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Preparation of porous carbon materials by polyphosphazene as precursor for sorption of U(VI)

Xiaopeng Liu^a, Yan Liu^{a,*}, Yun Wang^a, Dingzhong Yuan^a, Jinbiao Liu^b, Jia Wei Chew^{c,d,**}

^a State Key Laboratory of Nuclear Resources and Environment, East China University of Technology, Nanchang 330013, Jiangxi, China

^b Department of Chemistry, Jiangxi University of Science and Technology, Ganzhou 341000, Jiangxi, China

^c School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459, Singapore

^d Singapore Membrane Technology Center, Nanyang Environment and Water Research Institute, Nanyang Technological University, Singapore 639798, Singapore

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ABSTRACT

Polyphosphazene was synthesized by ultrasonic using 4,4-diaminodiphenyl ether and hexachlorocyclotriphosphazene (HCCP) as precursors. Next, it was further carbonized and functionalized to prepare the carboxylic-acid functionalized N, P co-doped carbon materials (NPCs-COOH). The structure of NPCs-COOH was characterized by FTIR, SEM and XPS. The sorption performance of NPCs-COOH for U(VI) in solution were determined under diverse factors including pH values, initial concentration, equilibrium time and reaction temperature. The results indicated that the optimal pH value was 5.0 and the equilibrium time was 60.0 min. The maximum sorption capacity from experimental results was 425.16 mg/g. The analysis results of the sorption thermodynamics and kinetics showed that the NPCs-COOH had excellent sorption performance so that it can be utilized on removal of U(VI) effectively in aqueous solution.

1. Introduction

Nuclear energy, as a clean and efficient energy, has become the main part to solve the increasing energy crisis [1–3]. U(VI) ions, which can reduce the biological activity of cells and even lead to carcinogenesis [4,5] due to the long half-life and high toxicity, is one of the major nuclear energy resources.

In recent decades, multifarious physical and chemical means have been applied to dislodge U(VI) from wastewater [6–8], such as membrane separation [9–11], ion-exchange [12,13], co-precipitation [14–16], solvent extraction [17,18], sorption [19–21] and so on. These methods have various defects such as low efficiency and secondary pollution though they have some advantages and applicability. However, as to the sorption method, many materials are used as adsorbents with the advantages of low cost, large sorption capacity, vast application range and good repeatability. Since the 19th century, due to the high porosity, low pollution and good physicochemical properties, many kinds of carbon materials have been widely used in the field of sorption, such as graphene oxides [22–24], carbon nanotubes [25–27], activated carbon [28], carbonaceous sphere [29] and carbon fiber [30].

However, they usually show poor sorption performance because of the lack of binding sites on surface. Thus, functionalization was carried out to overcome these defects. Wang et al. [31] treated mesoporous carbon (CMK-3) with sulfuric acid solution to prepare carboxyl functionalized mesoporous carbon (CMK-3-COOH). The maximum monolayer adsorption capacity of CMK-3-COOH and CMK-3 were 250.00 mg/g and 178.60 mg/g, indicating that oxidation increased the sorption capacity. Meanwhile, functionalization improved the selective removal performance of CMK-3 for U(VI). Subsequently, Zhang et al. [32] prepared sulfonated mesoporous carbon (CMK-3-SO₃H) by a vapor phase transfer method and the maximum sorption capacity of U(VI) on the mesoporous carbon after sulfonation increased from 133.51 mg/g to 186.22 mg/g. Experimental results showed that functionalization changed the pore structure and porosity of mesoporous carbon, and improved selective sorption performance. However, the complex synthesis process limits its wider application. Therefore, it is of great significance to find a much simpler method to synthesize carbon materials with abundant binding sites to combine with radionuclides.

Polyphosphazene is a neoteric kind of organic-inorganic polymer. Its main chain is the alternation of single bond and double bond between

* Corresponding author at: Yan Liu, State Key Laboratory of Nuclear Resources and Environment, East China University of Technology, Nanchang 330013, Jiangxi, China.

** Correspondence to: Jia Wei Chew, School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459, Singapore.

E-mail addresses: fzliuyan1986@163.com (Y. Liu), JChew@ntu.edu.sg (J.W. Chew).

