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Equilibrium, kinetic and thermodynamic study of cesium adsorption onto nanocrystalline mordenite from high-salt solution

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H I G H L I G H T S

- We have investigated the equilibrium, kinetic and thermodynamic properties of Cs adsorption by nano mordenite.
- The nano mordenite showed a fast adsorption rate and stable binding site for Cs even in high-salt solution.
- The nano mordenite can be successfully applied to the static adsorption condition.

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In this study, the equilibrium, kinetics and thermodynamics of cesium adsorption by nanocrystalline mordenite were investigated under cesium contamination with high-salt solution, simulating the case of an operation and decommissioning of nuclear facilities or an accident during the processes. The adsorption rate constants were determined using a pseudo second-order kinetic model. The kinetic results strongly demonstrated that the cesium adsorption rate of nano mordenite is extremely fast, even in a high-salt solution, and much faster than that of micro mordenite. In the equilibrium study, the Langmuir isotherm model fit the cesium adsorption data of nano mordenite better than the Freundlich model, which suggests that cesium adsorption onto nano mordenite is a monolayer homogeneous adsorption process. The obtained thermodynamic parameters indicated that the adsorption involved a very stable chemical reaction. In particular, the combination of rapid particle dispersion and rapid cesium adsorption of the nano mordenite in the solution resulted in a rapid and effective process for cesium removal without stirring, which may offer great advantages for low energy consumption and simple operation.

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1. Introduction

Radioactive liquid waste is mainly generated from the operation or decommissioning of nuclear facilities and unexpected accidents involving nuclear power plants (Ishikawa et al., 2013; Lee et al., 2014). Due to its high specific radioactivity and long half-life, radiocesium is one of the most hazardous and problematic materials for the environment as well as for human health (Dubourg, 1998; Ding et al., 2013). To date, numerous studies on cesium removal from waste solutions have been conducted to enhance the efficiency and applicability of such processes (Nilchi et al., 2011;

Karamanis and Assimakopoulos, 2007; Lin et al., 2001; Ding et al., 2013; Abdel Rahman et al., 2011). Waste solutions with higher radioactivity and long-lived radionuclides may be treated using adsorption, ion exchange, chemical precipitation, evaporation, reverse osmosis, filtration and solvent extraction (Abdel Rahman et al., 2011). Among the treatment technologies, adsorption and ion exchange have been considered to be the most effective methods for removal of high-level radioactive cesium from high-salt solutions, because the chemical concentration of cesium is much lower than that of matrix ions (Dubourg, 1998).

Zeolites are well-known crystalline aluminosilicate minerals with a porous structure that can accommodate a diversity of cations. Because these cations are rather loosely held and can be exchanged for other ions in a contact solution, zeolites have been commonly used as commercial adsorbents and catalysts. Mordenite

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is a zeolite mineral with two-dimensional pores, whose system consists of main channels of $6.5 \times 7.0 \text{ \AA}$ and tortuous pores of $2.6 \times 5.7 \text{ \AA}$ (Li et al., 2009). Mordeinite is one of the zeolite types with industrial applications in sorption and catalysis studies. Due to its high thermal and acid stability and catalytic activity, mordeinite has industrial importance in the refining and petrochemical catalytic processes (Bajpai, 1986). It has been also considered for applications in semiconductors, chemical sensors and nonlinear optics (Gilbert and Mosset, 1998). In addition, mordeinite has been used in the adsorptive separation of gas or solution mixtures (Shao et al., 2002). In the field of radioactive waste management, mordeinite is useful as an inorganic ion exchanger, with additional advantages such as high radiation resistance and exchange selectivity on specific radionuclides, e.g. cesium. The selectivity of monovalent cations by mordeinite is in the order of: $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$ (Ohnuki and Kozai, 2013), and the exchange selectivity of cesium by mordeinite is higher than that of most divalent cations (Chmielewska, 2014). Most of the related previous studies have been focused on bulk-scale mordeinite because of its high commercial availability as a granular form suitable for application in fixed-bed columns (Samanta, 1999; Borai et al., 2009).

Nanomaterials have extremely high specific surface areas, adsorption sites, and reactivity, whereas conventional bulk materials have some limitations (Sharma et al., 2009; Qu et al., 2013). Nano-sized zeolites also offer advantages in supramolecular catalysis, photochemistry, nanochemistry, electrochemistry and optoelectronics (Mintova and Valtchev, 1999). Zeolite nanocrystals can also be applied in the production of other geometries such as thin films, fibers and self-standing zeolite membranes (Zhu et al., 1998). Many studies and applications of the synthesis of nano-sized mordeinite for the aforementioned uses have been reported (Aly et al., 2012; Hincapie et al., 2004; Li et al., 2009), however, to the best of our knowledge, few studies have focused on the fundamental evaluation of mordeinite as an adsorbent in waste solution conditions. In environmental applications, waste solution treatment using nanoadsorbent in powder form in precipitation reactors with additional techniques to separate the nanoparticles may be considered (Sharma et al., 2009; Qu et al., 2013). Therefore, exploration of the adsorption characteristics of nano mordeinite itself is important.

