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The Adsorption Properties and Kinetics of Uranium(VI) with a Novel Fibrous and Polymeric Adsorbent Containing Amidoxime Chelating Functional Group from Seawater

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ABSTRACT

The adsorption properties of U(VI) with a new type of fibrous and polymeric adsorbent containing amidoxime chelating functional group (FPAO) from seawater was studied by the method of the static state adsorption at 25 °C. The optimum conditions of the adsorption were determined by investigating the influence of the concentrations of FPAO, U(VI), feed acidity, temperature, and the shape and size of FPAO on the adsorption equilibrium.

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The maximum adsorption capacity of U(VI) in theory was deduced to be 384.6 mg/g dry FPAO by Langmuir isothermic adsorption equation. Freundlich isothermic adsorption equation, expressed as $Q = 4.116[U(VI)]^{0.4293}$, shows that this process can taken place easily because the adsorption factor 1/n equals to 0.4293, which is in the region of 0.1–0.5. Meanwhile, the adsorption kinetics of U(VI) with FPAO was also studied. The rate equation of the adsorption reaction was determined as $-d[U(VI)]/dt = k[U(V)]FPAO]^{1.70}/[H^{+}]$ and the rate constant of the adsorption reaction k was calculated to be 0.5912 min^{-1} for pH 6.0 and ionic strength 0.1 mol/l. The activation energy of the adsorption reaction was calculated to be 28.54 kJ/mol. On the basis of the kinetics results, the adsorption mechanism of FPAO on U(VI) was discussed. The diffusion of uranium ion in internal of the adsorbent was thought to be the rate-controlling step.

Key Words: Fibrous adsorbent; Adsorption properties and kinetics; Amidoxime; Uranium; Seawater.

INTRODUCTION

Seawater is a moderately electrolytic solution and contains many kinds of metal ions. The concentrations of electrolyte, heavy metal ions, and pH value are about 0.6 mol/l, 10^8 mol/l and 8.1–8.3,[1] respectively. The concentration of uranium is only about 1.4($\times 10^{-8}$ mol/l (3.3 mg/m^3),[2] that is; at least 3×10^8 m^3 of seawater among 1.39×10^{18} m^3 of total volume of ocean contains only 1 ton of uranium, and this uranium principally exists in seawater in the form of $UO_2(CO_3)_3^{-4}$, which is the anionic tricarbonatouranate (VI) coordination compound with a high stability.[3] Even though the concentration of U(VI) is much lower, the total amount of uranium, 4–4.5 × 10^9 ton, stored in seawater is much larger.[4] So seawater is an inexhaustible resource for uranium. It can effectively supplement the shortage of uranium and satisfy the demand for uranium for nuclear power plants in the future. It is reported that if 1% of this amount of uranium can be recovered for use in nuclear power plants, the presently known resource will be multiplied by a factor of more than 10. Therefore, considering the anticipated depletion of uranium resource reserves in the future, the recovery of uranium from seawater or other solutions containing uranium waste has been carried out over the past four decades, with increased intensity over the past two decades, and resulting in much important progress and many inspiring achievements.[5–7]

Many research works about recovery of uranium from seawater using various inorganic[8,9] and organic[10,11] sobers, especially some containing chelating functional group adsorbents, e.g., 8-hydroxylquinoline, salicylic acid, resorcinol arsenic acid, phosphonic acid, amino-phosphoric acid, and aminocarboxylic acid have been widely studied since the mid 1950s. Some materials such as hydrous titanium oxide, titanium-activated carbon, and arsenic acid resin etc., were found to combine a relatively high adsorption capacity for uranium with low solubility in seawater. However, it is difficult to recover uranium from seawater because a significant disadvantage of these sobers is their low mechanical resistance against attrition, resulting in a decrease in repeating used times. So a cross-linked poly(acrylamidoxime) chelating adsorbent, which contain so-called amidoxime functional group, has been noticeably paid attention to for recovering uranium from seawater since nearly 20 years.[12,13] Various kinds of fibrous adsorbents containing amidoxime chelating functional group have been synthesized by methods of suspension polymerization and radiation-induced graft polymerization poly(acrylonitrile), followed by functionalization with hydroxylamine (HAN) in ethanol solution.[14,15] Experiments involving is the adsorption of uranium from seawater with spherical resin or bead and fibrous fiber or nonwoven fabric-chelating adsorbents containing amidoxime group indicate that it has very high selectivity, strong adsorption, ability and a large loading capacity on many metal ions, especially on uranium (VI) advantage over others. Furthermore, it is easy to operate and considerably safe for the environment. So the fibrous polymeric adsorbent containing amidoxime chelating functional group is considered the most promising for recovering uranium from seawater iin the near future.[16–20]

In order to economically recover enormous amount of uranium from seawater, in this paper the adsorption properties, kinetics, and a possible mechanism of U(VI) with a new type of fibrous and polymeric adsorbent containing amidoxime chelating functional group have been studied. Some of the adsorption parameters also have been obtained.

EXPERIMENTAL

Reagents

Fibrous and polymeric adsorbent containing amidoxime chelating functional group (FPAO) used in experiment was provided by Takasaki Research Establishment, Japan Atomic Energy Research Institute (JAERI). The average content of the amidoxime chelating functional group in FPAO was about 3.61 mmol/g dry FPAO. The adsorbent was cut into about 3 × 4 mm of small pieces, conditioned with 2.5% KOH solution at 80 °C for 60 min, washed with distilled water to natural form, and then equilibrated with a given pH value solution before used. U(VI) solution at different concentrations was prepared by a stock solution at NUCEF laboratory of JAERI. Other reagents used in experiments were of analytical grades and without further purification.

