Study on kinetics of adsorption of humic acid modified by ferric chloride on U(VI)

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Abstract: In order to reveal the adsorption mechanism of the ferric chloride modified humic acid on uranium, the influence of pH value and contact time of adsorption on uranium was studied through a series of batch experiments. Meanwhile, the adsorption kinetics was analyzed with pseudo-first order kinetic model and pseudo-second order kinetic model. The results show that adsorption is affected by the pH value of the solution and by contact time, and the best condition for adsorption on uranium is at pH=5 and the adsorption equilibrium time is about 80 min. Kinetics of HA-Fe adsorption on uranium accords with pseudo-second order kinetic model. The adsorption is mainly chemical adsorption, and complexes were produced by the reaction between uranium ions and the functional groups on the surface of HA-Fe, which can provide reference for further study of humic acid effecting on the migration of U(VI) in soil.

1. Introduction

Compared with water, wind and solar energy, nuclear energy has many advantages such as economy, stability and so on, a highly efficient cleanness, so many countries around the world are trying to develop nuclear energy [1]. With the rapid development of nuclear energy, demand for uranium increases significantly. However, a lots of uranium mill-tailings (UMT) are produced during uranium ore hydrometallurgy [2]. UMT interacts with water to produce acid mine drainage (AMD) that contains radionuclides such as uranium, radium-226 and thorium, among which uranium concentration is the largest, making serious threat to ecology and human health [3-4].

When ADM flows into the soil, part of the uranium can be accumulated in the soil due to physical, chemical and biological functions, namely the soil self-purification ability [5-6]. The other part of uranium is further migrated along with the flow of ADM and eventually is transferred into groundwater, leading to further expansion that the area is affected by uranium and causing serious harm to groundwater’s ecological security [7] which is what people most care about [8]. Humic acid, as an important part of organic matter in water and soil, has a high specific surface energy and is rich in -OH, -COOH and other active functional groups that are easy to form complexes with heavy metal ions, such as Pb, Hg, and U [9]. Studies have shown that the migration of uranium can be promoted by complexation and adsorption of humic acid in soil [10-11]. However, the soil also contains a lot of iron ions after the humic acid interacts with the iron ions, and how will it affect adsorption on uranium is one of the contents we intend to study.

In this work, ferric chloride was used to modify humic acid. The kinetics of adsorption of HA-Fe on uranium was studied by batch experiments of HA-Fe adsorption on uranium, which provide theory evidences for further study on the influence of humic acid on the migration of uranium in soil.
2. Materials and methods

2.1 Chemicals
All chemicals used in this study were analytical reagents. The chemicals were phosphoric acid, sulfuric acid, urea, ammonium iron sulfate, titanium trichloride, sodium nitrite, diphenylamine-4-sulfonic acid sodium salt, sodium hydroxide, sodium bicarbonate, sodium carbonate, tricalcium phosphate, ferric chloride hexahydrate and humic acid.

2.2 Modification of humic acid
The weighed 5 g humic acid powder was placed in 100 ml 2 mol/L ferric chloride solution, and soaked for 2 hours, then evaporated slowly at no more than 200 ℃ with electric furnace, finally its evaporated solid was washed to neutrality, dried into the sample vial and sealed. The humic acid modified by ferric chloride was abbreviated as HA-Fe.

2.3 Adsorption of HA-Fe on uranium
A certain concentration of uranium solution was taken in a series of 250 ml conical flasks, and 0.2 g of HA-Fe was added to each flask. According to different experimental purposes, the appropriate experimental conditions were selected. Following that, all flasks are stuffed with cork and labeled, then placed in the water bath oscillator at 160 r/min, then filtered after adsorption equilibrium. Finally, the concentration of uranium in the filtrate was determined. The adsorbed amount (qe) of HA-Fe on U can be given by the following relationship:

\[ q_e = \frac{(c_0 - c_e) \cdot v}{m} \]  

where \( q_e \) is the adsorbed amount (mg/g) of HA-Fe on uranium at equilibrium; \( c_0 \) and \( c_e \) are the the initial concentration (mg/L) of uranium in the solution at equilibrium and time t; \( v \) is the volume (mL) of the solution; \( m \) is the quality (g) of HA-Fe.

