用于放射性废水处理的高比表面多孔六氰合铁钛钾/二氧化硅小球的制备

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摘要: 采用一种新方法合成了由六氰合铁钛钾(PTH)与二氧化硅组成的多孔球形杂化材料。其过程分为两步: 首先将无定型二氧化钛接枝于球形二氧化硅载体的孔壁上; 然后利用 TiO^{2+} 和 $K_4[Fe(CN)_6]$ 的反应将孔道内的二氧化钛转化为 PTH。所制备的杂化材料通过低温氮吸附、XRD、FTIR 和 XPS 等方法进行了表征。结果表明 PTH 涂层被成功负载于二氧化硅小球的内部孔壁上。所得杂化材料在高酸度和高盐度的情况下仍然对 Cs^+ 离子表现出了很强的去除能力和很高的分配系数。

关键词: 二氧化硅小球; 杂化; 铯分配系数; 放射性废水

Preparation of High Surface Area Porous Potassium Titanium Hexacynoferrate/SiO₂ Bead for Radioactive Waste Water Treatment

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Abstract: Porous composite beads composed of potassium titanium hexacynoferrate (PTH) and silica was prepared with a method developed in this work. The method could be divided in two steps: the first was grafting amorphous titania onto the wall of pores in silica bead support, the second was converting the tinania inside the pores into PTH by the reaction between TiO^{2+} and $K_4[Fe(CN)_6]$. The as-made composites were characterized by low temperature nitrogen adsorption-desorption, XRD, FTIR and XPS. The results show that the PTH layer is coated successfully onto the wall of pores in silica bead. The as-made composites exhibit high Cs^+ removal ability and distribution coefficient even under high acidity and salinity.

Key words: silica bead; composite; cesium distribution coefficient; radioactive waste water

The importance of nuclear power industry has been much realized in recent years. However, the problem of disposing radioactive waste, especially the radioactive waste water generated from nuclear power industry must be properly solved. Radioactive waste water has many characteristics which make it notoriously hard to be treated with common methods.[1~3] First, the usually high acidic water will cause serious corrosion upon boiling when treated with vaporizing method; second, when the water is treated with ion-exchange resin the ion-exchanging sites of the resin will be rapidly exhausted by large amount of non-radioactive ions in water . A promising choice to solve the problem is to adsorb the radioactive ion (mainly Cs^+) in water with inorganic ion-exchange adsorbents.

Transition-metal-stabilized potassium hexacyanoferrate (TMPH) have been proved to be very good Cs^+ adsorbents under high salinity and acidity [1~7]. However,

they could hardly be used directly in treating radioactive waste solution with column operation because most of them are nano-scaled particles. Many works were dedicated to stabilize TMPH particles into porous silica support. The method of fabricating silica composites of potassium cobalt hexacyanoferrates[8~10], potassium zinc hexacyanoferrates[11], potassium(zinc, nickel or copper) hexacyanoferrates[12] have been reported. Composites convenient to be handled and applied could be successfully fabricated with these approaches, but there are still some problems to be solved. First, doping TMPH into porous silica with solvent vaporizing method demands repeated soaking process and vaporizing process, as a result, the preparing route is very complicated and time-consuming. Second, there is no chemical bond between porous silica and TMPH making the attachment unstable and prone to detachment. XU et al[13] reported the method of fabricating PTH bead with spherical TiO_2 particles as titanium precursor. The material showed obvious Cs removal ability and relative durability, but there are still shortcomings in the method. First, the spherical TiO_2 beads are not hard enough and some of them will be crashed in the following water treatment process. Second, the BET surface area of the TiO_2 bead is very low(14 $m^2 \cdot g^{-1}$), as a result, the ion exchange reaction between K^+ and Cs^+ could only occur on the thin surface layer of the sphere which reduces the mateials Cs uptake capacity and Cs removal ability.

