



Solid phase extraction of uranium(VI) onto benzoylthiourea-anchored activated carbon

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ABSTRACT

A new solid phase extractant selective for uranium(VI) based on benzoylthiourea anchored to activated carbon was developed via hydroxylation, amidation and reaction with benzoyl isothiocyanate in sequence. Fourier transform infrared spectroscopy and total element analysis proved that benzoylthiourea had been successfully grafted to the surface of the activated carbon, with a loading capacity of 1.2 mmol benzoylthiourea per gram of activated carbon. The parameters that affect the uranium(VI) sorption, such as contact time, solution pH, initial uranium(VI) concentration, adsorbent dose and temperature, have been investigated. Results have been analyzed by Langmuir and Freundlich isotherm; the former was more suitable to describe the sorption process. The maximum sorption capacity (82 mg/g) for uranium(VI) was obtained at experimental conditions. The rate constant for the uranium sorption by the as-synthesized extractant was 0.441 min^{-1} from the first order rate equation. Thermodynamic parameters ($\Delta H^0 = -46.2 \text{ kJ/mol}$; $\Delta S^0 = -98.0 \text{ J/mol K}$; $\Delta G^0 = -17.5 \text{ kJ/mol}$) showed the adsorption of an exothermic process and spontaneous nature, respectively. Additional studies indicated that the benzoylthiourea-anchored activated carbon (BT-AC) selectively sorbed uranyl ions in the presence of competing ions, Na^+ , Co^{2+} , Sr^{2+} , Cs^+ and La^{3+} .

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1. Introduction

As the most common radionuclide, uranium is considered to be not only an irreplaceable raw material for nuclear energy, but also a serious long-term potential environmental hazard because of its long half-life and high radiological and biological toxicity [1–3]. Since the 1950s, great efforts have been focused on new materials and technologies for separation of uranium(VI) from aqueous solution. Although liquid–liquid extraction (LLE) has been widely used in separation and/or recovery of uranium(IV) from U-containing aqueous solution so far [4–6], this technology is being applied with its insurmountable limitations due to heavy use of organic extractants and solvents and so on [7–9]. The researches on solid phase extraction (SPE) have steadily increased over recent years. In the field of separation of nuclides including uranium, the technology based on SPE can lead to superior applications properties such as high volume reduction ratio, larger cost-effectiveness, more reliable safety in practice, and, more importantly, environmental friendship [8–11].

SPE is the transfer of metals from the aqueous phase to the active sites of the adjacent solid phase; it can also be termed as solid–liquid extraction [3]. Solid phase extractants are composed of a solid matrix and a chelating component (molecule or functional group). The former offers the support for the chelating component and the latter takes charge of the affinity capacity and selectivity for target ions. So far, several solid phase extractants for selective adsorption and separation of uranium(IV) were reported. For example, activated carbon was impregnated with diarylazobisphenol (DAB) [12] or oxalic/succinic acids [13]; and silica gel was functionalized by sulfasalazine [9] or xanthate [14]; moreover, extractants based on polymeric matrix, like N,N-dibutyl-N'-benzoylthiourea impregnating Amberlite XAD-16 [2] and quinoline-8-ol anchoring polymeric resin beads [8], were also studied.

Technically, these chelating components were incorporated into the surface of the support by either impregnation (physical adsorption) or grafting (covalent bonding). Grafting technology, which changes surface functionality of solid matrix by well designed organic reactions (Covalently bonding process), provides more stable linking between chelating component and support, therefore, has been developing vigorously in recent years [15–18].

Comparing with the familiar inorganic matrixes in solid phase matrixes, such as alumina, silica, fluorisil, diatomaceous earth [3], and the polymeric resin support [2,8,10,19], activated carbon pos-

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esses more practical attributes including high surface area and porosity, greater thermo and radiation stability, and especially, rigid and stable porous structure in strong acidic solutions for the most situation in nuclear wastewater [12–13,20,21].

