

Effects of Ionic strength, Inorganic Ions and Humic acids on U (VI) removal by HAP modified Quartz Sand

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Abstract: Removal of U (VI) from aqueous solution by quartz sand loaded hydroxyapatite prepared by sol-gel method, discussed the effects of ionic strength, inorganic ions and humic acid and other hydrochemical parameters on the removal efficiency, using VISUAL MINTEQA to calculate the removal Mechanism of U (VI) occurrence Morphology. Analysis showed that the element ratio of P to Ca in EDS indicates that the composites are successfully prepared. The effect of ion strength shows that U (VI) is adsorbed to form an outer surface complex, the adsorption capacity decreased by $0.876\text{mg} \cdot \text{L}^{-1}$ (7.97%) at 20mM. Inorganic coexisting ions also have some effects, and the order of influence is $\text{Ca}^{2+} > \text{CO}_3^{2-} > \text{Na}^+$. Humic acid can obviously promote the removal of U (VI) by composites, but also reduce the inhibitory effect of Ca^{2+} and CO_3^{2-} on adsorption.

1. Introduction

Uranium is one of the most common radioactive substances in wastewater, which is a serious threat to the environment and human health. Major sources of uranium include nuclear raw material mining (uranium mining), nuclear energy activities, nuclear weapons testing, and nuclear waste disposal^[1-2]. Many nuclear wastes contain high levels of uranium. For example, the groundwater content in some Britain's energy facilities sector is as high as 1700 mg / L. In nature, U (IV) often exists as insoluble UO_2 and soluble in water as UO_2^{2+} cations (which is easier to enter the food chain and cause serious health problems)^[3-4].

Permeable Reactive Barrier (PRB) is a kind of in-situ restoration technology for groundwater pollution. In its representative precipitation media, the adsorption capacity of hydroxyapatite (HAP) for U (VI) can reach 1125.4 mg / g, theoretically. However, there is the problem of poor permeability caused by pore blockage, but the permeability of quartz sand can be greatly improved by using quartz sand as skeleton. At present, most of the studies on such materials are concentrated on pH, reaction, time and initial concentration^[5], but there are no data about basic hydrochemical parameters (such as ion strength, inorganic co-existing ion, natural organic matter (NOM)). Because of its unique chemical properties (such as the ability to combine with bicarbonate and NOM (such as humic acid (HA) and its morphology under different hydrochemical conditions), these information cannot be ignored. Generally speaking, the concentration range of NOM is 0.5mg/l (groundwater) to > 20mg/l (surface water). Moreover, the solubility of U (VI) is related to its various ligands^[6-7]. Based on previous research, this paper has a further studied on the effect of ion strength, inorganic coexistence ions and humic acid on the removal of U(VI) from hydroxyapatite supported by quartz sand.

2. Experiment

2.1. Reagents and materials

Hydrogen nitrate, sodium hydroxide, sodium chloride, calcium chloride, soda, ortho-phosphoric acid, calcium nitrate tetrahydrate, ammonia, humic acid, reagents are all analytical pure and purchased from Chinese Pharmaceutical Group Chemical Reagent Co., Ltd.

Preparation of uranium solution: U_3O_8 1.179g into 50ml beaker, heated with 6ml perchloric acid until solid disappeared, cooled with concentrated hydrochloric acid 1ml and drained to 1L capacity

flask. The concentration of 1g/L was diluted according to the experimental conditions.

Preparation of quartz sand loaded hydroxyapatite composites: the composites were synthesized by sol-gel method, the 240mL 0.25mol/L phosphate solution was placed in beaker, and the pH of the solution was adjusted to 10 by ammonia water, then add 150g quartz sand with particle size of 0.15-0.30mm, rotating speed of agitator is 300r / min, and slowly pouring into 1mol/L calcium nitrate solution of 100mL to ensure that pH is 10 in the preparation environment for 24 hours. Cleaning of composites made by 3000r/min centrifugation with deionized water after 5 minutes. Then repeat centrifugal cleaning for three times and put it in the oven to dry for 24 hours to be used^[8-9].