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phosphorus atom and nitrogen atom. Due to its excellent thermal stability and structural diversity, phosphazene has been widely used as flame retardant materials [33], catalyst [34], dye adsorbents [35] and so on. It was reported that the polyphosphazenes microspheres could remove cationic dyes from aqueous solution, which was the first investigation that polyphosphazenes microspheres can be used in separation and concentration field [36].

The polyphosphazenes in this paper were synthesized by direct reaction of hexachlorocyclotriphosphazene (HCCP) containing active P—Cl bonds with diamines under mild reaction conditions. Carboxylic acid functionalized N, P co-doped carbon materials (NPCs-COOH) were further prepared to manifold sorption sites for U(VI). The products were characterized by FTIR, SEM and XPS. In addition, a great deal of batch experiments was carried out to look into the effects of pH value, initial concentration, reaction time and temperature on the sorption properties of U(VI). The results showed the functionalization and doped heteratoms on NPCs-COOH could promote the sorption of U(VI).

2. Experimental

2.1. Materials

All reagents and chemicals, including HCCP, 4,4-diaminodiphenyl ether, acetonitrile, uranyl nitrate, absolute alcohol, chloroacetic acid, triethylamine (TEA), sodium acetate, potassium hydroxide, nitric acid, caustic soda and Arsenazo III, were purchased from Aladdin Chemistry Co., Ltd., China. All the reagents were analytical reagent.

2.2. Synthesis of NPCs-COOH

The synthesis route of NPCs-COOH is shown in Fig. 1. Firstly, 0.3453 g of 4,4-diaminodiphenyl ether, 2.0 mL of triethylamine and 0.2431 g of HCCP were poured into 150.0 mL acetonitrile. Then, put the solution into an ultrasonic bath (120 W, 40 Hz) and reacted at 50 °C for 5.0 h. The reaction mixture was centrifugated and white powder polyphosphazene was obtained.

After grinding the polyphosphazene, it was calcined for 2.0 h under N₂ atmosphere at 450 °C at a heating rate of 4 °C/min so that black solid powder (NPCs) was obtained.

20.0 mg of the NPCs and 5.0 mL of nitric acid were put into a stainless-steel cauldron at 120 °C for 5.0 h. Deionized water and ethanol were used for the filtration when it cooled down to room temperature. Finally, the product of NPCs-COOH was obtained after drying (Scheme 1).

Fig. 1. FTIR spectra of NPCs and NPCs-COOH.

2.3. Characterization

A TENSOR27 FTIR spectrometer was used to scan the Fourier Transform Infrared Spectroscopy (FTIR) spectra and the wave number ranged from 4000 to 400 cm⁻¹. The surface structure of the NPCs-COOH was observed by JEOL JSM-5900 Scanning Electron Microscopy (SEM). A Kratos Axis Ultra DLD was used to record X-ray Photoelectron Spectra (XPS) and the reference was C1s lined at 284.8 eV. The specific surface area and pore size of NPCs and NPCs-COOH were tested by surface area and pore size distribution analyzer (BET, Beijing Jin Ai Pu Technology Co., Ltd.).

2.4. Sorption experiment

A UV-VIS (757CRT, Tianjin Guanze Technol. Co., Ltd) was used to characterize the NPCs and NPCs-COOH by batch experiments. Moreover, the target pH was adjusted with 0.1 mol/L HCl and 0.1 mol/L NaOH. Firstly, 25.0 mL of uranium solution with different initial concentrations was measured and the initial pH value was adjusted. Then 5.0 mg of the adsorbent was added into the U(VI) solution and the solution was filtered after the specified reaction time. The concentrations of U(VI) ions were tested by the Spectrophotometry with Arsenazo III at 650 nm. The sorption capacity of adsorbent (q_e , mg/g) for U(VI) ions were computed by the following equation:

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

where C_0 is the original concentration of U(VI) solution (mol/L); C_e is the concentration of U(VI) solution (mol/L) after the specified time of reaction; V is the dosage of the U(VI) solution (mL); and m is the mass of adsorbent (mg).

