Evaluation of Sr and Cs ions adsorption capacities with zeolitic materials synthesized from various mass ratios of NaOH to coal fly ash

Jeong-Hak Choi¹, Chang-Han Lee^{2*}

¹Department of Environmental Engineering, Catholic University of Pusan, Busan 46252, Korea

²Department of Environmental Administration, Catholic University of Pusan, Busan 46252, Korea

ABSTRACT

The adsorptive aqueous removal of Sr^{2+} and Cs^+ was performed using zeolitic materials prepared with fused coal fly ash (CFA) using a hydrothermal method. The influence of the mass ratio of NaOH to CFA of 0.3-1.2 in the synthesis of zeolitic material was evaluated its crystallization properties by X-ray diffraction (XRD) analysis. The zeolitic materials synthesized at the mass ratio of NaOH to CFA of 0.6-1.2 could be identified to have the same location as the XRD peaks of Na-A zeolite at $2\theta = 7.18 - 34.18$. They appeared to be zeolitic materials which were crystalline particles with a cubic structure by scanning electron microscopy (SEM). The experimental adsorption data for Sr^{2+} and Cs^+ using the zeolitic materials were estimated satisfactory using pseudo-2nd-order kinetics and Langmuir isotherm models. The highest maximum adsorption capacities (q_m) of 147.6 mg/g for Sr^{2+} and 160.2 mg/g for Cs^+ were estimated by using the zeolitic material. This material demonstrated superior crystallinity and was synthesized at a mass ratio of NaOH to CFA of 0.6. Consequently, the zeolitic material prepared from the fused CFA through the hydrothermal method could be used effectively for the adsorption of Sr^{2+} and Cs^+ in aqueous solutions.

Keywords: Cesium, Coal fly ash, Crystallization, Strontium, Zeolitic materials

1. Introduction

Nuclear power plants contain significant radioactive waste with radionuclides. They are considered one of the most hazardous contaminants, and their treatment has received much attention. Radioactive wastes released into the aquatic environment are known to damage the ecosystem – as in the case of the nuclear power plant accident at Fukushima in 2011. Nuclear fission reactions produce large amounts of hazardous radionuclides such as Cs and Sr ions. The Cs and Sr ions are accidentally or routinely released [1]. They have been deemed hazardous because of their relatively long half-life of 30 years. Their accumulation potential in animals and plants threatens human health and the environment [2, 3].

The technologies for the removal of Cs and Sr ions that are effective and feasible remove the ions from contaminated water by inorganic sorbents [1, 2, 4-6]. Coal fly ash (CFA) is discharged

as solid waste from thermal power plants and recycled as raw materials, which are cement raw materials and concrete mixtures [7]. Various methods for reusing as source components are introduced because the main components of the CFA are SiO_2 and Al_2O_3 , which exist in the form of aluminosilicates in amorphous and crystalline phases such as quartz, mullite, and hematite [8]. Its composition allows it to become a precursor for the synthesis of zeolitic materials. Many studies have sought to improve the crystallinity of zeolitic materials with various synthetic conditions using the CFA [9-11]. Walek et al. [9] compared the synthesis efficiency of zeolitic materials according to the CFA and NaOH concentrations. Zeolitic materials were synthesized at a solid/liquid ratio of 4 in 2 M NaOH solution. Zeolitic materials have a relative crystallinity of 80% with the formation of a single-phase NaP1 zeolite. Yang et al. [10] prepared zeolitic materials with a relative crystallinity of 75.8% at a Na_2CO_3 and NaOH mass ratio of 2.8 in the zeolite synthesis

This is an Open Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

Copyright © 2022 Korean Society of Environmental Engineers

Received November 29, 2020 Accepted February 13, 2021

* Corresponding author

E-mail: chlee@cup.ac.kr

Tel: +82-51-510-0624

ORCID: 0000-0002-0641-1463

process. Ye et al. [11] synthesized zeolitic materials from fused sodium carbonate and CFA mixture by a hydrothermal method at high temperatures.