2.2. Analytical testing instruments

FE20pH meter, SHZ-82 gas-bath constant-temperature oscillator, JA1003-type one-thousandth of electronic balance, S312 stirrer, DGG-9070B electric-heating constant-temperature blast drying box, 722-type spectrophotometer, and S-520HTACHI-type scanning electron microscope.

2.3. Adsorption experiment

The uranium solution of 10ml100mg · L⁻¹ was accurately arranged in 100ml centrifugal tube, 0.02g composite material was put into 180r/min rotating speed at room temperature (298K) for 4 h, and the liquid was obtained after 0.22 μ m filter membrane filtration at room temperature (298K) for 4 h. after filtration with 0.22 μ m filter membrane, 0.5 mL culture medium was taken. Add 2 mL arsenazo III and 2 mL pH = 2. 5 chloroacetic acid-sodium acetate buffer was used to determine the residual concentration of U (VI) in distilled water for 15 min at a constant volume of 50 mL,.

The experimental conditions are as follows: (1) When the condition of pH of 4, the concentration of Na⁺, Ca⁺, CO₃²⁻ is 0mg/L, 1.25mg/L, 2.5mg/L, 5mg/L, 10mg/L, 20mg/L. The concentration of 3X6 was 1.25mm / L, 2.5mm / L, 5mm / L, 10mm / L and 20mm / L,, respectively. Under the condition of pH = 4, the concentration of 3X6). (2)When the condition of pH of 4, the concentration of Na⁺, Ca⁺, CO₃²⁻ is 5mM/L, the concentration of HA is 0mg / L, 1.25mg / L, 2.5mg / L, 5mg / L, 10mg / L, 20mg / L, and a group of blank groups (4X6) without impurity ions were added. All the reaction temperature is 25 °C.

The formulas for calculating equilibrium adsorption capacity Q and ion strength I are as follows:

$$q_e = (C_0 - C_t) \times V / M \quad (1)$$

$$I = 1/2 \sum m_i Z_i^2 \quad (2)$$

In the formula, C₀ is the initial concentration of U (VI) in solution, C_t is the t time concentration, mg/L; V is solution volume, L; M is HAP composite content, g ; m_i is mass molar concentration, mg/kg; Z_i is ion electricity price.

3. Results and analysis

3.1. Analysis of characterization results of SEM and EDS

The test conditions are as follows: the magnification of working voltage is 20 kV, the magnification is 250 and 1000 times. The results of scanning electron microscope are shown in fig. 1.

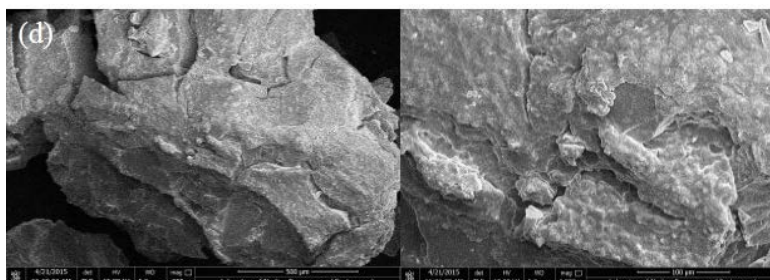


Fig.1 SEM images of composite materials.

It can be seen from fig. 1 that there are steps, holes and uneven peaks and valleys on the surface of the composite. The weight ratio of P to Ca is 1: 1.60, which is close to 1: 1.67 in the chemical formula of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. It is proved that quartz sand was successfully prepared by loading HAP.

