Simultaneous removal of aqueous Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$ by zeolites synthesized from low-calcium and high-calcium fly ash

X. D. Ji, Y. Y. Ma, S. H. Peng, Y. Y. Gong and F. Zhang

ABSTRACT

In this study, zeolites were synthesized from low-calcium (LCZ) and high-calcium (HCZ) fly ash, respectively. Subsequently, the zeolites were tested for their removal effectiveness for four aqueous cations, namely, Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$, as a function of contact time, pH value, adsorbent dosage, and initial concentration of heavy metals. Both zeolites were characterized by X-ray diffraction, X-ray fluorescence spectrometry, scanning electron microscopy, specific surface area, and cation exchange capacity. The results show that HCZ mainly consists of an unnamed zeolite (Na$_{6}$[AlSiO$_{4}$]$_{6}$·4H$_{2}$O), whereas LCZ mainly consists of faujasite-type zeolite. The optimum sorption conditions were pH = 6.0, adsorbent dosage = 1.0 g·L$^{-1}$; temperature = 25 °C; contact time = 100 min; and initial heavy metal concentration = 100 mg·L$^{-1}$. The sorption kinetics of the four aqueous cations on both LCZ and HCZ followed the pseudo-second-order kinetic model, and the sorption isotherm data fitted well with the Langmuir isotherm model. For LCZ, the maximum adsorption capacities of Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$ were 155.76, 197.86, 123.76, and 186.22 mg·g$^{-1}$, respectively. For HCZ, the values were 154.08, 183.15, 118.91, and 191.94 mg·g$^{-1}$, respectively. The zeolites were regenerated by NaCl solution (1 mol·L$^{-1}$) and showed high removal efficiency. In conclusion, zeolites produced by fly ash are promising materials for removing Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$ from wastewater.

Key words | adsorption, heavy metal, high-calcium fly ash, low-calcium fly ash, synthesized zeolite, wastewater

INTRODUCTION

Heavy metals are among the toxic contaminants in the environment that cause the most concern. These contaminants are mainly generated from metal plating, sewage sludge, mining operations, fertilizer industries, batteries, paper industries, etc., and pose hazards to the environment and human health. Wastewater from these industries normally contains zinc, copper, cadmium, and lead. The conventional methods available to remove heavy metals from wastewater include ion exchange (Kang et al. 2004; Kolodytyska et al. 2017), adsorption (Jusoh et al. 2007; Wang et al. 2007a, 2015; Kang et al. 2008), coagulation–flocculation (El Samrani et al. 2008; Teh et al. 2016), chemical precipitation (Ku & Jung 2001; Chen et al. 2009), flotation (Polat & Erdogan 2007; Albuquerque et al. 2012), and the electrochemical method (Wang et al. 2007b; Cui et al. 2015). Among these, the adsorption technique is the preferable approach because of its low cost, high efficiency, ease of operation, and potential for large-scale application.

