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Removal of radioactive cesium from solutions by zinc ferrocyanide

LI Bing¹ LIAO Jiali¹ WU Jiaojiao¹ ZHANG Dong² ZHAO Jun² YANG Yuanyou¹ CHENG Qiong² FENG Yue¹ LIU Ning^{1,*}

¹ Key Laboratory of Radiation Physics and Technology of Education Ministry of China, Institute of Nuclear Science and Technology, Sichuan University,

Chengdu 610064, China

² Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang 621900, China

Abstract Adsorption of ¹³⁴Cs from aqueous solution by zinc ferrocyanide, and the effect of experimental conditions on the adsorption were investigated. Preliminary results showed that zinc ferrocyanide was very efficient as an absorbent. Over 98% of ¹³⁴Cs could be removed by zinc ferrocyanide of 0.33 g·L⁻¹ from ¹³⁴Cs solution (*C*o) of 3.2~160.0 kBq·L⁻¹, with adsorption capacities (*Q*) of 9.6~463.0 kBq·g⁻¹. The adsorption equilibrium time was within one hour and the suitable pH ranged 1~10. No significant differences on ¹³⁴Cs adsorption were observed at 0~50°C, or in solutions containing Ca²⁺, Fe³⁺, Mg²⁺, HCO₃⁻, CO₃²⁻, Cl⁻ and SO₄²⁻, even though they are 1000 times higher than the anions or cations in groundwater. However, the adsorption rates decreased when solutions contained K⁺ or Na⁺. The adsorption process could be described by Freundlich and Langmuir adsorption equations.

Key words Zinc ferrocyanide, ¹³⁴Cs, Adsorption, Radioactive waste

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1 Introduction

Radioactive cesium nuclides are harmful to the environment and to human health. Among them, ¹³⁷Cs, with half-life of about 30 years, is of high radiotoxicity. Due to the high solubility of Cs-compounds, Cs can be up-taken by human body though food chain^[1]. They can be easily incorporated into the bone and the inner irradiation may cause bone sarcoma and leukemia^[2]. Therefore, removal of radiocesium from nuclear waste effluents is an important environmental issue for human health and nuclear waste management.

Many methods have been studied to eliminate this harmful element from nuclear waste solution and great progress has been achieved by electrochemical processes, membrane processes, and physico-chemical processes, such as co-precipitation, coagulation, ion exchange, and solvent extraction^[3]. Of these methods, inorganic ion exchange is one of the most prospective methods for removing cesium from radioactive waste solutions, due to the specific selectivity, thermal and radiation stabilities^[4,5]. Natural inorganic ion exchangers, such as montmorillonite and illite, have been studied extensively for decontamination of radiocesium wastewater^[6]. Some synthetic inorganic ion exchangers have been investigated, too^[7,8].

Zinc ferrocyanide (ZnFc), as an inorganic ion adsorbent^[7-9] usually in forms of $M_2Zn_3[Fe(CN)_6]_2$ (M=K, H) or $Zn_2Fe(CN)_6^{[10]}$, shows satisfactory adsorption capacity on some inorganic ions like $Cu(II)^{[11]}$, even on some organic compounds, such as o-aminophenol, o-nitrophenol^[12], 2,4-dinitrophenol, or 2,4,6-trinitrophenol^[13]. And several groups reported their work on Cs⁺ adsorption by $ZnFc^{[14-17]}$, though most of them focused on Cs⁺ removal or separation from high-level radioactive liquid waste (HLLW) and only a few experimental conditions were evaluated. In this paper, radiocesium was removed from low-level radioactive liquid waste (LLW), and the adsorption of Cs by ZnFc in different conditions was investigated.

^{*} Corresponding author. *E-mail address:* nliu720@scu.edu.en Received date: 2007-09-17

2 **Experimental**

2.1 Reagents and experimental solution

¹³⁴Cs (¹³⁴CsNO₃) aqueous solution, containing ¹³⁴Cs of 3.8 MBq·L⁻¹, was provided by the Nuclear Power Institute of China (NPIC). Diluted solutions were prepared using redistilled water. Other chemical regents were of analytical or chromatographic grade and were used without further purification.

