Preparation of ring crosslinked poly (p-nitrile) nanoparticles and Study on adsorption behavior of uranium (VI)

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Abstract. Cyclo crosslinked polyphosphazenes (PPNs) were prepared by Hexachlorocyclotriphosphazene (HCCP) with unique P = n structure and active p-cl group and green compound phloretin. The synthesis process of polyphosphazene nanospheres with Hexachlorocyclotriphosphazene as the main body and phloretin was discussed. The effects of pH value and solid-liquid ratio of solution on the adsorption of uranium by polyphosphazene nanospheres were studied. The results show that polyphosphazene nanospheres are off white powder in appearance and spherical in microstructure. When the pH value of the solution is 4 and the solid-liquid ratio is 0.5g · L⁻¹, the maximum adsorption rate of uranium is obtained.

1 INTRODUCTION

Adsorption method is a kind of wastewater treatment method that uses adsorbents with a large number of adsorption active groups to adsorb the radioactive substances in HLW to the surface. It is widely used in the treatment of HLW because of its advantages of simplicity, low cost and good effect. With the rapid development of social economy, environmental protection has become one of the most concerned hot spots in today's society. Among them, nuclear pollution is a widely concerned environmental problem, and uranium, the main resource of nuclear fuel, is one of the radioactive elements in waste liquid. Therefore, the search for a green material that can efficiently remove uranium by adsorption has a far-reaching impact on the future environmental protection. At present, diyun Chen [2] Research Group has studied the adsorption behavior of phosphate rock for uranium (VI) in mine sewage, the adsorption capacity is 0.1133mg · g⁻¹, and the removal rate of uranium (VI) is 76.89%. M. K. sureshkumar [3] prepared chitosan tripolyphosphate (CTPP) particles by liquid internal solid method. The adsorption capacity of CTPP particles for uranium (VI) was 236.9mg · g⁻¹. Xingcheng Ding [4] the research group prepared polyacrylonitrile (acrylonitrile) grafted with amidoxime chitosan and used it to adsorb uranium (VI) from aqueous solution, with the removal rate of 86.02%. M. H. khani [5] used the synthesized polypyrrole to adsorb uranium (VI) in waste water, and the adsorption capacity was about 87.72 mg · g⁻¹. In addition, polyphosphazene microspheres have attracted the attention and application of some researchers because of their superior characteristics to traditional adsorption materials. However, there are few studies and literature reports on the application of polyphosphazene materials in HLW at home and abroad. In this paper, He

hexachlorocyclotriphosphazene cophloretin nanospheres were synthesized with green inorganic material Hexachlorocyclotriphosphazene as the main body and green organic material phloretin, and characterized by SEM. Then, a series of single factor experiments were carried out to study the optimal pH value and solid-liquid ratio of the synthesized microspheres for uranium adsorption in aqueous solution.

2 Experimental methods

2.1 Experimental process

2.1.1 Preparation of cyclocrosslinked Hexachlorocyclotriphosphazene cophloretin nanospheres

Add 0.201 g Hexachlorocyclotriphosphazene and 0.4733 g phloretin into a 250 ml round bottom flask, pour in 100 ml acetonitrile solvent, disperse and dissolve in ultrasonic (100 W), add 4 ml triethylamine after dissolution, then pass in nitrogen as protective gas, vacuum the flask three times to remove oxygen, and react in ultrasonic (100 W) constant temperature water bath for 3 h. The device was transferred to an oil bath at about 60 °C for 12 h. The solution with the product was centrifuged to obtain solid. Then the crude product was cross washed with ethanol and distilled water for three times, and finally dried in an oven for 48 h to obtain crosslinked polyphosphazene microspheres. The synthesis route of cyclocrosslinked polyphosphazene phloretin nanospheres is shown in Fig. 1.

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Fig. 1 Synthesis process of cyclic cross-linked polyphosphazene-phloretin microspheres

2.1.2 Preparation of uranium (VI) standard solution

At first, 1g • L⁻¹ of uranium (VI) reserve solution was prepared, and then the reserve solution was gradually diluted to 60 mg • L⁻¹, 50 mg • L⁻¹, 40 mg • L⁻¹, 30 mg • L⁻¹, 20 mg • L⁻¹ and 10 mg • L⁻¹. Measure 1ml of each solution, add 1ml of arsenazo Tris, and prepare chloroacetic acid sodium acetate buffer solution with pH of 2.5 to titrate the above solution to the scale line. Use deionized water group as blank sample, measure three times in parallel on the visible spectrophotometer, record the corresponding absorbance data at each concentration, and then use Origin Software for linear fitting. A linear curve and a linear fitting equation can be obtained, which is the standard curve of uranium (VI) solution.

