

57 (2016) 29457–29466 December



Improved removal of Cd(II) from aqueous solution by synthesized nanozeolite

Thi-Huong Pham, Byeong-Kyu Lee*, Jitae Kim, Chi-Hyeon Lee

Department of Civil and Environmental Engineering, University of Ulsan, Daehakro 93, Nam-gu, Ulsan 680-749, Republic of Korea, email: phambary@gmail.com (T-H. Pham), Tel. +82 52 259 2864; Fax: +82 52 259 2629; emails: bklee@ulsan.ac.kr (B.-K. Lee), najitae 82@gmail.com (J. Kim), chibary782@naver.com (C.-H. Lee)

Received 16 December 2015; Accepted 5 February 2016

ABSTRACT

This study investigated the adsorption potential of synthesized nanozeolites for the removal of cadmium (Cd(II)) ions from aqueous solutions. The obtained adsorption results for Cd(II) removal indicate that the nanozeolites had higher surface area, pore volume, and adsorption capacity than commercial activated carbon (AC). The synthesized nanozeolites were well fitted with the Langmuir adsorption isotherm and the second-order reaction kinetic. Based on the Langmuir model, the maximum adsorption capacities of Cd(II) onto nanozeolite and AC were 189.6 and 171.2 mg/g at an optimum pH of 5.0, respectively. In the regeneration study of Cd(II)-loaded adsorbents, even after 10 cycles of adsorption–desorption, the identified desorption efficiencies of Cd(II) were 78.8 and 42.3% using nanozeolites and AC, respectively. Based on the adsorption characteristics of Cd(II), the synthesized nanozeolites could be utilized as a promising low-cost adsorbent for Cd(II) removal from water.

Keywords: Nanozeolite; Cd(II); Adsorption; Desorption

1. Introduction

Recently, heavy metals pollution has become the focus of much international attention, mainly because of the voluminous discharge into the environment from industrial activities. The primary threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury, and arsenic [1,2]. The presence of these heavy metals in the environment is of significant concern due to their toxicity and adverse health effects on humans and other living

creatures. Removing the toxic heavy metal contaminants from aqueous waste streams is one of the greatest matters of interest in the literature and studies.

Cadmium is one of the most toxic metals even in low concentrations. It is naturally produced in the environment and is a major contaminant. Cadmium is a particularly dangerous chemical as it can accumulate in individual organisms throughout the entire food chain [3–8]. Cadmium is classified as a human carcinogen and a teratogen agent impacting the lungs, kidneys, liver, and reproductive organs [9,10]. The primary source of cadmium pollution in wastewater is the discharge of waste from acid battery

^{*}Corresponding authors.

Presented at the 8th International Conference on Challenges in Environmental Science & Engineering (CESE-2015) 28 September–2 October 2015, Sydney, Australia

^{1944-3994/1944-3986 © 2016} Balaban Desalination Publications. All rights reserved.

manufacturing, metal plating, production of alkaline batteries, and electroplating. Some technologies and methods for heavy metal ion removal from wastewater have been developed, including ion exchange, evaporation and concentration, chemical precipitation, reverse osmosis, and adsorption [11–17]. From an economic and efficiency perspective, the adsorption method is regarded as one of the most promising and widely used methods due to its low operating costs, minimized sludge volumes, and high removal efficiencies of removal heavy metals [18,19].

Many adsorbent materials have been used for Cd (II) removal from contaminated water, such as activated carbon (AC), industrial and agricultural waste materials, nanomaterials (carbon nanotube and nanoscale iron) and polymers [20–24].

AC was first used to treat wastewaters and it is one of the most widely used adsorbents for removing heavy metals. However, its high regeneration cost poses an economical problem and there are a number of studies concerning the production of alternative adsorbents to replace AC. Many researchers have focused on various natural materials that are able to remove heavy metals from water [12,13,19]. Natural zeolites have attracted attention because they offer many advantages for removing heavy metals due to their valuable properties such as ion exchange and metals sorption capability [25-28]. Recent research interest in zeolites has been focused on different aspects in the synthesis of nanosized zeolites, which have favorable properties for adsorption. The surface area of nanocrystalline zeolites increase with decreasing particle size, which supports the application of nanozeolite for Cd(II) removal from industrial wastewaters.