A method was developed in this work to prepare PTH/SiO_2 composite with large surface area, high particle strength and good spherical degree. In this route, amorphous TiO_2 layer was coated onto the wall of pores in the porous silica bead. Then, being treated with $K_4[Fe(CN)_6]$, some of the amorphous TiO_2 inside the pores was converted into PTH. The as-made composites were assessed with their adsorbing ability upon Cs^+ under the disturbance of coexisting ion(H^+ and Na^+).

1　Experimental

1.1　Chemicals

Tetrabutyl titanate(Ti(OC$_4$H$_9$)$_4$), Cyclohexane(C$_6$H$_{12}$), potassium ferrocyanide trihydrate (K$_4$[Fe(CN)$_6$]·3H$_2$O)

were of analytical grade and purchased from Fluka. Two kinds of silica beads were obtained from Hailang Silica-gel Factory(Tsingtao, China), namely wide-pore silica bead(WP) and catalyst-support silica(CS). The water used in the present work was deionized water with $R >$ 18 MΩ.

1.2　Experimental procedure

1.2.1　Grafting amorphous TiO_2 layer onto the wall of pores in silica beads

The silica beads were washed with deionized water and dried under 100 ℃ in air for 12 h. The dried silica gel(10 g) were immersed into the mixture of 150 mL cyclohexane and 40 mL Ti (OC$_4$H$_9$)$_4$. The mixture was placed in a three-necked flask equipped with a condenser. It was heated to 80 ℃ under magnetic stirring and nitrogen gas protection. The reaction lasted for 24 h before the silica beads were separated and thoroughly washed with cyclohexane. Then the beads were dried in the air under 80 ℃ for 8 h. The resulting samples with WP and CS as supports were named as WP-Ti and CS-Ti, respectively.

1.2.2　Preparation of PTH/SiO$_2$ composite beads

WP-Ti and CS-Ti were soaked into the mixture of K$_4$[Fe(CN)$_6$] solution and HCl ($c_{K_4[Fe(CN)_6]}$=0.5 mol·L^{-1}, c_{HCl}=1 mol·L^{-1}). The liquid was stirred every 3 h and the reaction lasted for 24 h. The as-prepared glaucous composite beads were filtrated and washed thoroughly with deionized water before dried in air under 100 ℃ for 24 h. The composites with WP and CS as supports were named as WP-Ti-KFC and CS-Ti-KFC, respectively.

1.2.3　Determination of composition of WP-Ti-KFC and CS-Ti-KFC

About 0.1 g composite were leached with hot H$_2$SO$_4$(98%, 10 mL, 100 ℃) for 3 h. (CAUTION: highly toxic HCN was released during this process. It must be operated in well vented fume-hood). The remained solid were thoroughly washed with HCl(10%) and discarded. The resulting washing liquid was collected and its volume was adjusted to 1 000 mL with deionized water. The metal ion contents in the liquid were measured by atomic adsorption spectrometer(AAS 6 Vario, Analytik Jena AG, Germany) and the composition of the samples

were determined.

1.2.4　Measurement of Cs uptake capacity of WP-Ti-KFC and CS-Ti-KFC

To determine the Cs uptake capacity of the samples, about 0.2 g of each sorbent was soaked into 50 mL 0.01 mol·L^{-1} CsCl solution in polypropylene flask. The solutions were shaken in flask shaker for 24 h under 20 ℃. After separating the solids in the liquid with centrifugation at 3 000 r·m^{-1} for 10 min, the Cs$^+$ concentration in the resulting liquid were studied with atomic adsorption spectrometer (AAS 6 Vario, Analytik Jena AG, Germany). The Cs uptake capacities of the composites were calculated by the following formula:

$$q = (C_0 C_1) \times F \qquad (1)$$

where C_0: the initial concentration of Cs$^+$(mmol·mL^{-1})

C_1: the final concentration of Cs$^+$(mmol·mL^{-1})

F: the ratio of volume of solution to the mass of the composite added(mL·g^{-1})

