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Original Article

Removal of Cs^+, Sr^{2+}, and Co^{2+} Ions from the Mixture of Organics and Suspended Solids Aqueous Solutions by Zeolites

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ABSTRACT

Serving as an excellent adsorbent and inorganic ion exchanger in the water purification field, zeolite 4A has in this work presented a strong capability for purifying radioactive waste, such as Sr^{2+}, Cs^+, and Co^{2+} in water. During the processes of decontamination and decommissioning of suspended solids and organics in low-level radioactive wastewater, the purification performance of zeolite 4A has been studied. Under ambient temperature and neutral condition, zeolite 4A absorbed simulated radionuclides such as Sr^{2+}, Cs^+, and Co^{2+} with an absorption rate of almost 90%. Additionally, in alkaline condition, the adsorption percentage even approached 98.7%. After conducting research on suspended solids and organics of zeolite 4A for the treatment of radionuclides, it was found that the suspended clay was conducive to absorption, whereas the absorption of organics in solution was determined by the species of radionuclides and organics. Therefore, zeolite 4A has considerable potential in the treatment of radioactive wastewater.

1. Introduction

Nowadays, with the rapid development of the nuclear industry, a large amount of radioactive wastewater has been generated during the process of nuclear facility operation, maintenance, and decommissioning. Such water contains many radioactive metal ions, such as Sr^{2+}, Cs^+, and Co^{2+} [1,2]. In order to satisfy the demand for a safe and healthy environment, radioactive wastewater must be posttreated prior to further disposal into nature, so as to meet national standards [3].

This kind of wastewater usually contains high concentrations of radionuclides and complex components such as radioactive laundry wastewater [4], decontamination wastewater, and decommissioning wastewater [5]. Although the probability of nuclear accidents is extremely low, considerable

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quantities of radioactive liquid waste will be released if such accidents occur. The Fukushima accident discharged about 6.3×10^5–7.7×10^5 terabecquerels (TBq) of radioactive wastewater, which mainly contained radionuclides ^{134}Cs, ^{137}Cs, and ^{131}I, as well as organics, into the environment [6,7]. Even under normal operational conditions, radioactive wastewater containing a high concentration of suspensions and organics such as suspended clay, grease, and detergents (oxalic acid, citric acid) will be produced [8]. Hence, there is an urgent need to address the safety problems caused by radioactive wastewater.

There are several methods used to treat radioactive wastewater, such as flocculation, ion exchange, membrane technology, evaporation, and adsorption [9]. Because of its advantages in wastewater treatment, adsorption has received increasing attention [10]. Adsorption can reduce the application of organic solvents so as to make the operation process simpler and safer. Widely used adsorption materials include zeolite, vermiculite, and crystalline silicotitanate [11–13]. To be specific, vermiculite shows a very low adsorption efficiency (capacity), and crystalline silicotitanate requires artificial synthesis. As one type of inorganic material in this case, zeolites have been reported to be excellent adsorbents that can remove heavy metal ions from aqueous solutions [14–21]. Various advantages of zeolites have been reported, such as low price, large ion exchange capacity, excellent selectivity, and thermal stability as well as antiradiation stability [22–25]. The main mechanism for removing radionuclides is that cations in the zeolite structure can exchange with cations in the aqueous solutions freely through the cavities. Zeolite 4A shows an excellent adsorption property during artificial synthesis; the main crystal structure is zeolite A. Meanwhile, zeolites demonstrate stronger adsorption and exchange capacity because the network-like structure contains uniform small pores.

However, a systematic understanding of how suspended solids and organic matter participate in the adsorption process of zeolite in radioactive wastewater is still lacking. This paper attempts to show how effectively zeolite 4A can absorb radionuclides with different concentrations of suspended solids and organic matter.

2. Materials and methods

2.1. Chemicals and reagents

Cesium nitrate, strontium nitrate, cobalt nitrate, zeolite 4A, and sodium hydroxide were purchased from Tianjin Kermel Chemical Reagent Co., AR. Natural zeolite (Zhejiang, China; 200 meshes). Nitric acid, oxalic acid, and citric acid were purchased from Chengdu Jinshan Chemical Reagent Co., AR. Clay (Mianyang, Sichuan, China; 200 meshes) and sodium oleate (Klamar) were adopted.

