Study on cyclic crosslinked polyphosphazene microspheres and its adsorption behavior for uranium (VI)

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Abstract. Poly (cyclotriphosphazene-co-4,4 '- diaminodiphenylsulfone) (PZD) microspheres were synthesi zed by precipitation polymerization of Hexachlorocyclotriphosphazene (HCCP) and polyfunctional organic monomers. The products were characterized by FTIR, SEM-EDS, XPS and bet. The adsorption behavior of PZD microspheres for uranium (VI) in aqueous solution and the influence of adsorption behavior were disc ussed. The results show that the PZD microspheres have a certain adsorption capacity for uranium (VI) in a queous solution. When pH = 3.5, adsorption time is 6h, solid-liquid ratio is 2.0g • L-1 and initial concentra tion of uranium (VI) is 30mg • L-1, the adsorption rate of uranium reaches the maximum.

1 INTRODUCTION

At present, many methods have been developed to remo ve uranium (VI) from aqueous solution. However, many traditional methods have their own limitations. For exam ple, although membrane separation technology can effect ively remove uranium, the cost of this method is too high [1]. Chemical precipitation method is easy to operate an d low cost, but it is easy to cause secondary pollution [2]. Compared with the above two methods, adsorption meth od is widely favored because of its easy implementation, low cost and few secondary pollutants. Hai Nguyen tran [3] synthesized a new adsorbent for uranium (VI) adsorp tion by impregnating br PADAP onto multi walled carbo n nanotubes (MWCNTs). Xiangke Wang [4] has synthes ized magnetic titanate nanosheets (Fe3O4 @ TNS) to ad sorb uranium (VI) in wastewater, and the maximum adso rption capacity is relatively large. Ramzi zarrougui [5] us ed nonfluorinated ionic liquids (ILS) to extract uranium (VI) from radioactive wastewater. Polyphosphazenes are a kind of new polymer materials with unique P = n struc tural units and active p-cl groups. Their physical and che mical properties can be adjusted by nucleophilic substitu tion of functional groups. A poly (cyclotriphosphazene c o-4,4 '- diaminodiphenylsulfone) microsphere (PZD) was synthesized by precipitation polymerization of Hexachlo rocyclotriphosphazene (HCCP) and 4,4-diaminodiphenyl sulfone (DDS) under the protection of nitrogen and trieth ylamine (tea). The microspheres were used to adsorb ura nium (VI) from radioactive waste water.

2 Experimental methods

2.1 Experimental process

2.1.1 Preparation of PZD microspheres

65g HCCP and 4,4-diaminodiphenylsulfone (DDS) were dissolved in 200ml acetonitrile, and then the mixed solut ion was poured into a three port flask. After the solid wa s completely dissolved, nitrogen was used as protective g as. The three port flask was placed in an ultrasonic instru ment (200W, 40KHz) for ultrasonic reaction, and the rea ction temperature was set at 50 ℃. After 5 minutes of ult rasound, 3 ml triethylamine was added dropwise into the three port flask. After ultrasonic treatment for 6 hours, th e reaction system was transferred to an oil bath, heated i n an oil bath at 50 ℃ and stirred by magnetic force for 6 hours.

At the end of the reaction, the reaction product was centr ifuged in a centrifuge (800r / min) for 5 minutes, the sup ernatant was removed, and the white precipitate was was hed several times with anhydrous ethanol and deionized water. Finally, the washed solid material was dried in a v acuum drying oven at 60 ℃ for 48 hours to obtain the sy nthetic product.

2.1.2 Preparation of uranium (VI) standard solution

1 g • L-1 of uranium (VI) reserve solution was prepare d, and then the reserve solution was gradually diluted to 10 mg • L-1, 20 mg • L-1, 30 mg • L-1, 40 mg • L-1, 50 mg • L-1 and 60 mg • L-1. Measure 1ml of the a bove solution respectively, add 1ml of arsenazo Tris, titr ate it with chloroacetic acid sodium acetate buffer solutio n with pH = 2.5 to the scale line, take deionized water as blank sample, measure it in parallel for three times on th e visible spectrophotometer, and obtain the correspondin g absorbance at each concentration, which is linearly fitt ed by origin [6]. The linear fitting equation obtained is th

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e standard curve of uranium (VI) solution.