3.2. Uranyl species as a function of pH in Aqueous solution

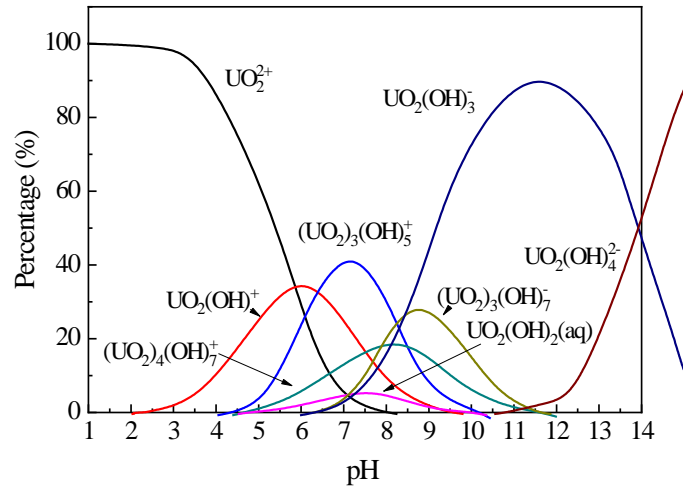


Fig. 2 The relative proportions of 100mg/L U (VI) in solution with different pH.

The distribution map of U (VI) occurrence morphology with pH in aqueous solution was calculated by VISUAL MINTEQA3.0 software. The pH doesn't change much during this experiment, which was 4 ~ 4.5. The main occurrence form of U (VI) in this range is UO_2^{2+} , $(\text{UO}_2)_2(\text{OH})_2^{2+}$. When pH is less than 3, H^+ and H_3O^+ in aqueous solution compete for adsorption sites^[10]. In addition, H^+ reacts with a large number of silicon hydroxyl groups carried on the surface of quartz sand. Protonation reaction ($\text{=SOH} + \text{H}^+ \rightleftharpoons \text{=SOH}^{2+}$)^[11] makes the adsorption capacity smaller under the condition of low pH. When pH is 3 to 4, with the increase of pH value, the amount of slow hydrolysis of, H^+ and H_3O^+ by UO_2^{2+} becomes smaller, and the adsorption capacity increases slowly. When pH is more than 4, the hydrolysis degree of UO_2^{2+} increases gradually and the radius of hydrated ions increases, which gradually hinders the substitution reaction of cations with them, and makes the adsorption capacity decrease again.

3.3. Ionic Strength

The effect of ionic strength on the adsorption of U (VI) by composites was studied by using NaCl as electrolyte.

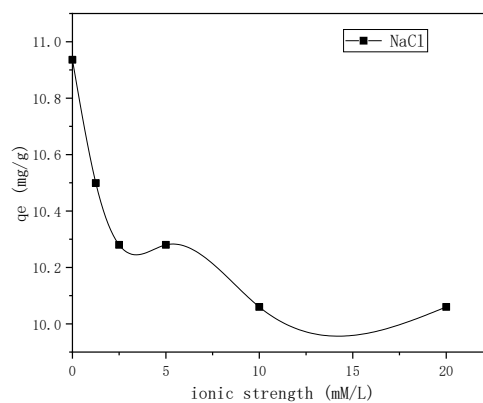


Fig. 3 Effect of ionic strength on composite materials.

The effect of ion strength on adsorption lies in changing adsorbents and electrostatic interaction

between agents; ion exchange between electrolyte ions with increased concentration competes with adsorbate ions; salting out effect of adsorbents; electrolytes, adsorbate ion pairing, and so on. As can be seen from fig.3, the amount of adsorption decreased by $0.876\text{mg}\cdot\text{L}^{-1}$ (7.97%) at 20 mM, so the ionic strength had an effect on the removal of uranium from the composite. In this experiment, there is a weak non-chemical bond between adsorbents and adsorbents (ion-pair interaction), and there is also the participation of water molecules between functional groups, which will form the complex (OSSC), adsorbents on the outer surface. There is electrostatic attraction between agents. With the increase of ion strength, sodium ion and chloride ion strongly shield the electrostatic attraction between uranyl ion and composite material, which makes it difficult to adsorb and rearrange uranyl ion on the surface of composite material. Moreover, sodium ion (supporting electrolyte ion) competes with uranyl ion to compete for the adsorption point site on the surface of the composite, that is, with the increase of NaCl concentration, the stronger the adhesion between Na and the composite surface^[12].