In view of the above, the current work focused on the synthesis and characterization of an extended activated carbon based solid phase extractant, benzoylthiourea grafted activated carbon (BT-AC). Benzoylthiourea was chosen as the chelating component because it is known to have strong tendencies to form complexes with uranyl ions through the N–CS–NH–CO–Ph chelating ligand as in LLE [2,22–24], and the ligand has seldom been investigated in SPE up to now. Of course, uranium(VI) sorption capability of the as-synthesized extractant was also investigated.

2. Experimental

2.1. Apparatus

PerkinElmer IR-843 spectrometer (USA) was used to obtain IR spectra. CARLO 1106 element analyzer (Italy) was used for carrying out CHN analysis. The initial and equilibrium concentration of Cs^+ were measured using atomic adsorption spectroscopy (AAS, Spectr AA220FS, USA), other metal ions in the solution were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Elemental, USA).

2.2. Reagents

A stock solution of uranium(VI) was prepared by dissolving appropriate amounts of standard U_3O_8 in nitric acid aqueous solution and diluted to desired concentration with deionized water. Activated carbon (AC) and tetrahydrofuran (THF) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Benzoyl isothiocyanate (98%) and 3-chloropropylaminehydrochloride were purchased from Acros Organics (USA). All other chemicals and reagents used were of A.R. grade and were used without further purification.

2.3. Synthesis of benzoylthiourea-anchored activated carbon

The designed Scheme 1 for the functionalization of AC by chemical grafting technique in this work is diagramed as below.

2.3.1. Pretreatment and oxidation of AC

A commercial AC was first heat-treated in muffle furnace at 500°C for 4 h under N_2 atmosphere, and then immersed in 10% (v/v) hydrochloric acid solution for 24 h so as to remove the metal ions and other impurities sorbed on it. The purified AC was subsequently suspended in 3.2 M nitric acid solution under stirring and heating at 373 K for 60 min. The resultant was filtered and washed with deionized water to neutral pH followed by ethyl alcohol, and dried at 393 K for 4 h. Then, the oxidized products were heat-treated at 573 K in air in order to enhance the hydroxyl capacity on AC,

and therefore the products with abounding hydroxyl (HO-AC) was obtained [25].

2.3.2. Preparation of 3-chloropropylamine modified AC

Typically, 2 g of HO-AC was dispersed in 100 mL THF. 1.2 g of 3-chloropropylamine was added to the reaction systems. After refluxed for 24 h under stirring, the resultant was filtered, washed by deionized water till pH value near neutrality and dried in a vacuum oven at 70°C for 4 h, and then 3-chloropropylamine modified AC ($\text{NH}_2\text{-AC}$) was ready for the next procedure.

2.3.3. Preparation of benzoylthiourea-anchored AC

The amine group on AC was converted into a multifunctional ligand by reaction with benzoyl isothiocyanate. Typically, $\text{NH}_2\text{-AC}$ and benzoyl isothiocyanate (mass ratio: 1:4) was refluxed in THF for 12 h. The resulting solid was filtered out and washed with 50 mL THF and 50 mL isopropanol, and then dried in the vacuum oven at 70°C for 10 h. Benzoylthiourea-anchored AC (BT-AC) was obtained as a final product.

2.4. Batch method for uranium sorption

The adsorption of uranium(VI) was carried out by contacting specified amount of BT-AC in 25 mL uranium(VI) solutions with different UO_2^{2+} concentration (20–200 mg/L) alone or blending with competing ions (Na^+ , Co^{2+} , Sr^{2+} , Cs^+ and La^{3+}) in a conical flask at adjusted pH. The flask was shaken (200 rpm) at specified temperature (T) for desired contact time (t). The solution was separated from the solids by centrifugation. Then the initial and the equilibrium concentration of tested ion(s) in supernatant were determined. The amount (Q , mg/g) of sorbed uranyl and/or other metal ions was calculated using the following equation:

$$Q = \frac{(C_0 - C_e) \times V}{W} \quad (\text{a})$$

where C_0 is the initial concentration of ion (mg/L), C_e is the equilibrium concentration of ion (mg/L), V is the volume of the testing solution (L), and W is the amount of sorbent (g).

