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Adsorption of cesium(I) using potassium zinc hexacyanoferrate and its application in simulated oilfield water

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Abstract

Potassium zinc hexacyanoferrate with the formula $K_2Zn_3[Fe(CN)_6]_2$ (KZnFc) was synthesized by a sol-gel method and characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The adsorption performances of KZnFc to Cs^+ in aqueous solution and simulated oilfield water were investigated. The effects of the various parameters like contact time, temperature, initial pH value of the solution, initial concentration of the cesium ion and other coexisting cations in the solution on the adsorption efficiencies of KZnFc have been studied systematically by batch experiments. Adsorption isotherm of KZnFc was studied and the fitted results indicated that the Langmuir model could well represent the adsorption process. Different thermodynamic parameters like Gibbs free energy, enthalpy and entropy of the adsorption process are also evaluated. The maximum adsorption capacity of Cs^+ onto KZnFc was found to be 4.049 mmol g^{-1}. About 96.13% of cesium in the simulated oilfield water could be absorbed by the synthesized KZnFc. This study will be helpful for understanding the adsorption mechanisms of cesium ion, and suggests that KZnFc could be used as potential adsorbent for adsorbing Cs^+ from oil field water of Nanyishan.

Keywords

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INTRODUCTION

The study of the separation of ^{137}Cs from low- and intermediate active nuclear waste solutions has received intensive interest, because ^{137}Cs is an important radioactive contaminant, can be easily absorbed by living organisms, has long half life ($t_{1/2}$ = 30.17 years) and causes serious radiological damage to human body[1-5]. Recent research indicated that the concentrations of cesium in salt lake brines and oil field water of the Qinghai–Tibet plateau are high (the ion concentrations of the brine of Zabuye Salt Lake in Tibet and the oilfield water of Nanyishan have found to be 12–21 mg/L and 88 mg/L, respectively), and this non-radioactive specie is currently found to be widely applied in the electronics, medication and defense industries[6-11]; therefore, it is essential to develop a convenient method to extract ^{137}Cs and non-radioactive cesium from liquid resources.

The conventional methods of separating cesium are adsorption[12-14], precipitation[15], extraction[16,17], and

ion exchange[5,18,19]. Adsorption technique has increasingly become popular because of its advantages such as: (i) simple to operate; (ii) high stability; and (iii) high selectivity[20,21]. Among the commonly used adsorbents, ferrocyanides[22-24] have received increased attention because of their high efficiency for separating alkali metal ions. To our knowledge, several groups reported their works on Cs^+ adsorption by ferrocyanides, but most of them focused on Cs^+ removal or separation it from radioactive liquid waste, and the studies on the experimental condition evaluation were very rare[12,25,26]. As parts of our ongoing efforts on the design and synthesis of novel adsorbent with high efficiency, we thus synthesized potassium zinc hexacyanoferrate $K_2Zn_3[Fe(CN)_6]_2$ (KZnFc). Herein, we report the synthesis of KZnFc and its adsorption behavior to Cs^+ from aqueous solution and the simulated oilfield water.

EXPERIMENTAL

Materials

All chemicals and reagents used in this work were of A.R grade, purchased from the Sinopharm Group Chemical Reagent Co. Ltd. of China and used without further purification. All the solutions were prepared using double distilled water. A PHS-3B digital pH meter (Shanghai Precision & Scientific Instrument Co., Ltd.) was used to measure pH value of solutions (adjusted by adding 0.2 M HCl or 0.2 M NaOH).

Preparation and characterization of KZnFc

The KZnFc was prepared as follows: potassium hexacyanoferrate (3.68 g), zinc nitrate (5.68 g), and distilled water (400 mL) were mixed under constant stirring to get a homogenous mixture. The mixture was then heated to 80 °C for 2 hours, and a light green gel was yielded. The gel was cooled down naturally, filtered, washed with KNO_3 (0.3 M) and double distilled water for three times, respectively. The resulted crude product was then heated in a preheated oven at 80 °C for 48h. The final KZnFc was obtained as light green particles (30 ~ 80 mesh).

JSM-5610LV SEM electron microscope was used for scanning electron microscopy (SEM). The sample was prepared by dispensing the alcohol suspension of the particles onto a stub. The mixture on the stub was allowed to dry at room temperature and was then coated with a thin gold film. XRD characterizations were determined using a Phillips Analytical X-ray spectrometer (X Pert Pro).