3.4. Inorganic coexisting ions

Fig. 4 shows the effect of Na^+ , Ca^{2+} and CO_3^{2-} on the adsorption of U (VI) in aqueous solution of the composite. The effect of Ca^{2+} on the adsorption of U (VI) in aqueous solution is greater, but that of Na^+ and CO_3^{2-} is less. Na^+ has a significant effect below 2.5mM (5.99%). Then the adsorption capacity is close to stable with the increase of concentration. Ca^{2+} has a significant effect. The adsorption capacity of $10.936\text{mg}\cdot\text{g}^{-1}$ decreased to $7.655\text{mg}\cdot\text{g}^{-1}$ (30%) at 10mM and to $6.124\text{mg}\cdot\text{g}^{-1}$ (44%) at 20mM. This is due to: first, Ca^{2+} ions compete directly with uranyl ions for adsorption sites. HAP adsorbs U (VI), in composites, and the adsorption mechanism of HAP is mainly dissolution precipitation and cation exchange in addition to complexation and physical adsorption. That is, UO_2^{2+} and Ca^{2+} , PO_4^{3-} of Ca^{2+} and PO_4^{3-} , aqueous solution formed by HAP in water form calcareous mica $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2$. The main reaction equations are (3) and (4). Second, the smaller the ionic radius of the hydrated ions in the solution, the higher the charge carried, the higher the ion polarization, and the higher the adsorption rate between the composite materials, and the ionic radius Ca^{2+} (99pm) is less than Na^+ , the charge is greater than Na^+ , and the competitiveness of the adsorption sites is strong^[13]. Third, the effect of Ca^{2+} as flocculant is stronger than that of Na^+ , which can promote the aggregation of HAP on the surface and reduce the specific surface area^[14]. The effect of CO_3^{2-} on the specific surface area is less because the pH value is 4, which has little effect at first, but with the increase of CO_3^{2-} concentration, the slow hydrolysis of CO_3^{2-} upregulated the existence of free CO_2 in pH, solution in the form of HCO_3^- , and the $\text{UO}_2(\text{CO}_3)_3^{4-}$ complex did not decompose completely, but gradually stabilized^[15].

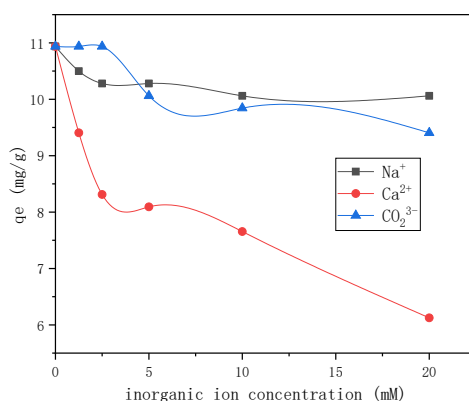
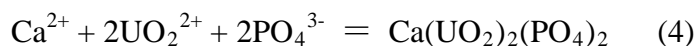
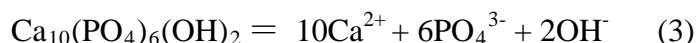


Fig. 4 Effect of inorganic ion concentration on composite materials.

3.5. Humic acid

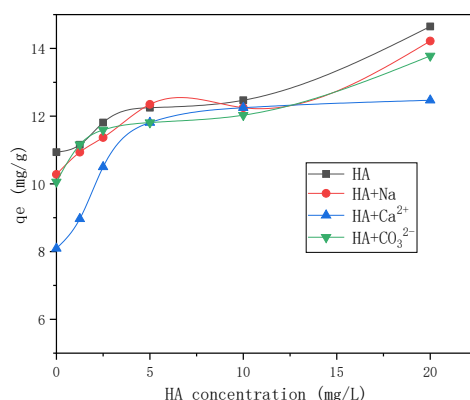


Fig .5 The influence of HA on composite materials.