3. Results and discussion

3.1. FTIR

Fig. 1 shows the FTIR spectra of NPCs and NPCs-COOH. For NPCs, the peaks at 1502 cm⁻¹ and 1605 cm⁻¹ were ascribed to C—N bonds and the stretching vibration of C=C bonds, respectively. The Ar—O—P bonds located at 1005 cm⁻¹, which indicated the successful polycondensation between 4,4-diaminodiphenyl ether and HCCP. For NPCs-COOH, the new peak at 1721 cm⁻¹ was the strong absorption peak of carboxyl. The new peak at 1394 cm⁻¹ was caused by the coupling of O—H in-plane bending vibration and C—O stretching vibration. It confirmed the successful carboxylic acid functionalization of NPCs.

3.2. SEM

SEM images of NPCs and NPCs-COOH were shown in Fig. 2. After carbonization at high temperature, the surface topography of NPCs became rough and porous (Fig. 2a), with an average diameter of about 2.2 μm. After carboxylic acid functionalization, the pore on the surface of NPCs-COOH (Fig. 2b) was obviously added and well-distributed, and the observed size was narrowed to about 1.1 μm. The surface was no longer relatively flat, and the gully with well-distributed aperture was formed, which greatly enlarged the specific surface area of NPCs-COOH to get more contacting chance with U(VI).

3.3. XPS

The chemical structure of NPCs and NPCs-COOH were characterized by XPS spectra. The peaks of NPCs and NPCs-COOH shown in Fig. 3(a) were devoted to O1s, N1s, C1s and P2p at 534.9, 400.5, 285.8 and 135.6 eV, respectively. After functionalization, C1s and O1s peaks intensities of NPCs-COOH increased owing to the carboxyl on the surface of NPCs-

Scheme 1. Synthesis route of NPCs-COOH

Fig. 2. SEM images of (a) NPCs and (b) NPCs-COOH.

COOH. Fig. 3(b) was the XPS spectra of NPCs-COOH after the sorption of U(VI). The new peak beside N1s was attributed to U4f, in which the double peaks at 395.9 and 386.1 eV were actually ascribed to U4f_{5/2} and U4f_{7/2}, respectively. Moreover, O1s peak intensity of NPCs-COOH-U was higher than that of NPCs-COOH. These could suggest that U(VI), in the form of UO₂²⁺, combined with NPCs-COOH successfully.

3.4. Pore structure

The parameters of the relevant pore structure are listed in Table 1. The BET specific surface areas (SBET) of NPCs and NPCs COOH were 623.74 and 432.75 m²/g while the corresponding pore volumes were 0.38 and 1.35 cm³/g, respectively. This indicated that functionalization decreased the SBET of NPCs, but greatly increased its pore volume. In addition, the average pore size of NPCs-COOH (10.42 nm) was much larger than that of NPCs (2.51 nm), which was favor for the sorption of uranium ions and the combination with more binding sites so that greatly improved the sorption capacity of the adsorbent.

3.5. pH values

As exhibited in Fig. 4a, the optimal pH for NPCs and NPCs-COOH to adsorb U(VI) were both 5.0 and the maximum sorption capacity was 64.18 mg/g and 243.47 mg/g, respectively. The sorption capacity of both adsorbents showed a tendency of increasing firstly and then decreasing with the increase of pH value. When the pH was low, the H⁺ concentration in the solution was high, which could occupy most of the binding sites in the form of H₃O⁺ resulting in the relatively low sorption

capacity. The H⁺ concentration started to drop with the increase of pH value, leading to the decrease of the competition ability of H⁺ so that the sorption capacity started to enhance. Fig. 4b shows the functional relationship between the uranium species distribution and pH value. As the pH value increased higher than 5.0, UO₂²⁺ species were hydrolyzed in the form of (UO₂)₃(OH)₅⁺ and (UO₂)₄(OH)₇⁺, resulting into the decline of sorption capacity. All these proved that the sorption process was primarily influenced by the pH values.