The aim of the present study was to identify the adsorption characteristics of Cd(II) on mesoporous AC and nanozeolites in aqueous solutions. Characterization techniques including scanning electron micrographs (SEM), FTIR, and surface area (BET) were used to describe the nanozeolite synthesized and AC. In addition, the effects of varying adsorbent dosage, solution pH, and contact time were also investigated.

2. Material and methods

Nanozeolite was synthesized based on the facile sol-gel method, which was reported in previous studies. Nanozeolite was prepared by mixing of 0.35 g NaOH and 0.147 g sodium aluminate salt in H₂O and aging it for 5 h at 20°C with magnetic stirring. After 6.6 g of silica sol was added drop wise, the resulting mixture was stirred at room temperature for 12 h to give a homogenous mixture that was then heated for 24 h at 180°C under autogenously pressure. The solid product was centrifuged and washed with deionized water until its pH reached 4.0. After being dried at 120°C for 12 h, the material was used for characterization and adsorption experiments [25,29]. The commercial AC used in this study was purchased from Daejung Chemical and Metals Co. Ltd, South Korea.

All of the chemicals used in this study were analytical reagent grades (obtained from Daejung Chemical and Metals Co. Ltd, South Korea) and were used as received without further purification. Aqueous solutions of Cd(NO₃)₂ were prepared by dissolving Cd(NO₃)₂ (Merck) in deionized distilled water. The pH measurements were performed with a digital pH meter (Orion 5Star). The concentration of Cd(II) ions was measured using an atomic absorption spectrophotometer (VARIAN AA240) at $\lambda = 326.1$ nm with a slit width of 1 nm under an air-acetylene flame. Scanning electron micrographs (SEM Hitachi 4700 microscope) were taken for the surface morphology analysis of the nanozeolites and AC. Infrared spectra (Perkin-Elmer infrared spectrophotometer) were used to identify the functional groups of these adsorbents using a Nicolet Nexus 470 FTIR spectrometer in the $4,000-500 \text{ cm}^{-1}$ region in transmission mode and IR samples were prepared in the form of pellets with KBr at ambient conditions. The specific surface area and porosity measurements of the nanozeolites and AC were carried out using adsorption isotherms obtained from the Micromeritics BET ASTP 2010 surface area and a porosity analyzer 27 at 77 ± 0.5 K under gas nitrogen atmosphere as well as by using the BET equation.

2.2. Adsorption experiments

Batch experiments for adsorption studies to remove Cd(II) ions from aqueous solutions were performed in 250 mL Erlenmeyer flasks, which were agitated in a shaking water bath (HST-205SW) at 120 rpm and room temperature of 20 ± 1 °C. After adsorption experiments, the samples were taken out, and filtered using Whatman 45 filter paper. The concentration of Cd(II) ions was measured using an atomic absorption spectrophotometer (VARIAN AA240) at $\lambda = 326.1$ nm.

The equilibrium Cd(II) uptake capacity was calculated using the following Eq. (1):

$$q_{\rm e} = [C_{\rm o} - C_{\rm e}] \times \frac{V}{W} \tag{1}$$

where q_e is the amount of Cd(II) adsorbed (mg/g) on the adsorbent, C_o is the initial concentration of Cd(II) (mg/L), C_e is the equilibrium concentration of Cd(II)

29459

in solution (mg/L), *V* is the volume of the solution used (L), and *W* (g) is the weight of the adsorbent used. The removal efficiency of Cd(II) ions (*R* %) by the nanozeolites in the aqueous solution was calculated using the following Eq. (2):

$$R \% = \frac{(C_{\rm o} - C_{\rm e})}{C_{\rm o}} \times 100$$
 (2)

2.2.1. Optimum adsorbent dose

To optimize the adsorption conditions, 0.1-0.10 g of the adsorbents (AC and nanozeolite) were shaken with 200 mL of solution containing 200 mg/L Cd(II) ions.

2.2.2. Optimization of pH

In order to evaluate the effect of pH on Cd(II) uptake by nanozeolite and AC, we adjusted the pH of the experimental solutions from 2.0 to 7.0. The solution pH values were adjusted to the required values with 0.1 M HNO₃ and 0.1 M NaOH. Solutions containing initial concentrations of 200 mg/L of Cd(II) ions and 0.5 g of adsorbent were used to determine the optimal pH.

2.2.3. Optimization of contact time

Adsorption experiments were performed in 100 mL of a solution of 200 mg/L Cd(II) and the contact time was varied from 10 to 300 min. After adsorption for a given reaction time, the concentration of Cd (II) remaining in the solution was analyzed.