Some researchers proposed experimental approaches to evaluate the removal performance of radioactive ions with adsorbents related to various zeolites [1, 5, 6]. The removal efficiencies of Sr^{2+} (69.0 mg/g) and Cs^+ (90.7 mg/g) using a synthetic Na-A zeolite was evaluated using equilibrium data. They were represented using the pseudo-2nd order kinetic and Langmuir models [5]. The adsorption of Cs^+ using a zeolitic material from a bio-slag demonstrated a superior fit to the Langmuir and Freundlich models in comparison with the Temkin isotherm. The adsorption capability of the zeolitic material was 51.02 mg/g [12]. The adsorption of Cs^{2+} , Co^{2+} , and Sr^{2+} from clinoptilolite (natural zeolite) could be fitted by the Langmuir isotherm model [1]. The adsorption capacities of Cs^{2+} , Co^{2+} , and Sr^{2+} were 2.93, 49.0, and 9.8 mg/g, respectively. Zeolitic materials with Na-A zeolite on the crystal surface were prepared from the CFA in Korea using the fusion/hydrothermal method [6]. It presented an adsorption capacity of 156.4 mg/g for Sr^{2+} . However, it was difficult to find a correlation between the crystallinity of the zeolitic materials and Sr^{2+} and Cs^+ adsorptions in previous studies.

This study focused on the synthesis of zeolitic materials and used them as adsorbents to remove Sr^{2+} and Cs^+ in an aqueous solution. The CFA obtained from the Y power plant was synthesized into zeolitic materials through the fusion/hydrothermal method. The dependence of the synthesis of zeolitic materials upon the mass ratio of NaOH to CFA was confirmed by analyzing their crystallinity and crystal morphology. The zeolitic materials prepared with various mass ratios of NaOH to CFA were applied as adsorbents for the aqueous removal of Sr^{2+} and Cs^+ . Model fittings were also performed with the experimental data using the adsorption kinetic models (i.e., pseudo-1st and 2nd-order kinetic models) and adsorption isotherm models (i.e., Langmuir and Freundlich isotherm models) to evaluate the adsorption characteristics and capacities of Sr^{2+} and Cs^+ by the synthesized zeolitic materials.

2. Materials and Methods

2.1. Materials

The CFA was collected as a raw material at the Y thermal power plant in Korea. It was dried at 105°C in Pyrex glass containers for 10 h. The standard Na-A zeolite sample (Z-CS) with CP grade was obtained from Cosmo Chemicals Co. Ltd (Korea). NaOH and NaAlO_2 (EP grade) were obtained from Daejung Co. Ltd. (Korea). Stock solutions for batch adsorption experiments were prepared with $\text{Sr}(\text{NO}_3)_2$ and CsNO_3 (ACS grade, Sigma-Aldrich, USA). Deionized water was used in all experiments.

2.2. Preparation of Zeolitic Materials

Zeolitic materials were prepared from the CFA according to the synthesis methods and conditions suggested in a previous study [13]. To increase the crystallinity of the zeolitic materials the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio was fixed at 2.5 and the mass ratios of

Fig. 1. Synthesis procedure for zeolitic materials.

NaOH to CFA were varied from 0.3 to 1.2. The synthesis procedure for the zeolitic materials is shown in Fig. 1. The synthesis experiments were performed using a 0.2 L flat-bottom stainless-steel reactor equipped with an anchor-blade agitator and a temperature controller.

Ten grams of the CFA and NaOH powder (3, 6, 9 and 12 g) were mixed and ground for 15 min in a mortar. They were fused at 550°C for 60 min. The fused materials were pulverized into powder using a mortar. The powder was added to 3.51 g of NaAlO_2 . Deionized water (100 mL) was added to the mixture of the fused materials and NaAlO_2 . The dispersed solution was aged and then crystallized in the reactor. The synthetic products after all synthetic procedures were washed with deionized water until the filtrate reached pH 10. They were dried at 110°C for 2 h in a dry oven.