Adsorption experiments

Stock solution of Cs^+ was prepared by dissolving CsCl (126.7 mg) in double distilled water (1.00 L). The concentration of Cs^+ was determined by using GBC-908 atomic absorption spectrophotometer (GBC Scientific Equipment Pty Ltd., Australia). Unless stated elsewhere, the experiments were carried out inside 250 mL iodine flasks, containing 100.0 mL solutions with desired amount of CsCl and adsorbent particle. The solutions were adjusted to neutral. The iodine flasks were then shaken by using a SHZ-C reciprocating shaker (Changzhou Guohua Co., Ltd., P.R. China; the shaking speed was set to 120 rpm). The adsorption time and temperature were set to 20 h and 25°C, respectively.

After adsorption, the mixtures were filtered and the concentrations of the cesium ion in the filtrates were determined by the GBC-908 Atomic Absorption Spectrometer according to the method described in the literatures[27]. The adsorption percentages (Ads.%) and amounts of Cs^+ adsorbed onto KZnFc (q, mmol/g; mmol of Cs^+ was absorbed by per gram of the dried KZnFc) were determined by using the following equations (Eq. 1 and Eq. 2):

$$\text{Ads.}(\%) = \frac{C_0 - C}{C_0} \times 100 \qquad (1)$$

$$q = (C_0 - C) \cdot \frac{V}{m} \qquad (2)$$

where C_0, C and C_e are the initial, final and equilibrium concentrations of Cs^+ in the solutions (mmol/L), respectively; V is the volume of the solution (L) and W is the dry weight of KZnFc used (g). When C_e is used instead of C in Eq. 2, q_e is obtained. All the adsorption experiments were conducted in duplicate, and the mean values were calculated.

RESULTS AND DISCUSSION

Characterization of $K_2Zn_3[Fe(CN)_6]_2$

The XRD measurement results of the synthesized adsorbent before and after the adsorption were shown in Figure 1. The XRD patterns of the Figure 1 revealed that the formula of the adsorbent was $K_2Zn_3[Fe(CN)_6]_2$ before the adsorption, whereas a mixture of $Cs_2Zn_3[Fe(CN)_6]_2$ and $Cs_2Zn[Fe(CN)_6]$ were obtained after the adsorption. Evidently, K^+ in the adsorbent was substituted by Cs^+. The patterns of XRD also showed that both species displayed nice crystal forms and were in high purity.

Usually, the crystallinity of the adsorbent is reduced and becomes amorphous after the adsorption process and the adsorption capacity of the adsorbent will decrease. The results of Figure 1 indicated that the synthesized adsorbent particles have good mechanical stability and they have not been destroyed during the whole adsorption process. The afterward adsorption experiments demonstrated that KZnFc could be reused.
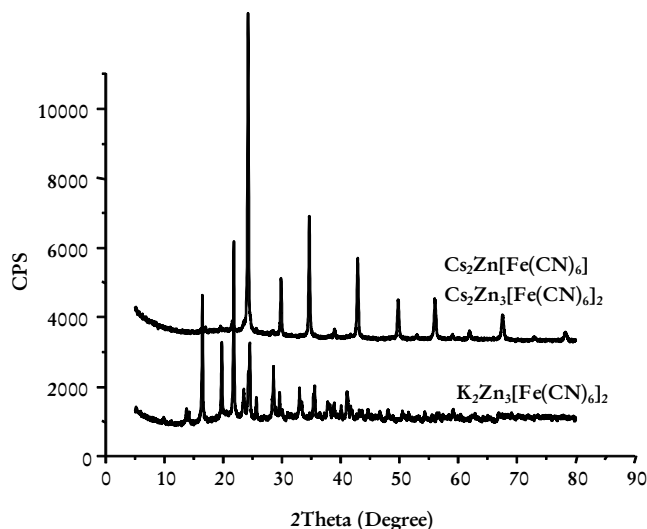

Figure 1 : X-ray diffraction pattern of KZnFc

The SEM images of the adsorbent particles before and after the adsorption were shown in Figure 2. It is clear that the adsorbent particle has a more homogeneous morphology after the adsorption than that before the adsorption.
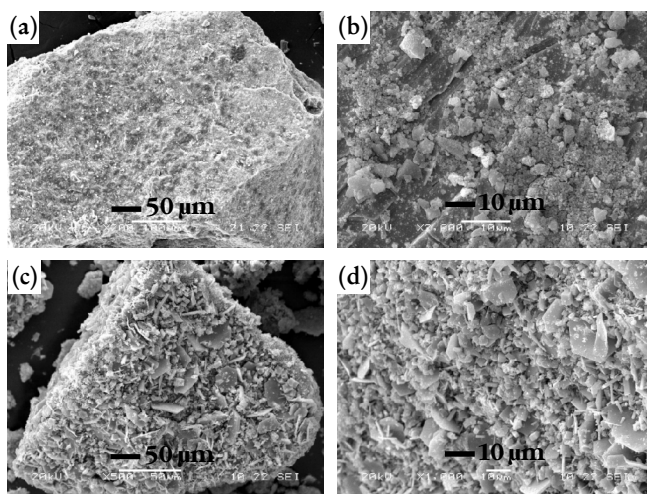