Adsorption Procedure and Measurement

A weighed amount of FPAO pre-equilibrated with a given pH value solution without containing U(VI) for at least 24 h and U(VI) solution with a given pH value were quickly mixed in 50 ml of triangle flask and shaken mechanically for a desired contact time in a thermostated water bath at the desired temperature. Preliminary studies showed that equilibrium of the adsorption of U(VI) was established in 30 min. In order to reach the adsorption equilibrium completely, the contact time used in the experiment was prolonged to 60 min. The pH value was controlled by addition of two kinds of different buffer solutions, $ClCH_2COOH—ClCH_2COONa$ and $Na_2B_4O_7—H_3BO_3—NaCl$, respectively. Ionic strength of the initial solution was kept at 0.1 mol/l by addition of a stock solution of sodium chloride. The amount of U(VI) adsorbed (Q_t) with FPAO was calculated as follows:

$$Q_t = ([U(VI)]_0 - [U(VI)]_t)\cdot V/W \quad (mg/g \text{ dry FPAO})$$

where $[U(VI)]_0$ and $[U(VI)]_t$ are the concentrations of U(VI) in feed solution at initial and at any time, respectively. V and W are the volume of U(VI) solution and the weight of the dried adsorbent. The concentration of U(VI) in the feed solution either at initial or at any time was measured by ICP-AES (Atomic Emission Spectrometer).

RESULTS AND DISCUSSION

The Influence of Acidity on the Adsorption of U(VI)

The influence of acidity of the feed solution, pH changes from 1.0 to 9.0, on the adsorption of U(VI) was studied at an ionic strength of 0.1 mol/l, FPAO and U(VI) concentrations of 7.260×10^{-3} mol/l and 128 ppm, respectively. The results are shown in Fig. 1. It is to been seen that the amount of U(VI) adsorbed with FPAO in the feed solution rapidly increases with increasing the pH values from pH 1.0 to 3.0, slowly increases from pH 3.0 to 6.0, reaches the maximum value at pH 6.0, and subsequently rapidly decreases from pH 6.0 to pH 9.0. So the optimum acidity is determined as pH 6.0. It shows that the following

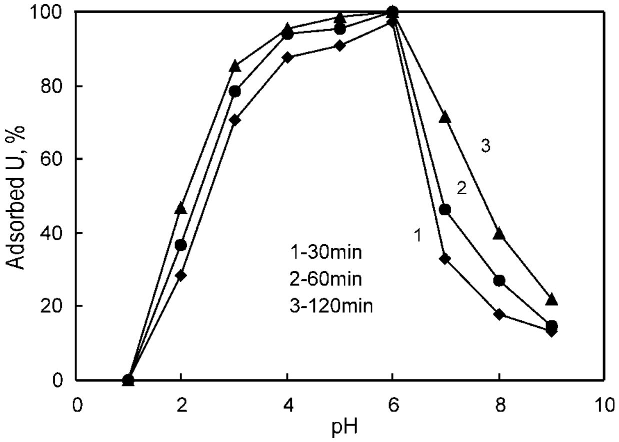

Figure 1. The influence of pH values on the adsorption. $W_{FPAO} = 0.10g$, $[U(VI)] = 128\,ppm$ and $\mu = 0.1\,mol/l$.

dissociation equilibrium exists in the adsorption process and increasing

$$R—C(NH_2)N—OH \leftrightarrow R—C(NH_2)N—O^- + H^+ \qquad (1)$$

pH value of the feed solution can accelerate the process of releasing proton to take place. As a result of this equilibrium, U(VI)-FPAO complex can thus be easily formed by following coordination reaction. So the amount of U(VI) adsorbed with FPAO increases with increasing when the acidity of

$$2R—C(NH_2)N—O^- + UO_2{}^{2+} \rightarrow UO_2(R—C(NH_2)N—O)_2 \qquad (2)$$

the feed solution changes from pH 1.0 to 6.0. However, when pH value is more than 6.0, the amount of U(VI) adsorbed with FPAO decreases obviously with increasing pH values, especially when pH value is 9.0 because of precipitation of U(VI).

The Influence of the Quantity of FPAO on the Adsorption of U(VI)

The influence of the quantity of FPAO on the adsorption of U(VI) was also studied under pH 6.0, the concentration of U(VI) 184.4 ppm and ionic strength 0.1 mol/l, respectively. The results are show in Figs. 2 and 3. It is to been seen that the adsorption percent of U(VI) increases rapidly with increasing the concentration of FPAO and contact time. When the contact time is 20 min, the adsorption percents of U(VI) are 57.8%,

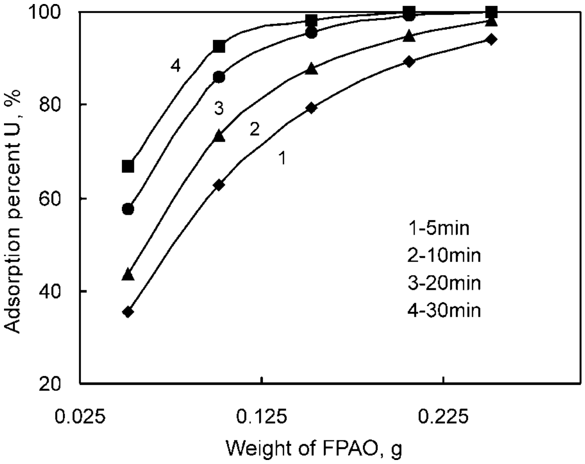

Figure 2. The relationship between the adsorption percent of U(VI) and the amount of FPAO. 1–5 min, 2–10 min, 3–20 min, 4–30 min, [U(VI)] = 184.4 ppm, pH = 6.0, and $\mu = 0.1$ mol/l.