1.2.5　Characterization of WP-Ti-KFC and CS-Ti-KFC

The powder XRD pattern of WP-Ti-KFC, CS-Ti-KFC, WP-Ti, CS-Ti, WP and CS were recorded in 2θ from 5° to 90° with a scanning step of 0.016 7° on PANalytical X′Pert PRO X-ray diffraction using Ni filtered Cu $K\alpha(\lambda=0.154\ 18$ nm) radiation at 40 kV and 30 mA. The nitrogen adsorption/desorption isotherms of the samples were measured at 77 K using a nitrogen adsorption instrument (ASIMP, Quantachrome, USA). The FTIR spectra of the samples were obtained using a Bruker RFS100 spectrometer. The spectra were recorded at the transmittance mode from 4 000 to 400 cm^1 at the resolution of 1 cm^1 using optical grade potassium bromide (KBr) as a background material. The X-ray photoelectron spectroscopy data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Mg $K\alpha$ radiation. The base pressure of the chamber was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

1.2.6　Determination of the Cs-uptake-behavior of the composites under interference of Na$^+$ and H$^+$

Distribution coefficients of the composite upon Cs were studied with batch experiment under the competition of co-existing ions (H$^+$ and Na$^+$). Proper amount of composite beads (0.2 g) were soaked into Cs$^+$ solution(50 mL, c_{Cs^+}=1 000 μg·L^{-1}). The c_{Na^+} in the liquid was adjusted with adding NaNO$_3$ or NaCl while c_{H^+} in the liquid was adjusted with HCl or HNO$_3$. The solutions were shaken in flask shaker for 24 h under 20 ℃. After separating the solids in the liquid with centrifugation at 3 000 r·m^{-1} for 10 min, the Cs$^+$ conce-ntration in the resulting liquid was measured with atomic adsorption spectrometer(AAS 6 Vario, Analytik Jena AG, Germany). The following equation was used to determine the distribution coefficients(K_d)

$$K_d = (C_0 - C_1)F / C_1 \qquad (2)$$

where C_0: the initial concentration of Cs$^+$(mmol·mL^{-1})

C_1: the final concentration Cs$^+$(mmol·mL^{-1})

F: the ratio of volume of solution to the mass of the composite added(mL·g^{-1})

2　Results and discussion

2.1　Composition of the composites

The compositions of the composites are listed in Table 1. It could be seen that the empirical formula of PTH in WP-Ti-KFC is very close to that in CS-Ti-KFC. XU et al[13] reported that the PTH prepared with reaction between amorphous TiO$_2$ and K$_4$[Fe (CN)$_6$] could be expressed as K$_{2x}$[(TiO)$_{2-x}$Fe(CN)$_6$](where x lies between 0.5 and 0.75). The results of the current work are in agreement with the above conclusion with x of 0.502 in WP-Ti-KFC and 0.504 in CS-Ti-KFC. It could be also observed from the Table 1 that not all of the Ti atoms react with K$_4$[Fe(CN)$_6$]. There are still some TiO$_2$ left in the composites. It is highly possible that these Ti atoms locate in the in ner part of TiO$_2$ layer that does not

Table 1　Composition of WP-Ti-KFC and CS-Ti-KFC

Sample	PTH composition	PTH load(g/100 g SiO$_2$)	TiO$_2$(g/100 g SiO$_2$)
WP-Ti-KFC	K$_{1.04}$[(TiO)$_{1.48}$Fe(CN)$_6$]	8.92	4.57
CS-Ti-KFC	K$_{1.08}$[(TiO)$_{1.46}$Fe(CN)$_6$]	15.33	4.11

undergo reaction with $K_4[Fe(CN)_6]$.