Fly ash is a by-product from coal combustion in power plants. Globally, over 750 million tonnes of fly ash is generated annually (Blissett & Rowson 2012), and the annual average utilization is estimated at 25% (Wang 2008). The remaining fly ash disposed in landfill not only occupies a large amount of land but also poses an increasing threat to the environment because of its fine structure and toxic compositions. One of the economically feasible solutions to this problem is to utilize fly ash for the synthesis of zeolite because of its high contents of silica and alumina (Shigomoto et al. 1993; Amrhein et al. 1996; Chang & Shih 1998; Hollman et al. 1999). Two methods are commonly used for synthesizing zeolite from fly ash, namely, the hydrothermal and fusion methods (Querol et al. 2002). The conventional hydrothermal method usually results in zeolite containing...
some fly ash residue, which could limit the adsorption capacity (Wang et al. 2009b). The fusion method includes an alkaline fusion stage before the hydrothermal process, and it can obtain zeolites that have more purity and a higher cation exchange capacity (CEC) (Shigomoto et al. 1993), and, therefore, a greater adsorption capacity for heavy metal in wastewater. Javadian et al. (2015) studied the adsorption behavior of Cd\(^{2+}\) from aqueous solution with zeolite synthesized from coal fly ash by employing the fusion method. These authors found that the adsorption kinetics followed the pseudo-second-order kinetic model, and the adsorption isotherm data fitted well with the Langmuir isotherm model, with a maximum sorption capacity of 26.25 mg·g\(^{-1}\). The sorbents were regenerated by NaOH, with a maximum desorption efficiency of 84%. Another study (Apiratikul & Pavanant 2008) compared the sorption process of Cu\(^{2+}\), Cd\(^{2+}\), and Pb\(^{2+}\) in a single-ion system with zeolite X synthesized from coal fly ash by using the fusion method. These authors found that the sorption kinetic data fitted the pseudo-second-order kinetic model well. The Langmuir and Dubinin–Radushkevich isotherms fitted the equilibrium sorption data well. The maximum adsorption capacity followed the order of Pb\(^{2+}\) (420.21 mg·g\(^{-1}\)) > Cd\(^{2+}\) (97.44 mg·g\(^{-1}\)) > Cu\(^{2+}\) (91.52 mg·g\(^{-1}\)). Izidoro et al. (2013) compared the adsorption behavior of Zn\(^{2+}\) and Cd\(^{2+}\) in single and binary systems with synthesized pure zeolites X and A from Brazilian fly ash with the fusion method. These authors discovered that Zn\(^{2+}\) was more easily adsorbed by zeolites than Cd\(^{2+}\). The adsorption capacity for zinc and cadmium was of the range 156–220 mg·g\(^{-1}\) and 57–195 mg·g\(^{-1}\), respectively. The adsorption effectiveness of zeolite A was less affected by the presence of competitive cations compared with zeolite X. The performance of synthetic zeolites was influenced by the fly ash properties. For instance, Zhang et al. (2011b) discovered that zeolite synthesized from low-calcium fly ash was more efficient for aqueous ammonium removal compared to zeolite synthesized from high-calcium fly ash.

Numerous studies have been conducted on the removal of a single heavy metal by synthesized zeolites (Apiratikul & Pavanant 2008; Li et al. 2014; Javadian et al. 2015); however, the real wastewater is usually a mixture of multiple heavy metal ions. The treatment method that could be used for effective removal of multiple heavy metals has not been widely investigated (Visa 2016). This study aims to explore the effectiveness of two types of synthesized zeolites from a waste material (low-cadmium and high-cadmium fly ashes) to remove Cu\(^{2+}\), Pb\(^{2+}\), Zn\(^{2+}\), and Cd\(^{2+}\) simultaneously from aqueous solutions. X-ray powder diffraction (XRD) analysis, X-ray fluorescence (XRF) spectrometry, scanning electron microscopy (SEM), specific surface area (SSA), and CEC tests were carried out to characterize the produced zeolites. The effects of the pH value, adsorbent dosage, contact time, and initial heavy metal concentration were tested to determine the optimal sorption conditions. In addition, adsorbent regeneration was studied for recycling applications.

**MATERIALS AND METHODS**

**Preparation of zeolites**

The low-calcium (LFA) and high-calcium (HFA) fly ash used in this study were obtained from a power plant located in the Hebei Province of China. The typical chemical compositions of the fly ash are listed in Table 1. An alkaline fusion method followed by hydrothermal treatment was adopted for the synthesis of zeolites (Shigomoto et al. 1993). In brief, 10 g of the fly ash was mixed with 12 g of NaOH powder (analytical reagent grade) and calcined in a nickel crucible at 600 °C for 3 h. The solids were then ground and poured into a flask, followed by the addition of distilled water to form a mixture containing 17.25% solids (w/w). The mixture was stirred for 2 h at 80 °C to form an aluminosilicate gel, and was subsequently poured into a stainless alloy autoclave and crystallized in an oven at 100 °C for 9 h. After the crystallization process, the precipitated samples were extracted and washed with distilled water until the pH of the samples was 8 to 9. Finally, the resultant samples were dried at 100 °C for 12 h in an oven and sieved through a 100 mesh (<150 μm) for further studies.

**Physical and chemical characterization**

The chemical compositions of the fly ash and synthesized zeolites were determined by XRF (Siemens model D5000, Germany). The crystalline compositions were identified through XRD (Rikaku D/max-RB, Rikaku, Japan). The samples were scanned from 2° to 70° with a step size of 0.02°·s\(^{-1}\). The morphological structures were obtained by using SEM (S-3000N, Hitachi, Japan). The SSAs were determined by N\(_2\) adsorption at 77 K by using QuadraSorb SI (Cantata Instruments Co., State, USA). The CEC was measured according to the ammonium acetate method (Alloway 1990).