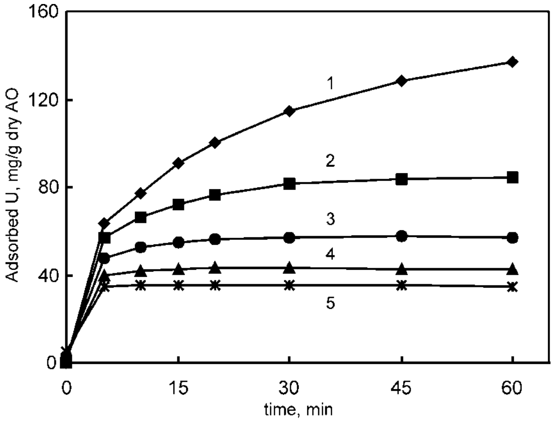

Figure 3. The influence of the concentration of adsorbent on the adsorption. 1–0.0515 g, 2–0.1011 g, 3–0.1542 g, 4–0.2055 g, 5–0.2508 g, [U(VI)] = 184.4 ppm, pH = 6.0, and $\mu = 0.1$ mol/l.

86.1%, 95.5%, 99.1%, and 100% respectively for the amount of FPAO changes from 0.0515 g to 0.2508 g. However, the amount of U(VI) adsorbed with FPAO increases very slowly with increasing the concentration of FPAO before the amount of FPAO on U(VI) absorbed reaches the saturated state. It indicates that FPAO possesses a larger adsorption capacity on U(VI).

The Influence of the Concentration of U(VI) on the Adsorption of U(VI)

The influence of the concentration of U(VI) from 50 ppm to 300 ppm on the adsorption of U(VI) was studied at pH 6.0, the amount of FPAO of 0.015 g and 0.1 g and ionic strength of 0.1 mol/l, respectively. The results are shown in Figs. 4 and 5. From figures, the adsorption percent of U(VI) increases rapidly with increasing concentration of U(VI) when the amount of FPAO is 0.015 g and subsequently slowly increases. It indicates the adsorption of the fibrous adsorbent FPAO on U(VI) gradually approaches its maximum adsorption capacity. However, the amount of U(VI) adsorbed slowly increases in the form of linearity with increasing concentration of U(VI) when the amount of FPAO is 0.1 g, and the adsorption percent of U(VI) also decreases with increasing concentration of U(VI). When the contact time is 20 min, the adsorption percent of U(VI) gradually

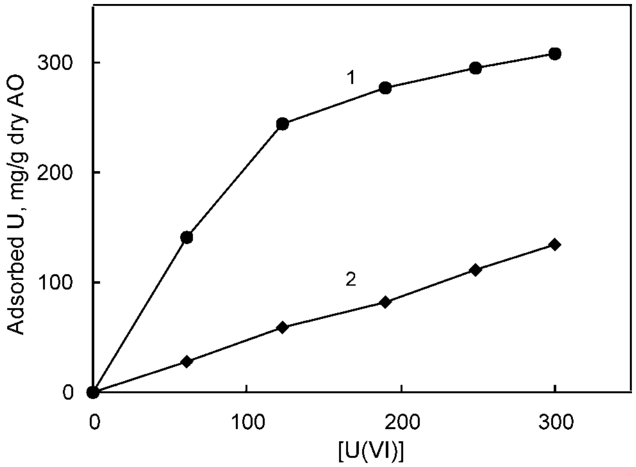

Figure 4. The relationship between the amounts of U adsorbed and the concentration of U. pH = 6.0 and $\mu = 0.1$ mol/l, W_{FPAO}: 1–0.015 g, 2–0.10 g.

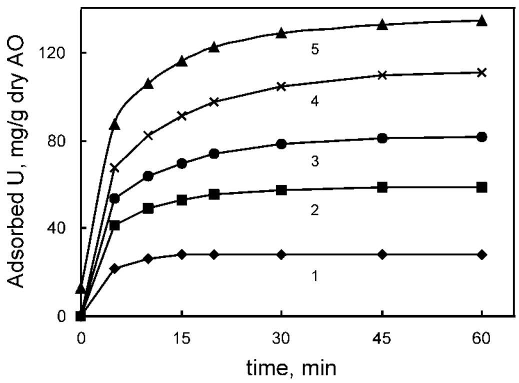

Figure 5. The influence of the concentration of U(VI) on the adsorption. 1–59.0995ppm, 2–124.8895ppm, 3–179.715ppm, 4–250.9075ppm, 5–295.4975ppm, $W_{FPAO} = 0.1g$, pH = 6.0 and $\mu = 0.1$ mol/l.

decreases from 99.8% to 81.3% under the concentration of U(VI) changes from 59 ppm to 300 ppm. It shows the saturated adsorption capacity of U(VI) is far not reached in excess of FPAO.