2.2.4. Optimization of Cd(II) initial concentration

Batch tests were conducted at different initial concentrations of Cd(II) ions ranging from 10 to 1,000 mg/L with an adsorbent dose of 0.5 g and a reaction time of 150 min.

2.3. Adsorption isotherm

Isotherm studies were performed using different concentrations of Cd(II) ions (10-1,000 mg/L) at 20° C ± 1. To simulate adsorption isotherms, two commonly used models, the Langmuir and Freundlich isotherms were selected for use in this study.

2.3.1. Langmuir isotherm

The Langmuir isotherm is valid for monolayer sorption due to its surface, which has a finite number of identical sites that can be expressed as follows (Eq. (3)):

$$\frac{C_{\rm e}}{q_{\rm e}} = \frac{1}{bQ_{\rm max}} + \frac{1}{C_{\rm e}Q_{\rm max}} \quad \text{(Linear form)} \tag{3}$$

where q_e is the equilibrium adsorbate loading on the adsorbent (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), Q_{max} is the maximum adsorption capacity (mg/g) representing the monolayer adsorption capacity, and *b* is the relative energy (intensity) of adsorption, also known as the binding constant (L/mg).

In particular, the Langmuir isotherm can be explained with a dimensionless constant separation factor or equilibrium parameter R_L , which is defined by the following equation:

$$R_{\rm L} = \frac{1}{1 + bC_{\rm o}} \tag{4}$$

where *b* is the Langmuir constant (L/mg) and C_o is the initial concentration of Cd(II) (mg/L).

A value of $0 < R_L < 1$ indicates that it is a favorable adsorption process, while $R_L > 1$ shows that it is an unfavorable adsorption, $R_L = 1$ means linear adsorption, and $R_L = 0$ signifies irreversible adsorption.

2.3.2. Freundlich isotherm

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The linearized form of the Freundlich equation is as follows (Eq. (5)):

$$\ln q_{\rm e} = \ln K_{\rm F} + \frac{1}{n} \ln C_{\rm e} \quad (\text{Linear form}) \tag{5}$$

where q_e is the amount of Cd(II) adsorbed per unit of adsorbent at the time of equilibrium (mg/g), C_e is the equilibrium concentration of Cd(II) in solution (mg/L), and K_F ((mg/g) (L/mg)^{1/n}) and *n* are isotherm constants for the capacity and intensity of adsorption, respectively.

2.4. Desorption and reuse of adsorbents

0.5 g adsorbents were poured into 100 mL Cd(II) ion solution (200 mg/L) and agitated for 150 min.

Then, these adsorbents loaded with Cd(II) ions were poured into 100 mL EDTA solutions (0.5 M) for desorption of the adsorbed Cd. These procedures were repeated, producing ten consecutive sorption and desorption cycles. The percentage of desorption was calculated with the following Eq. (6):

% Desorption =
$$\frac{(C_e - C_d)}{C_e} \times 100$$
 (6)

where C_d (mg/L) represents the final Cd(II) ions concentration identified in the desorption medium. After desorption, the nanozeolites and AC were washed with distilled water and reused for another adsorption cycle.

3. Results and discussion

3.1. SEM analysis

The SEM images of the nanozeolites and AC are shown in Fig. 1(A) and (B). It can be observed that the surface morphology of the nanozeolites with a tetrahedral structure was different from that of the AC. The surface morphology of nanozeolites exhibited particle sizes around 90–100 nm, which was composed of very small nanocrystals. However, the surface morphology of AC appeared to contain mainly flat multilayers with a small number of pores.

3.2. FTIR analysis

FTIR spectra were used to investigate the functional groups present in the nanozeolites and AC. Figs. 2A and 2B shows the FTIR spectra of the nanozeolites and AC in the range of 500–4,500 cm⁻¹. The characteristic peaks of nanozeolites with tetrahedral rings were observed at the

wavenumber of 550–580 cm⁻¹ [33]. A strong peak around the wavenumber of 1,000 cm⁻¹ represented the Si-O stretch. The small peaks around the wavenumber of 1,650 cm⁻¹ are linked to the adsorbed water in the nanozeolites. The broad band range from 3,320 to $3,600 \text{ cm}^{-1}$ can be assigned to the O–H stretching vibrations of the hydrogen-bonded molecules. The broad stretch in this wavenumber range is attributed to the loosely bound water molecules hydrogen-bonded Si-OH groups in nest defects produced by vacancies of Al in the zeolite structure. In the FTIR spectra of AC, the wide band located in the range of 3,200–3,450 cm⁻¹ was identified as the stretch peak of hydroxyl groups associated with hydrogen bonding. The band at $1,630 \text{ cm}^{-1}$ was an indicative peak for the stretching vibration of C=O bonds associated with carboxylic acids or esters present in the AC. The band at approximately 2,900 cm⁻¹ corresponded to a C-H vibration, while a band at $1,158 \text{ cm}^{-1}$ was assigned to a C-O vibration.

