Investigation of U(VI) Adsorption Kinetics on Montmorillonite Clay

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Abstract

This study investigates the adsorption behavior of U(VI) in aqueous solutions by bentonite. The static adsorption method is employed to explore the effects of various factors on the adsorption of uranium by bentonite, including adsorption time, pH, initial concentration, ionic environment, and solid-liquid ratio. The adsorption distribution coefficient under different conditions is determined, and the variation patterns of the adsorption distribution coefficient are further analyzed.In the static adsorption experiments with bentonite, the following observations are made: (1) The equilibrium adsorption between bentonite and U(VI) is reached after 12 hours of adsorption time. (2) The adsorption distribution coefficient (Kd) initially increases and then decreases as the concentration of uranium standard solution increases. (3) The maximum adsorption efficiency is achieved at a solid-liquid ratio of 1:300, and the adsorption rate increases most rapidly at a solid-liquid ratio of 1:150. (4) Different ions in the solution have varying degrees of inhibitory effects on the adsorption of U(VI) by bentonite. Anions generally exhibit stronger inhibitory effects than cations, with CO3²- and Ca²⁺ showing significant inhibition, and NO³⁻ and SO4²⁻ exhibiting certain inhibitory effects. K+ and Na+ have a moderate inhibitory effect on uranium adsorption, while Mg²+ has negligible inhibitory effect. (5) The best adsorption performance is observed at pH 5, and the adsorption distribution coefficient shows an increasing trend followed by a decreasing trend as the pH value increases. (6) The adsorption of uranium by bentonite is better described by the pseudo-second-order kinetic model, as it considers not only external diffusion and surface adsorption but also internal diffusion.

Keywords

Bentonite; Adsorption Characteristics; U(VI).

1. Introduction

With the continuous development of nuclear science and technology, it has brought not only great economic benefits and energy convenience to humanity, but also numerous hazards. The various radioactive wastes generated by nuclear science and technology have entered the natural environment, posing risks to human health and causing irreversible damage to the environment. Therefore, the safe and effective treatment of these issues has become a global challenge. Uranium, as the main raw material for the nuclear industry and the primary disposal target for high-level radioactive waste, is of great significance to study the adsorption characteristics of uranium-containing radioactive wastewater in bentonite for the prevention and control of uranium hazards[1].

Uranium is a highly toxic element, and its hazards mainly include chemical toxicity and radiological hazards [4]. In terms of human health, the chemical toxicity of uranium has a greater impact than its radiological hazards. The chemical toxicity of uranium is mainly due to its accumulation in various

organs such as the liver and skeletal system after entering the body, leading to renal failure and toxic lesions. It can cause organ failure, such as in the brain, liver, and heart, leading to death. The radiological hazards of uranium are mainly due to its extremely long half-life and the production of other harmful progeny during the decay process, such as radium, thorium, radon, etc. The α , β , γ particles produced can irradiate organs, damage the lungs, cause mutations in cell membranes, and lead to diseases such as cancer. In the process of treating uranium-containing radioactive wastewater, this study adopts the adsorption method, which can remove radioactive nuclides from the wastewater and recover rare metals. This method has good treatment efficiency for low-concentration radioactive nuclides and can also effectively treat heavy metal wastewater [2-5].

This experiment mainly focuses on the adsorption kinetics of U(VI) by bentonite. The main research contents are as follows: This experiment investigates the adsorption performance of bentonite for uranium in aqueous solutions, exploring the effects of factors such as adsorption time, amount of bentonite, initial uranium solution concentration, pH value of the solution, and concentration of added ions on the adsorption performance of uranium by bentonite[6].