Determination of the Adsorption Rate Constant

Freundlich Isothermic Adsorption Equation

According to the Freundlich isothermic adsorption equation

$$Q = k_d[\mathrm{U(VI)}]^{1/n} \qquad (3)$$

$$\mathrm{lgQ} = 1/\mathrm{nlg}[\mathrm{U(VI)}] + \mathrm{lg}k_d \qquad (4)$$

the relationship between the adsorption capacity of FPAO on U(VI) and the concentration of U(VI) was investigated and a graph of lgQ vs. lg[U(VI)] is shown in Fig. 6. From Fig. 6, the slope of resultant straight line is 0.4293, that is, 1/n = 0.4293. It shows the adsorption process of U(VI) with FPAO very easily takes place because 0.4293 is in the region of 0.1–0.5. The rate constant of the adsorption reaction was calculated to be $k_d = 4.116$. So the Freundlich isothermic adsorption equation can be expressed as $Q = 4.116[\mathrm{U(VI)}]^{0.4293}$ under experimental conditions.

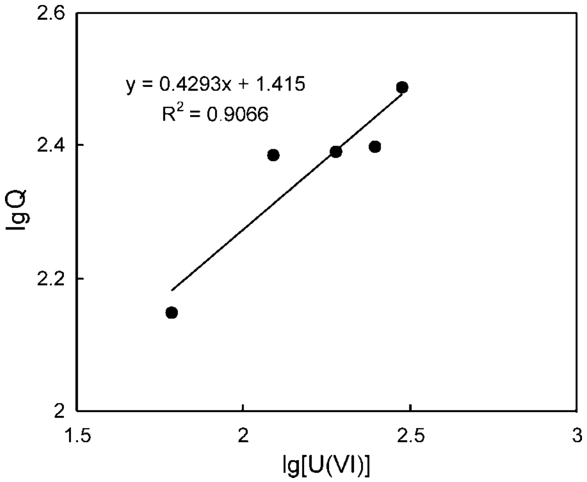

Figure 6. The relationship between the adsorption capacity of U(VI) and the concentration of U(VI). $W_{FPAO} = 0.015g$, pH = 6.0 and $\mu = 0.1\,mol/l$.

Langmuir Isothermic Adsorption Equation

According to Langmuir isothermic adsorption equation

$$1/Q = 1/(k_a Q_{max})\cdot 1/[U(VI)] + 1/Q_{max} \tag{5}$$

the relationship between the amount of U(VI) adsorbed with FPAO and the concentration of U(VI) was also investigated and a graph of 1/Q vs. 1/[U(VI)] is shown in Fig. 7. From the slope of resulting straight line and its cutting distance, the maximum adsorption capacity (Q_{max}) of FPAO on U(VI) and the rate constant of the adsorption reaction (k_a) were calculated to be 384.6 ppm and 9.078×10^{-3}, respectively.

The Influence of the Shape and Size of FPA on the Adsorption of U(VI)

In order to further investigate the adsorption ability of FPAO on U(VI) and effectively recovery U(VI) from seawater and especially from the enriched uranium solution, the influence of the shape and size of the adsorbent, square and round-shaped, on the adsorption of U(VI) was studied in the batch process when other conditions were fixed. Fig. 8 shows that the amount of U(VI) adsorbed increases with an increase in the adsorption

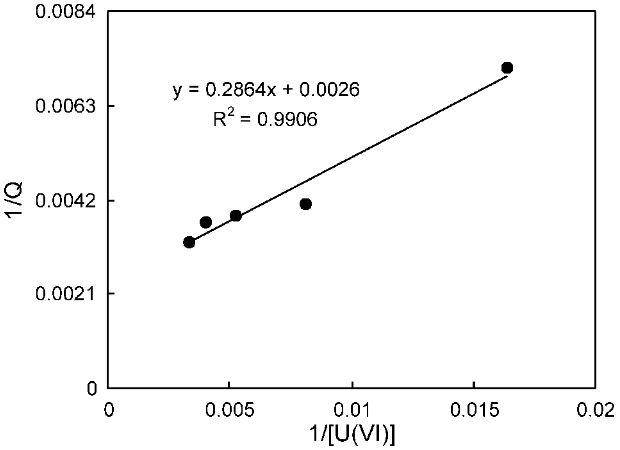

Figure 7. The relationship between the adsorption capacity of FPAO and the concentration of U(VI). $W_{FPAO} = 0.015g$, $pH = 6.0$ and $\mu = 0.1\,mol/l$.

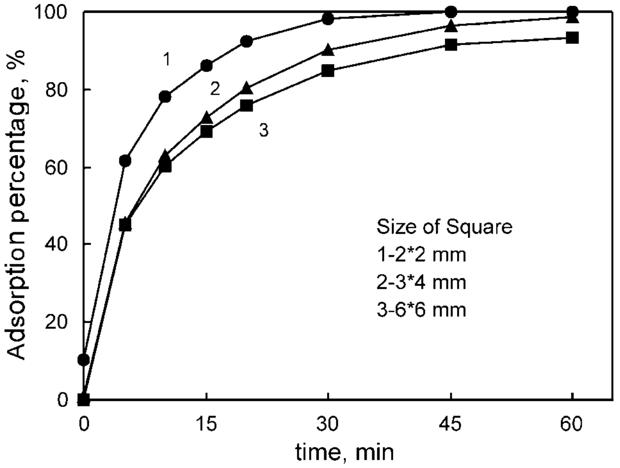

Figure 8. The influence of the shape and size of FPAO on the adsorption of U(VI). $W_{FPAO} = 0.1g$, $pH = 6.0$, $[U(VI)] = 113\,ppm$ and $\mu = 0.1\,mol/l$.