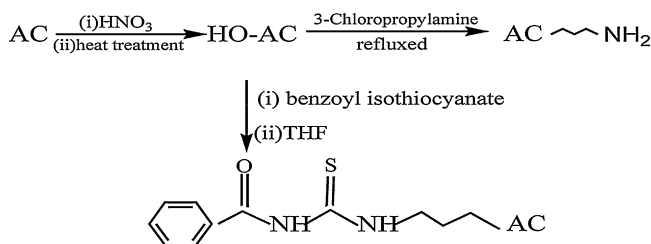
All experiments were carried out in duplicate.

3. Results and discussion

3.1. Characterization studies

3.1.1. FT-IR

The IR spectrum of BT-AC was compared with that of HO-AC, $\text{NH}_2\text{-AC}$ and unmodified AC (Fig. 1). Two bands, in the range of $1600\text{--}1500\text{ cm}^{-1}$ and $3600\text{--}3200\text{ cm}^{-1}$ assigned to the stretching mode of $\text{C}=\text{C}$ groups of aromatic ring and O–H (hydroxyl group)



Scheme 1.

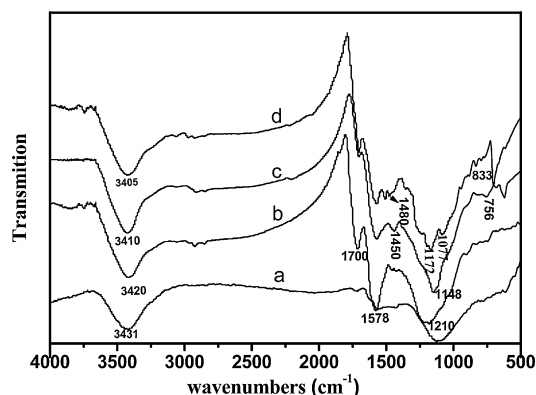


Fig. 1. FT-IR spectra for unmodified AC (a), HO-AC (b), $\text{NH}_2\text{-AC}$ (c), and BT-AC (d).

Table 1
Element analysis of as-prepared solid phase extractant.

	C%	N%	H%	S%
Raw AC	89.20	0.26	1.86	– ^a
HO-AC	68.98	0.78	1.92	– ^a
NH ₂ -AC	68.30	2.83	2.73	– ^a
BT-AC	69.38	4.38	3.33	3.81

^a Under detection limit.

and/or N–H (anchored aliphatic primary amine) respectively, were observed in all spectra. Compared with the plot of unmodified AC (Fig. 1a), the phenolic stretching frequency at 3420 cm⁻¹ and a new frequency at 1700 cm⁻¹ (C=O) appeared in that of HO-AC after oxidation (Fig. 1b). A new frequency at 1450 cm⁻¹ together with band at 756 cm⁻¹ clearly supports the presence of primary amino groups on the surface of NH₂-AC (Fig. 1c) [18]. The bands at 1077 cm⁻¹ and 1480 cm⁻¹ in BT-AC attributed to the C=S stretching vibration mode (Fig. 1d) [12]. In addition, the shift of the vibration (C–O) of phenolic group, from 1210 cm⁻¹ in the HO-AC to 1148 cm⁻¹ in NH₂-AC and 1177 cm⁻¹ in BT-AC indicated the participation of the phenolic group in the functionalization. The above points confirmed the functionalization of AC with benzoylthiourea after hydroxylation, amidation and reaction with benzoyl isothiocyanate.

3.1.2. CHNS

Elemental analysis was performed for each stage of the synthesis to check the extent of ligand functionalization. The results are given in Table 1. The significant increase of N content in NH₂-AC and BT-AC supported the results from IR analysis. Appearance of S content only in BT-AC further confirmed that benzoylthiourea was successfully anchored onto the surface of the AC. The loading ratio of benzoylthiourea was found to be 1.2 mmol benzoylthiourea per gram of AC corresponding to 3.81% of S content based on unmodified AC.

