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Kinetic and thermodynamic studies on the adsorption of U(VI) onto humic acid

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ABSTRACT

Humic acid was applied to the adsorption of U(VI) from aqueous solution. Adsorption kinetics was determined from the experimental data, and the results showed that pseudo-second-order kinetic model matched well for the adsorption of U(VI) onto humic acid. Thermodynamic parameters including free energy, enthalpy, and entropy of adsorption were obtained, and all the results were in favor of the adsorption. It was found that the adsorption rate was the best at pH 5.0. It can be concluded from FT-TR spectra that there is chemical adsorption in the U adsorption.

Keywords: Humic acid; Uranium; Adsorption; Kinetic studies; Thermodynamic studies

1. Introduction

Humic substances are ubiquitous natural macromolecule organic materials which can be found in many upland streams, coal, peat, and dystrophic lakes. Humic acid is one of the major components of humic substances which contribute to various stages of soil and plant development, is biologically active in soil and play important roles in plant stimulation. The average humic acid weight is more than hundreds of thousands [1], besides, it has a backbone of aromatic and aliphatic residues with numerous substituents such as ketones, OH groups, carboxylic acid groups, amino acids/peptides, saccharides, and amino saccharides [2]. Moreover, it is found that because of the adsorption ability of humic acid, it can interact with radioactive nuclides, and affect their speciation, migration–sedimentation redox, or other chemical behavior [3,4].

Therefore, humic acid plays a significant role in the geochemical behavior and migration of uranium and other actinide ions in the geosphere [5,6]. Hence, the impact of humic acid on the stability and solubility of U(VI) solid phases and species predominantly formed is of particular interest.

Chemists and geologists have researched on the adsorption of humic acid with uranium and transuranic elements. Some studies have shown that in the migration process, U exists in form with UO_2^+, which can exchange H^+ of absorbed HA. There are many factors which have effect on the adsorption of uranium onto humic acid, especially the effect of pH which is more significant [7]. Meanwhile, different concentrations of HA will have different effects on the chemical form of the radionuclides [8,9].

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In the past few decades, scholars of uranium and transuranic elements have made a lot of research on the chemical form and the migration of the interaction between the humic substances with uranium and transuranic elements. However, due to the different source and extraction method, the composition and nature of humic acid are different, which results in different adsorption ability and different interaction mechanism. With the development of nuclear science and nuclear industry, in-depth study of nuclear waste disposal site medium humus and its regularity, and mechanism of interaction with uranium and transuranic elements is necessary. In order to achieve the safety assessment of nuclear waste disposal, the research can provide a more comprehensive reliable basic data. In this work, the effect of the amount of the insoluble humic acid, shaking time, pH value, and concentration of U(VI) on the adsorption were discussed, in order to explore the best adsorption conditions.

2. Experiments

2.1. Apparatus

The absorbance at 650 nm was measured on a Perkin-Elmer lambda 17 UV–vis spectrophotometer (P-E Co., America) with 10 mm cells for the determination of concentration of uranium. Fourier transform infrared (FT-IR) spectra were taken with a Spectrum One FT-IR spectrophotometer (Perkin-Elmer, America) at room temperature.

2.2. Reagents

Uranium dioxide (UO_2) and humic acid were obtained from Chinese academy of geological sciences. Nitric acid and arsenazo were both of analytical reagent grade, made in China.

About 0.1405 g UO_2 was dissolved to 250 mL 5–8% nitric acid, and the concentration of U(VI) was determined by Chinese academy of geological sciences. About 0.0395 g arsenazo was dissolved with water to 100 mL, and 0.04% arsenazo concentration was obtained.

2.3. Experiment

Arsenazo was used as chromogenic reagent for uranium solution with absorption peak at 650 nm, and the absorbance intensity is directly proportional to the concentration of uranium solution. Based on the relationship between absorbance and concentration of uranium solution, concentration of uranium in solution can be determined. Series of different concentrations of uranium solution were prepared by standard uranium solution. One milliliter was taken to be diluted to 10 mL, and three drops of chromogenic reagent arsenazo was added, then the absorbance at 650 nm was measured to obtain linear relationship curve: $C = A \times 42.78929 - 0.48464$, where A is the absorbance, C is the concentration of uranium. The calculation formula of the adsorption efficiency is: $\eta = (C_0 - C_e)/C_0$, where C_0 represents the initial concentration of U(VI), and C_e represents the residual concentration of U(VI) after adsorption.

3. Results and discussion

3.1. Effect of HA amount

Fig. 1 is the effect of the HA amount on the adsorption. It shows that when HA amount is 0.015 g, the adsorption efficiency is the highest. However, when HA amount is over than 0.015 g, adsorption efficiency declines. It can be explained when the amount is less than 0.015 g, the uranyl ion cannot be sufficiently adsorbed and when the amount is higher than this value, the adsorption reached homeostasis. When humic acid amount is larger, it can adsorb U(VI) rapidly. After it reaches the saturation adsorption, desorption happens and it starts to release U(VI), so that the residual U(VI) concentration increases, the adsorption efficiency decreases.