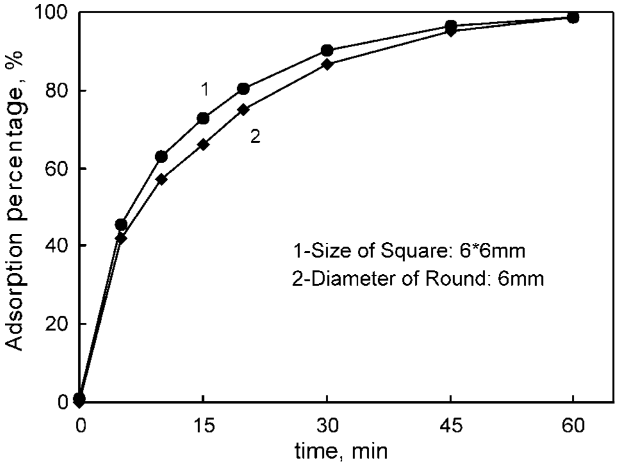

Figure 9. The influence of the shape and size of FPAO on the adsorption. $W_{FPAO} = 0.1g$, pH = 6.0, [U(VI)] = 113 ppm and $\mu = 0.1$ mol/l.

time when the size of square adsorbent is 2 × 2 mm, 3 × 4 mm and 6 × 6 mm, respectively. After a rapid increase in the initial period, the adsorption of U(VI) decreases gradually until it reaches 100% within 30 min in the case of 2 × 2 mm. In the same contact time the adsorption percentages with 3 × 4 mm and 6 × 6 mm were 85% and 90%, respectively. The adsorption percentage of U(VI) with 2 × 2 mm is apparently much higher than that of 3 × 4 mm and 6 × 6 mm. So the order of adsorption ability of U(VI) with different square-shaped adsorbent is 2 × 2mm > 3 × 4 mm > 6 × 6 mm. It shows that the smaller size of adsorbent is beneficial to the adsorption of U(VI).

Figure 9 shows the effect of size of adsorbent, square and round-shaped, on the adsorption properties of U(VI). It is to be seen that the amount of U(VI) adsorbed increases with increasing the contact time at the initial adsorption step, either using, a square-shaped adsorbent or a round-shaped one. However, the adsorption ability of the square-shaped adsorbent on U(VI) seems slightly higher than that of the round one before 30 min, and the adsorption percentages of U(VI) with them are 90% and 86%, respectively. After 30 min, there is no obvious difference in the adsorption percentage of U(VI) with both square and round flat shaped adsorbent.

The Influence of Temperature on the Adsorption of U(VI)

The influence of temperature (25–45 °C) on the adsorption of U(VI) with FPAO was investigated for the weight of FPAO 0.1 g, pH 6.0 and the concentration of U(VI) varied from 111 ppm to 132 ppm (Fig. 10). The results show that the adsorption process of FPAO on U(VI) was an endothermic reaction because the amount of U(VI) adsorbed increases with increasing temperature.

According to $-\ln(1-F) = k_b t$, $F = Q_t/Q_\infty$, a graphs of $-\ln(1-F)$ vs. t is shown in Fig. 11. From Fig. 11, the adsorption equations at different temperatures are listed as follows:

$$25^\circ\mathrm{C}: \quad -\ln(1-F) = 0.1114t \quad \gamma = 0.9961$$

$$30^\circ\mathrm{C}: \quad -\ln(1-F) = 0.1388t \quad \gamma = 0.9932$$

$$35^\circ\mathrm{C}: \quad -\ln(1-F) = 0.1411t \quad \gamma = 0.996$$

$$40^\circ\mathrm{C}: \quad -\ln(1-F) = 0.1800t \quad \gamma = 0.9916$$

$$45^\circ\mathrm{C}: \quad -\ln(1-F) = 0.2287t \quad \gamma = 0.9984$$

The results show that the adsorption process of U(VI) with FPAO is a chemical adsorption because of the linearity between $-\ln(1-F)$ and t.

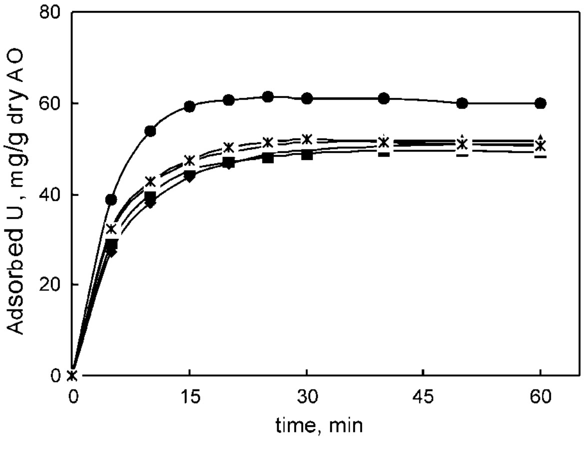

Figure 10. The influence of temperature on the adsorption. 25°C(◆), 30°C(■), 35°C(▲), 40°C(●) and 45°C(∗), $W_{FPAO} = 0.1$g, pH = 6.0, [U(VI)] = 111 ppm for 25 °C, 30 °C, 35 °C and 45 °C, [U(VI)] = 132 ppm for 40 °C and $\mu = 0.1$ mol/l.