2. Materials and Methods

Bentonite is a type of clay mineral, with montmorillonite being its main component. It is widely distributed throughout the country and has a large storage capacity. Bentonite is known as "universal clay" because of its excellent physicochemical properties, and it finds extensive applications in industries such as petroleum, papermaking, chemicals, food, drilling, casting, agriculture, ceramics, and pharmaceuticals [7]. It is also referred to as bentonite or swelling clay. Bentonite is a 2:1 type layered silicate mineral, and its main component, montmorillonite, has a unit cell structure consisting of two tetrahedral sheets (SD) and an octahedral sheet (AlO or AlOH) sandwiched between them, connected by shared oxygen atoms. The high-valence silicon-aluminum ions inside the bentonite undergo ion exchange reactions with the low-valence cations inside, resulting in a permanent negative charge on the montmorillonite. To achieve charge balance, bentonite has the ability to adsorb cations, giving it two properties: ion exchange capacity and strong adsorption capability. The bentonite used in this experiment is Inner Mongolia Gaomiaozi bentonite, abbreviated as GMZ bentonite.

The main reagents used in this experiment include U(VI) stock solution, prepared using U_3O_8 analytical grade at a concentration of 100 mg/L according to the GBW04201 method, deionized water for experimental purposes, as well as HCl, NaOH, HNO₃ solutions, and azobenzene III solution. These reagents are utilized for various purposes such as preparing standards, adjusting pH levels, and facilitating chemical reactions.

Instrument Name	Model	Quantity	Manufacturer
Electronic pH Meter	DZS-708L	1	Shanghai Yidian Scientific Instrument Co., Ltd
High-speed Centrifuge	L500	1	Hunan Xiangyi Laboratory Instrument Development Co., Ltd.
Benchtop Thermostatic Oscillator	CHA-S(A)	1	Jintan Kexi Instrument Co., Ltd.
Laboratory Water Purification System	WP-UP-III- 10	1	Sichuan Wotter Water Treatment Equipment Co., Ltd.
Precision Electronic Balance	FA2004A	1	Shanghai Liangping Instrument Co., Ltd.
UV-Visible Spectrophotometer	UV-3150	1	Shimadzu Corporation, Japan

 Table 1. Experimental Instruments

Using blank reagent as a reference, a full wavelength (350nm-800nm) scan was performed on a UV-visible spectrophotometer to analyze and identify the maximum absorption wavelength at 652nm in the obtained UV-visible spectrum. Different volumes (0μ L, 100μ L, 200μ L, 400μ L, 600μ L, 800μ L, 1000μ L) of 100μ g/mL uranium standard solution were sequentially added to 25.0 mL volumetric flasks. Then, 0.5 mL of 0.5 mol/L HCl solution and 2.0 mL of 0.1% mass concentration of diazotized sulfanilic acid III color reagent were added. The solutions were diluted with ultrapure water to a final volume and prepared as uranium standard solutions with concentrations of 0.4μ g/mL, 0.8μ g/mL, 1.6μ g/mL, 2.4μ g/mL, 3.2μ g/mL, and 4.0μ g/mL, respectively. Each solution was transferred to a colorimetric dish with a thickness of 1.0cm, and the absorbance at a wavelength of 652nm was measured using a UV-visible spectrophotometer. The uranium standard curve was plotted by using the uranium standard solution concentration as the x-axis and the absorbance value as the y-axis. The fitted equation of the curve is as shown in the figure below.

$$y=0.2324x+0.02192$$
 (1)



Fig.1 The standard curve for uranium

3. Results and Discussion

3.1 Experimental Study on the Adsorption Equilibrium Time of Uranium in Bentonite

Weighing 0.04g of bentonite, 11 portions were separately placed into 11 centrifuge tubes with a volume of 10mL each. Then, 7.2mL of deionized water was added to each tube containing the soil sample. The tubes were sealed and shaken at 220r/min and 25°C for 2 hours, followed by a 24-hour static settling period. Subsequently, 0.8mL of uranium standard solution with a concentration of 400ug/mL was added to each centrifuge tube. After sealing the tubes, they were placed on an oscillator tilted at an angle and continuously shaken at 220r/min and 25°C for 12 hours. At 1h, 2h, 4h, 6h, 8h, 10h, 12h, 16h, 24h, 32h, and 48h, the tubes were taken out and centrifuged at 3000rpm for 60 minutes. Then, 1mL of the supernatant was extracted using a pipette and analyzed using a spectrophotometer.