3.2. Uranium-sorption behavior of BT-AC

3.2.1. Effect of pH

The batch tests for adsorption of uranyl ions on BT-AC were performed at different pH values ranging from 1.0 to 5.0 in two parallel samples. As plot shown in Fig. 2, the uranium(VI) sorption capacity increases steeply with increase in pH value. This suggests that the pH value of testing solution is one of the most significant factors for the quantitative separation of UO₂²⁺ ions by BT-AC.

Besides, it should be noted that uranyl ion may convert to other species (such as UO₂OH⁺ and (UO₂)₂(OH)₂²⁺) at lower acidity [26]. So the pH value in this study was limited in the range of 1.0–5.0 for the maximum uranium(VI) initial concentration of 200 mg/L according to solubility calculation [27].

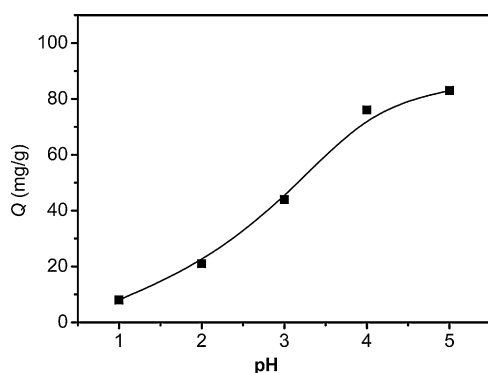


Fig. 2. Effect of pH on sorption of UO₂²⁺, C₀ = 200 mg/L, t = 120 min, T = 293 K.

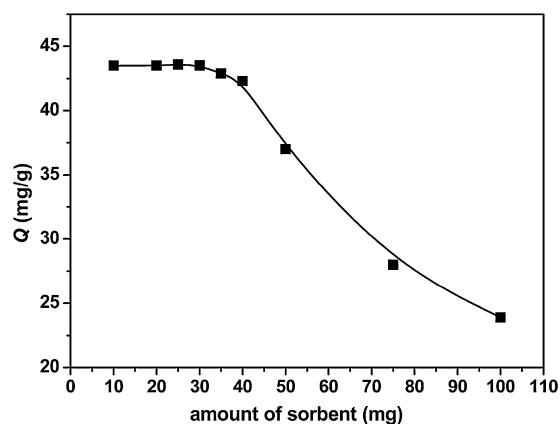


Fig. 3. Effect of amount of sorbent on sorption of uranyl ions, C₀ = 100 mg/L, pH 4.5, t = 60 min, V = 25 mL, T = 293 K.

3.2.2. Effect of amount of sorbent

Effect of the amount of BT-AC on the uptake of uranyl ion was examined in batch tests. The removal efficiency of the uranyl ion was tested with different amounts of BT-AC from 10 to 100 mg in 25 mL U-containing solution (Fig. 3). The results revealed that the sorption capacity of uranyl ion was quantitative from 10 to 30 mg of BT-AC. Beyond 30 mg, the sorption capacity slowly decreased as the amount of sorbent was increased. So the solid–liquid ratio of 1:1 (mg:mL) under the given test conditions was appropriate for quantitative sorption of U(VI) in this sorption system.

3.2.3. Effect of contact time

The sorption amount of uranium(VI) onto BT-AC as a function of contact time was shown in Fig. 4. The uranium(VI) sorption amount increased rapidly during the first 10 min and then gradually tended to equilibrium. It is worth noting that approximately 90% of the maximum sorption capacity was achieved within 5 min.