2.2 XRD analysis of WP-Ti-KFC and CS-Ti-KFC

The powder XRD patterns of WP-Ti-KFC, CS-Ti-KFC, WP-Ti, CS-Ti, WP and CS are shown by Fig.1. The powder XRD pattern of PTH sample with composition of $K_{1.1}[(TiO)_{1.45}Fe(CN)_6]$ (prepared with the method reported by Xu et al. [13]) is also shown for comparison. Sample WP and CS exhibit no characteristic peak corresponding to their amorphous crystal structure of silica. There are also no characteristic peaks in the XRD patterns of WP-Ti and CS-Ti because the titania layers coated on their inner surface are amorphous. The characteristic peaks very close to those of $K_{1.1}[(TiO)_{1.45}Fe(CN)_6]$ in the XRD pattern of WP-Ti-KFC and CS-Ti-KFC reveal the existence of PTH component. Because there are only slight crystal structure difference between the PTH component in WP-Ti-KFC, CS-Ti-KFC and $K_{1.1}[(TiO)_{1.45}Fe(CN)_6]$, their XRD patterns were quite similar. The low intensity of PTH characteristic peaks in WP-Ti-KFC and CS-Ti-KFC implies that the PTH particles generated on the inner surface of the two samples are in very small scale.
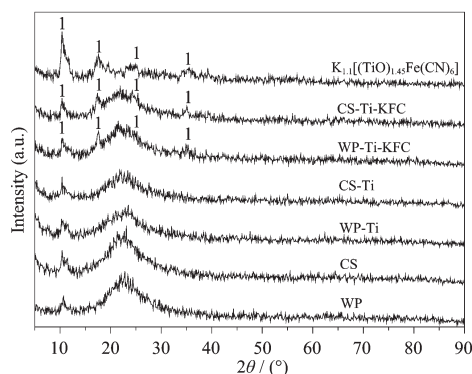
2.3 BET surface area of WP-Ti-KFC and CS-Ti-KFC

Fig.2 shows the nitrogen adsorption and desorption isotherms of WP, CS, WP-Ti-KFC and CS-Ti-KFC. According to the classification of IUPAC, the adsorption isotherms of WP and WP-Ti-KFC could be approximately classified as type IV, which is commonly linked to mesopores with capillary condensation taking place during the nitrogen adsorption. At the same time, the adsorption isotherms of CS and CS-Ti-KFC could be approximately sorted as type I, usually detected in microporous solids having relatively small external surface[14]. It could be seen that the saturated adsorbed amount of WP-Ti-KFC and CS-Ti-KFC are lower than that of WP and CS, respectively. The reason might lie in the possibility that the TiO_2 and PTH layer inside of the pores of WP and CS reduces the surface area and pore volume. The BET results are listed in Table 2. After loaded with PTH, the WP-Ti-KFC and CS-Ti-KFC exhibit lower surface area, smaller average pore size and less pore volume than those of WP and CS.
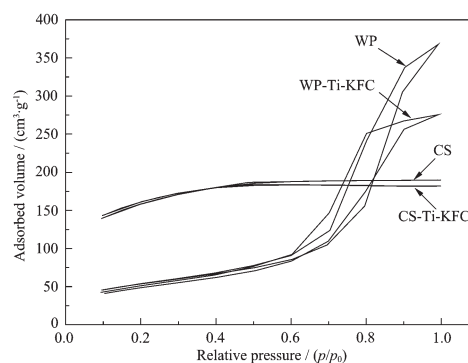

Fig.1　XRD patterns of samples

Fig.2　Nitrogen adsorption/desorption isotherms of WP, CS, WP-Ti-KFC and CS-Ti-KFC

Table 2　Nigrogen adsorption-desorption results of samples

Sample name	Pore volume[a] / (mL·g⁻¹)	Average pore size / nm	BET surface area / (m²·g⁻¹)
WP	0.56	12.2	185
WP-Ti-KFC	0.43	10.0	171
CS	0.30	2.3	520
CS-Ti-KFC	0.28	2.2	517

[a] Cumulative pore volume(1.5 nm < pore size < 200 nm)