3.3. BET analysis

Table 1 presents the BET analysis results for the nanozeolites and AC. The specific surface area (698.19 m²/g) of the nanozeolites was even higher than that of AC (680.68 m²/g). However, the pore sizes of the nanozeolites and AC were 3.07 and 1.12 nm, respectively. The increased pore size of the nanozeolites also facilitates adsorption because the large Cd(II) molecules would be able to bind to the adsorption site of the nanozeolites more easily, leading to improved adsorption capacity of Cd(II) as compared with AC.

3.4. Effect of adsorbent dose

Adsorbent dosage is also an important parameter because it determines the capacity of an adsorbent for



Fig. 1. SEM images of nanozeolite (A) and AC (B).



Fig. 2A. FTIR spectrum of AC.



Fig. 2B. FTIR spectrum of nanozeolite.

a given initial concentration of the adsorbate. The effect of adsorbent dose on the adsorption of Cd(II) ions by nanozeolites and AC were studied using different doses in the range of 0.1-1.0 g (see in Fig. 3). When the dose was increased from 0.1 to 0.7 g, the adsorption removal efficiency of Cd(II) increased from 18 to 92% and from 20 to 98% for AC and nanozeolites, respectively.

Any further increase in the dose only negligibly increased the sorption. In general, a higher adsorbent dose increases the availability of adsorption sites and hence the adsorption of adsorbates. However, some of the adsorption sites may be blocked at high adsorbent doses. Thus, the optimum dose for Cd(II) removal using nanozeolites and AC was around 0.6–0.7 g.

3.5. Effect of solution pH

Solution pH is an important parameter in adsorption process as it is capable of influencing the adsorption process due to changes in the surface charge of the adsorbent used. The effect on the adsorption of Cd(II) using nanozeolites and AC was investigated in the pH range of 2.0-7.0. Adsorption of Cd(II) at pH values greater than 7.0 was avoided due to the presence of insoluble cadmium hydroxide precipitates in the solution. Fig. 4 shows the effect of pH on the adsorption removal efficiency of Cd(II) using nanozeolites and AC adsorbents. It can be seen that the adsorption removal efficiency of Cd(II) by nanozeolites and AC increased with increasing pH under pH conditions ranging from 2.0 to 5.0 but decreased after pH 5.0. The maximum removal efficiency of Cd(II) was 92 and 96% for AC and nanozeolites at pH 5.0, respectively. Conversely, at lower pH values ranging from 2.0 to 3.0, the lower adsorption of Cd(II) was attributed to the competition between H⁺ and Cd(II) ions on active sites of the adsorbent surface, which weakened the adsorption capacity of Cd(II) onto the surface of the adsorbents. With higher pH values ranging from 4.0 to 5.0, the concentration of available H⁺ ions in the solution decreased dramatically, resulting in less competition between the Cd(II) and H⁺ ions for more negative charges on the adsorbent surface as compared with the lower pH range of 2.0-3.0. However, the surface of the nanozeolite and AC has the points of zero charge (pH_{pzc}) at pH 4.91 and 4.68, respectively.

It starts to build a partial negative charge at pH higher than pH_{pzc} and the decrease in proton concentration with increasing pH could increase the electrostatic attraction between the negative charged surface of the adsorbent and the positive charge of adsorbed, thus increasing the removal efficiency.

Table 1 Surface area and pore volume of nanozeolite and AC

Materials	$S_{\rm BET}~({\rm m}^2/{\rm g})$	V pores (cm ³ /g)	Pore size (nm)	
Nanozeolite	698.19	0.0369	3.07	
AC	680.68	0.0287	1.12	



Fig. 3. Effect of adsorbent dose.



Fig. 4. Effect of solution pH.

Over pH 5.0, the increase in the solution pH produces more OH⁻, which could compete with active negative or nonbonding sites on the adsorbent surfaces for Cd(II) adsorption [30]. Thus, fewer Cd(II) ions would be adsorbed onto the active sites of the adsorbent. Therefore, pH 5.0 was selected as the optimum solution pH for Cd(II) removal.