2.2. Adsorption studies

2.2.1. Types of zeolites

In brief, 1 g natural zeolite and 1 g zeolite 4A were added to 100 mL simulated radioactive waste solution containing Sr^{2+}, Cs^+, and Co^{2+}. The concentrations of the ions were 1 mg/L each. Then, the suspension was stirred at ambient temperature. In order to measure the absorption efficiency when the adsorption had proceeded to 45 min, 60 min, 120 min, and 180 min, 10-mL solution samples at each time point were passed on for the next analysis. Samples and initial solution were treated with a centrifugal machine for 5 min at 4500 rpm simultaneously. After centrifugation, the supernatant was filtered. Subsequently, the concentration of radionuclides after filtration was analyzed.

2.2.2. Influencing factors of adsorption

At ambient temperature, 1 g natural zeolite and 1 g zeolite 4A were added into 25 mL simulated radioactive waste solution containing Sr^{2+}, Cs^+, and Co^{2+}, respectively. The nuclide concentration was 1 mg/L, and the solutions were adjusted with the pH value range or the concentration of suspended solids and organic matter. The suspension was stirred for 1 hr, and then 10 mL was extracted for centrifugal separation to analyze the concentration of radionuclides.

2.2.3. Analysis

To evaluate the absorption level, the concentrations of Sr^{2+}, Cs^+, and Co^{2+} were analyzed by plasma emission spectroscopy mass spectrometry (inductively coupled plasma-mass spectrometry) (Agilent 1200/7700x). The X-ray diffraction (XRD) technique was used to analyze the changes in the zeolite crystal structure prior to and after the adsorption process. The instrument type was an X'Pert PRO made by PANalytical B.V. located in Eindhoven of Netherlands.

2.2.4. Experimental calculation

The adsorption efficiency of zeolite 4A (adsorption percentage, R) was calculated using the following equation [26]:

$$R = \frac{C_0 - C_t}{C_0}, \tag{1}$$

where C_0 and C_t are the concentrations of simulated radionuclides in the solution prior to and after adsorption.

3. Results and discussion

3.1. Role of zeolite structure

3.1.1. Effect of zeolite types and chemical components

The weight contents of SiO_2 and Al_2O_3 in zeolite 4A were 54.6% and 27.8%, respectively, and the sodium ions were the main skeleton of the zeolite. In contrast, the weight contents of SiO_2 and Al_2O_3 of the natural zeolites were 78.35% and 12.88%, respectively. The elemental aluminum and silicate made up more than 90% of the total, indicating that this material contained few impurities. The molar ratio of Al to Na in the zeolite 4A was 1.86; for the natural zeolite, that ratio was 31.4. It was shown that a charge compensating cation other than Na^+ exists. Meanwhile, natural zeolite had no chlorine in it; it mainly contained clinoptilolite and very small amounts of mordenite zeolite, quartz, etc. This natural zeolite came from a deposit in Zhejiang. The main ingredient of both zeolite 4A

Table 1 – Chemical components of natural zeolites and zeolite 4A (wt.%).

Chemical components	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3
Zeolite 4A	11.67	2.77	27.8	54.6	0.14	0.13	0.22	0.38	0.54	0.18	0.03	1.51
Natural zeolite	0.41	0.95	12.88	78.35	0.03	0.15	–	1.77	3.49	0.21	0.08	1.52

and natural zeolite was SiO_2. The zeolite 4A samples were all zeolite-A, as confirmed by jade analysis. The main chemical components of the natural zeolites and zeolite 4A are shown in Table 1.

3.2. *Effect of adsorption efficiency*

It was observed in this experiment that the structural difference can affect the adsorption properties of zeolites. In this section, the adsorption efficiency was investigated by measuring the R value of the three ions, Cs, Sr, and Co. Fig. 1A shows that the tendencies of Cs^+ adsorption of zeolite 4A and natural zeolites were very similar; after 60 min of adsorption time, the two curves almost reached adsorption equilibrium with 91% adsorption efficiency. Fig. 1B reveals that the tendencies of Sr^{2+} adsorption by zeolite 4A nearly reached the adsorption equilibrium after 45 min; the adsorption equilibrium of natural zeolites was almost reached after 180 min, which means that zeolite 4A has a higher adsorption efficiency. Fig. 1C indicates that Co^{2+} adsorption by zeolite 4A, because its adsorption efficiency was more than 98%, required less time to reach the adsorption equilibrium compared with the natural zeolites. Therefore, zeolite 4A has an obvious advantage in terms of adsorption efficiency, and zeolite 4A was chosen in this study to adsorb simulated radionuclides in aqueous solution.