According to Fig 2, it can be observed that within 6 hours, the adsorption distribution coefficient increases significantly with time. During this period, there are plenty of adsorption sites available for

uranium adsorption. Some metal ions can also undergo ion exchange with uranium, facilitating its adsorption. After 4 hours, the adsorption distribution coefficient continues to increase, but the rate of increase decreases. At around 12 hours, the adsorption distribution coefficient stabilizes and shows almost no change. This indicates that the bentonite sample has reached adsorption saturation, and 12 hours can be considered as the adsorption equilibrium time for bentonite. To ensure adsorption equilibrium, the experimental duration was set to a maximum of 48 hours.



Fig.2 The Influence of Adsorption Time on the Adsorption Distribution Coefficient

3.2 Experimental Study on the Adsorption of Uranium in Bentonite at Different Initial Concentrations

Weigh 0.04g of bentonite for each of the 7 samples and place them in separate 10mL centrifuge tubes. Add 7.8mL, 7.6mL, 7.4mL, 7.2mL, 6.8mL, 6.4mL, and 6.0mL of deionized water to the respective tubes containing the bentonite samples. Seal the tubes and shake them at 220r/min and 25°C for 2 hours, followed by a 24-hour static settling period. Then, add 0.2mL, 0.4mL, 0.6mL, 0.8mL, 1.2mL, 1.6mL, and 2.0mL of 400ug/mL uranium standard solution to the tubes containing the bentonite samples to adjust the uranium concentrations to 10ug/mL, 20ug/mL, 30ug/mL, 40ug/mL, 60ug/mL, 80ug/mL, and 100ug/mL, respectively. After sealing the tubes, place them on an oscillator tilted at an angle and shake them continuously at 220r/min and 25°C for 12 hours. At the end of the shaking period, centrifuge the tubes at 3000rpm for 60 minutes. Use a pipette to extract 1mL of the supernatant from each tube. Analyze the extracted supernatant using a spectrophotometer to determine the uranium concentration.

The experiment was conducted with initial uranium standard solution concentrations of 10 ug/mL, 20 ug/mL, 30 ug/mL, 40 ug/mL, 60 ug/mL, 80 ug/mL, and 100 ug/mL. Fig 3 shows that as the initial concentration of the uranium standard solution increases from 10 ug/mL to 100 ug/mL, the adsorption distribution coefficient initially increases with the uranium concentration. The adsorption distribution coefficient reaches its maximum at a uranium standard solution concentration of 40 ug/mL and then decreases with further increases in uranium concentration. The overall trend of the curve is an initial increase followed by a decrease. This indicates that as the uranium concentration increases from 10

ug/mL to 40 ug/mL, the adsorption distribution coefficient continuously increases. This is because, under the condition of a constant amount of bentonite, there are a large number of adsorption sites available in the bentonite, allowing for rapid adsorption and ion exchange with uranium in the solution. When the concentration reaches 40 ug/mL, the adsorption distribution coefficient reaches its maximum, indicating the optimal adsorption effect. However, as the uranium concentration continues to increase, the amount of uranium in the solution exceeds the capacity of the fixed adsorption sites on the bentonite. As a result, the adsorption quickly reaches saturation, and the excess uranium in the solution remains in the form of free hydrated ions. Therefore, the adsorption distribution coefficient gradually decreases.