Fig. 5 shows that HA can obviously promote the adsorption of U (VI) in aqueous solution of composites. In addition, HA reduces the inhibition of Ca^{2+} and CO_3^{2-} on adsorption. In theory, HA may inhibit adsorption because HA can form soluble binary complexes $\text{UO}_2\text{HA}(\text{II})$ and ternary complexes $\text{UO}_2(\text{OH})\text{HA}$ by complexing with uranyl ions. However, the pH is 4 ~ 4.5. Under the condition of weak acidity, the surface of HA has large negative electricity, the negative electromotive force is large, and the electrostatic adsorption of uranyl ion is also large. HA contains humic acid and fulvic acid. Humic acid had the strongest adsorption capacity of U (VI) at pH 3.5~6.5 and formed precipitation. Under weak acid condition, humic acid migrated in the form of uranyl complex ion of fulvic acid [16]. Besides, $-\text{COOH}$, $-\text{C}_6\text{H}_5$, $-\text{OH}$, $-\text{O}-\text{CH}$ in HA also has adsorption and redox effects on U (VI). Once again, Na^+ , CO_3^{2-} has little effect on the adsorption of U (VI) in aqueous solution of composites, but HA greatly reduces the competitive effect of Ca^{2+} , such as $5\text{mM}\text{Ca}^{2+}$. HA increased from $0\text{mg}\cdot\text{L}^{-1}$ to $20\text{mg}\cdot\text{L}^{-1}$ (from $8.092\text{mg}\cdot\text{g}^{-1}$ to $12.47\text{mg}\cdot\text{g}^{-1}$). This is due to the fact that, first, the Ca^{2+} complexes with the HA to the extent that it competes with the adsorption sites of the uranium-containing ions; secondly, the Ca^{2+} is bound to the surface of the composite material by binding to the adsorbed HA molecules, and is further combined with the U (VI) as a ligand-exchange site in the aqueous solution. In addition, due to the competitive complexation of HA with uranyl ion, although the effect is much smaller than that of Ca^{2+} , HA also slightly reduces the inhibitory effect of CO_3^{2-} on the adsorption of U (VI) by composites (from $10.06\text{mg}\cdot\text{g}^{-1}$ to $13.78\text{mg}\cdot\text{g}^{-1}$) [17].

4. Conclusion

The removal effect of HAP loaded with quartz sand on U (VI) in aqueous solution was studied by static test when the initial pH was 4. The ion strength and inorganic coexisting ions in the solution were discussed. The effects of humic acid and pH 4 ~ 4.5 U (VI) in aqueous solution on the removal efficiency were obtained as follows.

(1) The characterization results show that HAP has been successfully loaded on quartz sand in the newly synthesized composites.

(2) The ion strength has a certain effect on the removal of U (VI) by the composites. In addition to the chemical bond, there is also the effect of hydrogen bond or van der Waals force in the adsorption process.

(3) Inorganic coexisting ions in the solution have a certain effect on the removal process, and the order of influence is $\text{Ca}^{2+} > \text{CO}_3^{2-} > \text{Na}^+$. All of them inhibit the removal of uranium, in which Ca^{2+} (44%) and its obvious, Na^+ (5.99%) and CO_3^{2-} (14%).

(4) Humic acid can obviously promote the removal of U (VI) from aqueous solution of composites, and also reduce the inhibitory effect of Ca^{2+} and CO_3^{2-} on the adsorption of U (VI) by

composites.

In this paper, the effect of different water chemistry parameters on the adsorption of U (VI) on the composite material is studied. The common ions and the humic acid concentration in the real condition are reduced as much as possible. However, as the PRB material is applied to the practical application, it is also necessary to further study the parameters such as the specific permeability coefficient at different flow rates through the penetration experiment.

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