2.3. Characterization

The crystallization properties of the synthetic materials were determined using an X-ray diffractometer (XRD, D8 Advance, Bruker AXS). The CFA, commercial Z-CS, and the prepared materials were analyzed with XRD patterns using a powder diffractometer with $\text{Cu-K}\alpha$ radiation. The samples were scanned under conditions of radiation wavelength (λ) of 1.54 Å, diffraction angle $5^\circ < 2\theta < 50^\circ$, and time constant of 0.02° steps (3 s per step). The crystal morphology of the CFA and zeolitic materials was observed by a scanning electron microscopy (SEM, Hitachi S-4200). For SEM, the samples were mounted on a copper slab with double-sided tape and then coated with a thin layer of platinum.

2.4. Adsorption Experiments

The adsorption experiments for Sr^{2+} and Cs^+ were performed in 50 mL-volumed conical centrifuge tubes (Falcon, 352070) at 25 °C. Powdered commercial Na-A zeolite (Z-CS) or the prepared zeolitic material of 0.02g was added to each conical centrifuge tube containing 50 mL of Sr^{2+} or Cs^+ stock solution. The mixed samples were stirred at 180 rpm using a shaking incubator (VS-8480SF, Vision Scientific Co., Ltd.). During the adsorption reaction, the

mixture was removed at regular intervals for the adsorption kinetic analysis and centrifuged for 3 min at 3,000 rpm (VS-5500i centrifuge, Vision Scientific Co., Ltd., Korea). After the centrifugation, the Sr^{2+} and Cs^{+} concentrations in the supernatant were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS 7900, Agilent). The initial pH was adjusted to 5.0 by adding 0.1 M of HCl or NaOH. The pH measurements were conducted using a pH meter (model 420A, Orion).

The amount of Sr^{2+} and Cs^{+} removed by the Na-A zeolite and zeolitic materials was calculated using Eq. (1).

$$q = \frac{(C_0 - C_t) V}{W} \quad (1)$$

where q (mg/g) is the adsorption capacity of Sr^{2+} or Cs^{+} at time t , C_0 and C_t (mg/L) are the Sr^{2+} or Cs^{+} concentrations at the $t = 0$ and t , respectively, W (g) is the dosage of the adsorbent, and V (L) is the volume of the solution.

3. Results and Discussion

3.1. Synthesis of Zeolitic Materials from CFA

Zeolitic materials were synthesized with mass ratios of NaOH to CFA varying from 0.3 to 1.2 via the synthesis procedure of our previous study [13]. The crystallization properties of the prepared materials were determined by XRD analysis and compared with that of the commercial Na-A zeolite (Z-CS) as a standard material. The XRD patterns of the raw material (CFA), the prepared materials, and the commercial Z-CS are shown in Fig. 2. The XRD result of the prepared sample with mass ratio of NaOH to CFA of 0.3 showed a different peak pattern and relatively weak peak intensities compared to those of the other prepared zeolitic materials and Z-CS. The XRD peaks of quartz and mullite were only observed in the sample with a mass ratio of NaOH to CFA of 0.3. Therefore, it was concluded that the zeolitic material could not be synthesized successfully at a mass ratio of NaOH to CFA of 0.3. The 2θ values of 20.82 and 26.62 indicated the XRD peak of quartz and the 2θ value of 35.24 indicated the XRD peak of mullite. Murayama et al. [14] suggested that Na-A zeolite could not be synthesized through hydrothermal synthesis with a NaOH concentration of 0.5 M or less and only alumina and silica existed as the crystal forms. Previous study [15] reported the zeolitic material was able to be synthesized from the CFA using a fusion/hydrothermal method under low-alkali mass ratio of NaOH to CFA of 0.6. At the mass ratio of NaOH to CFA of 0.9, some of the XRD peak corresponding to quartz (2θ value of 26.62) remained. However, at the mass ratio of NaOH to CFA of 0.6-1.2, the 2θ values changed to 21.72, 27.11, and 34.21, which is the XRD peak corresponding to Na-A zeolite. They could be identified as a successful synthesis of zeolitic materials because the peaks appeared at the same positions as those of the Na-A zeolite [16] in the 2θ range of 7.18 to 34.18.