3.2. Effect of pH

The effect of pH is shown in Fig. 2. With the changes in pH, adsorption rate first increases and then decreases.

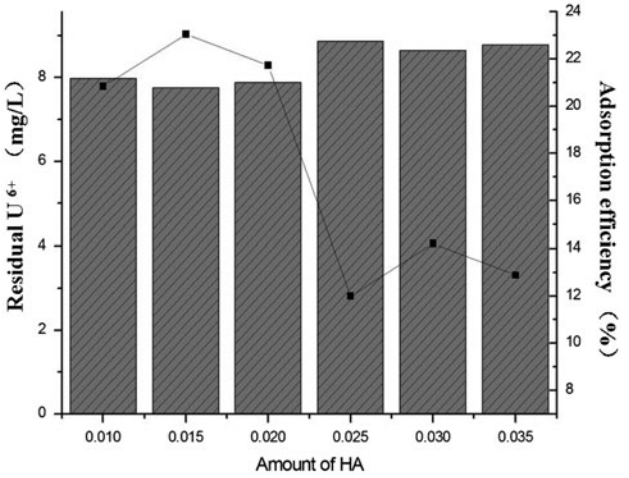

Fig. 1. Effect of HA amount on the U adsorption.

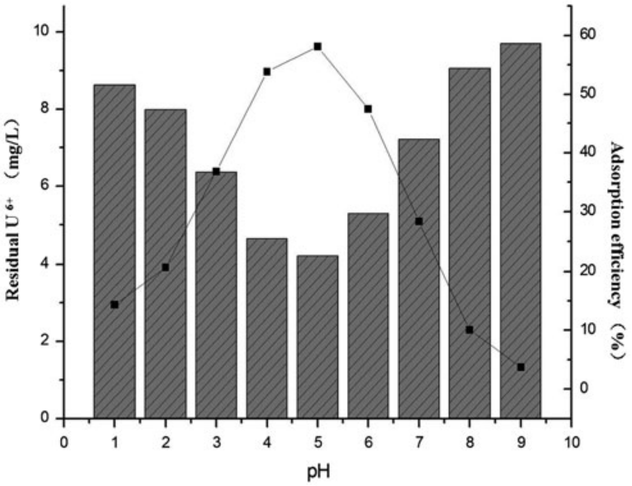

Fig. 2. Effect of pH on the U adsorption.

When pH 5, the adsorption rate is the highest. In weak acidic condition, the adsorption of uranium is the best. When the concentration of H^+ is large in strongly acid conditions, uranyl ion and H^+ form a strong competitive adsorption, and thus the efficiency of adsorption decreases; in strong alkaline conditions, humic acid may be dissolved, and the adsorption efficiency will reduce. The saturation sorption of uranium on HA can be calculated to be 502.78 mg/g.

3.3. Kinetic models

The adsorption model which describes the sorption of a solute onto a solid surface can be expressed in the following way:

$$dq/dt = k_1(q_e - q_t) \tag{1}$$

where k_1 is the apparent pseudo-first-order constant (min^{-1}), q_t is the extent of sorption at time t (in mg g^{-1}), and q_e is the extent of sorption at equilibrium (mg g^{-1}). This law is used to describe processes in which the reaction rate, dq_t/dt, is proportional to the number of available sorption sites, $(q_e - q_t)$. The linear, integrated form of this equation for the boundary conditions; $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, can be written as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

Hence, the rate equation is obeyed when a linear relationship exists between $\log(q_e - q_t)$ and t, in which case k_1 may be estimated from the gradient of the plot. Similarly, the expression can be used to describe adsorption processes in which the reaction rate is proportional to the square of the number of available adsorption sites.

$$dq_t/dt = k_2\,(q_e - q_t)^2 \tag{3}$$

where k_2 is the apparent pseudo-second-order rate constant (in g $\text{mg}^{-1}\,\text{min}^{-1}$), and can be integrated and rearranged thus:

$$t/q_t = 1/\left(k_2\, q_e^2\right) + t/q_e \tag{4}$$

radient of a linear plot of t/q_t against t.

The applicability of the pseudo-first- and pseudo-second-order kinetic models to U adsorption by HA has been tested by fitting the experimental data to the models by least squares regression analysis (as shown in Figs. 3 and 4, respectively). The apparent pseudo-rate constants, k_1 and k_2, integrated rate equations, and corresponding squares of the correlation coefficients, R^2, are listed in Table 1. High correlations between the experimental data for the adsorption of U(VI) by humid acid and the pseudo-second-order kinetic model are indicated by R^2 values of 0.9922: whereas, R^2 values of 0.9763 were obtained by fitting the U adsorption data to the pseudo-first-order model and demonstrate that this model affords a less appropriate description of the adsorption process.