3.3. *Effect of zeolite 4A structure*

In order to study the structural changes of zeolite 4A prior to and after adsorption, the samples were analyzed with XRD. The lamp was made of Cu. The K-Alpha2/K-Alpha1 ratio was 0.5; the XRD patterns of zeolite 4A prior to and after adsorption are shown in Fig. 2. Moreover, the figure also shows the structural changes of zeolite 4A prior to and after the adsorption of Cs^+, Sr^{2+}, and Co^{2+}. In the figure, zeolite 4A for Sr^{2+} adsorption has the strongest diffraction peaks. The position of the diffraction peaks was determined by considering the intensity of the diffraction peak, whereas the crystal cell parameters were determined using the Bragg equation.

$$2d \sin\theta = n\lambda \tag{2}$$

Using jade analysis, the chemical formula of zeolite 4A was found to be $Na_2Al_2Si_{2.5}O_96\cdot 2H_2O$; zeolite 4A was of Na type; the average constant was 25.5599. The chemical formula of zeolite 4A was $Na_{96}Al_{96}Si_{96}O_{384}216H_2O$ after the adsorption of Cs^+, Sr^{2+}, and Co^{2+}; the average constants were 25.5511, 24.7961, and 29.3178. After the adsorption, zeolite 4A had the same chemical formula, and Co^{2+} had the largest average constants.

In the patterns, the simulated radionuclides entered the crystal structure of zeolite 4A, resulting in changes of the diffraction peaks and lattice distortion [27,28]. Adsorption and

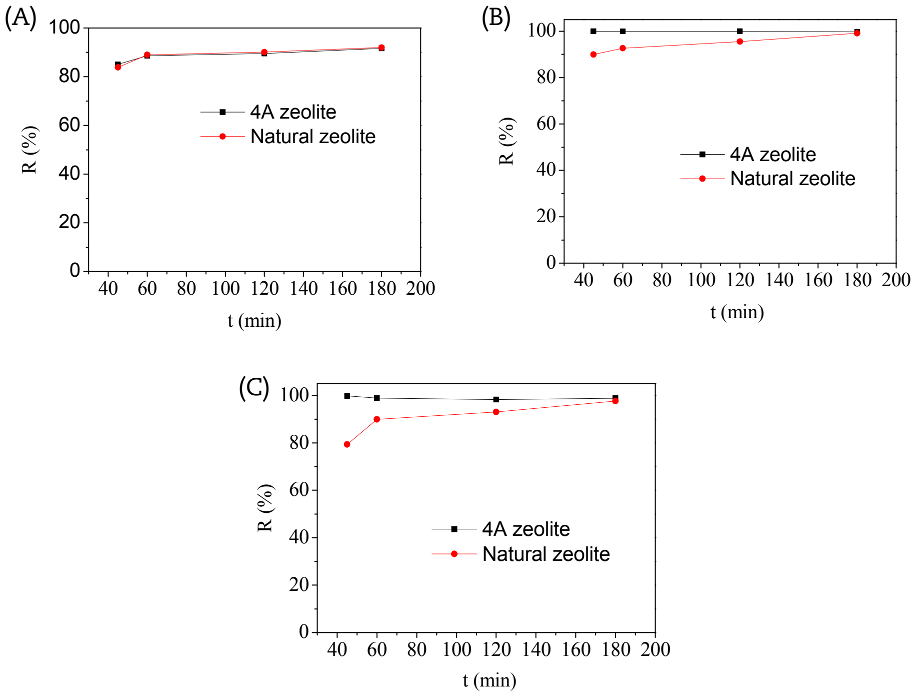

Fig. 1 – Adsorption ability comparison between zeolite 4A and natural zeolite. (A) Cs^+ adsorption. (B) Sr^{2+} adsorption. (C) Co^{2+} adsorption.

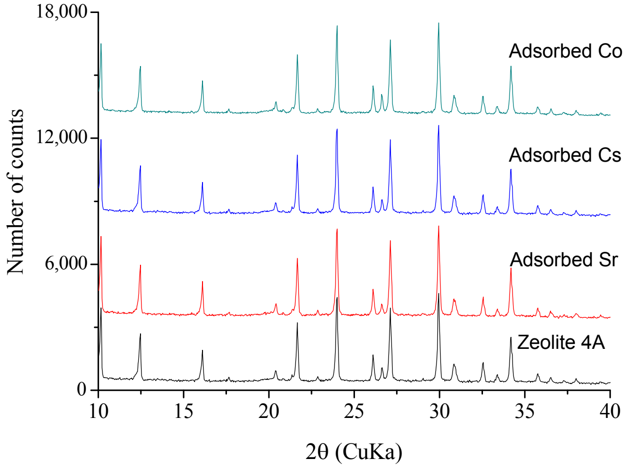

Fig. 2 – **Effect of structure changes of zeolite 4A prior to and after adsorption. Co = cobalt; Cs = cesium; Sr = strontium.**

ion exchange were the main radionuclide removal mechanisms stimulated by zeolite 4A in radioactive wastewater.