The kinetics for sorption of U(VI) on BT-AC was found to follow the first order rate expression given by Lagergren [12]:

$$\log(q_e - q) = \log q_e - \left(\frac{K_{\text{ads}}}{2.303} \right) t \quad (b)$$

where q_e and q are the amounts of metal ions sorbed per gram of BT-AC at equilibrium and at time 't', respectively, and K_{ads} is the sorption rate constant. The linear plots of $\log(q_e - q)$ versus 't' in Fig. 5 suggested the applicability of the above equation for sorption of U(VI) on BT-AC. The K_{ads} value calculated from the slope of the plot was 0.441 min⁻¹ for U(VI). The high sorption rate constant might result from fast coordination of uranyl ion with benzoylthiourea ligand immobilized on AC. The activation

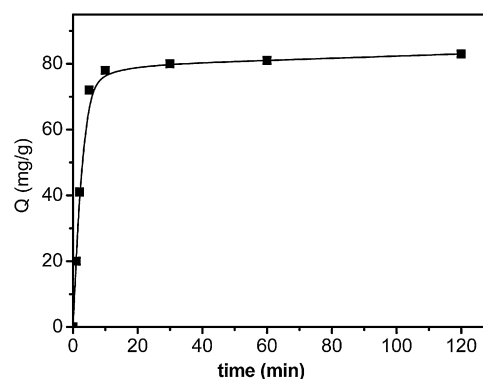


Fig. 4. Effect of time on sorption of UO₂²⁺, C₀ = 200 mg/L, pH 4.5, T = 293 K.

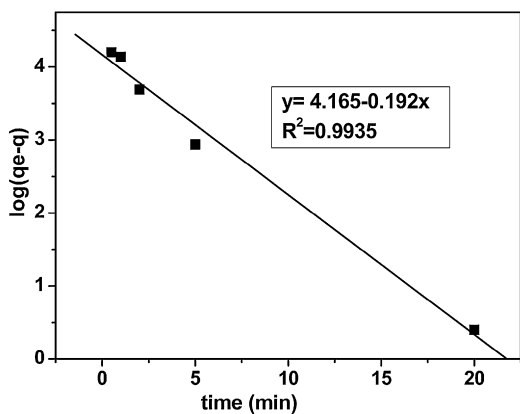


Fig. 5. Lagergren plot for the sorption of uranium(VI). $C_0 = 200$ mg/L, pH 4.5, $T = 293$ K.

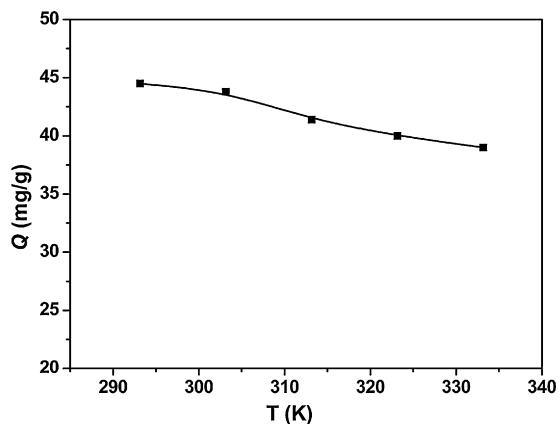


Fig. 6. Effect of temperature on the sorption of U(VI) on BT-AC. $C_0 = 100$ mg/L, pH 4.5, $t = 60$ min.

energy (E_a) calculated using Arrhenius equation [28,29] was found as 8.5 kJ mol $^{-1}$.

3.2.4. Effect of temperature

The sorption of uranium(VI) onto BT-AC was carried out by agitating the testing solution in a temperature-controllable incubation shaker at 293.15, 303.15, 313.15, 323.15 and 333.15 K. The curve in Fig. 6 shows that uptake of uranium(VI) reduced with increasing temperature. The values of ΔH^0 and ΔS^0 were calculated from the slopes and intercepts of linear regression of $\ln K_d$ versus $1/T$ (Fig. 7),