3.6. Effect of contact time

Fig. 5 shows the effect of different contact times, ranging from 10 to 300 min, on the adsorption of Cd (II) by nanozeolites and AC at the solution pH of 5.0. The adsorption of Cd(II) ions onto the nanozeolites and AC was rapid and nearly complete after 120 min, at 88.44 and 97.68%, respectively. As time elapsed, little further adsorption was achieved until 300 min,



Fig. 5. Effect of contact time.

specifically, 89.24 and 98.48% of Cd(II) removal by AC and nanozeolites, respectively. The Cd(II) adsorption rate was high at the beginning of the adsorption experiment (the first stage: 30–120 min) because a greater number of adsorption sites was initially available for Cd(II) adsorption. After the surface or the pores of the adsorbent was blocked by adsorbed Cd, the remaining vacant surface sites had low availability for further Cd(II) adsorption or removal. This is because of repulsion among the Cd(II) molecules adsorbed on the adsorbent surface and those in the bulk phase, leading to slow adsorption of the adsorbate. The Cd(II) adsorption equilibrium appeared to be reached within 120 min.

3.6.1. Adsorption kinetics

Adsorption kinetics is one of the most important datasets for elucidating the removal/adsorption mechanism of Cd(II) ions and assessing the adsorption performance of the adsorbents. Two kinetic models, namely the pseudo-first-order and pseudo-secondorder models, were applied to the experimental data to predict the adsorption kinetics.

The pseudo-first-order equation assumes that the solute uptake rate is directly proportional to the difference between saturation concentration and the uptake amount of Cd(II) ions with time.

From Table 2, it can be observed that there were a lager difference in the adsorption equilibrium capacities between the calculation values (12.88 and 21.96 mg/g using nanozeolite and AC, respectively) and the experimental data (48.30 and 49.02 using nanozeolite and AC, respectively). However, the pseudo-first-order model provided a poor fit ($R^2 = 0.74 - 0.69$ by the nanozeolites and AC) for the

	First-order kinetic model			Second-order kinetic model			
Adsorbent	q _{e,exp} (mg∕g)	q _{e,cal} (mg∕g)	R^2	k_1	q _{e,cal} (mg∕g)	R^2	<i>k</i> ₂
Nanozeolite AC	48.30 49.02	12.88 21.96	0.74 0.69	$\begin{array}{c} 2.48 \times 10^{-2} \\ 1.79 \times 10^{-2} \end{array}$	47.73 49.52	0.98 0.99	1.63×10^{-3} 1.04×10^{-3}

Comparison of the first- and second-order adsorption rate constants and calculated and experimental qe values of Cd(II)

Note: exp and cal stand for experimental and calculated, respectively.

experimental data obtained. These results represent the adsorption data are not following by the firstorder kinetic model.

The calculation of Cd(II) adsorption capacities by using nanozeolite and AC based on the second-order kinetic were 47.73 and 49.52, respectively. Also, the experimental data was perfectly fitted to the pseudo-second order kinetic model, with high R^2 -values of 0.98 and 0.99 for nanozeolites and AC, respectively. These results indicate that the adsorption of Cd(II) by the nanozeolite and AC from the aqueous solution followed the second-order kinetic model rather than the first-order model [24,30].

3.7. Effect of initial concentration

Table 2

In this study, the effects of initial Cd(II) ion concentration on the adsorption capacity of nanozeolites and AC were determined by varying the initial Cd(II) concentration between 10 and 1,000 mg/L. The removal efficiency decreased with the increase in the initial Cd(II) concentration range of 10-1,000 mg/L. The concentration of Cd(II) ions reached saturation at around 300 mg/L. At low initial concentrations below 300 mg/L of Cd(II) ions, the surface areas and the adsorption sites available for Cd(II) removal were relatively high and thus the Cd(II) ions were easily adsorbed and removed. At high initial concentrations of Cd(II) ions (above 300 mg/L), the removal efficiency of Cd(II) using nanozeolites and AC were significant decreased and the removal efficiency of Cd(II) tended to be constant. These results indicate that all of the sites for active adsorption for a given amount of the adsorbent were fully adsorbed by Cd(II) ions. This behavior can be attributed to an increasing degree of saturation sorbent sites above a certain concentration of Cd(II) ions. Increases in the ratio of Cd(II) ions/adsorbents cause the saturation of binding sites on the adsorbent surface, resulting in decreased adsorption efficiency for Cd(II) ions onto the adsorbents. The identified removal efficiency of Cd(II) by the nanozeolites range of (98.7-24.19% with initial concentration from 10 to 1,000 mg/L) were higher than that by AC (96.3–20.06% with the same condition). The result of FTIR analysis indicated that the nanozeolites had substantially more hydroxyl functional groups than AC, which is a favorable condition for removing Cd(II) ions from aqueous solutions. The nanozeolites also had high surface area and pore size compared with AC, leading to more adsorption on the Cd(II) ions (Fig. 6).