**Batch sorption experiments**

Stock solutions of Zn\(^{2+}\), Cu\(^{2+}\), Cd\(^{2+}\), and Pb\(^{2+}\) at 1,000 mg·L\(^{-1}\) were prepared by using CuCl\(_2\), ZnCl\(_2\), CdCl\(_2\), and Pb(NO\(_3\))\(_2\).
The initial Zn$^{2+}$ solution was adjusted to 6.0. Concentrations ranged from 10 to 200 mg·L$^{-1}$ were 100 mg·L$^{-1}$ at 25 °C with 1 mol·L$^{-1}$ HCZ 33.65 12.62 11.70 15.00 0.79 0.46 0.70 0.31 23.16 LFA 53.30 16.98 8.57 3.14 0.60 0.97 0.60 0.10 0.08

10 to 200 mg·L$^{-1}$ HFA 37.95 14.52 16.73 17.86 1.09 1.44 1.09 0.44 1.24 LCZ 43.55 16.27 10.07 3.69 2.96 0.71 0.99 0.12 21.10 LFA, low-calcium fly ash; LCZ, zeolites synthesized from LFA; HFA, high-calcium fly ash; HCZ, zeolites synthesized from HFA.

Calculation of adsorption capacity and removal efficiency

The sorption capacity and the removal efficiency of Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$ by the synthesized zeolites (mg·g$^{-1}$) were calculated by Equations (1) and (2), respectively.

Adsorption capacity ($q_e$) = $\frac{C_o - C_e}{W} \times V$ (1)

Removal efficiency (%) = $\frac{C_o - C_e}{C_o} \times 100$ (2)

where $C_o$ and $C_e$ are the initial and equilibrium Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$ concentrations (mg·L$^{-1}$), respectively, $V$ is the solution volume (L), and $W$ is the mass of the adsorbent (g).

Adsorbent regeneration

Two grams of heavy-metals-saturated zeolite was regenerated with 25 mL NaCl solution (1 mol·L$^{-1}$). The mixture was stirred at 180 rpm at 25 °C for 1.5 h, and subsequently centrifuged and filtered with a 0.45 μm cellulose acetate membrane. The steps mentioned above were repeated three times. The solid samples obtained were dried at 60 ℃ for 12 h and subsequently sieved through a 100 mesh for further work.

To evaluate the performance of the regenerated zeolites for Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$ removal, the conditions were the same as those of the original sorption experiments.

RESULTS AND DISCUSSION

Characterization of fly ash and synthesized zeolite

The chemical compositions of the fly ash and the synthesized zeolites are listed in Table 1. Based on the classification for fly ash used as construction material in China (GB/T 1596-2005), the CaO content of LFA and HFA is <5% and >15%,
respectively. Here, the LFA contained 3.14% CaO and the HFA contained 17.86% CaO. The LFA contained 53.50% SiO₂ and 16.98% Al₂O₃, while the HFA contained 37.95% SiO₂ and 14.52% Al₂O₃. The Fe₂O₃ content of HFA was 16.73%, approximately twice that of the LFA (8.57%). According to the American Society for Testing and Materials (ASTM C618), the LFA is Class F fly ash (SiO₂ + Al₂O₃ + Fe₂O₃ > 70%), whereas the HFA is Class C fly ash (50% < SiO₂ + Al₂O₃ + Fe₂O₃ < 70%). Compared with the fly ash, the silica and alumina content in the synthetic zeolites decreased, which is ascribed to the incomplete dissolution of the silicon and aluminum in the fly ash during the alkali hydrothermal reaction. However, the Na₂O of LCZ and HCZ (zeolites synthesized from LFA and HFA, respectively) increased because an alkali was used during the synthesis.

The XRD patterns of fly ash, synthesized zeolites, and the adsorption saturated zeolites are shown in Figure 1. The XRD pattern of LFA showed the presence of quartz and mullite, whereas the predominant phases of HFA were quartz, CaO, magnesium oxide, and anhydrite. In the XRD pattern of the LCZ, the main crystals were faujasite-type zeolite, zeolite P, an unnamed zeolite (Na₂O·Al₂O₃·3SiO₂·6H₂O), and thermonatrite, whereas HCZ mainly consisted of the unnamed zeolite (Na₆(AlSiO₄)₆·4H₂O) and thermonatrite.