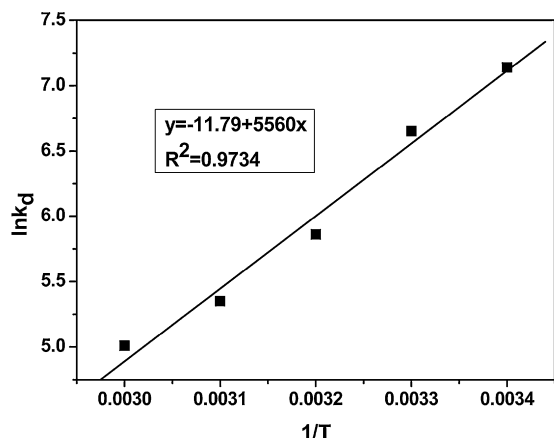


Fig. 7. Plot of $\ln K_d$ vs. $1/T$ for U(VI) adsorption on BT-AC.

Table 2

Thermodynamic parameters for uranium adsorption on BT-AC.

ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)	ΔG^0 (kJ/mol)				
		293.15 K	303.15 K	313.15 K	323.15 K	333.15 K
-46.2	-98.0	-17.5	-16.5	-15.3	-14.5	-13.6

using the relations [28,29]:

$$K_d = \frac{\text{amount of metal in adsorbent}}{\text{amount of metal in solution}} \cdot \frac{V}{M} \quad (c)$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (d)$$

where K_d is the distribution coefficient (mL/g), ΔS^0 is standard entropy, ΔH^0 is standard enthalpy, T is the absolute temperature (K), and R is the gas constant (J mol $^{-1}$ K $^{-1}$). The standard free energy values were calculated from:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (e)$$

where ΔG^0 is the standard Gibbs free energy. The values of ΔH^0 , ΔS^0 and ΔG^0 are given in Table 2. The negative values of ΔH^0 and the decrease in the value of ΔG^0 with rise in temperature showed that the sorption was favoured at low temperature, and the negative free energy values ΔG^0 indicated the feasibility of the process and its spontaneous nature without an induction period.

3.2.5. Sorption isotherm

In order to understand the sorption behavior of BT-AC for uranyl ions, the equilibrium data were evaluated according to the Langmuir isotherms under the experimental condition. The Langmuir equation, which has been successfully applied to many sorption processes [10–12], is given by

$$\frac{C_e}{Q_m} = \frac{1}{kb} + \frac{C_e}{b} \quad (f)$$

where C_e is the equilibrium concentration (mg/L), Q_m is the amount sorbed (mg/g) at equilibrium, b and k are the Langmuir constants related to monolayer maximum capacity (mg/g) and energy of sorption (L/mg) separately. A linear plot of C_e/Q_m versus C_e based on the data from the batch tests for sorption isotherm (Fig. 8-1a) is given in Fig. 8-2. The correlation coefficient for the plot in Fig. 8-2 was found to be 0.9914 indicating a well fit of the experimental data with Langmuir mode. b and k were found as 113.76 mg/g and 0.010 L/mg, respectively. The basic characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter, R_L which is defined by

$$R_L = \frac{1}{1 + kC_0} \quad (g)$$

where k is a Langmuir constant and C_0 is the initial concentration of uranium(VI) [10]. The value of $0 < R_L < 1$ indicates favourable sorption of uranium(VI) onto BT-AC (Table 3).

On the other hand, the Freundlich model stipulates that the ratio of solute sorbed to the solute concentration is a function of the solution. The Freundlich isotherm is an empirical model that is based on

Table 3

Separation factor, R_L .

Initial uranium(VI) concentration (mg/L)	R_L value
20	0.833
40	0.714
50	0.667
100	0.500
150	0.400
200	0.333