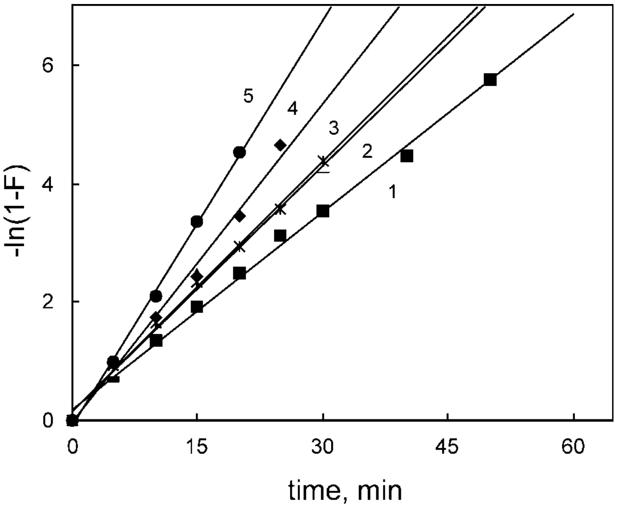

Figure 11. The relationship between $-\ln(1-F)$ and t. 1–25 °C, 2–30 °C, 3–35 °C, 4–40 °C, 5–45 °C, pH = 6.0, $W_{FPAO} = 0.10g$, [U(VI)] = 111 ppm for 25 °C, 30 °C, 35 °C and 45 °C, [U(VI)] = 132 ppm for 40 °C and $\mu = 0.1$ mol/l.

The Adsorption Kinetics of U(VI)

Verification of Pseudo-First Order with Respect to the Concentration of U(VI)

In experiments, the adsorption reaction of U(VI) with FPAO can be assumed as a pseudo-first order with respect to the concentration of U(VI) under the condition that a large excess of FPAO is present over U(IV), i.e., $[U(VI)] \ll [FPAO]$. In order to prove this hypothesis, the adsorption kinetics of U(VI) with FPAO were carried out under conditions in which acidity was pH 6.0 and ionic strength μ was 0.1 mol/l. The typical results are shown in Fig. 12.

It shows plots of $\ln([U(VI)]/[U(VI)]_0)$ vs. contact time t as straight lines passing through the origin with slope equaling $-k'$. Therefore, the hypothesis about the first order of the adsorption reaction with respect to the concentration of U(VI) is fully proved to be correct. The relationship among rate constant of the adsorption reaction k, overall rate constant of the adsorption reaction k', and the concentration of FPAO and acidity can be expressed as follows:

$$k' = k[FPAO]^m[H^+]^n \tag{6}$$

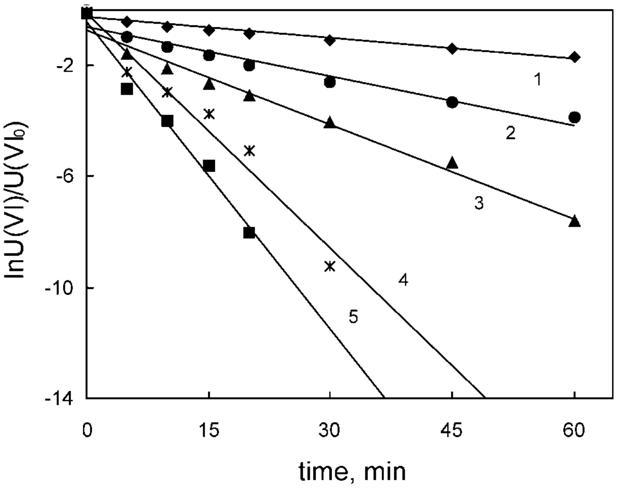

Figure 12. Verification of pseudo-first order with respect to the concentration of U(VI). 1–0.0515 g, 2–0.1011 g, 0.1524 g, 0.2055 g, 5–0.2508 g, [U(VI)] = 184 ppm, pH = 6.0 and $\mu = 0.1$ mol/l.

Where m and n are the reaction orders of adsorption reaction with respect to the concentration of FPAO and H^+.

Determination of the Reaction Orders with Respect to Concentration of FPAO and H^+

According to Eq. (6), the following equation can be obtained

$$\lg k' = m\lg[\mathrm{FPAO}] - n\mathrm{pH} + \lg k \qquad (7)$$

The influence of the concentration of FPAO on the adsorption reaction of U(VI) with fixed concentrations of U(VI) and H^+ has been studied. A graph of lg k' vs. lg[FPAO] is shown in Fig. 13. The slope of the resultant straight line is 1.70 with the correlation coefficient 0.9751. It shows that the order with respect to the concentration of FPAO is 1.70, i.e., m = 1.70. Similarly, the influence of the acidity (pH varied from 2 to 6) on the adsorption reaction with constant concentrations of FPAO and U(VI) has also been studied. A plot of lg k' vs. pH is shown in Fig. 14. From Fig. 15 the slope of the resulting line is 0.96 with the correlation coefficient 0.9961. It shows that the reaction order with respect to the acidity is negative one, i.e., n = −1. Therefore, the rate equation