3.6. Sorption kinetics fitting

As shown in Fig. 5, the sorption capacity of NPCs and NPCs-COOH initially increased and reached maximum value at about 80.0 min and 60.0 min, respectively. In the initial stage of the sorption, the binding sites of NPCs and NPCs-COOH were ample. After a period of time, the binding sites that could participate in the reaction were completely occupied so that the sorption capacity hardly changed. After functionalization, NPCs-COOH reached equilibrium in even shorter time, which indicated that abundant porous structure and more binding sites could accelerate the process of U(VI) adsorbed on NPCs-COOH.

To study the effect of time on sorption process, the related data were fitted by some kinetic models, such as pseudo-first-order (PFO) and pseudo-second-order (PSO). The models obeyed the following equations:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

Fig. 3. XPS survey spectra of (a) NPCs and NPCs-COOH; (b) NPCs-COOH-U; (c) C1s; (d) O1s; (e) N1s and (f) P2p.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where q_t (mg/g) is the sorption capacity at time t ; k_1 (min^{-1}) and k_2 ($\text{mg}^{-1} \cdot \text{min}^{-1}$) are the rate constants of PFO model and PSO model, respectively.

The relevant parameters were listed in Table 2 by converting the

kinetic fitting curves of NPCs and NPCs-COOH in Fig. 6. R^2 values of PSO model for NPCs and NPCs-COOH were 0.9866 and 0.9994, while those of the PFO model were 0.7862 and 0.9375, respectively. Besides, the theoretical sorption values of the PSO model (q_{cal}) for NPCs (72.46 mg/g) and NPCs-COOH (250.14 mg/g) were much closer to the actual values of 67.42 mg/g and 246.58 mg/g. All these indicated that the sorption process between adsorbent and U(VI) was mainly chemical sorption.

Table 1

Pore structure parameters of NPCs and NPCs-COOH.

Adsorbent	SBET (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
NPCs	623.74	0.38	2.51
NPCs-COOH	432.75	1.35	10.42

3.7. Initial concentrations

As shown in Fig. 7, the sorption capacity of NPCs and NPCs-COOH increased with the raise of initial concentration initially. When the corresponding initial concentrations was 100 mg/L, NPCs and NPCs-COOH reached the maximum sorption capacity of 69.47 mg/g and 425.16 mg/g, respectively. At low concentrations of U(VI) solution, the amount of U(VI) ions was relatively small while that of binding sites was adequate so that few U(VI) ions could combine with adsorbents and the

sorption capacity was low. With the increase of initial concentration, all the binding sites which can take part in the combination were occupied and the sorption capacity did not increase. Besides, the maximum sorption capacity of NPCs-COOH was higher than that of NPCs, which indicated that carboxylic acid functionalization can promote the combination of U(VI) ions and adsorbents.

3.8. Sorption isotherm fitting

The sorption property of NPCs and NPCs-COOH were assessed by Langmuir and Freundlich models and obeyed the following equations:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (4)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

Fig. 4. (a) Influence of solution pH on U(VI) sorption by NPCs and NPCs-COOH; (b) functional relationship between U(VI) species and pH values. ($T = 298.15$ K, $m = 5.0$ mg, $V = 25.0$ mL, $t = 30.0$ min and $C_0 = 50$ mg/L).

Fig. 5. Influence of contact time of solution on U(VI) sorption by NPCs and NPCs-COOH ($T = 298.15$ K, $m = 5.0$ mg, $V = 25.0$ mL, pH = 5.0 and $C_0 = 50$ mg/L).

Table 2

Kinetic parameters of pseudo-first-order and pseudo-second-order kinetic models of U(VI) by NPCs and NPCs-COOH.

Adsorbent	$q_{e,exp}(mg/g)$	Pseudo-first-order model			Pseudo-second-order model		
		$q_{1,cal}(mg/g)$	$k_1(/min)$	R^2	$q_{2,cal}(mg/g)$	$k_2(g/mg \cdot min)$	R^2
NPCs	66.42	99.68	0.0023	0.7862	72.46	0.014	0.9866
NPCs-COOH	246.58	223.62	0.0467	0.9375	250.14	0.003	0.9994

where C_e (mg/L) is the equilibrium concentration and q_m (mg/g) is the maximum capacity; q_e (mg/g) is the sorption capacity when the reaction reached sorption equilibrium; K_L represents the constant of affinity with the binding site on the adsorbent; K_F is a constant relevant to the Freundlich models; and n is the dependence of sorption process on equilibrium concentration.