2.4 FTIR analysis

Fig.3 displays the FTIR spectra of the samples. WP and CS exhibit the features typical for amorphous

silica with main absorption bands at ca. 1 220, 1 070~1 090, 800, 455 cm⁻¹ due to the anti-symmetric and symmetric stretching modes of Si-O-Si lattice unites and
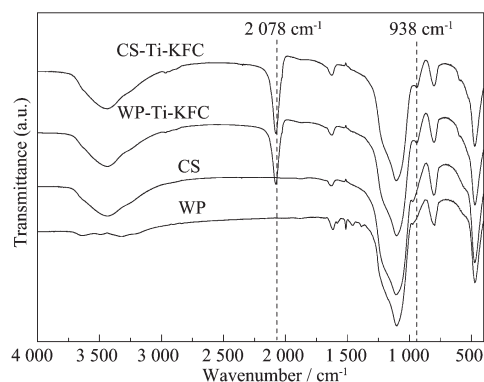
Fig.3　FTIR spectra of samples

to deformation modes of SiO_4 tetrahedral group, respectively. Different from those of WP and CS, spectra of WP-Ti-KFC and CS-Ti-KFC show a peak at 938 cm^{-1} that could be safely attributed to characteristic vibration due to the formation of Ti-O-Si bonds [15]. Furthermore, obvious absorption band at 2 078 cm^{-1} are detected in both WP-Ti-KFC and CS-Ti-KFC, strongly supporting the conclusion that $Fe(CN)_6^{4-}$ groups were stabilized onto the composites.

2.5　XPS analysis

X-ray photoelectron spectroscopy analyses were conducted to show the surface elements and binding environment of titanium atoms. The N1s spectra of WP-Ti-KFC and CS-Ti-KFC are all obtained at the BE of 398.0 eV attributed to nitrogen in transition metal coordinated cyano groups [16]. It proves that $Fe(CN)_6^{4-}$ groups are stabilized on the surface of the composites.

Fig.4 shows the XPS spectra in the Ti2$p_{1/2}$/Ti2$p_{3/2}$ binding energy region. The peak shape implies the presence of more than one environment of titanium atoms. The curve fitting is possible with two components for each peak (458.4/464.0 eV and 459.3/465.0 eV).
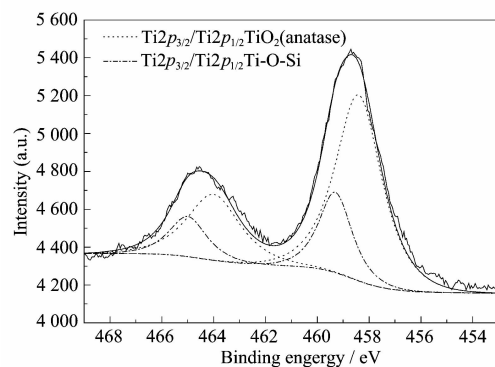
Fig.4　XPS spectra of Ti2p of CS-Ti-KFC

The largest peak (located at 458.4/464.0 eV) is consistent with the reported binding energy of Ti(IV) atom in pure anatase-phased titanium [17], and possibly with the Ti(IV) atom in TiO^{2+} ion stabilized in the PTH crystal lattice. The binding energy of the second contribution coincides with that of titania closely associated with silica where TiO_2 moieties are connected with SiO_2 via the Ti-O-Si bonds [18].