The SEM images of the raw material (CFA), the prepared samples, and the commercial Z-CS are shown in Fig. 3. CFA (a) consisted of spherical particles. The raw spherical particles were changed

Fig. 2. XRD patterns of CFA, prepared materials (mass ratios of NaOH to CFA of 0.3-1.2), and commercial zeolite (Z-CS).

into rough and porous particles at the mass ratio of NaOH to CFA of 0.3 (b). Moreover, the surface roughness gradually developed on the originally smooth spherical particles according to the alkali fusion process with the synergism of NaOH. The surface of the spherical particle was covered with the aggregate of cubic crystals at a mass ratio of NaOH to CFA of 0.6 (c). The cubic crystals on the particles decreased at the mass ratio of NaOH to CFA of 0.9 (d). Some of the cubic crystals were changed into sodalite crystals at the mass ratio of NaOH to CFA of 1.2 (e). From the SEM results, the prepared samples with the mass ratio of NaOH to CFA from 0.6 to 1.2 appeared to be zeolitic materials which were similar in morphological structure to the commercial Z-CS (Na-A zeolite (f)). The XRD patterns (Fig. 2) of the zeolitic materials with the mass ratios of NaOH to CFA from 0.6 to 1.2 were confirmed to be crystalline particles with the cubic structure of Na-A zeolite. The crystalline particle morphologies were similar shape to those of the zeolitic materials prepared from the CFA [14,17-18] and volcanic rocks [13]. Na-A zeolite and sodalite crystals were generated simultaneously from coal fly ash under high alkali conditions (Na_2CO_3 and NaOH) using fusion/hydrothermal synthesis [10].

3.2. Adsorption Kinetic Analysis

To analyze the adsorption kinetics of Sr^{2+} and Cs^{+} with zeolitic materials, pseudo-1st-order and pseudo-2nd-order kinetic models were applied to fit the experimental adsorption data. The pseudo-1st-order model for the adsorption kinetic analysis of solutes in aqueous solution to adsorbents is expressed as follows [19]:

$$\frac{dq}{dt} = k_1 (q_e - q) \quad (2)$$

where q and q_e are the adsorption capacities (mg/g) at any time and equilibrium, respectively, and k_1 is the adsorption rate constant (1/h) for the pseudo-1st-order model. Integrating Eq. (2) for the boundary conditions $t = 0$ to t and $q = 0$ to q gives:

Fig. 3. SEM images of CFA ($\times 10,000$), prepared materials ($\text{NaOH/CFA} = 0.3\text{--}1.2$) ($\times 15,000$), and commercial zeolite (Z-CS) ($\times 15,000$) ((a) CFA; (b) $\text{NaOH/CFA} = 0.3$; (c) $\text{NaOH/CFA} = 0.6$; (d) $\text{NaOH/CFA} = 0.9$; (e) $\text{NaOH/CFA} = 1.2$; (f) Z-CS).

$$\ln(q_e - q) = \ln(q_e) - k_1 t \quad (3)$$

The pseudo-2nd-order model for the adsorption kinetic analysis of solutes from liquid to adsorbent phases is expressed as follows [5]:

$$\frac{dq}{dt} = k_2 (q_e - q)^2 \quad (4)$$

The integration of Eq. (4) for the boundary conditions $t = 0$ to t and $q = 0$ to q gives:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where k_2 is the adsorption rate constant (g/mg·h) for the pseudo-2nd-order model. A linear equation was then obtained from Eq. (5).