Fig. 8 shows the fitting curves of NPCs and NPCs-COOH and the corresponding data are listed in Table 3. The fitting curves indicate that the sorption processes of NPCs and NPCs-COOH are more consistent with the Langmuir model ($R^2 = 0.9944$ and $R^2 = 0.9812$, respectively) than the Freundlich model ($R^2 = 0.9778$ and $R^2 = 0.9376$, respectively), which shows that the combination of U(VI) and adsorbents is monolayer sorption. Table 4 shows the sorption properties of other carbon materials for U(VI). The corresponding data showed great superiority of NPCs-COOH, as the maximum sorption capacity calculated by Langmuir model was much higher and the equilibrium time was even shorter than the carbon materials listed in Table 4 under certain conditions.

Fig. 6. (a) Pseudo-first-order and (b) pseudo-second-order sorption kinetics of U(VI) by NPCs and NPCs-COOH ($T = 298.15$ K, $m = 5.0$ mg, $V = 25.0$ mL, $\text{pH} = 5.0$ and $C_0 = 50$ mg/L).

Fig. 7. Influence of initial concentration of solution on U(VI) sorption by NPCs and NPCs-COOH ($T = 298.15$ K, $m = 5.0$ mg, $V = 25.0$ mL, $t = 30.0$ min and $\text{pH} = 5.0$).

3.9. Thermodynamic calculations

Fig. 9 reveals the effect of temperature on sorption process that the sorption capacity of NPCs and NPCs-COOH increased laxly with the raise of temperature. Related thermodynamic calculation was carried out using the following equations:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (6)$$

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

where ΔH ($\text{J}\cdot\text{mol}^{-1}$), ΔS ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), ΔG ($\text{J}\cdot\text{mol}^{-1}$) and T (K) are the enthalpy, entropy, Gibbs free energy change and absolute temperature, respectively. According to the slope and intercept of the fitting curves shown in Fig. 9b, the relative thermodynamic parameters were calculated and listed in Table 5. In the sorption process of uranium by NPCs and NPCs-COOH, the values of ΔH were positive while those of ΔG were negative, indicating that the sorption processes were endothermic and spontaneous processes, respectively. Besides, the positive values of ΔS illustrated that the disorder of the two-phase interface increased during the sorption process. Moreover, the absolute value of ΔG enlarged with the temperature rose, proving that ascending of temperature was instrumental in the sorption process because of the stable chemical

Table 3

Langmuir and Freundlich isothermal sorption fitting parameters of NPCs and NPCs-COOH adsorbed uranium.

Adsorbent	Langmuir			Freundlich		
	K_L	$q_m(\text{mg/g})$	R^2	K_F	n	R^2
NPCs	0.121	217.30	0.9944	5.12	1.02	0.9778
NPCs-COOH	0.015	666.70	0.9812	1.39	1.16	0.9376

Fig. 8. (a) Langmuir and (b) Freundlich isotherms of U(VI) adsorbed by NPCs and NPCs-COOH.

Table 4

Sorption performances of NPCs-COOH and other carbon materials for U(VI).

Adsorbents	Temp. (K)	pH	Sorption capacity (mg/g)	Equilibrium time	Isotherm model	Ref.
NPCs-COOH	298.15	5.0	666.70	60.0 min	Langmuir	-
PAF	293.15	5.0	115.31	1.0 h	Langmuir	[37]
Fe-SC-800	298.15	3.5	148.99	30.0 min	Langmuir	[38]
CNT-TBP	298.15	5.0	166.60	3.0 h	Langmuir	[39]
EDTA-mGO	298.15	5.5	277.43	100.0 min	Langmuir	[40]
NH3-GO	298.15	6.0	80.13	3.0 h	Langmuir	[41]
PAM/GO	295.15	5.0	166.12	6.0 h	Langmuir	[42]

bonds between U(VI) and binding sites on adsorbents.