Figure 2 : SEM of KZnFc before and after adsorption: (a) & (b) SEM of KZnFc before the adsorption; (c) & (d) SEM of the synthesized adsorbent after the adsorption.

Adsorption equilibrium time

The studies involving different contact time were employed in determining the equilibrium time of the adsorbent particles. The amount of Cs^+ adsorbed by KZnFc versus the adsorption time was exhibited in

Figure 3. It was established that adsorption occurred rapidly in the first 5 h, after which time, there was only very slight increase of the adsorption percentage of Cs^+. 20 h of contact time was found sufficient to acquire equilibrium. According to the results of Figure 3, the adsorption time was fixed at 20 h for the followed experiments. The results of Figure 3 also demonstrated that almost 90% adsorption occurred within the first 5 h of contact, which is understood that the initial concentrations of the metal ions were relatively high and the probability of collision between K^+ on the adsorbent and Cs^+ in the solution was higher. With the approaching of the equilibrium, the probability of collision between K^+ and Cs^+ was decreased, therefore the rate of Cs^+ adsorption decreased.
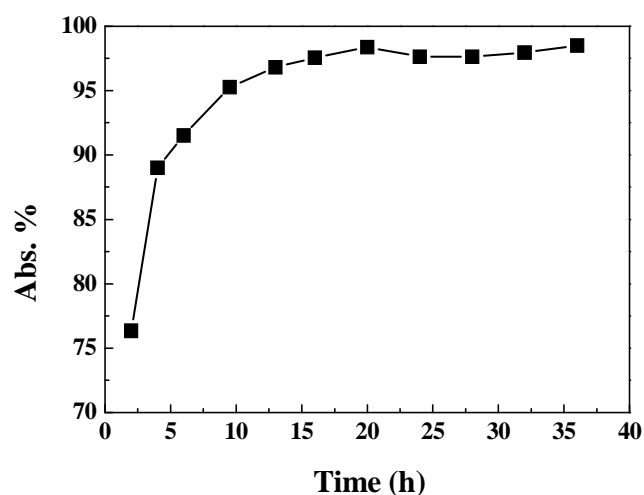

Figure 3 : Effect of time on adsorption efficiency

Effect of pH on the adsorption of Cs^+

Effect of pH on adsorption of Cs^+ has been studied for adsorbent particles over a range of 2.0-12.0. Figure 4 showed the plot of adsorbed percentage of Cs^+ versus initial pH values of the solutions. The results presented in Figure 4 showed that the absorbent percentage main-
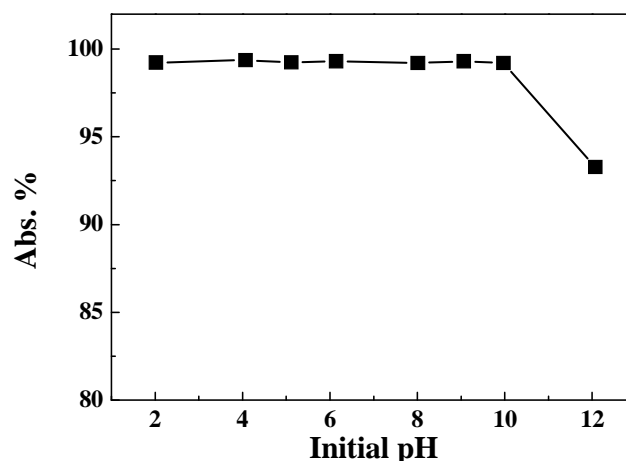

Figure 4 : Effect of pH on adsorption efficiency

tained constant (>99%) in the pH range of about 2.0 ~ 10.0 and then decreased sharply with increase of the pH values of the solutions. This results indicated that the pH range of 2.0 ~ 10.0 is favored for the absorption.