The experimental adsorption data of Sr^{2+} and Cs^+ using the synthesized zeolitic material (mass ratio of NaOH to CFA of 1.2) and the results of model fitting by the pseudo-1st and 2nd-order kinetic models are shown in Fig. 4. The adsorption capacities of Sr^{2+} and Cs^+ with the prepared zeolitic material increased gradually for the first 30 min, after which they reached adsorption equilibrium within 120 min. Other contact time results reported that the adsorption capacities of Zn^{2+} by Na-A zeolite and Cu^{2+} by a ligand-embedded conjugate material reached equilibrium within approximately 120 min and 50 min, respectively [20, 21]. The kinetic parameters of Sr^{2+} and Cs^+ obtained from estimating the experimental data to Eq. (3) and (5) are summarized in Table 1.

In the pseudo-1st and 2nd-order kinetic models, the plot of $\ln(q_e - q)$ versus t and t/q versus t gives a linear line with a slope of k_1

Fig. 4. Kinetic results and model fittings for the adsorption of Sr^{2+} and Cs^+ using the zeolitic material synthesized with the mass ratio of NaOH to CFA of 1.2 (adsorbent dosage = 0.02 g/0.05 L).

and $1/q_e$ and intercept of $\ln(q_e)$ and $1/k_2 q_e^2$, respectively. q_e , k_1 , and k_2 were calculated from the slope and intercept of the kinetic models. As shown in Table 1, the q_e values estimated with the pseudo-1st-order kinetic model differed considerably from the experimental adsorption capacities ($q_{e,exp}$) calculated directly from the experimental data, whereas the q_e values by the pseudo-2nd-order model fitting showing high correlations (r^2) were similar to the $q_{e,exp}$ in both cases of Sr^{2+} and Cs^+ adsorption. The r^2 values of the pseudo-2nd-order model for Sr^{2+} and Cs^+ were 0.9979 and 0.9991, respectively. Consequently, the adsorp-

Table 1. Adsorption Kinetic Parameters of Sr^{2+} and Cs^+ Using the Zeolitic Material Synthesized with the Mass Ratio of NaOH to CFA of 1.2

Ion	C_0 (mg/L)	$q_{e,\text{exp}}$ (mg/g)	pseudo-1 st -order kinetic model			pseudo-2 nd -order kinetic model		
			q_e (mg/g)	k_1 (1/h)	r^2	q_e (mg/g)	k_2 (mg/g·h)	r^2
Sr^{2+}	50	118.0	70.9	0.0166	0.8733	123.0	0.0056	0.9979
Cs^+	50	78.4	51.5	0.0822	0.9201	78.4	0.0469	0.9991

tion kinetics for Sr^{2+} and Cs^+ using the zeolitic material could be well estimated by the pseudo-2nd-order kinetic model. El-Rahman et al. [22] reported that the experimental adsorption results of Sr^{2+} and Cs^+ with a Na-A zeolite prepared from the CFA were described to the pseudo-2nd-order kinetic model better than the pseudo-1st-order model. El-Kamash [5] also mentioned that the adsorptive removal kinetics of Sr^{2+} and Cs^+ using a Na-A zeolite could be predicted more accurately with the pseudo-2nd-order model.

3.3. Adsorption Isotherm Analysis

The adsorption equilibrium data of Sr^{2+} and Cs^+ were obtained experimentally and then the Langmuir and Freundlich models were applied for the adsorption isotherm analysis.

Langmuir model is expressed as follows [23]:

$$q_e = \frac{k_L q_m C_e}{1 + k_L C_e} \quad (6)$$

where q_m is the maximum adsorption capacity (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), and k_L is the Langmuir constant (L/mg).

Freundlich model is expressed as follows [24]:

$$q_e = k_F C_e^{1/n} \quad (7)$$

where k_F and $1/n$ are the Freundlich constants ((mg/g)(L/mg)^{1/n}) and a constant indicating the adsorption strength, respectively.