3.4. FT-IR spectra

The FT-IR spectra of HA before and after U adsorption were shown in Fig. 5. There are carboxyl

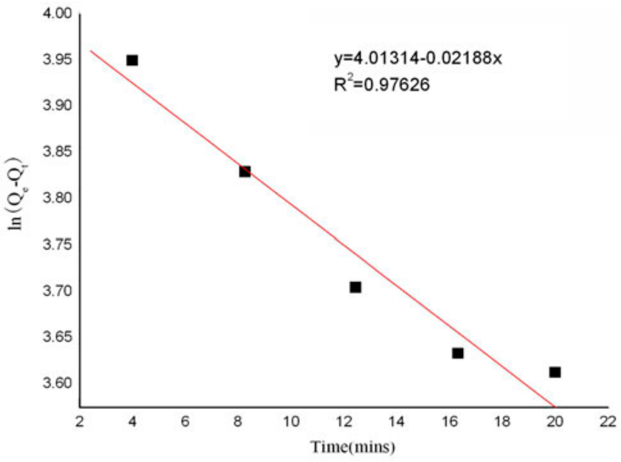

Fig. 3. Pseudo-first-order kinetic model fitted to experimental data for the U adsorption by HA.

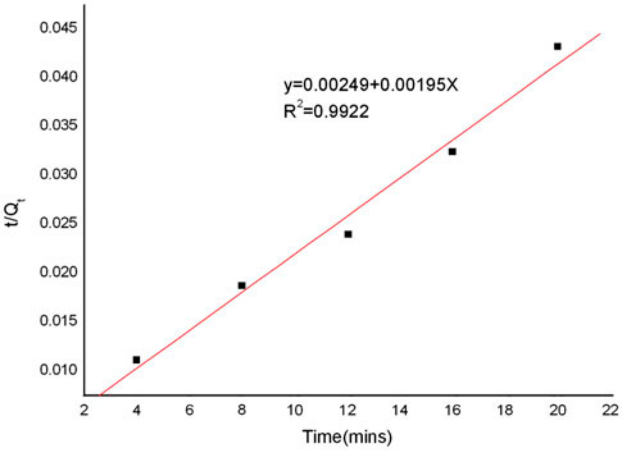

Fig. 4. Pseudo-second-order kinetic model fitted to experimental data for the U adsorption by HA.

Table 1
Kinetic and statistical data for the pseudo-rate models

Pseudo-first-order model		
k_1 (min^{-1})	Integrated rate equation	R^2
0.0101	$\ln(q_e - q_t) = -0.0219t + 4.0131$	0.9763
Pseudo-second-order model		
k_2 (g mg^{-1} min^{-1})	Integrated rate equation	R^2
0.00152	$t/q_t = 1.95 \times 10^{-3}t + 2.49 \times 10^{-3}$	0.9922

and phenolic hydroxyl groups in the molecular structure of humic acid. The peak at 3,500 cm^{-1} belongs to hydroxyl groups, but it disappears after U adsorption, which results from the coordination between –OH and U(VI) [10,11]. UO_2^{2+} is a typical hard Lewis acid and displays a strong affinity for oxygen-containing donor [12]. Hence, the oxygen atoms in these hydroxyl groups of HA provided coordination sites for uranium species [13].

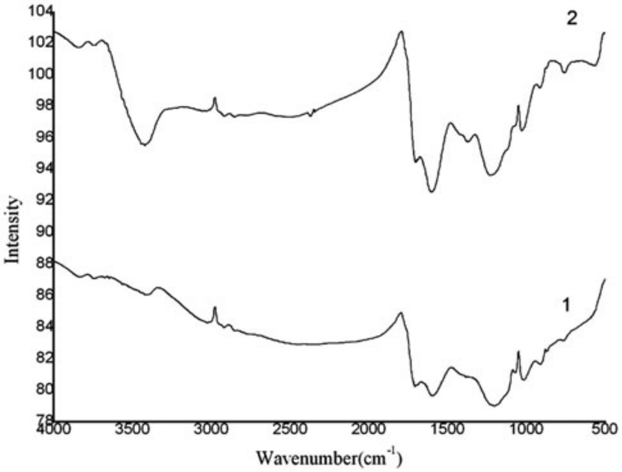

Fig. 5. FT-TR spectra of HA. (1) Before adsorption and (2) after adsorption.

The absorption peak at 1,650 cm^{-1} redshift after U adsorption, and it can be explained that the energy which C=O peak vibration required becomes low, therefore, the group is more unstable. The O atoms of C=O in humic acid coordinate with uranyl ion, so that the C=O bond becomes weak, vibration frequency decrease. It can be concluded that there is coordination in the U adsorption.

4. Conclusion

In this work, adsorption of U(VI) onto humic acid was studied. The results indicate that pseudo-second-order kinetic model matched much better with the adsorption of U(VI) onto humic acid compared with pseudo-first-order kinetic model. The thermodynamic parameters, including free energy, enthalpy, and entropy of adsorption, were calculated from the result of isotherms, suggesting that the adsorption of U(VI) onto humic acid was a process with negative free energy change, negative enthalpy change, and positive entropy change. The adsorption rate was the best at weak acid condition pH 5.0, because uranyl ion and H$^+$ form a strong competitive adsorption in strong acid condition, while humic acid could be dissolved in strong alkaline conditions. Furthermore, it was found that there is coordination in the U adsorption. Therefore, the results can help study the epigenetic deposition of uranium during the formation of humic acid on the transport and enrichment of uranium chemical and physical boundary conditions in geology.

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