3.4. *Role of chemical environment*

The adsorption capacity of zeolite 4A might be affected by the different levels of pH, and by suspended solids and organic matter during the adsorption process.

3.4.1. *Effects of pH value*

The effect of the solution pH value on the zeolite 4A adsorption ability of simulated radionuclides is shown in Fig. 3. The adsorption efficiency improved with the increase of the pH value in the solution. In an acidic environment, the positively charged H^+ in the solution might affect the ability of zeolite 4A to adsorb simulated radionuclides. Identical valence states of Cs^+ and H^+ might have the greatest impact on Cs^+ adsorption. The adsorption rate (R) of Cs^+ was found to increase from 99.0% to 99.8% when the pH increased from 4.0 to 12.0 in the solution. The R value of Sr^{2+} increased from 98.9% to 99.9% when the pH increased from 4.0 to 12.0 in the solution. The R value of Co^{2+} increased from 98.7% to 99.6% when the pH increased from 4.0 to 12.0 in the solution. Therefore, the simulated radionuclide adsorption via zeolite 4A was more appropriately modeled in the alkaline environment.

3.4.2. *Effects of concentration of suspended solids*

Radioactive wastewater was usually suspended by the local clay, which means that the radioactive wastewater produced in the process of decontamination or decommissioning usually contains local soil suspensions. The clay contained mainly kaolinite and very small amounts of mica, quartz, gibbsite, etc. The effect of suspended solids (Mianyang, Sichuan, China; 200 meshes) on the simulated radionuclide adsorption ability by zeolite 4A is shown in Fig. 4. The suspended solid significantly impacted the Co^{2+} adsorption. The blank experimental results demonstrate that the clay could not adsorb the simulated radionuclides because it had a certain charge, which increased the simulated radionuclides adsorption by zeolite 4A.

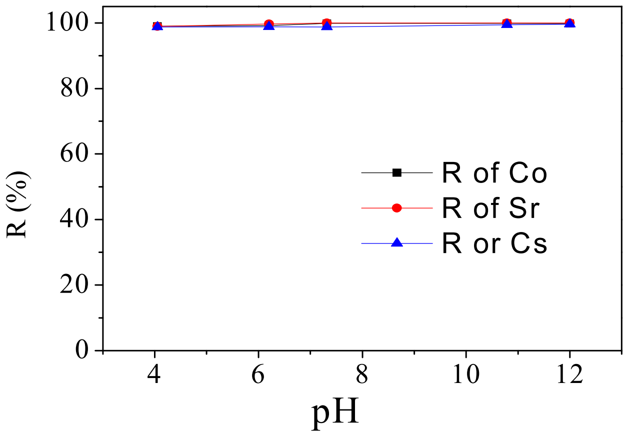

Fig. 3 – **Adsorption efficiency affected by pH in the aqueous solutions. Co = cobalt; Cs = cesium; Sr = strontium.**

3.4.3. *Effect of concentration of organic acid*

The decommissioning and decontamination processes of nuclear facilities generate radioactive wastewater containing sodium oleate, oxalic acid, and citric acid. However, the organic acids can remove radioactive contamination from metal surfaces. The effects of organic acids such as sodium oleate, oxalic acid, and citric acid on zeolite 4A adsorption of simulated radionuclides are shown in Fig. 5. Sr^{2+} adsorption by zeolite 4A was slightly influenced by these three kinds of organics. It was observed that sodium oleate and oxalic acid had little influence on Cs^+ adsorption, but the adsorption efficiency of zeolite 4A on Cs^+ decreased rapidly with the increase of citric acid concentration in the solution. It might be possible to increase the adsorption efficiency of zeolite 4A on Co^{2+} by increasing the sodium oleate concentration or by rapidly decreasing the rising concentration of oxalic acid and citric acid in the aqueous solutions. There could be complex formations between citrate and oxalate with divalent cations, such as Co^{2+}. R decreased when the acids were added because of the pH decrease.