The experimental adsorption data of Sr^{2+} and Cs^+ and model fitting data are shown in Fig. 5. Model fitting was performed for both the commercial zeolite (Z-CS) and the zeolitic materials synthesized with various mass ratios of NaOH to CFA. The adsorption isotherm parameters for the Langmuir and Freundlich models were estimated for all adsorption cases and are presented in Table 2. The r^2 values of the Langmuir model were found to be comparatively higher than those of the Freundlich model. The q_m for Sr^{2+} estimated by the Langmuir model was 123.6-147.6 mg/g at the mass ratio of NaOH to CFA of 0.6-1.2, and 16.9 mg/g at the mass ratio of NaOH to CFA of 0.3. For the adsorption of Cs^+ , the q_m values were calculated as 124.9-160.2 mg/g at the mass ratio of NaOH to CFA of 0.6-1.2, and 17.9 mg/g at the mass ratio of NaOH to CFA of 0.3. From these results, it was found that zeolitic material was not successfully synthesized at the mass ratio of NaOH to CFA of 0.3 and its function as an adsorbent was not sufficiently exhibited. Notably, q_m was shown to be higher at the mass ratio of NaOH to CFA of 0.6 than at mass ratios of 0.9 and 1.2 in both adsorption cases of Sr^{2+} and Cs^+ and its q_m value was 147.6 mg/g and 160.2 mg/g, respectively. These results indicate that the zeolitic materials covered with homogeneous cubic crystals synthesized at the mass ratio of NaOH to CFA of 0.6 (Fig. 3(c)) can be a better adsorbent than those synthesized at mass ratios of 0.9 and 1.2 (Fig. 3(d) and (e)). The q_m values for Sr^{2+} and Cs^+ using natural zeolite (clinoptilolite) by the Langmuir model were calculated to 9.80 and 49.02 mg/g, respectively [1]. Consequently, the synthesized zeolitic material with a mass ratio of NaOH to CFA of 0.6 in this study could be a superior adsorbent for the aqueous removal of Sr^{2+} and Cs^+ .

Fig. 5. Adsorption isotherm results and model fittings for the adsorption of (a) Sr^{2+} and (b) Cs^+ using the zeolitic materials synthesized with the mass ratios of NaOH to CFA of 0.3-1.2 and commercial Z-CS (adsorbent dosage = 0.02 g/0.05 L).

Table 2. Adsorption Isotherm Parameters of Sr^{2+} and Cs^{+} Using the Zeolitic Materials Synthesized with the Mass Ratios of NaOH to CFA of 0.3-1.2 and Commercial Z-CS

Mass ratio	Ion	Langmuir model			Freundlich model		
		q_m (mg/g)	k_L (L/mg)	r^2	k_F (mg/g(L/mg) $^{1/n}$)	$1/n$	r^2
Z-CS	Sr^{2+}	226.5	1.3289	0.9864	99.6973	0.4845	0.6378
	Cs^{+}	134.3	0.1602	0.9759	19.0853	0.5665	0.8653
0.3	Sr^{2+}	16.9	0.0757	0.9765	3.3514	0.3361	0.9804
	Cs^{+}	17.9	0.0368	0.7950	1.3316	0.5400	0.9256
0.6	Sr^{2+}	147.6	0.8190	0.9886	51.8145	0.3288	0.8207
	Cs^{+}	160.2	0.1237	0.9915	20.3749	0.5343	0.9716
0.9	Sr^{2+}	123.6	0.4117	0.9982	31.1806	0.3958	0.8895
	Cs^{+}	136.5	0.1051	0.9966	14.9079	0.5652	0.9393
1.2	Sr^{2+}	132.2	0.9261	0.9966	48.6992	0.3065	0.8482
	Cs^{+}	124.9	0.1281	0.9977	17.1865	0.4989	0.9676

Fig. 6. Comparison of the adsorption capacities of Sr^{2+} and Cs^{+} by the prepared zeolitic materials and commercial Z-CS.