Fig. 6. Effect of initial Cd(II) concentration.



Fig. 7. Values of the equilibrium parameter $R_{\rm L}$ for the Langmuir isotherm.

Adsorbent	Langmuir isothe	Langmuir isotherm			Freundlich isotherm		
	$q_{\rm max} ({\rm mg}/{\rm g})$	<i>b</i> (L/mg)	R^2	1/n	$K_{\rm F} (({\rm mg/g}) ({\rm L/mg})^{1/n})$	R^2	
Nanozeolite	189.25	0.034	0.99	0.39	4.02	0.89	
AC	171.62	0.068	0.98	0.35	3.38	0.88	

Langmuir and Freundlich adsorption isotherms for adsorption of Cd(II) on nanozeolite and AC

3.7.1. Adsorption isotherms

Two adsorption isotherm models, the Langmuir and Freundlich isotherms, were used to investigate the adsorption systems. In general, an adsorption isotherm model is distinguished by the respective parameters that indicate the affinity and surface properties of the particular adsorbent used. Table 3 shows the parameters for each adsorption isotherm. The Langmuir isotherm model is based on the assumption that all adsorption sites are alike and equally energetic, making the surface homogeneous. The Langmuir constant (Q_{max}) represents monolayer saturation at equilibrium when the adsorbent surface is covered by Cd (II) molecules and helps to explain the adsorption performance. The Langmuir adsorption model provided the best fit for the experimentally determined data with respect to the adsorption of Cd(II) ions (R^2 ranging from 0.999 to 0.998). However, the correlation between the Freundlich isotherm, a heterogeneous adsorption system ($R^2 = 0.898 - 0.889$), and the experimental data for Cd(II) removal was much lower than that of the Langmuir isotherm. This indicates that Cd(II) removal by the adsorbents (nanozeolites and AC) better followed the Langmuir isotherm, a monolayer equilibrium system. The values of $R_{\rm L}$ (see in



Fig. 8. Adsorption-desorption cycles.

Fig. 7) for the adsorption of Cd(II) were found to be between 0 and 1, and these data also fit reasonably well with the Langmuir isotherm in the adsorption studies. This result implies a monolayer adsorption of Cd(II) on the nanozeolite and AC. This can be explained by the fact that nanozeolite and AC have high surface area (Table 1), and high monolayer sorption occurs on adsorbent surfaces.

From the fitting of experimental data using the Langmuir isotherm, the obtained maximum adsorption capacity of Cd(II) was (189.25 mg/g) and (171.62 mg/g) using nanozeolites and AC, respectively.

3.8. Adsorption-desorption cycles

Recovery of Cd(II) ions from the loaded adsorbent is an important characteristic for proper disposal and reuse of adsorbents. In order to minimize the cost of the entire recovery process, the adsorbed Cd(II) needs to be desorbed and the adsorbent should then be regenerated for further adsorption-desorption cycles. In this study, 0.5 M EDTA was chosen as the desorption medium for the Cd-loaded adsorbents. Fig. 8 shows the desorption efficiencies of Cd(II) ions from Cd(II)-loaded nanozeolites and AC using 0.5 M EDTA. After 10 cycles (adsorption-desorption), the desorption efficiency of Cd(II) ions was 78.86 and 42.34% from the nanozeolites and AC, respectively. Even after 10 consecutive cycles, the adsorbents retained stable phases and the adsorption capacity of Cd(II) ions decreased by 34.07 and 19.84% from the initial adsorption capacity for AC and nanozeolites, respectively. The decreased adsorption uptake of the nanozeolites was relatively low compared with AC, indicating that nanozeolites can be a good adsorbent for the removal of Cd(II) from water with high uptake rates and great usability.