2.1.3 Effect of pH value on adsorption of uranium (VI) by cyclocrosslinked polyphosphazene nanospheres

10ml of 30mg • L⁻¹ uranium (VI) solution was accurately measured. The pH of the solution was adjusted by HNO₃ and NaOH respectively to be 2,3,0,4,0,5,0,6,0 respectively. 20mg of HCRP co-pgm nanoparticles were added respectively. The reaction solution was separated by ultra-fine filter membrane after the oscillation was completed, and 1ml of filtrate was transferred into 10ml volumetric flask, and 1ml of arsenazo III (0.05wt%) reagent was added into the volumetric flask with a pipette. Then, the buffer solution of chloroacetic acid sodium acetate with pH of 2.5 was added to the scale line by the drop of rubber head dropper. The absorbance of filtrate was determined by uv-2100 spectrophotometer. The effect of pH on the adsorption of uranium (VI) by the ring crosslinked polyphosphate root skin nanomicrospheres was analyzed. The calculation formula of adsorption quantity (q) and removal rate [6].

$$Q(\text{mg g}^{-1}) = \frac{(C_0 - C_e)V}{m} \quad (1.1)$$

$$R(\%) = \frac{(C_0 - C_e)}{C_0} \quad (1.2)$$

Where, q is the adsorption capacity (mg • g⁻¹), C₀ and C_e represent the concentration of uranium (VI) ion

before and after adsorption (mg • L⁻¹), V is the volume of uranium (VI) solution (L), and M is the amount of adsorbent (g).

2.1.4 Effect of solid-liquid ratio on adsorption of uranium (VI) by cyclocrosslinked polyphosphazene nanospheres

The pH of 30mg • L⁻¹ uranium (VI) solution was accurately measured, and the pH of the solution was adjusted to 3.5. 5mg, 10mg, 15mg, 20mg, 25mg and 30mg ring crosslinked polyphosphate nanomicrospheres were added respectively. The reaction solution was separated by ultra-fine filter membrane after the vibration was completed. 1ml of filtrate was transferred into 10ml volumetric flask, and 1ml of arsenazo III (0.05wt%) reagent was added into the volumetric flask with a pipette. Then, the buffer solution of chloroacetic acid sodium acetate with pH of 2.5 was added to the scale line by the drop of rubber head dropper. The absorbance of filtrate was determined by uv-2100 spectrophotometer. The effect of solid-liquid ratio on the adsorption of uranium (VI) by the ring crosslinked polyphosphate root skin nanosphere was analyzed.

3 Results and discussion

3.1 Characterization of cyclocrosslinked Hexachlorocyclotriphosphazene co phloretin nanospheres by SEM-EDS

Fig.2 Scanning electron microscopic study of pre adsorption ring crosslinked polyphosphazene phloretin nanospheres

Fig.3 Scanning electron microscopic study of pre adsorption ring crosslinked polyphosphazene phloretin nanospheres

Fig.4 Scanning electron microscopic study of pre adsorption ring crosslinked polyphosphazene phloretin nanospheres

It can be seen from figures 2, 3 and 4 that the material presents regular and uniform spherical shape, which is in line with the initial conjecture on the structure of cyclocrosslinked Hexachlorocyclotriphosphazene co phloretin nanospheres.

3.2 Establishment of standard curve of uranium (VI) solution

Fig.5 Uranium standard curve

It can be seen from figure 5 that in the range of 10-60mg • L⁻¹, there is a good linear relationship between the concentration of uranium (VI) and its absorbance ($R^2 = 0.9992$), and the linear equation can be obtained, as shown in formula 2.1

$$A = 0.019C_e + 0.0346 \quad (2.1)$$

Where a is the absorbance of uranium (VI) and C_e (mg L⁻¹) is the concentration of uranium (VI). When the

absorbance of unknown uranium (VI) solution is known, the fitted equation can be used to calculate its concentration.