In this study, we aim to examine the adsorption properties of nanocrystalline mordeinite for cesium removal from high-salt aqueous solution during a batch study. Equilibrium, kinetic and thermodynamic constants were obtained by applying the modeling methods for cesium adsorption. Comparative studies were performed for the cesium adsorption rate and the capacity of nano and micro-sized mordeinites.

2. Materials and methods

2.1. Materials

The sample solutions for the adsorption experiments were prepared by dissolving cesium chloride (Sigma-Aldrich, CsCl 99.9%) in seawater collected from the Korean East Sea with initial Cs concentrations of 1 and 100 mg/L. The solution initially had high-salt conditions with Na and Cl concentrations of 10,675 mg/L and 19,700 mg/L, respectively, and other major ions including Mg, K, Ca, SO_4 and Br (1200 mg/L, 424 mg/L, 420 mg/L, 2610 mg/L and 73 mg/L, respectively). This was considered as a high-salt solution contaminated by Cs.

Two types of pure mordeinite were used for this study. A commercially available mordeinite (Alfa Aesar, Zeolite mordeinite, sodium) was sonicated for 2 h to obtain nano-sized mordeinite through disaggregation of the particles. The producer of the

commercial mordeinite has reported the median size of the aggregated mordeinite particle is $3.5 \mu\text{m}$, however the nanoparticles exist as stable colloids in water after the sonication pre-treatment, excepting for minor portion of microparticles settled down. The colloidal nano mordeinite was used for comparison with micro-sized mordeinite synthesized in our lab. The mordeinite was synthesized using the following hydrothermal method modified from previous methods (Kim and Ahn, 1991; Aly et al., 2012). Briefly, 2.43 g of sodium hydroxide (Merck, NaOH >99%) was dissolved in 68.6 mL of deionized water (Millipore, Direct-Q3), and then 3.8 g of aluminum nitrate (Merck, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 98.5%) and 9 g of fumed silica (Aldrich, SiO_2 0.2–0.3 μm) were sequentially added to the mixture and stirred for 1 h at 400 rpm. The batch composition of the gel was $6 \text{ Na}_2\text{O}:\text{Al}_2\text{O}_3:30 \text{ SiO}_2:780 \text{ H}_2\text{O}$. The prepared gel was then transferred to a Teflon-lined stainless steel autoclave and placed in a furnace at $180 \text{ }^\circ\text{C}$ for 5 days. The products were thoroughly washed with deionized water to $\text{pH} < 10$ and then dried in an oven at $95 \text{ }^\circ\text{C}$ for 24 h.

2.2. Characterization of mordeinites

Powder X-ray diffraction (XRD; Bruker D2 Phaser, Germany) was used for identification of the prepared mordeinites. Particle morphology and size were examined using scanning electron microscopy (SEM; SEC SNE-4500M, Korea), and elemental composition was measured using electron dispersive spectroscopy (EDS; Bruker QUANTAX, Germany). Mordeinite particle size was determined on the basis of particle dispersibility in solution. Mordeinite nanoparticles exist as stable colloids in deionized water; therefore, the mean volume diameter of the colloidal sample was measured by dynamic light scattering (DLS; Malvern ZS90, UK), which allowed exact measurement of the nanometer size of the particles dispersed in the solution. However, the mean size of micro mordeinite was determined using laser diffraction (LD; Microtrac S3500, Japan), since most of the particles settled to the bottom within several seconds. The laser diffraction method has a detection range of 0.7–1000 μm in fluidized solution conditions.

2.3. Adsorption experiments

Batch adsorption experiments were conducted for different m/V s (g-mordeinite/L) under shaking conditions for 2 h at room temperature. All experiments were repeated in triplicate. Following the experiments, the samples were collected by filtering supernatants through a 0.2- μm membrane (Advantec, DISMIC-13) and diluted with deionized water to appropriate concentrations prior to analysis by atomic absorption spectroscopy (AAS; PerkinElmer Analyst 900F, USA). To ignore the matrix effect of high-salt conditions on Cs quantification in AAS analysis, a constant level of seawater-based standard solution was used. In the case of low Cs quantification, inductively coupled plasma-mass spectrometry (ICP-MS; PerkinElmer Elan DRC ii, USA) was used. This instrument was an adequate measure for Cs analysis of the samples collected from the experiments using 1 mg/L initial Cs concentration, because its detection limit of Cs was 10 ng/L. The Cs removal results are given as adsorption yields (A , %) and distribution coefficients (K_d , mL/g) based on the following equations:

$$A = (C_i - C_f)100 / C_i \quad (1)$$

$$K_d = (C_i - C_f)1000V / C_f m \quad (2)$$

where C_i (mg/L) is the initial Cs concentration, C_f (mg/L) is the final

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