2.1.3 Effect of pH value on adsorption of uranium (VI) by PZD microspheres

10 ml of 30 mg • L-1 uranium (VI) solution was accura tely measured. The pH of the solution was adjusted to 2, 3.0, 4.0, 5.0 and 6.0 with HNO3 and NaOH respectively. 20 mg PZD microspheres were added respectively, and t he adsorption time was 6 h under the condition of oscilla tion rate of 120 rpm and temperature of 25 ℃. After the oscillation, the reaction solution was separated by ultrafil tration membrane. 1 ml of filtrate was transferred into a 10 ml volumetric flask, and then 1 ml of arsenazo Ⅲ (0. 05 wt%) chromogenic agent was transferred into the vol umetric flask with a pipette gun, Then add chloroacetic a cid sodium acetate buffer solution with pH of 2.5 dropwi se to the scale line, and determine the absorbance of the f iltrate by uv-2100 spectrophotometer, so as to analyze th e effect of pH on the adsorption of uranium (VI) by cycl ocrosslinked polyphosphazene phloretin nanospheres. Ca lculation formula of adsorption capacity (q) and removal rate [6] are as follows:

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

$$R(\%) = \frac{(C_0 - C_e)}{C_0} \quad (2)$$

Where, q is the adsorption capacity (mg • g-1), C0 and CE represent the concentration of uranium (VI) ion befor e and after adsorption (mg • L-1), V is the volume of ur anium (VI) solution (L), and M is the amount of adsorbe nt (g).

2.1.4 The effect of solid-liquid ratio on adsorption of uranium (VI)by PZD microspheres

Accurately measure 10ml of 30mg • L-1 uranium (VI) solution and adjust the pH of the solution to 3 5. 5mg, 10 mg, 15mg, 20mg, 25mg and 30mg PZD microspheres w ere added respectively. Under the condition of oscillation rate of 120rpm and temperature of 25 ℃, the adsorption was vibrated for 6h. After the oscillation, the solid-liquid separation of the reaction solution was carried out by ult rafiltration membrane. 1ml of the filtrate was transferred into a 10ml volumetric flask, and then 1ml of arsenazo Ⅲ (0.05wt%) chromogenic agent was transferred into th e volumetric flask by pipette gun. Then the pH 2.5 chlor oacetic acid sodium acetate buffer solution was added dr opwise to the scale line with a rubber tipped burette, and the absorbance of the filtrate was determined by uv-2100 spectrophotometer, so as to analyze the effect of solid-li quid ratio on the adsorption of uranium (Ⅵ) by cyclicall y crosslinked polyphosphazene phloretin nanospheres.

2.1.5 Effect of initial concentration of uranium (VI) o n adsorption of uranium (VI) by PZD microspheres

The concentration of 10 mg • L-1, 20 mg • L-1, 30m g • L-1, 40 mg • L-1 and 50 mg • L-1 of uranium (V I) solution was accurately measured. The pH of the soluti on was adjusted to 3.5 with HNO3 and NaOH respective ly. 20 mg PZD microspheres were added. The shaking ra te was 120 RPM and the adsorption time was 6 h at 25℃. After shaking, the reaction solution was separated b y ultrafiltration membrane. 1 ml of filtrate was put into a 10 ml volumetric flask, Then, 1 ml arsenazo Ⅲ (0.05w t%) chromogenic agent was transferred by pipette gun an d added into volumetric flask. Then, chloroacetic acid so dium acetate buffer solution with pH of 2.5 was added dr opwise with rubber tip dropper to make volume to the sc ale line. The absorbance of the filtrate was determined b y uv-2100 spectrophotometer to analyze the effect of init ial concentration on the adsorption of uranium (VI) by P ZD.

3 Results and discussion

3.1 Characterization of PZD microspheres

3.1.1 Infrared characterization of PZD microspheres

The absorption peaks at 3361cm - 1 and 3215cm - 1 are t he stretching vibration peaks of - NH2. This indicates tha t the polymerized PZD microspheres contain a certain a mount of - NH2 group. Obviously, the two strong absorp tion peaks of 1593 cm-1 and 1500 cm-1 are the absorptio n peaks of C = C in aromatics. 1300 cm-1 and 1103 cm- 1 are characteristic absorption peaks of o = s = O stretchi ng vibration of sulfodiphenol group. The characteristic a bsorption peak of P = n stretching vibration is at 1143cm -1. 880cm-1 is the stretching vibration peak of p-n and 9 31cm-1 is the stretching vibration peak of ar-n-p. due to t he formation of ar-p-n, it can be preliminarily inferred th at HCCP and DDS have polymerized to form a new subs tance.