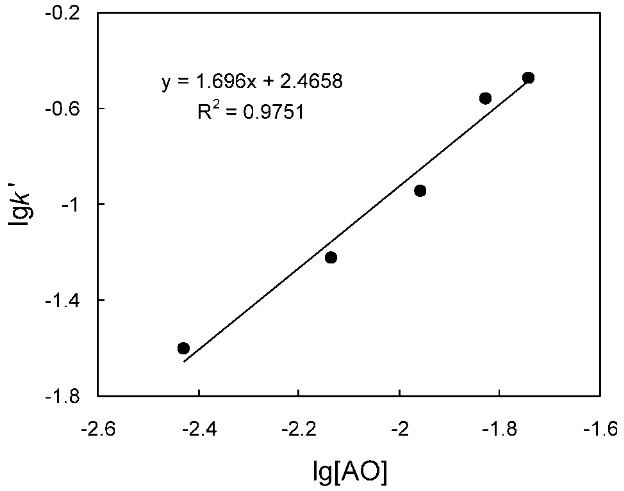

Figure 13. The relationship between lg k' and lg[FPAO]. [U(VI)] = 184.4 ppm, pH = 6.0 and $\mu = 0.1$ mol/l.

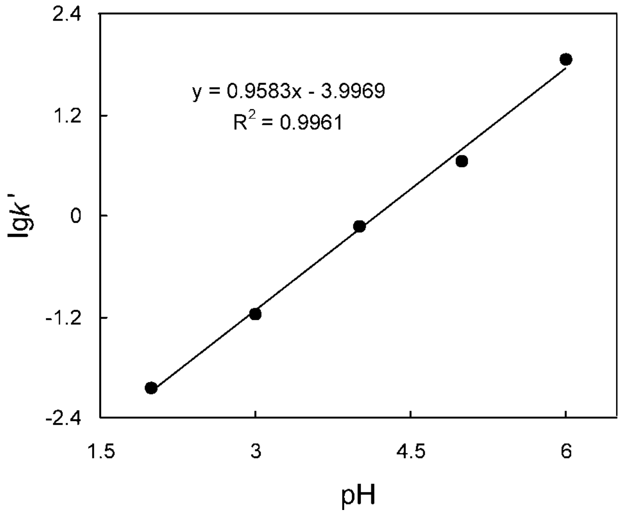

Figure 14. The relationship between lg k' and pH value. $W_{FPAO} = 0.1$g, [U(VI)] = 128 ppm and $\mu = 0.1$ mol/l.

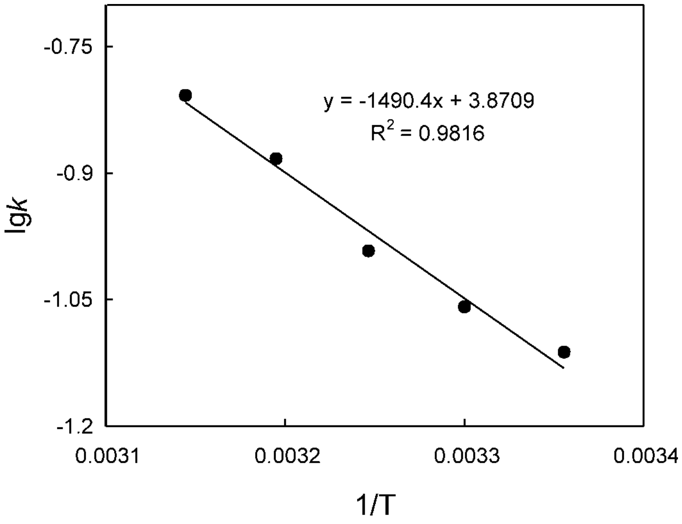

Figure 15. The relationship lg k and 1/T. pH = 6.0, W_{FPAO} = 0.10g, [U(VI)] = 111 ppm for 25 °C, 30 °C, 35 °C and 45 °C, [U(VI)] = 132 ppm for 40 °C and $\mu = 0.1$ mol/l.

of the adsorption reaction between FPAO and U(VI) can be written as:

$$-d[U(VI)]/dt = k[U(VI)][FPAO]^{1.7}/[H^+] \tag{8}$$

From Eq. (8), the rate constant and overall rate constants of the adsorption reaction k and k' were calculated (Table 1). From Table 1, the rate constant could be determined to be $k = 0.5912\,\text{min}^{-1}$.

Table 1. Rate constants k' and k of the adsorption reaction at 25 °C.

[FPAO], mol/l	pH value	k', min^{-1}	k, min^{-1}
7.266×10^{-3}	2.0	0.1306	0.6704
7.259×10^{-3}	3.0	0.3124	0.5904
7.288×10^{-3}	4.0	0.8882	0.6157
7.317×10^{-3}	5.0	1.9165	0.4873
7.353×10^{-3}	6.0	6.3534	0.5922

Determination of the Activation Energy

The investigation of the influence of temperature on the adsorption of U(VI) with FPAO revealed that the adsorption process was an endothermic reaction (Fig. 10). Furthermore, Fig. 12 shows that the adsorption reaction order with respect to the concentration of U(VI) was the first. In order to further obtain the activation energy of the adsorption reaction on the basis of the kinetics results above mentioned, the relationship between the rate constant of the adsorption process and temperature was studied (Fig. 15). From the slope of the plot of lg k vs. 1/T, according to the Arrhenius Law $\mathrm{dln}k/\mathrm{dT} = \Delta E/RT^2$, the activation energy of the adsorption reaction of FPAO on U(VI) is calculated to be $\Delta E = 28.54\,\mathrm{kJ/mol}$.