3.3 Experimental Study on the Adsorption of Uranium in Bentonite at Different Initial Concentrations

Weigh 0.04g of bentonite for each of the 6 samples and place them in separate 10mL centrifuge tubes. Add 7.2mL of water solutions with pH values of 2, 4, 6, 7, 8, and 10 to the respective tubes containing the bentonite samples. Seal the tubes and shake them at 220r/min and 25°C for 2 hours, followed by a 24-hour static settling period. Then, add 0.8mL of uranium solution to each tube containing the bentonite samples. After sealing the tubes, place them on an oscillator tilted at an angle and shake them continuously at 220r/min and 25°C for 12 hours. At the end of the shaking period, centrifuge the tubes at 3000rpm for 60 minutes. Use a pipette to extract 1mL of the supernatant from each tube. Analyze the extracted supernatant using a spectrophotometer.

Fig 4 shows the effect of clay on the adsorption distribution coefficient of uranium under different pH conditions. The effect of pH on the adsorption distribution coefficient of uranium by clay is significant. At lower pH values, the competition between H+ ions and uranyl ions for the active sites on the clay surface leads to a lower adsorption capacity and distribution coefficient. However, as the pH increases, the concentration of H⁺ ions decreases, resulting in an increase in the negative charge on the clay surface. This enhances the complexation ability of the clay with uranyl ions, leading to an increase in the adsorption distribution coefficient. However, at higher pH values, the species composition of uranium changes, and the formation of $UO_2(CO_3)_3^{4-}$ and $UO2(OH)^{3-}$ ions causes electrostatic repulsion with the clay surface, reducing the adsorption efficiency. Additionally, the precipitation of carbonate uranium complexes and the formation of $UO_2(OH)^{3-}$ ions further decrease

the adsorption distribution coefficient. Therefore, excessively high or low initial pH values are not favorable for uranium adsorption.





3.4 Experiment on the Influence of Different Solid-to-Liquid Ratios on Uranium Adsorption

In this experiment, 0.2g, 0.1g, 0.08g, 0.05333g, 0.04g, 0.02666g, and 0.02g of bentonite were weighed and transferred into 7 centrifuge tubes with a volume of 10mL each. Then, 7.2mL of distilled water was added to each centrifuge tube containing the bentonite samples. The tubes were sealed, and the solid-to-liquid ratios were set as 1:40, 1:80, 1:100, 1:150, 1:200, 1:300, and 1:400, respectively. The tubes were then subjected to shaking at a speed of 220r/min and a temperature of 25°C for 2 hours, followed by a 24-hour settling period. After the settling, 0.8mL of uranium solution was added to each centrifuge tube containing the bentonite samples. The tubes were closed and placed on an inclined oscillator, shaking continuously at 220r/min and 25°C for 12 hours. After the shaking, the tubes were centrifuged at 3000rpm for 60 minutes. Then, 1mL of the supernatant was extracted using a pipette, and the uranium concentration was measured using a spectrophotometer.

The effect of solid-to-liquid ratio on uranium adsorption is quite significant, as evident from the graph. As the solid-to-liquid ratio decreases, the adsorption distribution coefficient increases, indicating better adsorption performance. However, between the ratios of 1:40 and 1:100, a large amount of bentonite is required, but the adsorption distribution coefficient is low, indicating poor adsorption performance. This suggests that the dispersion of bentonite particles is not good, leading to significant spatial hindrance and low utilization of adsorption sites on the bentonite surface. At a solid-to-liquid ratio of 1:150, the adsorption distribution coefficient shows the fastest growth rate, indicating the optimal dispersion of bentonite particles and a high utilization of adsorption sites. After the solid-to-liquid ratio falls below 1:200, the growth rate of the adsorption distribution coefficient, resulting in poorer uranium adsorption performance.



Fig.5 The effect of different solid-to-liquid ratios on the adsorption distribution coefficient.