3.1.2 XPS characterization of PZD microspheres

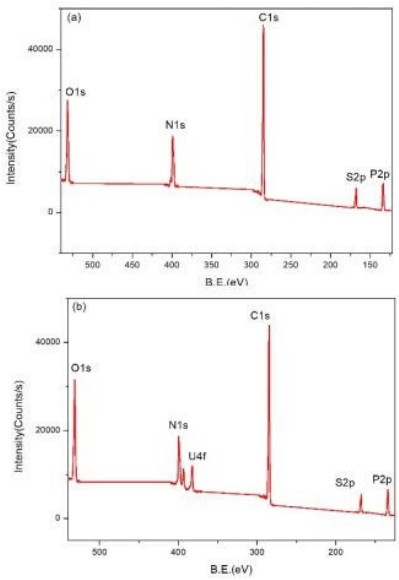

Fig.1XPS spectra of the PZD microspheres before(a) and after (b) adsorption

In order to determine the composition of the elements in PZD microspheres, XPS was used. The XPS spectrum of PZD microspheres is shown in Fig.1 It can be seen from figure a that the surface of PZD microspheres is compos ed of C, N, O, P and S elements, in which Cl, N, O, P an d S elements account for 63.93%, 11.33%, 11.52%, 6.9 4% and 6.27% respectively. It can be seen from figure B that the peak of uranium (VI) appears obviously after ads orption, and the proportion of uranium (VI) is 0.33%, wh ich indicates that PZD microspheres have a certain adsor ption effect on uranium (VI) in aqueous solution.

3.1.3 Bet characterization of PZD microspheres

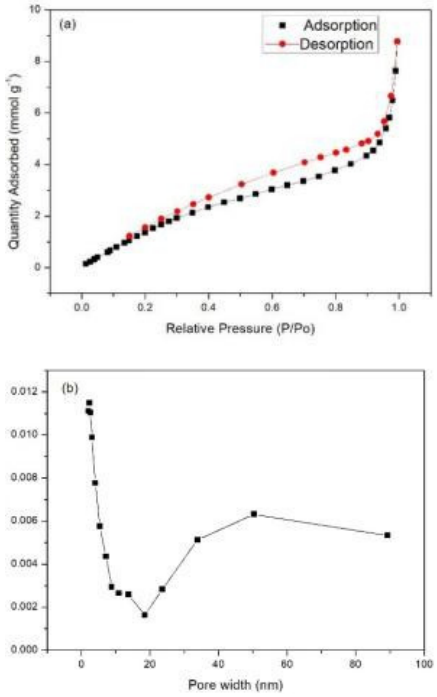

Fig.2 Nitrogen adsorption-desorption isotherm obtained at 77K for the PZD（b）The pore size distribution curve of the PZD

In order to determine the specific surface area and pore s ize of PZD microspheres, the PZD microspheres were ch aracterized by bet. As shown in Figure 2.4, the BET spec ific surface area of PZD microspheres is 10.42m2/g, the t otal pore volume is 0.012cm3/g, and the pore size is 5.21 nm, which is a mesoporous material. It can be seen that t he specific surface area of the adsorption material is goo d, which can provide a certain adsorption site for the ads orption of uranium (VI) [7].

3.1.4 Characterization of PZD microspheres by SE M-EDS

Accurately measure 10ml of 30mg • L-1 uranium (VI) solution and adjust the pH of the solution to 3.5. 5mg, 10.It can be seen from figure 6 that the material presents a r egular and uniform ball shape. However, after adsorption, the material becomes irregular and even flat. It can be se en from Fig.7 that there is one more uranium element on the PZD microspheres after adsorption than before, whic h further indicates that the PZD has successfully adsorbe d uranium (VI) on its surface.