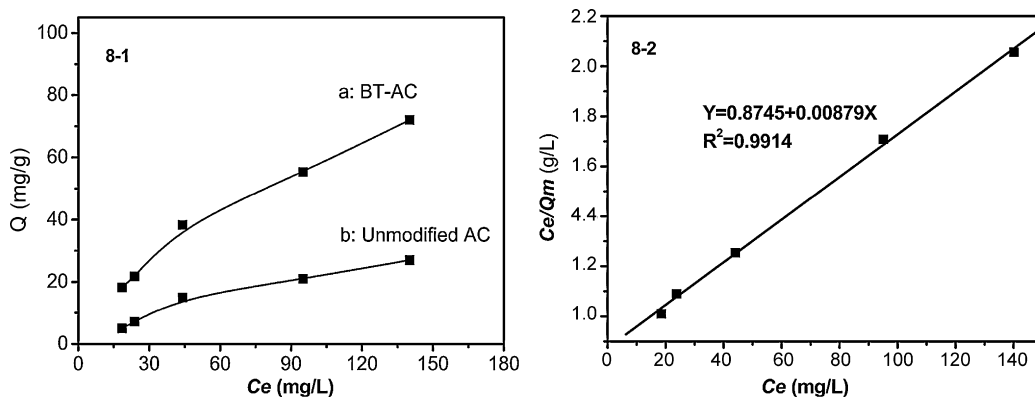


Fig. 8. Langmuir sorption isotherm of U(VI) (1) and the linear fitting (2) based on data in 8-1a after the transformation by the Langmuir Eq. (f), $t = 60$ min, pH 4.5, $T = 293$ K.

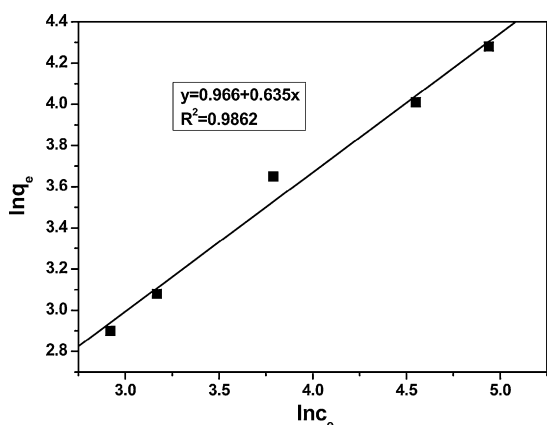


Fig. 9. Freundlich plots for the adsorption of uranium(VI), $C_0 = 200$ mg/L, pH 4.5, $t = 60$ min, $T = 293$ K.

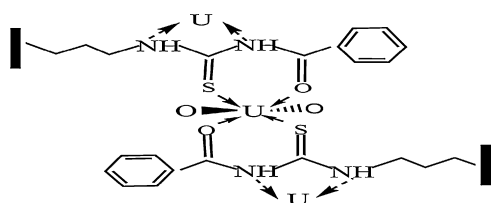
sorption on heterogeneous surfaces and is given as follows [28,29]:

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

where K_F and n are the Freundlich constants, which represent sorption capacity and sorption intensity, respectively. A plot of $\ln q_e$ versus $\ln C_e$ would result in a straight line with a slope of $(1/n)$ and intercept of $\log K_F$ as seen in Fig. 9. The constants K_F and n were found to be 2.63 and 1.57, respectively. The value of $1 < n < 10$ shows a favourable sorption of uranium(VI) onto BT-AC [30].

Comparing the two isotherm models described above, Langmuir isotherm is more suitable to characterize the uranium-sorption behavior of BT-AC according to values of R^2 .

Besides, the data from the experiment also showed much higher uranyl-affinity of BT-AC (Fig. 8-1a) with the maximum sorption capacity (82 mg/g) three times more than that of unmodified AC (Fig. 8-1b). The possible coordination mechanism for the interaction between uranyl ions and the ligands on BT-AC may be illustrated by the following Scheme 2.



Scheme 2.

The as-prepared sorbent provides O, S, N-donor ligands with which uranyl ions readily form complexes [31,32].