3.10. Selective sorption performance

Under practical condition, aqueous solution contain many metal ions, which can compete with U(VI) to bind with the binding sites on the surface of NPCs-COOH. In order to explore the selective sorption performance of NPCs-COOH for U(VI), the U(VI) solution containing competitive ions of Pb^{2+} , Ba^{2+} , V^{2+} , Sr^{2+} , Co^{2+} , Ni^{2+} and Eu^{3+} was selected for sorption experiment under the conditions of $\text{pH} = 5.0$, $T = 298.15 \text{ K}$, $t = 120.0 \text{ min}$ and initial concentration of various ions was 100 mg/L . The results shown in Fig. 10 indicated that NPCs-COOH had high selectivity for sorption on U(VI) in the presence of competitive ions and it was promising to be used to remove uranium from aqueous solution.

3.11. Sorption mechanisms

In Fig. 3b, the appearance of U4f peak illustrated the successful combination of U(VI) and adsorbents. Fig. 4c–f are the C1s, O1s, N1s and P2p XPS spectra of adsorbent and Table 6 are the relative data. After the process of sorption, the binding energy of C–N, C–C, pyrrole/pyridone-N, quaternary-N and pyridine-N-oxide bonds did not change, which showed that nitrogen element and C–C bonds were

hardly involved in the sorption process. Almost all the other peaks shifted and the corresponding peaks intensities were decreased. Specifically, it was found that the binding energies of C=O and C–O belonged to carboxylic acid functional groups with P–C, P–N, P–O bonds were decreased after sorption. The results implied that the carboxylic acid functional group and phosphorus element in NPCs-COOH took part in the coordination with U(VI).

4. Conclusions

To sum up, carboxylic acid functional group carbon material (NPCs-COOH) was synthesized in a simple way. The experimental results showed that the carboxylic acid functionalization enhanced the sorption capacity by producing not only more binding sites but also effective pore structure. Moreover, the doped heteroatoms and carboxyl of NPCs-

Fig. 10. Results of selective sorption of NPCs-COOH in specified U(VI) solution ($T = 298.15 \text{ K}$, $m = 5.0 \text{ mg}$, $V = 25.0 \text{ mL}$, $C_0 = 100 \text{ mg/L}$, $t = 120.0 \text{ min}$ and $\text{pH} = 5.0$).

Fig. 9. (a) Effect of temperature on the sorption of U(VI) ($m = 5.0 \text{ mg}$, $V = 25.0 \text{ mL}$, $C_0 = 50 \text{ mg/L}$, $t = 30.0 \text{ min}$ and $\text{pH} = 5.0$); (b) thermodynamics of U(VI) sorption by NPCs and NPCs-COOH.

Table 5

The thermodynamic parameters for U(VI) adsorbed by NPCs and NPCs-COOH.

Adsorbent	$\Delta H \text{ (KJ/mol)}$	$\Delta S \text{ (J/K-mol)}$	$\Delta G \text{ (KJ/mol)}$				
			283.15 K	293.15 K	303.15 K	313.15 K	323.15 K
NPCs	5.0008	32.8552	-4.3014	-4.6298	-4.9584	-5.2789	-5.6074
NPCs-COOH	8.0906	47.7988	-5.2081	-5.9168	-6.3902	-6.8681	-7.3462

Table 6

The parameters for XPS survey spectra of NPCs-COOH and NPCs-COOH-U.

Materials	Carbon element				Oxygen element		
	C-C	C=O	C-O	C-P/ C-N	C-O	P-O	C=O
NPCs-COOH	284.4	288.1	287.2	285.2	532.7	532.9	531.6
NPCs-COOH-U	284.4	287.9	287.1	285.2	532.4	532.7	531.3

Materials	Nitrogen element			Phosphorus element		
	Pyrrolic/ pyridone- N	Quaternary- N	Pyridinic- N-oxide	P-C	P-N	P-O
NPCs-COOH	395.5	400.5	402.1	132.3	132.8	133.7
NPCs-COOH-U	395.5	400.5	402.1	132.1	132.6	133.4

COOH displayed a synergistic effect to promote the combination with U (VI). This work indicates that the NPCs-COOH has the potential as an efficient adsorbent to dislodge U(VI) from aqueous solution.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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