2.6　Proposed preparing mechanism of the as-made composites

The process to prepare WP-Ti-KFC and CS-Ti-KFC is illuminated with Fig.5. When the porous silica beads are immersed into the $Ti-(OC_4H_9)_4$ solution under heating and stirring, $Ti-(OC_4H_9)_4$ molecules undergoes hydrolysis with the H_2O adsorbed on the wall of pores in silica-bead-support. As a result, the as-generated TiO_2 layer is formed on the wall of pore in the support. When the TiO_2/SiO_2 composite beads are treated with $K_4[Fe(CN)_6]$ solution (containing HCl), PTH layer is formed with the reaction between $K_4[Fe(CN)_6]$ and TiO^{2+} ions (from amorphous TiO_2 layer treated with HCl). In another word, the amorphous TiO_2 acts as cement to bind the PTH layer onto the silica support. As a result, the porous composites with a very thin layer of PTH coated on their wall of pores are obtained. Because the PTH particles are finely dispersed onto the inner surface of the porous composites, they might exhibit good performance in capturing the Cs^+ in liquid.
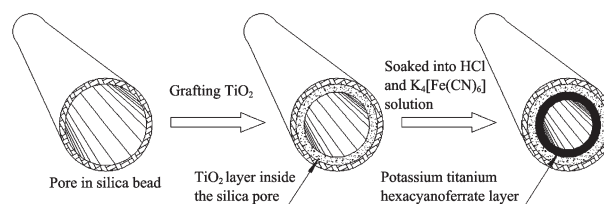

Fig.5　Proposed preparing mechanism of the composites

2.7　Cs uptake capacity of the composites

It is found that the Cs uptake capacity of WP-Ti-KFC and CS-Ti-KFC is 0.244 mmol·g^{-1}(composite) and 0.391 mmol·g^{-1}(composite), respectively. The Cs uptake capacity of WP and CS are 0.068 mmol·g^{-1} and 0.083 mmol·g^{-1}, respectively. The theorical Cs uptake capacity calculated from the empirical formula of PTH in WP-Ti-KFC and CS-Ti-KFC is 0.236 mmol·g^{-1}(composite) and

0.378 mmol·g⁻¹(composite), respectively (assuming that all of the K atom in the composites are replaced by Cs). There might be two reasons for the results that the empirical Cs uptake capacities are slightly higher than the theorical Cs uptake capacity: first, the porous silica support could make some contribution in Cs adsorption; second, some H^+ that could participate the ion-exchange exist in the PTH crystal lattice in the composites, so the Cs^+ in liquid could exchange with both K^+ and H^+, and the Cs uptake capacities of the composites are higher than their K^+ contents. It could be safely concluded that because the PTH particles are finely dispersed onto the wall of pores in the composites, adequate contact between the Cs^+ in the liquid and the K^+ in the PTH nano-crystal are obtained, as a result, almost all the K^+ could participate the ion-exchange reaction.

The Cs uptake capacities of WP-Ti-KFC and CS-Ti-KFC are much higher than the results of Terada et al. [8] who reported the Cs uptake capacity of 0.019 mmol·g⁻¹(composite) when the load of composite was 0.029 g-PCH/g-composite. Mardan et al.[10] reported Cs uptake capacity of 0.38 mmol·g⁻¹(composite) with the load of 1.386 g-potassium cobalt hexacyanoferrate/g-SiO₂. The high Cs uptake capacity of the samples in this work is related to their higher state of dispersion of the PTH crystal and larger surface area.

2.8 Determination of Cs distribution coefficient of samples under the presence of Na^+ and H^+

The distribution coefficient(K_d) upon Cs^+ under the presence of H^+ and Na^+ of as-made composites were assessed. When goal ion is in trace concentration and co-existing ions are in maro-concentration, K_d is usually chosen as a useful parameter to investigate the uptake ability of an ion-exchanger [10]. Here, all the K_d are measured with batch adsorption experiment in which the original concentration of Cs^+ before adsorption is 1 000 µg·L⁻¹.