All glassware for the adsorption experiments were routinely rinsed with 0.5 mol·L⁻¹ HNO₃ and washed extensively with redistilled water. A digital pH meter was used to measure pH value of solutions, which were adjusted by adding 0.2 mol·L⁻¹ HNO₃ or 0.2 mol·L⁻¹ NaOH.

2.2 Preparation of ZnFc

To a conical flask of 1.0 L containing freshly prepared 0.3 mol·L⁻¹ K₄Fe(CN)₆ solution of 800 mL, 50mL ZnCl₂ solution of 0.3 mol·L⁻¹ was added dropwise under stirring. The reaction systems were treated hydrothermally at 80°C for 2 h. After 4 days of maturing at room temperature, the mixture was filtered. The product was washed with redistilled water and allowed to dry at 70~80°C. Energy dispersive X-ray analysis on an SEM (scanning electronic microscope, at Analytical and Testing Center of Sichuan University, China) indicated that the compound had the mass ratio of K⁺:Fe²⁺:Zn²⁺=22.4:32.6:45.0. Thus, and referring to Ref.[10], the product was K₂Zn₃[Fe(CN)₆]₂.

2.3 Adsorption experiments

The ZnFc was added to the ¹³⁴Cs solution of

definite radioactive concentrations in desired pH values. The mixture was shaken on a rotary shaker at 200 r·min⁻¹ and 25 °C for 1 h, except described otherwise. The mixture was centrifuged at 4000 r·min⁻¹ for 15 min. After the supernatant liquid was removed, the ¹³⁴Cs radioactivity was measured by an automatic counter with a NaI well detector.

The adsorption rate (R) and adsorption capacity of the dry absorbent (Q) were calculated as

$$R = (1 - C/C_0) \times 100\% \tag{1}$$

$$Q = (C_0 - C)/m \tag{2}$$

where C_0 is the initial ¹³⁴Cs concentration (kBq·L⁻¹), *C* is the final ¹³⁴Cs concentration in the solution, *m* is the concentration (g·L⁻¹) of ZnFc.

3 Results and discussion

3.1 Effect of pH or acidity on¹³⁴Cs adsorption

The effect of pH or acidity on ¹³⁴Cs adsorption was investigated by changing the system's initial pH from 1 to 12 or acidity from 0.5 mol·L⁻¹ to 1 mol·L⁻¹. As shown in Table 1, at pH 1~10, the adsorption rate could be up to 98.0%, whereas it begun to decrease at pH 11 and was only 2.3% at pH 12. The ZnFc dissolved gradually in the solution of pH \leq 10, and dissolved almost completely at pH 12, giving rise to dropping adsorption rates above pH 10. And the acidity increased with decreasing adsorption rate. For example, with 0.5 mol·L⁻¹ HNO₃ in the solution, the adsorption rate of ¹³⁴Cs by ZnFc was 91.0%, but at 1 mol·L⁻¹ HNO₃ it dropped to 52.0%. This might be because that H⁺ and Cs⁺ had a strong competitive adsorption when the acidity exceeded 0.5 mol·L⁻¹.

Table 1 Effect of pH or acidity on ¹³⁴Cs adsorption by ZnFc (adsorption experiments was performed as $C_0(^{134}Cs)=20 \text{ kBq}\cdot\text{L}^{-1}$ and $m(\text{ZnFc})=0.33 \text{ g}\cdot\text{L}^{-1})$

Adsorption	$HNO_3 / mol \cdot L^{-1}$		pH											
parameters	1	0.5	1	2	3	4	5	6	7	8	9	10	11	12
R / %	52.0	91.0	98.6	98.2	99.5	98.9	98.0	98.8	98.1	98.5	98.4	99.2	90.5	2.3
$Q / kBq \cdot g^{-1}$	31.2	54.8	59.2	58.9	59.7	59.3	58.4	59.9	58.8	59.1	59.0	59.5	54.3	1.4

3.2 Effect of contact time (*t*) on 134 Cs adsorption

The effect of contact time on ¹³⁴Cs adsorption by ZnFc (Fig.1) showed that the ¹³⁴Cs adsorption was closely related to contact time, especially at the first 60

min. The adsorption rate increased rapidly with time at the first, reaching 93.7% at 5 min, and then grew slowly towards an equilibrium, being 99.6% at 60 min. Based on this result, the contact time was set at 1 h for other adsorption experiments, except described otherwise.