Adsorption isotherms

The adsorption isotherms for the adsorption of Cs^+ ion from aqueous solutions onto the adsorbent particles were obtained by determining the effects of initial concentration and temperature on the adsorption of Cs^+. Figure 5 presented the experimental adsorption isotherms of Cs^+ at three different temperatures onto the adsorbent particles. It can be seen that the adsorption amount of Cs^+ increases with increase of the initial ion concentration, but decreases with increase of temperatures from 25 to 65°C. These results demonstrated that the adsorption reaction is an exothermic process and relatively lower temperature is beneficial for the adsorption.
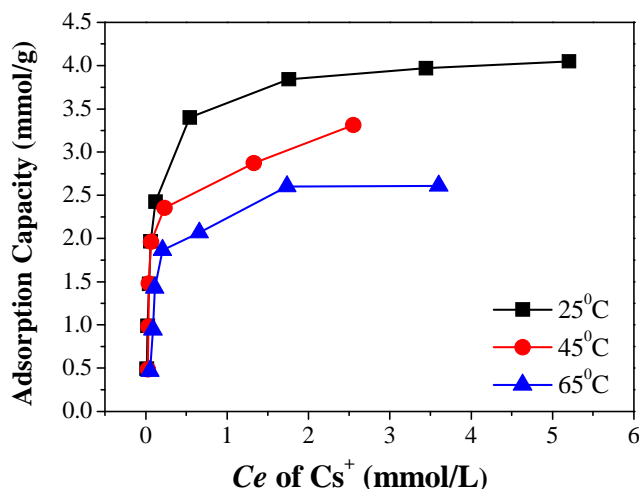

Figure 5 : Sorption isotherms of Cs^+ at 25°C, 45°C and 65°C

Up to date, a number of adsorption isotherm models have been reported, among which Langmuir model and Freundlich model are used commonly. They can be described in the forms of Eq. 3 and Eq. 4, respectively.

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

$$q_e = K_F C_e^{1/n} \tag{4}$$

where Q_m (mmol g^{-1}) is the maximum adsorption capacity, K_L, K_F, $1/n$ are the isotherm constants, C_e is the equilibrium concentration and q_e is the amount of Cs^+ adsorbed at equilibrium. The corresponding data for the equilibrium adsorption of Cs^+ onto KZnFc at 25°C, 45°C, 65°C and the model parameters were listed in TABLE 1. The adsorption data at 25°C were fitted by Langmuir and Freundlich adsorption equa-

tions (Figure 6). The correlation coefficients showed that the Langmuir model well represents the adsorption process. The theoretical value of the maximum adsorption capacity of Cs^+ onto KZnFc at 25°C is 4.016 mmol g^{-1}, which agrees with the observed value of 4.049 mmol g^{-1} very well. These all confirmed that the adsorption of Cs^+ onto KZnFc follows the Langmuir isotherm model.

TABLE 1 : Langmuir and Freundlich isotherm constants

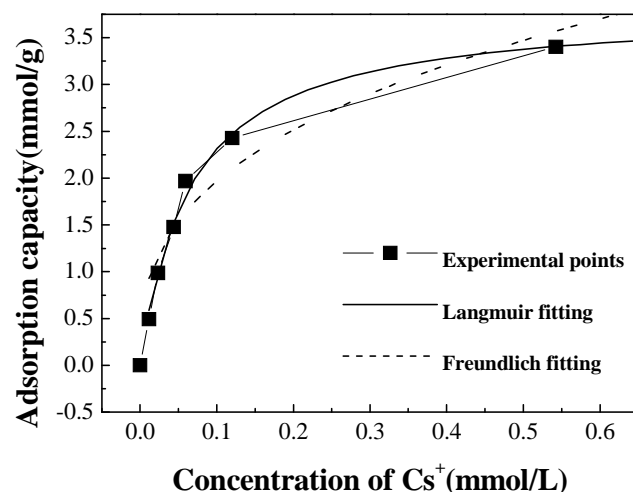| T (°C)	Langmuir			Freundlich		
	q_m (mmol g^{-1})	K_L (L mmol^{-1})	R^2	K_F	$1/n$	R^2
25	4.016±0.053	13.73±0.80	0.9966	3.145±0.185	4.723±0.03	0.8882
45	3.193±0.215	16.02±3.86	0.9456	2.753±0.232	4.360±0.05	0.8354
65	2.732±0.147	7.198±1.42	0.9668	2.109±0.163	4.109±0.06	0.8216

