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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 anti-radiation 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]:

$$R = \frac{C_0 - C_t}{C_0}, \qquad (1)$$

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