Fig.1 Effect of contact time on 134 Cs adsorption by ZnFc ($C_0=20$ kBq·L⁻¹, m=0.33 g·L⁻¹, pH=8).

3.3 Effect of temperature (T) on ¹³⁴Cs adsorption

As shown in Fig.2, no significant differences on 134 Cs adsorption by ZnFc were observed at 0~50°C, with all the adsorption rates being above 98%. This indicated that the temperature was not a primary factor to influence 134 Cs adsorption. So the adsorption experiments were performed at room temperature.



Fig.2 Effect of temperature on 134 Cs adsorption by ZnFc ($C_0=20$ kBq·L⁻¹, m=0.33 g·L⁻¹, pH=8).

3.4 Effect of ZnFc concentration (m) on ¹³⁴Cs adsorption

The effect of ZnFc concentration (m) on ¹³⁴Cs adsorption was shown in Fig.3. The adsorption rate increased with *m*, being 82.1% and 98% at $m=0.1 \text{ g}\cdot\text{L}^{-1}$ and $m=0.33 \text{ g}\cdot\text{L}^{-1}$, respectively, and tended to an equilibrium. It seems that the amount of ¹³⁴Cs ions was too few to be captured easily by ZnFc when the adsorption rate was above 98%. In contrast, the adsorption capacity declined with increasing *m*, being 164 kBq·g⁻¹ when the absorbent concentration was 0.1 g·L⁻¹, whereas it was 6 kBq·g⁻¹ when the absorbent concentration was 3.3 g·L⁻¹. This is because of the fixed mass of initial 134 Cs in solutions of different ZnFc concentrations.



Fig.3 Effect of ZnFc concentration on 134 Cs adsorption (C_0 =20 kBq·L⁻¹, pH=8).

3.5 Effect of 134 Cs concentration (C_0) on the adsorption

Effect of ¹³⁴Cs concentration on adsorption (Fig.4) showed that in $3\sim 160 \text{ kBq}\cdot\text{L}^{-1}$ of initial ¹³⁴Cs concentration (C_0), the amount of ¹³⁴Cs adsorbed by 0.33 g·L⁻¹ ZnFc increased with the ¹³⁴Cs concentration, with adsorption capacities of 8.8 kBq·g⁻¹ to 463.2 kBq·g⁻¹, while the adsorption rate almost kept constant at an average value of 98.0%. It could be seen that the adsorption capacities for ¹³⁴Cs had not reached saturation within this range. In other words, the adsorption of ¹³⁴Cs on ZnFc was favorable at all the given concentrations.

Langmuir and Freundlich adsorption equations, which relate to equilibrium adsorbate concentration in the sorbent phase and bulk fluid phase, were used to evaluate the effect of ¹³⁴Cs concentration (C_0) on the adsorption.



Fig.4 Effect of 134 Cs concentration on 134 Cs adsorption by ZnFc (*m*=0.33 g·L⁻¹, pH=8).

The Freundlich adsorption equation is in the form of $Q=kC_0^{1/n}$, where k and n are Freundlich constants related to degree of adsorption capacity and adsorption strength, Q is the amount of metal ions adsorbed on the unit mass of the absorbent (kBq·g⁻¹), C_0 is the concentration of initial metal ions (kBq·L⁻¹). Taking the logarithmic form of the equation should give a right line, so as to evaluate the constants k and n. Taking experimental data of different ¹³⁴Cs concentrations into the Freundlich equation, we have the results in Fig.5. The ¹³⁴Cs adsorption equation could be evaluated by $lgQ=0.9936lgC_0+0.476$, with its correlation coefficient of r=0.9998. Using equation $Q=kC_0^{1/n}$, one has $k(^{134}Cs)=2.99$ and $n(^{134}Cs)=1.01$.