Comparing with the known similar research results reported previously, the uranium(VI) capacity of BT-AC is much higher than that of succinic acid immobilized Amberlite XAD-4 (12.3 mg/g) [10], carboxylic acid impregnated carbonized apricot stone (CAS) (2.39 mg/g) [13], diarylazobisphenol impregnated AC (18.72 mg/g) [12] and ZnCl_2 modified AC (28.49 mg/g) [33], and lower than the two extractants, *N,N*-dibutyl-*N'*-benzoylthiourea impregnated Amberlite XAD-16 (214.2 mg/g) [2] and benzoylthiourea immobilized on silica gel (202.3 mg/g) [22]. However, except those made by impregnating methods, polymeric substrate based SPE sorbent may be intolerance to heat and radiation and the ones based on silica gel substrate tends to dissolve at pH values < 2 [21]. It could be understood that the sorption behaviors of uranium(VI) on different SPE extractants mainly depend on the sorts and structure types of selected chelating ligands, the preparing method (impregnation or grafting), as well as the supporting materials used.

3.2.6. Effect of competitive ions

The effects of coexisting mono-, di- and trivalent cations on the uptake of U(VI) by both BT-AC and unmodified AC were examined to evaluate the selectivity of the BT-AC towards U(VI) (Fig. 10). In the presence of competing cations, the total sorption capacity of BT-AC reached 0.64 mmol/g for all ions, which was 40% higher than that of unmodified AC (0.38 mmol/g), and more than 70% of the increased quantity based on the total sorption capacity of the unmodified AC was attributed to the additional sorption of the U(VI) by BT-AC under the same experimental conditions. Moreover, compared the maximum absorption capacity (82.0 mg/g) of BT-AC in "pure" uranium(VI) system with the U(VI) absorption amount of 66.64 mg/g

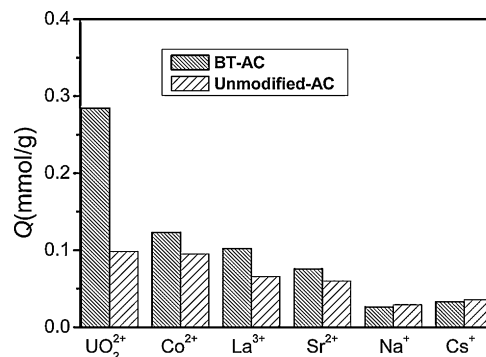


Fig. 10. Competitive adsorption of coexistent ions on BT-AC and unmodified AC. (0.84 mmol/L of initial concentration for UO_2^{2+} , 5 mmol/L for Na^+ , 1 mmol/L for other ions, pH 4.5, $t = 60$ min, $T = 293$ K).

in this multi-ion system, it was clear that the competing ions used in the present study have almost no significant influence on the uptake of U(VI) by BT-AC under the experimental conditions used. The result of the competing sorption test exhibits the following affinity sequence: $\text{UO}_2^{2+} > \text{Co}^{2+} > \text{La}^{3+} > \text{Sr}^{2+} > \text{Cs}^+ > \text{Na}^+$ for the as-synthesized extractant. It could also be seen obviously from Fig. 10 that the unmodified AC used in this study has almost no special affinity to UO_2^{2+} , whereas the resulting product showed highly selective sorption for uranyl ion. All the above suggests a significant role of benzoylthiourea ligand on BT-AC in selective sorption for uranyl ion.

4. Conclusions

In the present work, a new uranium selective solid phase extractant had been developed using commercial AC and an excellent uranium chelating ligand, benzoylthiourea, through grafting technology. The preparation method was simple and the raw materials were cheap and commercially available. Sorption behavior of the as-synthesized extractant for uranium(VI) was examined by batch tests. The extractant had excellent affinity and selectivity for uranium(VI) even in the solution containing a great deal of competing ions. The lower activation energy calculated from Arrhenius equation supports the results obtained from batch tests for effect of contact time. The fast sorption kinetics might be attributed to the coordination between benzoylthiourea on BT-AC and uranyl ion. Thermodynamics studies showed that the sorption progress was exothermic and spontaneous without an induction period. The resulting product would be a promising candidate for solid phase extraction of uranium(VI) from U-contaminated wastewater. The proposed method based on benzoylthiourea-anchoring onto AC provides a valuable reference for the grafting approach of chelating ligands onto various carbonaceous materials.

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