4. Conclusion

The synthesized nanozeolites were successfully used to remove Cd(II) from an aqueous solution. The adsorption data were well described by the Langmuir

Table 3

isotherm model. The identified maximum adsorption capacity of Cd(II) by nanozeolites was 189.25 mg/g based on the Langmuir isotherm. The regeneration process showed that, even after 10 adsorption–desorption cycles, the desorption efficiency of Cd(II) by the nanozeolites was 78.86%. The adsorbents retained stable phases and the adsorption capacity of Cd(II) ions decreased by only 19.84% from the initial adsorption capacity for the nanozeolites. The high adsorption capacity of the nanozeolites indicates its utility as a cost-effective alternative sorbent for expensive AC for water purification of Cd-contaminated wastewaters.

Acknowledgment

This work (C0193571) was supported by the Business for Cooperative R&D between Industry, Academy, and Research Institute funded by the Korea Small and Medium Business Administration in 2014.

References

- [1] K. Ji, J. Kim, M. Lee, S. Park, H.J. Kwon, H.K. Cheong, J.Y. Jang, D.S. Kim, S. Yu, Y.W. Kim, K.Y. Lee, S.O. Yang, I.J. Jhung, W.H. Yang, D.H. Paek, Y.C. Hong, K. Choi, Assessment of exposure to heavy metals and health risks among residents near abandoned metal mines in Goseong, Korea, Environ. Pollut. 178 (2013) 322–328.
- [2] C. Luo, C. Liu, Y. Wang, X. Liu, F. Li, G. Zhang, X. Li, Heavy metal contamination in soils and vegetables near an e-waste processing site, south China, J. Hazard. Mater. 186(1) (2011) 481–490.
- [3] T.G. Ammari, Utilization of a natural ecosystem biowaste; leaves of Arundo donax reed, as a raw material of low-cost eco-biosorbent for cadmium removal from aqueous phase, Ecol. Eng. 71 (2014) 466–473.
- [4] H. Benhima, M. Chiban, F. Sinan, P. Seta, M. Persin, Removal of lead and cadmium ions from aqueous solution by adsorption onto micro-particles of dry plants, Colloids Surf., B 61 (2008) 10–16.
- [5] Y. Ding, D. Jing, H. Gong, L. Zhou, X. Yang, Biosorption of aquatic cadmium(II) by unmodified rice straw, Bioresour. Technol. 114 (2012) 20–25.
- [6] D. Obregón-Valencia, M.dR. Sun-Kou, Comparative cadmium adsorption study on activated carbon prepared from aguaje (*Mauritia flexuosa*) and olive fruit stones (*Olea europaea* L.), J. Environ. Chem. Eng. 2(4) (2014) 2280–2288.
- [7] T. Dong, L. Yang, M. Zhu, Zh Liu, X. Sun, J. Yu, H. Liu, Removal of cadmium(II) from wastewater with gas-assisted magnetic separation, Chem. Eng. J. 280 (2015) 426–432.
- [8] Y. Liu, T. Xiao, Z. Ning, H. Li, J. Tang, G. Zhou, High cadmium concentration in soil in the Three Gorges region: Geogenic source and potential bioavailability, Appl. Geochem. 37 (2013) 149–156.