Fig.5 Freundlich adsorption of 134 Cs by ZnFc.

The Langmuir adsorption equation is given by: $C_0/Q=(1/kb)+C_0/k$, where k and b are Langmuir constants related to degree of adsorption strength, Q is the amount of metal ions adsorbed on the unit mass of the absorbent (kBq·g⁻¹), C_0 is the concentration of initial metal ions (kBq·L⁻¹). The reciprocal form of the equation gives a right line to evaluate constant k and b. The results by taking experimental data of different ¹³⁴Cs concentrations into the Langmuir adsorption equation for isothermal were shown in Fig.6. The ¹³⁴Cs adsorption equation could be evaluated by $1/Q=0.331/C_0+0.0003$, with r=0.9999. For equation $C_0/Q=(1/kb)+C_0/k$, $k(^{134}Cs)=3333.3333$, $b(^{134}Cs)=0.0009$.

These results show that the adsorption behavior of ¹³⁴Cs on ZnFc can be described by both the Langmuir adsorption equation and the Freundlich adsorption equation.



Fig.6 Langmiur adsorption of 134 Cs by ZnFc.

3.6 Effect of coexistent ions on ¹³⁴Cs adsorption

Effects of K⁺, Na⁺, Ca²⁺, Fe³⁺, Mg²⁺, HCO₃⁻, CO₃²⁻, Cl⁻ and SO₄²⁻ on ¹³⁴Cs adsorption by ZnFc were summarized in Table 2. It showed that the Ca²⁺, Fe³⁺, Mg²⁺, HCO₃⁻, CO₃²⁻, Cl⁻ and SO₄²⁻ had no significant influence on the adsorption of ¹³⁴Cs as $C_0(^{134}Cs)=20$ kBq·L⁻¹, m(ZnFc)=0.33 g·L⁻¹ and pH=8, even though the concentrations of these ions or cations are 1000 times higher than in groundwater. The adsorption rates of ¹³⁴Cs by ZnFc were still up to 98.0%.

 Table 2
 Effect of coexistent ions on ¹³⁴Cs adsorption by ZnFc

Ions	Content / mg·L ⁻¹	<i>R / </i> %
K^+	0.8	98.0
	8	96.7
	800	79.6
Na ⁺	3	98.0
	30	97.3
	3000	94.7
Ca ²⁺	40	98.2
	4000	98.1
Fe ³⁺	0.02	99.1
	20	98.0
Mg^{2+}	0.02	99.2
	20	99.5
HCO ₃	1400	98.3
CO3 ²⁻	140	98.5
Cl	6	98.3
SO ₄ ²⁻	450	98.9

* Ions' concentration referred to the ions concentration in groundwater.

**The adsorption experiments were performed as $C_0(^{134}Cs)=20$ kBq·L⁻¹, m(ZnFc)=0.33 g·L⁻¹, pH=8.

However, K^+ and Na^+ , especially K^+ could inhibit the adsorption of ¹³⁴Cs by ZnFc, possibly due to their similar chemical properties to Cs⁺, and competition with Cs⁺ for adsorption by ZnFc in solution. For example, when the concentration of K⁺ (in groundwater) increased from 0.8 mg·L⁻¹ to 800 mg·L⁻¹, the adsorption rate declined from 98.0% to 79.6%. And when the Na⁺ concentration increased from 3 mg·L⁻¹ (the concentration of Na⁺ in groundwater) to 3000 mg·L⁻¹, the adsorption rate decreased slightly from 98% to 94.7%.

4 Conclusion

Zinc ferrocyanide was a very efficient absorbent for ¹³⁴Cs, and the adsorption process of ¹³⁴Cs on zinc ferrocyanide could be described by Freundlich adsorption equation as well as Langmuir adsorption equation. Additionally, the adsorption behavior of ¹³⁴Cs by zinc ferrocyanide in aqueous solution was affected by many experimental conditions. All the results would be useful for the treatment of low-level radioactive liquid waste containing radioactive cesium. However, it should be further investigated for further practical application.

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