Available online at www.sciencedirect.com
ScienceDirect
Nuclear Science and Techniques 19 (2008) 88–92

NUCLEAR
SCIENCE
AND
TECHNIQUES

Removal of radioactive cesium from solutions by zinc ferrocyanide

LI Bing[1] LIAO Jiali[1] WU Jiaojiao[1] ZHANG Dong[2] ZHAO Jun[2]
YANG Yuanyou[1] CHENG Qiong[2] FENG Yue[1] 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 ^{134}Cs 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 ^{134}Cs could be removed by zinc ferrocyanide of 0.33 g·L^{-1} from ^{134}Cs solution (*Co*) 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 ^{134}Cs adsorption were observed at 0~50℃, or in solutions containing Ca^{2+}, Fe^{3+}, Mg^{2+}, HCO_3^-, CO_3^{2-}, Cl^- and SO_4^{2-}, 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, ^{134}Cs, Adsorption, Radioactive waste

CLC numbers O614.35, X13

1 Introduction

Radioactive cesium nuclides are harmful to the environment and to human health. Among them, ^{137}Cs, 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.cn

Received date: 2007-09-17

2 Experimental

2.1 Reagents and experimental solution

^{134}Cs ($^{134}CsNO_3$) aqueous solution, containing ^{134}Cs 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} HNO_3 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} HNO_3 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} $K_4Fe(CN)_6$ solution of 800 mL, 50mL $ZnCl_2$ solution of 0.3 mol·L^{-1} was added dropwise under stirring. The reaction systems were treated hydrothermally at 80℃ 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℃. 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^+:Fe^{2+}:Zn^{2+}=22.4:32.6:45.0. Thus, and referring to Ref.[10], the product was $K_2Zn_3[Fe(CN)_6]_2$.

2.3 Adsorption experiments

The ZnFc was added to the ^{134}Cs solution of definite radioactive concentrations in desired pH values. The mixture was shaken on a rotary shaker at 200 r·min^{-1} and 25℃ 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 ^{134}Cs 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

$$R=(1-C/C_0)\times 100\% \qquad (1)$$

$$Q=(C_0-C)/m \qquad (2)$$

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

3 Results and discussion

3.1 Effect of pH or acidity on ^{134}Cs adsorption

The effect of pH or acidity on ^{134}Cs 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≤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} HNO_3 in the solution, the adsorption rate of ^{134}Cs by ZnFc was 91.0%, but at 1 mol·L^{-1} HNO_3 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 ^{134}Cs adsorption by ZnFc (adsorption experiments was performed as C_0(^{134}Cs)=20 kBq·L^{-1} and m(ZnFc)=0.33 g·L^{-1})

Adsorption parameters	HNO_3 / mol·L^{-1}		pH											
	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·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 ^{134}Cs adsorption by ZnFc (Fig.1) showed that the ^{134}Cs 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.