well fitted into four peaks, C=O,

P=O, -OH, and C-O-P, which can be identified at 530.29, 531.19, 532.76, 533.21 eV, respectively (Cai et al. 2017, 2019). It was shown that the position of these O-donor function groups changes after U(VI) uptake. Specifically, the binding energy of P=O, C=O, and -OH bonds were shifted higher values. In contrast, the peak position of C-O-P changed slightly after U(VI) uptake. These phenomena indicated that the adsorption is primarily attributed to U(VI) coordinated with P=O rather than the C-O-P. Similarly, the high-resolution N 1s spectrum (Fig. 7d) was resolved into two peaks 399.58, 399.11 eV, corresponding to NH, NH₂⁺ (Park et al. 2010), respectively. After U(VI) adsorption, the position of NH was shifted (about 0.63 eV) to higher energy, implying that the lone pair of electrons on the N atom of NH group was shared with the U(VI). These results suggested that the adsorption of U(VI) is mainly induced by inner-sphere surface complexation between U(VI) and -OH, -NH and P=O groups of the t-DOPOR and electrostatic interaction and as depicted in Fig. 8.

Fig. 7 (a) XPS survey scans of t-DOPOR before and after U(VI) uptake (b) high resolution scans of P 2p spectra before and after (c) high resolution scans of O 1s spectra before and after. (d) high resolution scans of N 1s spectra before and after U(VI) uptake.

Fig. 8 Possible adsorption mechanism between t-DOPOR and U(VI)

Conclusions

In this work, a novel t-DOPOR was prepared via radiation technology to selectively separate U(VI) from acidic solution. As the chosen functionalized monomer, t-DOPO with abundant functional group, such as -OH, -NH and P=O, which have strong affinity to U(VI). Characterization of the t-DOPOR through different techniques confirmed that t-DOPO is successfully modified on cellulose, and the introduction of t-DOPO endows the cellulose with chemical stability and rich functional group. The t-DOPOR possesses a notable affinity and selectivity toward U(VI) over other lanthanides and heavy metal ions under acidic conditions from simulated radioactive wastewater, especially due to the strong synergistic effect of cellulose and t-DOPO. The U(VI) sorption process on t-DOPOR accorded with the Langmuir isotherm model and pseudo-second-order kinetic model, revealing a monolayer chemisorption. Besides, t-DOPOR exhibited good recyclability and highly salt resistant. Finally, the adsorption and favorable selectivity of t-DOPOR toward U(VI) were attributed to the inner-sphere surface complexation between U(VI) and surface-grated -OH, -NH and P=O groups. Notably, t-DOPOR could separate selectively U(VI) in column experiment, and efficiently remove the trace amount of U(VI) from simulated groundwater, which is expected to apply to the separation and remediation of U(VI) from actual environment. The experiment finding also indicated DOPO derivative could use as a novel class of suitable ligand for removal of U(VI) from aqueous solution and pave the way for the further application of DOPO in adsorption field.

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Compliance with ethical standards

Conflict of interest

The authors declare that they have no conflicts of interest.

Human or animal rights

This article does not contain any studies with human participants or animals performed by any of the authors.

Informed consent

Informed consent was obtained from all individual participants included in the study.

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