The q_m values of the zeolitic materials prepared with various mass ratios of NaOH to CFA and the commercial zeolite (Z-CS) are compared in Fig. 6. The q_m of the zeolitic material with a mass ratio of NaOH to CFA of 0.6 for Sr^{2+} (147.6 mg/g) was approximately 35% lower than that of the commercial Z-CS (226.5 mg/g), however, the q_m of the zeolitic material for Cs^{+} (160.2 mg/g) was higher than that of the Z-CS (134.3 mg/g). In a previous study on the adsorptive removal of Sr^{2+} and Cs^{+} using a Na-A zeolite synthesized from the CFA, the maximum adsorption capacity of the Na-A zeolite was reported to be 303.00 mg/g for Sr^{2+} and 207.47 mg/g for Cs^{+} [5]. Therefore, the zeolitic material synthesized from the CFA in this study seems to be an efficient adsorbent for the removal of Sr^{2+} and Cs^{+} . It can also be a cost-effective adsorbent through synthesis under low alkali conditions.

4. Conclusions

Zeolitic materials were successfully prepared from coal fly ash (CFA) via the fusion and hydrothermal method by changing the

mass ratio of NaOH to CFA. In the XRD and SEM analyses, the prepared zeolitic materials confirmed the morphological structure with highly crystalline particles covered with cubic crystals. Zeolitic materials with the XRD peak pattern of Na-A type zeolite could be synthesized at the mass ratios of NaOH to CFA of 0.6-1.2, and the zeolitic materials were covered with cubic crystals much more homogeneously at a mass ratio of NaOH to CFA of 0.6, which is a cost-effective, synthetic condition to synthesize zeolitic materials from CFA. The prepared zeolitic materials were used as adsorbents for the removal of Sr^{2+} and Cs^{+} in an aqueous solution. The experimental adsorption data for Sr^{2+} and Cs^{+} were described well by the Langmuir isotherm model, and the zeolitic material synthesized with the mass ratio of NaOH to CFA of 0.6 exhibited the highest maximum adsorption capacity (q_m) in both Sr^{2+} and Cs^{+} adsorption. Furthermore, the q_m of the prepared material with a mass ratio of 0.6 was even higher than that of the commercial Z-CS in Cs^{+} adsorption. As a result, it could be suggested that the zeolitic materials prepared from CFA through the fusion and hydrothermal method can be applied as an adequate for the removal of Sr^{2+} and Cs^{+} .

Acknowledgments

This paper was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2017R1D1A1B03030350) and by Research Fund offered from Catholic University of Pusan in 2018.

Author Contributions

J.H.C. (Professor) conducted the adsorption experiments and wrote the manuscript; C.H.L. (Professor) synthesized adsorbents, performed the adsorption experiments and wrote the manuscript.