The measured distribution coefficients of Cs^+ in varying concentrations of HNO₃, NaNO₃, HCl and NaCl solutions for the composites are given in Table 3. Because HNO₃ is usually used in nuclear industry in dissolving spent fuel elements and rinsing operation, it is selected as the H^+ source in the experiments to investigate K_d under the disturbance of H^+. The K_d of the composites upon Cs^+ under the presence of HNO₃ in the concentration range 0.1~1 mol·L⁻¹ is larger than 4 566 mL·g⁻¹-composite. When the concentration of HNO₃ was increased to 1 mol·L⁻¹, an acute decrease is observed in the K_d of the composite upon Cs^+. Some researchers attribute the phenomena to the competitive effect of H^+ upon the adsorption of Cs^{+}[19]. However, when HCl is chosen as the H^+ source, K_d higher than 624 750 are obtained even though the concentration of HCl is 1 mol·L⁻¹. The results strongly support the conclusion that it is not so much the competition effect of H^+ as the oxidation of HNO₃ that disturbs the adsorption of Cs^+. When the PTH particles are oxidized by HNO₃, the ferrocyanide groups ($Fe(CN)_6^{4-}$) in the composite are converted into ferricyanide groups ($Fe(CN)_6^{3-}$), at the same time, K^+ are expelled from the PTH crystal and the Cs-adsorption ability of the composites is apparently decreased.

Under the presence of Na^+ in the concentration range of 0.1~1 mol·L⁻¹, the measured K_d upon Cs^+ lies

Table 3 Distribution coefficient(K_d) of composites upon Cs^+ under the competition of Na^+ and H^+

Sample name	Concentration of co-existing ions / (mol·L⁻¹)	Distribution coefficient (Kd (mL·g⁻¹)-composite)			
		Co-existing ion			
		H⁺(HNO₃)	H⁺(HCl)	Na⁺(NaNO₃)	Na⁺(NaCl)
WP-Ti-KFC	0.1	>624 750[a]	>624 750[a]	60 127	67 159
	0.5	33 94	>624 750[a]	29 705	38 586
	1.0	4 566	>624 750[a]	24 857	22 807
CS-Ti-KFC	0.1	>624 750[a]	>624 750[a]	66 648	65 332
	0.5	44 582	>624 750[a]	30 410	35 973
	1.0	5 710	>624 750[a]	26 877	27 186

[a] The Cs^+ concentration after the batch adsorption experiment is below the detection limit of the atomic adsorption spectrometer (0.4 µg·L⁻¹). The figure 624750 is the K_d when Cs^+ concentration after the batch adsorption experiment is 0.4 µg·L⁻¹

between 67 159~22 807 mL·g^{-1}-composite. Compared with H$^+$, Na$^+$ exhibited stronger competition against Cs$^+$. It is clear that even under disturbance of Na$^+$ with concentration of 1 mol·L^{-1}, the composites could also capture the Cs$^+$ in the liquid successfully. The higher Cs-adsorbing ability of CS-Ti-KFC than that of WP-Ti-KFC could be attributed to its larger surface area and higher PTH content.

3　Conclusions

Spherical por ous PTH/SiO$_2$ particles were prepared with two steps: first, grafting amorphous TiO$_2$ layer onto the wall of pores in silica beads; second, converting the amorphous TiO$_2$ into PTH with the reaction between TiO^{2+} and K$_4$[Fe(CN)$_6$]. Two kinds of silica beads(WP and CS) were utilized as support. The empirical formula of PTH stabilized into the WP and CS could be expressed as K$_{1.04}$[(TiO)$_{1.48}$Fe (CN)$_6$] and K$_{1.08}$[(TiO)$_{1.46}$Fe (CN)$_6$]. The Cs uptake capacity of the composite with CS as support is 0.391 meq·g^{-1} (composite).

It is found that under the presence of HNO$_3$ in the concentration range of 0.1~1 mol·L^{-1}, the distribution coefficient K_d is larger than 4 566 mL·g^{-1}-composite. When Na$^+$ is the co-existing ion with concentration range of 0.1~1 mol·L^{-1}, the K_d lies between 67 159~ 22 807 mL·g^{-1}-composite. The composites exhibit very good performance in adsorbing Cs$^+$ in liquid even under the ion-competition of H$^+$ and Na$^+$.

It is also found that it is not so much the competition effect of H$^+$ as the oxidation of HNO$_3$ that disturbs the adsorption of the composites upon Cs$^+$. Compared with H$^+$, Na$^+$ is stronger in competing against Cs$^+$ for the adsorption sites in the composites.

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