Figure 6 : Adsorption isotherms at 25°C

Thermodynamic treatment of adsorption data

As showed in Figure 5, the adsorption of Cs^+ onto KZnFc decreased with increase in temperature, which indicated the exothermic nature of the adsorption process. Various thermodynamic parameters were also calculated using following equations:

$$\Delta G^0 = -RT \ln K \tag{5}$$

$$\Delta H^0 = -R\left(\frac{T_2 T_1}{T_2 - T_1}\right) \ln \frac{K_2}{K_1} \tag{6}$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \tag{7}$$

Where ΔH^0 is the change in enthalpy; ΔS^0 the change in entropy; ΔG^0 the change in Gibbs free energy; K, K_1 and K_2 are the Langmuir constants at 25°C, 45°C and 65°C, respectively. The calculated data have been depicted in TABLE 2. A negative ΔG^0 value confirms the feasibility of the process and spontaneous

nature of adsorption. Negative value of ΔH^0 indicates the exothermic nature of the process, while the negative ΔS^0 shows decreased randomness of the process.

TABLE 2 : Thermodynamic parameters for the uptake of Cs (I) on potassium zinc hexacyanoferrate

Temperature (°C)	ΔG^o (kJ mol^{-1})	ΔH^o (kJ mol^{-1})	ΔS^o (J mol^{-1})
25	-6.491	-5.958	1.666
45	-7.333	-	-
65	-5.539	-	-

The application of KZnFc in simulated oilfield water

The adsorption of Cs$^+$ onto KZnFc in the aqueous solution in the presence of coexisted cations and in the simulated oilfield water were studied by varying the species of the competing cations and preparing the simulated oilfield water, in which the concentration of the K$^+$, Na$^+$, Ca^{2+}, Mg^{2+}, NH$_4^+$ and Rb$^+$ are almost the same as that of the real oilfield water of Nanyishan. The changes of adsorption efficiencies of Cs$^+$ along with the changes of the concentrations of the coexisting K$^+$, Na$^+$, Ca^{2+}, Mg^{2+}, NH$_4^+$ and Rb$^+$ ions were given in TABLE 3. The results indicated that the selectivity of KZnFc towards cesium ion was slightly affected by the presence of competing ions, especially for NH$_4^+$ and Rb$^+$. It is understood that the ionic charge and radius of these two ions are much closer to that of Cs$^+$, and the concentrations of these two ions are much higher than that of Cs$^+$. Therefore, they are competing for the active sites in the surface of the adsorbent particle.

TABLE 3 : Effect of concomitant elements on adsorption efficiency

Number	Number	Multiple of Concentration	Adsorption Efficiency (%)
1$^\#$	Pure	1	98.37
2$^\#$	K$^+$	1000	94.65
3$^\#$	Na$^+$	4000	97.86
4$^\#$	Ca^{2+}	2000	99.00
5$^\#$	Mg^{2+}	150	98.41
6$^\#$	NH$_4^+$	150	91.65
7$^\#$	Rb$^+$	2	95.60
8$^\#$	Simulative oilfield water	/	96.13

a: 1$^\#$ is the pure solution, in which only Cs$^+$ is added; in 2$^\#$~7$^\#$, the ratios of M^{n+}:Cs$^+$(M^{n+} = K$^+$, Na$^+$, Ca^{2+}, Mg^{2+}, NH$_4^+$, Rb$^+$) are the similar rate as in the real oilfield water in Nanyishan; in 8$^\#$, all the coexisting cations were mixed in the rates mentioned in 2$^\#$~7$^\#$.

CONCLUSIONS

KZnFc particles were prepared and characterized, and their adsorption performances onto Cs$^+$ ion from the aqueous solution and the simulated oilfield water were investigated. The effects of the various parameters like contact time, temperature, pH, initial concentration of the cesium ion and other coexisting cations on the adsorption efficiencies of KZnFc have been studied systematically by batch experiments. Almost 90% adsorption occurred within the first 5 h. The equilibrium adsorption amount of Cs$^+$ was found to increase with increase of the initial ion concentration but decrease with increase in temperature. The suitable experimental conditions for the adsorption are summarized as follows: adjusting initial pH value of the solution to 2~10; setting adsorption time as 20 h, and lowering adsorption temperature. The Langmuir model fitted the adsorption of Cs$^+$ onto KZnFc very well. Thermodynamic parameters were calculated and the negative value of Gibbs free energy and enthalpy clear indicated that the adsorption process is exothermic and feasible, respectively. The results of this study would be helpful in understanding the adsorption mechanisms for adsorbing Cs$^+$ by KZnFc, and suggests that KZnFc could be used as potential adsorbent for adsorbing Cs$^+$ from oil field water of Nanyishan.

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