3.2 Effect of pH value on adsorption of uranium (VI) by PZD microspheres

When the pH is less than 3.5, with the increase of pH val ue, the adsorption capacity of PZD microspheres for ura nium (VI) increases gradually. This may be due to the ex istence of a large number of positively charged H + in th e uranium solution under strong acid conditions, and thes e positively charged hydrogen ions may be easier to com bine with the adsorption sites in PZD microspheres, resul ting in protonation of PZD microspheres, The protonated microspheres will repel the positively charged uranium (VI) ions, which is not conducive to the adsorption of ur anium (VI) in solution by PZD microspheres [8]. Howev er, when the pH of the solution is higher than 4, the adso rption capacity of PZD microspheres for uranium present s a downward trend. This is because when the pH value e xceeds 4, uranium (VI) is easy to hydrolyze, even to for m negatively charged (UO2) 3 (OH) 7 -, and the appeara nce of this ion will produce repulsive force with the PZD surface, resulting in the decrease of the adsorption stren gth of the adsorbent. In conclusion, when the pH value o f the solution is 3.5, the adsorption behavior of PZD micr ospheres is the best, and the optimal adsorption capacity is about 12.79 mg • g-1.

3.3 Effect of solid-liquid ratio on adsorption of urani um (VI) by PZD microspheres

In order to study the effect of solid-liquid ratio on the ad sorption of uranium (Ⅵ) by PZD microspheres, experiments were carried out under the conditions of initial conc entration of uranium (Ⅵ) 30 mg • L-1, shaking adsorpti on for 6 h, pH = 3.5, volume of uranium (Ⅵ) solution 10 ml and adsorbent dosage (5-30 mg). It can be seen that with the increase of solid-liquid ratio (M / V), the remov al rate of uranium (VI) by PZD microspheres gradually i ncreases, and when the solid-liquid ratio is greater than 2. 0 g • L-1, it gradually tends to be flat, and the removal rate is 86%. This may be due to the existence of a certain "shielding effect [9]" on the surface of the adsorbent aft er reaching a certain amount of adsorption, which has a c ertain repulsion to the remaining uranium (VI) ions. At t his time, due to the decrease of the concentration of uran ium (VI) ions, there is not enough driving force to offset the repulsion force. Therefore, it can be inferred that the best adsorption condition is when the solid-liquid ratio is 2.0 g • L-1.

3.4 Effect of initial concentration of uranium (VI) on adsorption of uranium (VI)

When the initial concentration of uranium (VI) ion is in t he range of 10-30 mg • L-1, the adsorption capacity of PZD microspheres for uranium (VI) increases with the in crease of uranium (VI) ion concentration. When the initi al concentration of uranium (VI) ion in the solution is gr eater than 30 mg • L-1, the increase of adsorption capa city gradually slows down. It may be that when the conc entration of uranium (VI) ion is high, the number of effe

ctive collisions between uranium (VI) ion and adsorbent is increased, and the driving force of mass transfer in soli d-liquid phase is improved, so more uranium (VI) ions ar e combined with PZD adsorbent. When the initial conce ntration of U (VI) in the solution is in the range of 10 ~ 5 0 mg • L-1, the removal rate of U (VI) by PZD microsp heres decreases slowly. It may be that at a higher concen tration of uranium (VI) ion, after uranium (VI) ion reach es a certain concentration, due to the increased competiti on of uranium (VI) ion in the adsorption sites, the adsorp tion sites on the adsorbent that can combine with metal i ons reach saturation [10].

4 Conclusion

In this experiment, PZD microspheres, a new adsorbent, were synthesized by precipitation polymerization. The P ZD microspheres were used to adsorb uranium (Ⅵ) in w astewater. The influence of pH value, solid-liquid ratio, i nitial solution concentration on adsorption of uranium (Ⅵ) by PZD microspheres was studied by single factor method. The results show that PZD microspheres have c ertain adsorption capacity for uranium (Ⅵ) in aqueous s olution. The removal rate was over 85%, and the adsorpt ion capacity was close to 12.19mg · g-1. The best conditi ons for adsorption of uranium (Ⅵ) in the waste liquid by PZD microspheres are: pH = 3.5, adsorption time is 6h, solid-liquid ratio is 2.0g · L-1, and initial concentration o f uranium (Ⅵ) is 30mg · L-1.

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