2.4 Analytical method
The concentration of uranium in solution was analyzed by ammonium vanadate titrimetric method of the standard QB/T73707-2003 [12].

3. Results and discussion

3.1 Influence of different pH value on adsorption HA-Fe of on uranium
The influence of different pH value on adsorption of HA-Fe on U is illustrated in Fig.1. The Fig.1 shows the adsorption is effected significantly by the pH value of the solution. The adsorbed amount of uranium is relatively small and its rising speed is relatively slow when pH value is not more than 3, and the main reason is that most of the adsorption sites of HA-Fe are occupied by the hydrogen ions in the solution. The adsorption amount increases rapidly when pH =3~4, and this is mainly because adsorption amount is improved by the hydrogen ions of uranyl ions attaching to the adsorbents’ surface. The adsorbed amount of uranium reaches the peak (5.65mg/g) at pH=5. The adsorption capacity decreases gradually when pH value is more than 5, resulting from that the adsorption sites are occupied by hydrogen ions from iron ions hydrolysis so that the adsorption on U was inhibited.
3. 2 Influence of contact time on adsorption of HA-Fe on Uranium

The influence of contact time on adsorption of HA-Fe on Uranium is shown in Fig. 2. The contact time has a great effect on the adsorption of HA-Fe on uranium, and the equilibrium time is about 80 min. The adsorbed amount increases obviously with the increase of contact time when contact time is no more than 50 min, and this is mainly due to the solvent diffusion of the initial adsorption, which means that the main uranium is instantaneously adsorbed by surface holes of HA-Fe [13-14]. The adsorption amount continues to rise and the rising trend slows relatively when t=50~80 min, and this is mainly because the surface holes adsorption sites were gradually occupied by uranyl ions and complexes were formed by uranium interaction with the surface-active groups of HA-Fe. The adsorption amount is almost constant when t>80 min, namely adsorption equilibrium time is 80 min, resulting from that the steric hindrance between uranium ion of free state and active adsorption sites of HA-Fe was increased gradually [6].

In order to investigate the adsorption mechanism, the kinetics of adsorption of HA-Fe on uranium was studied by pseudo-first order and pseudo-second order kinetic models. Linear form of pseudo-first order and pseudo-second order kinetic equation can be represented as [15]:

Pseudo-first order kinetic equation:
\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]  
(2)

Pseudo-second order kinetic equation:
\[ \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} \]  
(3)

where \( q_e \) and \( q_t \) is the amount (mg/g) of HA-Fe sorbed onto U at equilibrium and time t; \( k_1, \text{min}^{-1} \), \( k_2, (\text{g.mg}^{-1} \cdot \text{min}^{-1}) \) are the rate constants of pseudo-first order and pseudo-second order kinetic equation. According to the formulas (2) and (3), the experimental data are fitted by \( \ln(q_e-q_t) \) to t and \( t/q_t \) to t respectively, and the results are shown in Fig. 3 and Fig. 4:
The Fig. 3 and Fig. 4 show the fitting correlation coefficient \((R^2=0.96073)\) of pseudo-second order kinetic equation is slightly more than that \((R^2=0.95028)\) of pseudo-first order kinetic equation. So the pseudo-second order kinetic model describes the process of HA-Fe adsorption on uranium better than pseudo-first order kinetic model, meanwhile the result also suggests the adsorption of HA-Fe on uranium is that chemical adsorption was slightly more than other adsorption, which uranium ions react with the functional groups on the surface of HA-Fe to produce complexes [16-17].

4. Conclusion
The following remarks are concluded:
This experiment is mainly studied that uranium was adsorbed by HA-Fe under different experimental conditions. Adsorption is affected by the pH value of the solution, and the best condition for adsorption of HA-Fe on uranium is at pH=5. The adsorption equilibrium time is about 80 min.

The adsorption kinetics analysis shows that the pseudo-second order kinetic model described process of HA-Fe adsorption on uranium better than pseudo-first order kinetic model. Moreover, the adsorption of HA-Fe on uranium is mainly chemical adsorption that complexes were produced by the reaction between uranium ions and the functional groups on the surface of HA-Fe.

Acknowledgement
The project was funded by the National Natural Science Foundation of China (grant No.11275092).

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