References

- Smiciklas I, Dimovic S, Plecas I. Removal of Cs^{1+} , Sr^{2+} and

- Co²⁺ from aqueous solutions by adsorption on natural clinoptilolite. *Appl. Clay Sci.* 2007;35:139-144.
2. Wang M, Xu L, Peng J, Zhai M, Li J, Wei G. Adsorption and desorption of Sr (II) ions in the gels based on polysaccharide derivatives. *J. Hazard. Mater.* 2009;171:820-826.
 3. Munthali MW, Johan E, Aono H, Matsue N. Cs⁺ and Sr²⁺ adsorption selectivity of zeolites in relation to radioactive decontamination. *J. Asian Cera. Soc.* 2015;3:245-250.
 4. Vereshchagina TA, Vereshchagin SN, Shishkina NN, Vasilieva NG, Solovyov LA, Anshits AG. Microsphere zeolite materials derived from coal fly ash cenospheres as precursors to mineral-like aluminosilicate hosts for 135,137Cs and 90Sr. *J. Nucl. Mater.* 2013;437:11-18.
 5. El-Kamash AM. Evaluation of zeolite A for the sorptive removal of Cs⁺ and Sr²⁺ ions from aqueous solutions using batch and fixed bed column operations. *J. Hazard. Mater.* 2008;151:432-445.
 6. Lee CH, Park JM, Lee MG. Adsorption characteristics of Sr(II) and Cs(I) ions by zeolite synthesized from coal fly ash. *J. Environ. Sci. Int.* 2014;23:1987-1998.
 7. Gollakota ARK, Volli V, Shu CH. Progressive utilisation prospects of coal fly ash: A review. *Sci. Total Environ.* 2019;672:951-989.
 8. Bieseki L, Penha FG, Pergher SBC. Zeolite A synthesis employing a Brazilian coal ash as the silicon and aluminum source and its applications in adsorption and pigment formulation. *Mater. Res.* 2013;16:38-43.
 9. Wałek TT, Saito F, Zhang Q. The effect of low solid/liquid ratio on hydrothermal synthesis of zeolites from fly ash. *Fuel* 2008;87:3194-3199.
 10. Yang L, Qian X, Yuan P, et al. Green synthesis of zeolite 4A using fly ash fused with synergism of NaOH and Na₂CO₃. *J. Clean. Prod.* 2019;212:250-260.
 11. Ye Y, Zeng X, Qian W, Wang M. Synthesis of pure zeolites from supersaturated silicon and aluminum alkali extracts from fused coal fly ash. *Fuel* 2008;87:1880-1886.
 12. Khandaker S, Toyohara Y, Saha GC, Awual MR, Kuba T. Development of synthetic zeolites from bio-slag for cesium adsorption: Kinetic, isotherm and thermodynamic studies. *J. Water Process Eng.* 2020;33:101055.
 13. Lee MG, Park JW, Kam SK, Lee CH. Synthesis of Na-A zeolite from Jeju Island scoria using fusion/hydrothermal method. *Chemosphere* 2018;2017:203-208.
 14. Murayama N, Yamamoto H, Shibata J. Mechanism of zeolite synthesis from coal fly ash by alkali hydrothermal reaction. *Int. J. Miner. Process* 2002;64:1-17.
 15. Choi JH, Lee CH. Adsorption and desorption characteristics of Sr, Cs, and Na Ions with Na-A zeolite synthesized from coal fly ash in low-alkali condition. *J. Environ. Sci. Int.* 2019;28:561-570.
 16. Treacy MMJ, Higgins JB. Collection of simulated XRD powder patterns for zeolites. Elsevier: Amsterdam; 2001.
 17. Tanaka H, Fujii A. Effect of stirring on the dissolution of coal fly ash and synthesis of pure form Na-A and -X zeolites by two step process. *Adv. Powd. Tech.* 2009;20:473-479.
 18. Wang CF, Li JS, Wang LJ, Sun XY. Influence of NaOH concentrations on synthesis of pure-form zeolite A from fly ash using two-stage method. *J. Hazard. Mater.* 2008;155:58-64.
 19. Lagergren S. Zur theorie der sogenannten adsorption gelöster stoffe, Kungliga Svenska Vetenskapsakademiens. *Handlingar* 1898;24:1-39.
 20. Nibou D, Mekatel H, Amokrane S, Barkat M, Trari M. Adsorption of Zn²⁺ ions onto NaA and NaX zeolites: Kinetic, equilibrium and thermodynamic studies. *J. Hazard. Mater.* 2010;173:637-646.
 21. Awual MR, Hasan MM, Khaleque MA, Sheikh MC. Treatment of copper(II) containing wastewater by a newly developed ligand based facial conjugate materials. *Chem. Eng. J.* 2016;288:368-376.
 22. El-Rahman KMA, El-Sourougy MR, Abdel-Monem NM, Ismail IM. Modeling the sorption kinetics of cesium and strontium ions on zeolite A. *J. Nuclear Radiochem. Sci.* 2006;7:21-27.
 23. Langmuir I. The adsorption of gases on plane surface of glass, mica and platinum. *J. Am. Chem. Soc.* 1918;40:1361-1403.
 24. Freundlich HMF. Over the adsorption in solution. *J. Phys. Chem.* 1906;57:385-470.