3.5 The Experiment on the Influence of Different Ion Concentrations on Uranium Adsorption.

Take 0.04g of bentonite and place it into 8 centrifuge tubes with a volume of 10mL each. Then, add a specific amount of NaCl, KCl, CaCl₂, MgCl₂, Na₂SO₄, NaNO₃, Na₂CO₃, and NaHCO₃ into the centrifuge tubes containing the bentonite samples to prepare 0.05mol/L solutions of each chemical. Add 7.2mL of distilled water and seal the tubes. Shake them at a speed of 220r/min and a temperature of 25°C for 2 hours, followed by a 24-hour settling period. Then, add 0.8mL of uranium standard solution with a concentration of 400ug/mL into each centrifuge tube. Close the tubes and place them on an inclined oscillator, shaking continuously at 220r/min and 25°C for 12 hours. After the shaking, centrifuge the tubes at 3000rpm for 60 minutes. Then, use a pipette to extract 1mL of the supernatant and measure it using a spectrophotometer.

From Fig 6, it can be observed that all 8 different ions have a certain inhibitory effect on the uranium adsorption by bentonite, but their inhibitory effects vary. Overall, anions have a stronger inhibitory effect than cations. Among the anions, $CO_3^{2^-}$ and HCO^{3^-} have a significant inhibitory effect on uranium adsorption, while NO^{3^-} and $SO_4^{2^-}$ have a certain inhibitory effect but not as significant as the former. Among the cations, Ca^{2^+} shows the most pronounced inhibitory effect on uranium adsorption, while K^+ and Na^+ have a moderate inhibitory effect, and Mg^{2^+} has almost no inhibitory effect on uranium adsorption.



Fig.6 The adsorption distribution coefficients of various solutions at a concentration of 0.05mol/L.

3.6 Experiment on the Effect of CO32- and Ca2 + on the Adsorption of Uranium

Based on the previous experiment and literature research, it was found that CO_3^{2-} and Ca^{2+} have the most significant impact on uranium adsorption. Therefore, these two ions were selected as the research targets, and the following concentration gradients were determined for the experiment. Take 0.04g of bentonite and place it into 8 centrifuge tubes with a volume of 10mL each. Then, add different amounts of Na₂CO₃ and CaCl₂ into the centrifuge tubes containing the bentonite samples to prepare solutions with concentrations of 0.01mol/L, 0.03mol/L, 0.05mol/L, 0.07mol/L, 0.08mol/L, and 0.1mol/L, respectively. Add 7.2mL of distilled water and seal the tubes. Shake them at a speed of 220r/min and a temperature of 25°C for 2 hours, followed by a 24-hour settling period. Then, add 0.8mL of uranium standard solution with a concentration of 400ug/mL into each centrifuge tube. Close the tubes and place them on an inclined oscillator, shaking continuously at 220r/min and 25°C for 12 hours. After the shaking, centrifuge the tubes at 3000rpm for 60 minutes. Then, use a pipette to extract 1mL of the supernatant and measure it using a spectrophotometer.

From the graph, it can be observed that CO_3^{2-} and Ca^{2+} have a significant inhibitory effect on uranium adsorption, and they are the two ions with the strongest inhibitory effect among the 8 ions studied. To explore the change in inhibitory effect with increasing ion concentration, we conducted experiments.

From Fig 7, it can be observed that $CO_3^{2^-}$ has a stronger inhibitory effect on uranium adsorption compared to Ca^{2+} , and both ions show an enhanced inhibitory effect with increasing ion concentration, with $CO_3^{2^-}$ exhibiting a more pronounced effect. Mechanistically, $CO_3^{2^-}$ undergoes hydrolysis in aqueous solutions to generate OH^- , which can react with UO_2^{2+} in the solution to form $UO_2(OH)_3^-$ and $UO_2(CO3)_3^{4-}$, both of which are not easily adsorbed by bentonite. Additionally, the formation of the uncharged precipitate UO_2CO_3 also contributes to the inhibitory effect .The strong inhibitory effect of Ca^{2+} on adsorption is partly attributed to its ion exchange capacity, but it is not the primary influencing factor. Ca^{2+} can react with anions in bentonite to form some large particles, which can cover the surface of bentonite and occupy the active binding sites, thereby hindering the adsorption of U(VI). With an increase in Ca^{2+} concentration, more of these large particles are formed, resulting in a stronger inhibitory effect on bentonite adsorption.



