



## Novel application of nanozeolite for radioactive cesium removal from high-salt wastewater



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### ABSTRACT

Finding a striking peculiarity of nanomaterials and evaluating its feasibility for practical use are interesting topics of research. We investigated the application of nanozeolite's outstanding reactivity for a rapid and effective method for radioactive cesium removal in the wastewater generated from nuclear power plant accident, as a new concept. Extremely fast removal of cesium, even without stirring, was achieved by the nanozeolite at efficiencies never observed with bulk materials. The nanozeolite reached an adsorption equilibrium state within 1 min. Cesium adsorption by nanozeolite was demonstrated at reaction rates of orders of magnitude higher than that of larger zeolite phases. This observation was strongly supported by the positive correlation between the rate constant ratio ( $k_{2,\text{bulk}}/k_{2,\text{nano}}$ ) and the initial Cs concentrations with a correlation coefficient ( $R^2$ ) of 0.99. A potential drawback of a nano-adsorbent is the difficulty of particle settling and separation because of its high dispersivity in solution. However, our results also demonstrated that the nanozeolite could be easily precipitated from the high-salt solution with ferric flocculant. The flocculation index reached a steady state within 10 min. A series of our experimental results met the goal of rapid processing in the case of emergency by applying the well-suited nanozeolite adsorption and flocculation.

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## 1. Introduction

The treatment of wastewater containing radionuclides has become one of the most significant challenges facing the nuclear industry, which was highlighted from the generation of a large volume of radioactive wastewater and its release into surrounding soil, groundwater, and seawater after the severe accident at Fukushima, Japan in 2011 (ANS, 2012; Kosaka et al., 2012). Because high-salt and high-level radioactive wastewater in large quantities can be generated after emergency cooling the damaged reactors, a problem was caused by several small and large leakages of wastewater from the treatment system and storage tanks that were hurriedly installed in the early stages of the incident (ANS, 2012; TEPCO, 2012a). Therefore, to minimize the storage of wastewater and release of radionuclides into the environment, a novel emergency treatment system capable of rapid, effective, and convenient operation is required, followed by recycling of treated water back

into the reactors.

Radioactive cesium is the most crucial and problematic element of the radionuclides because of its abundance in the target wastewater and the hazards presented by its high specific radioactivity and long half-life (Dubourg, 1998; TEPCO, 2012b). Although there are a number of methods for purifying the waste solutions, ion exchange and adsorption have been considered to be the most effective methods for removal of radioactive cesium from the high-salt and high-level radioactive wastewater. The method is the most effective because the chemical concentration of cesium is relatively low despite its high radioactivity, whereas the concentrations of background ions are high (Dubourg, 1998). The major existing on-site wastewater treatment system at Fukushima site is also based on cesium adsorption by column operation using zeolites as the adsorbent (Sylvester et al., 2013). Zeolites or zeolitic materials have been preferred over organic materials for the treatment of high-level radioactive liquid waste because of their radiological and thermal stability as inorganic adsorbents (Plazinski and Rudzinski, 2009).

Nanoadsorbent-based wastewater treatment offers a promising approach to overcome current drawbacks and provide outstanding

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performances on the contaminant removal from wastewater in many different industrial applications (Qu et al., 2013). Nanomaterials have extremely high specific surface areas, adsorption sites, and reactivity, whereas conventional bulk materials have chemical and biogeochemical limitations in terms of surface area, active sites, and reaction kinetics (Sharma et al., 2009; Bosch et al., 2012; Qu et al., 2013). Research on nanozeolite has focused on chemical sensors, thin films, enhanced catalysts, and macrostructure composite materials (Hedlund et al., 1997; Choi et al., 2000; Pan et al., 2009; Serrano et al., 2009). In wastewater treatment applications, nanozeolite has been used in membrane processes for the removal of metal ions, where the main goal is to increase the hydrophilicity of the membrane (Jawor and Hoek, 2010; Pendergast and Hoek, 2011). A few studies have investigated water treatment using nanoadsorbent in powder form in slurry reactors with an additional separation unit to recover the nanoparticles (Sharma et al., 2009; Qu et al., 2013), although the minute particle of the nanoadsorbent size poses a challenge. In the same manner, a number of advantages of nanomaterials, especially nanozeolites, need to be explored in various fields of scientific research. To the best of our knowledge, although interests in the various applications of nanoadsorbents including nanozeolite have been attracting growing interest, there has been no research on the use of nanozeolite in the treatment of radioactive wastewater. Moreover, a precipitation method based on adsorption–flocculation mechanisms offers a promising design approach to an emergency treatment system. In this study, the cesium adsorption properties of nanochabazite (a form of zeolite) were determined and compared to those of bulk chabazite. A feasibility study on the application of the adsorption–flocculation process was also conducted in a real environmental setting where radioactive contamination by cesium was present.