A Possible Adsorption Mechanism

From the kinetics of the adsorption of FPAO on U(VI), the following mechanism of the adsorption was represented as follows:

$$UO_2{}^{2+}{}_{(aq)} \leftrightarrow UO_2{}^{2+}{}_{(s)} \tag{9}$$

$$UO_2{}^{2+}{}_{(s)} \leftrightarrow UO_2{}^{2+}{}_{(i)} \tag{10}$$

$$UO_2{}^{2+}{}_{(i)} + 2{-}C(NH_2)NOH \leftrightarrow UO_2({-}C(NH_2)O)_{2(i)} + 2H^+ \tag{11}$$

Where (aq), (s), and (i) present uranium ions in deep solution, surface, and internal of the fixed phase (e.g., adsorbent), respectively.

When the adsorption procedure takes place, U(VI) ion in bulk solution first needs to move to the surface of the adsorbent, that is, from the aqueous phase to the surface of the fixed phase. It is a faster step because of the smaller resistance in solution. So Eq. (9) is a mobile equilibrium of U(VI) and a quick step in the adsorption mechanism.

Eq. (11) is a complex equilibrium of U(VI) with FPAO. It involves a chelating reaction between U(VI) ion that had already immersed into internal of FPAO and the functional groups, e.g., $-NH_2$ and $-OH$, contained in FPAO. It is a faster process because the coordination reaction of U(VI) ion and N or O atom is a chemical process and the activation energy in this procedure is very small.

Eq. (10) is a diffusion process of U(VI) ion from the surface of the fixed phase to internal of the fixed phase, which is believed to be the rate-controlling step in the entire adsorption process since this procedure is very slow. For cross-linked fibrous adsorbents possessing high molecular weight and structure, hydrous U(VI) ion with a heavy ion atmosphere and bigger volume is very difficult to diffuse from the surface of the adsorbent to internal of FPAO with a narrow and small cavity. So there is considerably big resistance inside FPAO. The activation energy in this process is thus believed to be much higher. In experiments, although the velocity of the mechanical shaker increases to around 160 RPM, the increasing of the adsorption rate of FPAO on U(VI) is still not quick. Of course, this conclusion further needs to be proved by dynamics state, e.g., column operation experiments.

CONCLUSIONS

Amidoxime possessing a very strong coordination ability on U(VI) and many metal ions is a double-functional group compound containing $-NH_2$ and $=N-OH$. In order to research the possibility of recovery U(VI) from seawater, enriched uranium solution, or radioactive waste liquid, the adsorption behavior of the fibrous adsorbent containing amidoxime-chelating functional group (FPAO) on U(VI) was investigated by ICP at 25°C. The results show that: (1) the acidity has a considerably strong effect on the adsorption of FPAO on U(VI). The amount of U(VI) adsorbed increases with increasing pH value when pH changes from 1.0 to 6.0. However, the percent of U(VI) adsorbed with FPAO rapidly decreases after pH 6.0. So the optimum pH value is 6.0 for the adsorption of U(VI) with FPAO. (2) The amount of U(VI) adsorbed also increases with increasing the concentrations of U(VI) and FPAO, and adsorption behavior can be expressed with isothermic adsorption equations of both Freundlich and Langmuir. The Freundlich isothermic adsorption equation, $Q = 4.116[U(VI)]^{0.43}$, shows that the adsorption process of FPAO on U(VI) very easily takes place because $0.1 < 0.43 < 0.5$. By Langmuir isothermic adsorption equation, the maximum adsorption capacity of FPAO on U(VI) in theory is calculated to be 384.6 ppm. (3) The size of FPAO has a noticeable effect on the adsorption of U(VI), and the order is $2 \times 2\,\text{mm} > 3 \times 4\,\text{mm} > 6 \times 6\,\text{mm}$. For the shape of FPAO, the order of effect on U(VI) is square-shaped FPAO, slightly greater than that of round-shaped. (4) Temperature experiments show that the adsorption process is an endothermic reaction, and the adsorption behavior of FPAO on U(VI) at different temperatures can all be described by $-\ln(1 - F) = kt$. The activation energy of the adsorption reaction is calculated to be $\Delta E = 28.54\,\text{kJ/mol}$. (5) By investigating the effect of concentration of U(VI), FPAO, and acidity on the adsorption process, the rate equation of kinetics in the experiment is determined as $-d[U(VI)]/dt = k[U(VI)][FPAO]^{1.7}/[H^+]$, and the rate constant of adsorption k is $35.47 s^{-1}$ for pH 6.0 and ionic strength 0.1 mol/l. (6) The adsorption mechanism is discussed. The diffusion of U(VI) in internal of FPAO is believed to be the rate-controlling step. However, the adsorption mechanism may be considerably complicated because the order of the adsorption reaction with respect to the concentration of FPAO is 1.70. The detailed mechanism of the adsorption needs to be further investigated.

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