Fig.7 Effects of CO₃²⁻ and Ca²⁺ Concentrations on Adsorption Partition Coefficients

3.7 Adsorption Kinetic Model of U (VI) on Bentonite

As shown in Fig 8, it is the graph of the pseudo-first-order kinetic fitting of U(VI) adsorption on bentonite. Fig 9 shows the graph of the pseudo-second-order kinetic fitting of U(VI) adsorption on bentonite. The corresponding kinetic linear models are as follows:

$$ln(q_e - q_t) = lnq_e - k_{1t} \tag{2}$$

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

The equilibrium adsorption capacity (qe) and rate constants (k1 and k2) for U(VI) adsorption on bentonite were calculated using the pseudo-first-order and pseudo-second-order kinetic models. The results obtained were qe=0.00125 and k1=0.1032 for the pseudo-first-order model, and qe=0.00318 and k2=0.00324 for the pseudo-second-order model.By analyzing and fitting the experimental data to the kinetic models, it was found that the adsorption of uranium on bentonite is better described by the pseudo-second-order kinetic model, while the pseudo-first-order kinetic equation provides a poorer description. This can be attributed to the broader considerations of the pseudo-second-order kinetic model, which takes into account not only external diffusion and surface adsorption but also internal diffusion. The adsorption of uranium on bentonite is a complex and comprehensive reaction process. Therefore, the results suggest that the adsorption of uranium on bentonite is governed by multiple mechanisms, and the pseudo-second-order kinetic model provides a more comprehensive description of the adsorption process. These findings contribute to a better understanding of the adsorption behavior of U(VI) on bentonite and can be valuable for designing and optimizing adsorption processes for uranium removal.



Fig.8. Quasi-first-order kinetic model of adsorption



Fig.9 Quasi-second-order kinetics of adsorption

4. Results and Discussion

The main objective of this experiment was to investigate the effects of bentonite dosage, pH value, initial concentration, adsorption time, and different ion concentrations on the adsorption of uranium by bentonite. The following conclusions were drawn:

1) The equilibrium adsorption time of bentonite for uranium solution was found to be 12 hours.

2) The initial concentration of uranium solution had an impact on the adsorption efficiency of bentonite. The adsorption distribution coefficient increased gradually as the uranium concentration increased up to 40 mg/L. However, beyond this concentration, the adsorption distribution coefficient showed a decreasing trend.

3) The fastest increase in adsorption distribution coefficient was observed at a solid-liquid ratio of 1:150. After the solid-liquid ratio dropped below 1:200, the increase in adsorption distribution coefficient stabilized.

4) The pH value had a significant effect on the adsorption distribution coefficient of uranium solution by bentonite. The adsorption distribution coefficient sharply increased within the pH range of 2-5. However, beyond pH 5, the adsorption distribution coefficient decreased with increasing pH value.

5) Both anions and cations exhibited inhibitory effects on the adsorption of uranium solution by bentonite. Among them, $CO3^{2-}$ and Ca^{2+} showed strong inhibitory effects, while NO₃- and SO₄²⁻ exhibited moderate inhibitory effects. K⁺ and Na⁺ had a moderate inhibitory effect on uranium adsorption, while Mg²⁺ had minimal inhibitory effect.

6) The inhibitory effect of ions on the adsorption of uranium by bentonite increased with increasing concentrations of $CO3^2$ - and Ca^{2+} .

7) By comparing the first-order and second-order kinetic equations for the adsorption of uranium solution by bentonite, it was found that the adsorption process of uranium by bentonite was better described by the second-order kinetic equation.

In summary, the experimental results demonstrated that the adsorption of uranium by bentonite is influenced by various factors including dosage, pH value, initial concentration, adsorption time, and

different ion concentrations. The findings provide valuable insights for the design and optimization of uranium removal processes using bentonite.

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