## 2. Experimental section

### 2.1. Chabazite

Four types of chabazite were used for this study. A commercially available chabazite, AW500 manufactured by Linde (Sigma–Aldrich, Molecular sieve, 1.6 mm pellet) was used for comparison with pure synthesized chabazite. The AW500 pellet was ground and sieved to less than 212  $\mu\text{m}$  to produce AW500-powder. Pure chabazite was synthesized from the decomposition of a commercial grade of zeolite Y (Sigma–Aldrich, LZ-Y62, powder) following the method suggested by Bourgogne et al. (1985). Moreover, 99.1 mL of deionized water (Millipore, Direct-Q 3) was mixed with 13.4 mL of 45 wt% potassium hydroxide solution, and 12.5 g of zeolite Y was added to the mixture and shaken for 30 s in a polypropylene bottle (250 mL, Nalgene). The batch composition of the gel was 0.17  $\text{Na}_2\text{O}:2.0 \text{K}_2\text{O}:\text{Al}_2\text{O}_3:5.18 \text{SiO}_2:224 \text{H}_2\text{O}$ . The gel was then placed in an oven at 368 K for 4 days. The products were washed by deionized water with sonication and dried in an oven at 333 K for more than 48 h. The product synthesized by this procedure shows sub-micron crystallites with hundreds of nanometers (Bourgogne et al., 1985). For the synthesis of micro-sized chabazite (CHA-micro), the existing method for nanochabazite (CHA-nano) production was modified in this study. The batch composition and mixture conditions were identical to those in the procedure already described. However, the synthesis temperature was decreased to 358 K, and the crystallizing period was increased to 14 days. All the prepared chabazites were then ion exchanged to the sodium form using 1 M NaCl solution at 333 K with a solution comprising chabazite ratio of 50 mL/g in eight ion exchange cycles, each lasting more than 9 h. This yielded sodium-exchanged chabazites (Smith et al., 2001; Ridha et al., 2009).

### 2.2. Characterization of chabazite

The particle sizes of the prepared chabazites were determined on the basis of particle dispersibility in deionized water. CHA-nano was a very stable colloidal phase in solution; therefore, the mean volume diameter of the colloidal sample could be measured by dynamic light scattering (DLS; Malvern ZS90, UK), which allowed exact determination of the nanometer size of particles dispersed in the solution. Conversely, the CHA-micro and AW500-powder were measured by laser diffraction (LD; Microtrac S3500, Japan), because most of the particles settled to the bottom. This gave a detection range of 0.7–1000  $\mu\text{m}$  in a fluidized solution condition.

Powder X-ray diffraction (XRD; Bruker D2 Phaser, Germany) was used for identification of the prepared chabazites. Particle morphology and size were examined by scanning electron microscopy (SEM; SEC SNE-4500M, Korea).

### 2.3. Batch adsorption tests

The sample solutions for the batch 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 100 and 10 mg/L for the nonradioactive experiments, and 1 mg/L and 1  $\mu\text{g/L}$  with  $^{137}\text{Cs}$  as a tracer level for the radioactive experiments. The seawater was used after filtration, and it had initial Na and Cl concentrations of 10675 and 19700 mg/L, respectively, as well as a range of other ions including Ca, K, Mg, Br, and  $\text{SO}_4$ . This was considered as a Cs contaminated condition with high-salt content. Adsorption experiments were conducted for different m/Vs (g-chabazite/L) under shaking or static conditions for 2 h at room temperature. All experiments were repeated in triplicate, and running blanks were measured for experimental accuracy. After the experiments, the samples were collected by filtering supernatants through a 0.2  $\mu\text{m}$  membrane (Advantec, DISMIC-13) and diluted with deionized water to form appropriate concentrations prior to analysis by atomic absorption spectroscopy (AAS; PerkinElmer AAnalyst 900F, USA) and inductively coupled plasma-mass spectrometry (ICP-MS; PerkinElmer Elan DRC ii, USA) for the nonradioactive samples and multi channel analyzer (MCA; Oxford TC702, UK) for radioactive samples. To ignore the matrix effect on Cs in the AAS analysis of the seawater samples, a constant level of seawater-based standard solution was used. The Cs adsorption results are given as adsorption yields (A, %) and distribution coefficients ( $K_d$ , mL/g) and are based on the following equations:

$$A = \frac{(C_i - C_f)100}{C_i} \quad (1)$$

$$K_d = \frac{(C_i - C_f)1000V}{C_f m} \quad (2)$$

where  $C_i$  (mg/L) is the initial Cs concentration,  $C_f$  (mg/L) is the final Cs concentration from the supernatant solution,  $V$  (L) is the solution volume, and  $m$  (g) is the mass of chabazite used. The Cs adsorption capacity ( $q$ , mg/g) of chabazites with  $m/V = 1$  (1 g-chabazite/L dose) for 2 h was calculated from the mass balance as follows:

$$q = \frac{(C_i - C_f)V}{m} \quad (3)$$

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