Therefore, the removal of radionuclides in radioactive wastewater by zeolite 4A was complicated and required

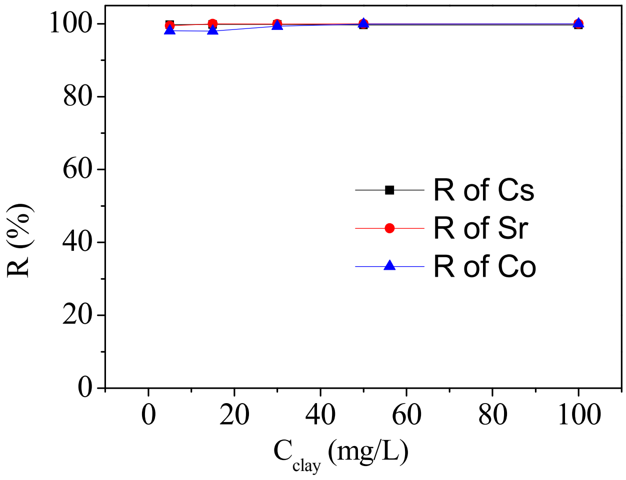

Fig. 4 – **Adsorption efficiency affected by concentration of suspended solids. Co = cobalt; Cs = cesium; Sr = strontium.**

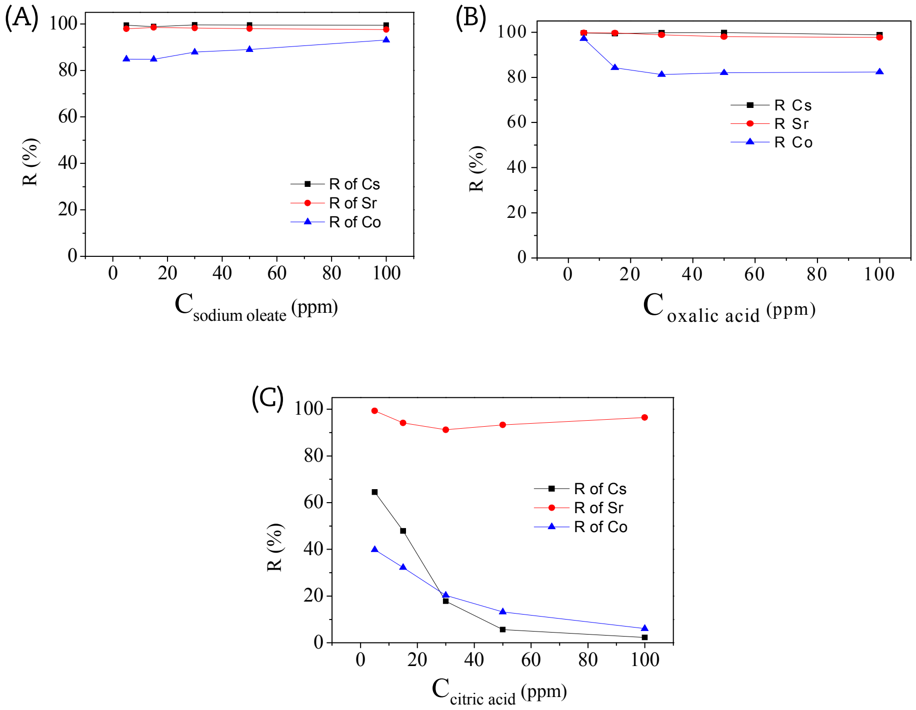

Fig. 5 – Adsorption efficiency affected by concentration of organics. Co = cobalt; Cs = cesium; Sr = strontium.

pretreatment of the water according to the water composition, such as the type of radionuclides and the contained organic species.

4. Conclusion

With experiment simulations on radionuclides in solution adsorbed by zeolite 4A, the results obtained were as follows:

(1) Removal of Cs^+ by zeolite 4A and natural zeolites leads to almost the same adsorption equilibrium time and adsorption efficiency. However, the adsorption of Sr^{2+} and Co^{2+} by zeolite 4A presents more advantages in the adsorption equilibrium time and adsorption efficiency because the adsorption efficiency surpasses 90% after a shorter adsorption time than is necessary for natural zeolite.
(2) Adsorption and ion exchange are the main removal mechanisms used by zeolite 4A in radionuclides wastewater.
(3) The pH value in aqueous solutions can affect the adsorption ability of zeolite 4A; a higher adsorption efficiency is obtained in an alkaline environment.
(4) Charged clay will increase the adsorption capacity of zeolite 4A. The effect of zeolite 4A on the process of adsorbing simulated radionuclides mixed with organics is determined by the types of organics and simulated radionuclides.
(5) Zeolite 4A has an advantage in complex radioactive wastewater treatment that contains suspended solids and organics.

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