3.3 Effect of pH value on adsorption of uranium (VI) by cyclophosphazene nanoparticles

One of the key factors for the adsorption of uranium (VI) by the cyclocrosslinked HCH co-pgm nanoparticles is the pH value in the wastewater containing uranium, which has a great influence on the adsorption behavior. The pH value not only affects the binding sites on the adsorbent surface, but also affects the morphology of the adsorbate in the solution [1]. The relationship between the pH value of solution and the adsorption amount of uranium (VI) is shown in Figure 6, which has an effect on the adsorption of uranium (VI) by microspheres. It can be seen from the figure that when the pH is less than 2.0, the corresponding adsorption amount is zero, indicating that when the pH is lower than 2.0, the microspheres have no adsorption effect on uranium containing wastewater. When the pH is less than 4 and greater than 2, the adsorption amount increases with the increase of pH value. The adsorption capacity of U (VI) by the cyclocrosslinked ppn-pgms increases gradually. The above phenomena may be due to the presence of a large amount of hydrogen ions in uranium solution under acidic conditions, which may be easier to bind with the adsorption sites in the cyclocrosslinked ppn-gpm nanoparticles, which leads to the particle of the microspheres, which is due to the repelling of the same

-sex charge, The particles will repel the positively charged uranium (VI) ions, which is not conducive to the adsorption of uranium (VI) [7] in the solution of the microspheres, so this trend is presented. When the pH value of the solution is 4, the content of hydrogen ion in the solution decreases gradually. At this time, a large number of active adsorption sites are preferentially combined with uranium (VI) ions with positive charge, thus obtaining the maximum adsorption capacity. However, it can be seen from the figure that the adsorption of uranium by the microspheres will decrease when the pH of the solution continues to increase and is greater than 4. It is possible that uranium (VI) is easy to hydrolyze in this pH range, and even form $(UO_2)_3(OH)_7$ with negative charge. The appearance of such ions may produce repulsion with the surface of the ring crosslinked hch-co-gpn nanoparticles, which also leads to the decrease of the adsorption strength of the adsorbent. Therefore, when the pH value of the solution is 4, the adsorption behavior of the cyclocrosslinked ppn-gpm nanoparticles to uranium (VI) is the best. At this time, the best adsorption capacity is 39.33mg • g⁻¹, and the removal rate reaches 65.86%.

Fig.6 The effect of pH on adsorption of uranium

Fig.7 The effect of solid-to-liquid ratio on adsorption of uranium

3.4 Effect of solid-liquid ratio on adsorption of uranium (VI) by cyclocrosslinked Hexachlorocyclotriphosphazene co phloretin nanospheres

The ratio of solid to liquid affects the economic benefit of adsorption behavior. Too high or too low ratio of solid to liquid is unfavorable to adsorption behavior. For this experiment, when the solid-liquid ratio is too large, not only the excess adsorbent will be wasted, but also the adsorption capacity will be reduced [8], and the removal rate will not increase significantly, or even decline. When the solid-liquid ratio is low, the adsorption rate of the adsorbent for uranium (VI) will slow down, and even can not absorb the remaining uranium (VI) ions in the solution. In order to study the effect of solid-liquid ratio on the adsorption of uranium (VI) by cyclohexachlorocyclotriphosphazene co phloretin nanospheres, the initial concentration of uranium (VI) was $3 \text{ g} \cdot \text{L}^{-1}$, the adsorption time was 2 h, and the pH value was adjusted to 4.0. The volume of uranium (VI) solution was 10 ml, and the mass of adsorbent was 4-8 mg. It can be seen from the influence of solid-liquid ratio on adsorption of uranium (VI) by microspheres in Fig. 7 that with the increase of solid-liquid ratio (M/V), the removal rate of uranium (VI) by cyclohexachlorocyclotriphosphazene co phloretin nanospheres gradually increases, and when the solid-liquid ratio is greater than $0.54 \text{ g} \cdot \text{L}^{-1}$, it gradually tends to be flat, and in a slight decline, the removal rate is 62.13%. This may be due to the existence of a certain "shielding effect [9]" on the surface of the adsorbent after reaching a certain adsorption capacity, which has a certain repulsive effect on the remaining uranium (VI) ions. At this time, due to the decrease of the concentration of uranium (VI) ions, there is not enough driving force to offset the repulsive force. Therefore, after the concentration of $0.54 \text{ g} \cdot \text{L}^{-1}$, the removal rate gradually decreased. It is speculated that the best removal rate is 62.13% when the solid-liquid ratio is $0.54 \text{ g} \cdot \text{L}^{-1}$.

4 Conclusion

In this study, a novel adsorbent, cyclocrosslinked Hexachlorocyclotriphosphazene co phloretin nanospheres, was synthesized and characterized by SEM. A series of single factor experiments were carried out to study the adsorption conditions of the synthesized microspheres for uranium in aqueous solution. The results showed that when the solution pH value was 4 and the solid-liquid ratio was $0.5 \text{ g} \cdot \text{L}^{-1}$, the adsorption behavior of cyclophosphazene phloretin nanospheres for uranium (VI) was the best.

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