- [9] R.A. Anayurt, A. Sari, M. Tuzen, Equilibrium, thermodynamic and kinetic studies on biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Lactarius scrobiculatus*) biomass, Chem. Eng. J. 151(1–3) (2009) 255–261.
- [10] D. Alidoust, M. Kawahigashi, S. Yoshizawa, H. Sumida, M. Watanabe, Mechanism of cadmium biosorption from aqueous solutions using calcined oyster shells, J. Environ. Manage. 150 (2015) 103–110.
- [11] J. Song, H. Kong, J. Jang, Adsorption of heavy metal ions from aqueous solution by polyrhodanine-encapsulated magnetic nanoparticles, J. Colloid Interface Sci. 359(2) (2011) 505–511.
- [12] G. Venkatesan, U. Senthilnathan, S. Rajam, Cadmium removal from aqueous solutions using hybrid eucalyptus wood based activated carbon: Adsorption batch studies, Clean Technol. Environ. Policy 16(1) (2014) 195–200.
- [13] A.F. Fouladi Tajar, T. Kaghazchi, M. Soleimani. Adsorption of cadmium from aqueous solutions on sulfurized activated carbon prepared from nut shells, J. Hazard. Mater. 165(1–3) (2009) 1159–1164.
- [14] M. Savasari, M. Emadi, M.A. Bahmanyar, P. Biparva, Optimization of Cd(II) removal from aqueous solution by ascorbic acid-stabilized zero valent iron nanoparticles using response surface methodology, J. Ind. Eng. Chem. 21 (2015) 1403–1409.
- [15] D. Mohan, C.U. Pittman Jr., M. Bricka, F. Smith, B. Yancey, J. Mohammad, P.H. Steele, M.F. Alexandre-Franco, V. Gómez-Serrano, H. Gong, Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production, J. Colloid Interface Sci. 310(1) (2007) 57–73.
- [16] M. Ahmad, A.U. Rajapaksha, J.E. Lim, M. Zhang, N. Bolan, D. Mohan, M. Vithanage, S.S. Lee, Biochar as a sorbent for contaminant management in soil and water: A review, Chemosphere 99 (2014) 19–33.
- [17] J. Sun, F. Lian, Z. Liu, L. Zhu, Z. Song, Biochars derived from various crop straws: Characterization and Cd(II) removal potential, Ecotoxicol. Environ. Saf. 106 (2014) 226–231.
- [18] H. Yaacoubi, O. Zidani, M. Mouflih, M. Gourai, S. Sebti, Removal of cadmium from water using natural phosphate as adsorbent, Proc. Eng. 83 (2014) 386–393.
- [19] F.Y. Wang, H. Wang, J.W. Ma, Adsorption of cadmium(II) ions from aqueous solution by a new lowcost adsorbent—Bamboo charcoal, J. Hazard. Mater. 177(1–3) (2010) 300–306.
- [20] M. Irani, A.R. Keshtkar, M.A. Moosavian, Removal of cadmium from aqueous solution using mesoporous PVA/TEOS/APTES composite nanofiber prepared by sol–gel/electrospinning, Chem. Eng. J. 200–202 (2012) 192–201.
- [21] M. Ajmal, R.A.K. Ali Khan Rao, S. Anwar, J. Ahmad, R. Ahmad, Adsorption studies on rice husk: Removal and recovery of Cd(II) from wastewater, Bioresour. Technol. 86 (2003) 147–149.
- [22] M.E. Argun, S. Dursun, M. Karatas, M. Gürü, Activation of pine cone using Fenton oxidation for Cd(II) and Pb(II) removal, Bioresour. Technol. 99 (2008) 8691.
- [23] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water Res. 33 (2008) 2469–2479.

29466

- [24] T.H. Pham, L. Byeong-Kyu, K. Jitae, L. Chi-Hyeon, N.Ch. Meng, Acid activation pine cone waste at diffrences temperature and selective removal of Pb²⁺ ions in water, Process Saf. Environ. Prot. 100 (2016) 80–90.
- [25] O.A. Abdel Moamen, I.M. Ismail, N. Abdelmonem, R.O. Abdel Rahman. Factorial design analysis for optimizing the removal of cesium and strontium ions on synthetic nano-sized zeolite, J. Taiwan Inst. Chem. Eng. 55 (2015) 133–144.
- [26] P. Šharma, M. Sharma, R. Tomar, Na-HEU zeolite synthesis for the removal of Th(IV) and Eu(III) from aqueous waste by batch process, J. Taiwan Inst. Chem. Eng. 44 (2013) 480–488.
- [27] D. Novembre, B. Di Sabatino, D. Gimeno, M. Garcia-Vallès, Synthesis of Na–X zeolites from tripolaceous deposits (Crotone, Italy) and volcanic zeolitised

rocks (Vico volcano, Italy), Microporous Mesoporous Mater. 75 (2004) 1–11.

- [28] H. Liu, S. Peng, L. Shu, T. Chen, T. Bao, R.L. Frost, Magnetic zeolite NaA: Synthesis, characterization based on metakaolin and its application for the removal of Cu²⁺, Pb²⁺, Chemosphere 91 (2013) 1539–1546.
- [29] M. Abrishamkar, A. Izadi, Nano-ZSM-5 zeolite: Synthesis and application to electrocatalytic oxidation of ethanol, Microporous Mesoporous Mater. 180 (2013) 56–60.
- [30] J.S. Kwon, S.T. Yun, J.H. Lee, S.O. Kim, H.Y. Jo, Removal of divalent heavy metals (Cd, Cu, Pb, and Zn) and arsenic(III) from aqueous solutions using scoria: Kinetics and equilibria of sorption, J. Hazard. Mater. 174(1–3) (2010) 307–313.