Figure 1 shows the XRD patterns of LCZ and HCZ after the reaction with the heavy metals. The result shows that the saturated LCZ consists of Cu-exchanged and Pb-exchanged zeolites, and Cd(OH)(NO₃). This result illustrates that Cu²⁺ and Pb²⁺ have been exchanged with LCZ. In respect of Cd(OH)(NO₃), the HNO₃ was used to adjust the pH of the heavy metal solution, and the pH value of LCZ was 8 to 9 (Cd(NO₃)₂ + OH⁻ → Cd(OH)(NO₃) + NO₃⁻). The XRD patterns of the saturated HCZ indicate that there were Cu₄(PO₄)₂O, Cd(H₂PO₂)₂, and Zn₃(PO₄)₂ after the reaction. The results illustrate that the removal of Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ by synthesized zeolites involves ion exchange and formation of insoluble precipitate.

Morphological analyses were carried out with SEM. As shown in Figure 2, the fly ash shows the presence of micro-particles in the shape of smooth balls (Figure 2(a) and 2(c)). After treatment with the fusion method, the spheres deformed, and the smooth surfaces changed into various crystal shapes (Figure 2(b) and 2(d)). The SSA were 0.07 m²·g⁻¹ for both LFA and HFA, which dramatically increased to 3.26 m²·g⁻¹ for LCZ and 8.56 m²·g⁻¹ for HCZ.

The CEC values of LFA and HFA were 1.20 and 0.94 mEq·g⁻¹, respectively, while the synthesized zeolites increased to 3.06 and 3.56 mEq·g⁻¹, respectively. The increase in the SSA and CEC values of zeolites compared to fly ashes indicates that the synthetic zeolites were favorable for the removal of metal ions (He et al. 2016).

**Effect of contact time**

Figure 3 shows the effect of contact time on the Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ removal efficiencies by LCZ and HCZ. The sorption displays a rapid initial removal rate (<60 min) and, subsequently, slows down until the sorption equilibrium at 90 min. The fast removal efficiency at the initial stage is attributable to all the adsorbent sites being available and the solute concentration gradient being high. As regards LCZ, the removal efficiency of Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ reached 87.96%, 97.47%, 75.29%, and 100.00% after 100 min, respectively. In respect of HCZ, the removal efficiency slightly decreased to 87.57%, 96.30%, 70.10%, and 99.99%, respectively. The contact time for the subsequent experiments to reach equilibrium was 100 min. The equilibrium pH was 6.30 for LCZ, and 6.32 for HCZ.

**Effect of pH**

The results in Figure 4 show that as the pH of the solution increased from 2.0 to 7.0, the removal efficiency by LCZ and HCZ increased. However, a further increase of pH to 12.0 had a negligible effect on the removal efficiency. As regards LCZ, the Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ removal efficiency increased by 18.57%, 10.57%, 38.21%, and 8.51%, respectively, when the pH increased from 2.0 to 12.0. Similarly, in respect of HCZ, the removal efficiency increased by 18.20%, 10.31%, 37.80%, and 8.69%, respectively. Moreover, the effect of pH on the removal of the four cations by LCZ and HCZ followed the order Cd²⁺ > Zn²⁺ > Cu²⁺ > Pb²⁺. This can be explained by the hydrogen ion having a high concentration when the pH decreases, intensifying the competition for the exchange sites (Zhang et al. 2007, 2013; Yusof et al. 2010). The concentration of the hydrogen ion decreases when the pH increases, and heavy metal ions transform insoluble hydroxides. In this instance, the zeolite not only adsorbs heavy metal ions but also accelerates the sedimentation of hydroxide (Wang et al. 2009a).

**Effect of adsorbent dosage**

Figure 5 shows the effect of the zeolite dosage on Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ removal. The increase in the dosage of LCZ and HCZ from 0.5 to 5.0 g·L⁻¹ resulted in an enhanced removal efficiency of the four cations; however, the adsorbent
Capacity decreases. For instance, the removal efficiency of Zn$^{2+}$ by LCZ increases from 60.98% to 99.95% when the amount of adsorbent increases from 0.5 to 5.0 g·L$^{-1}$. The maximum removal efficiency occurs at an adsorbent dosage of 2.5 mg·L$^{-1}$. However, the Zn$^{2+}$ adsorption capacity decreases from 121.95 to 19.99 mg·g$^{-1}$. The increase in Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$ removal efficiency can be explained by the increase in the surface area and the adsorption sites of LCZ and HCZ. As regards the removal efficiency and adsorbent capacity of the four cations, the optimum adsorbent dosage was 1.0 mg·L$^{-1}$. The Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$ removal efficiency was 87.96%, 97.47%, 75.29%, and 100.00%, respectively, by LCZ, and 87.57%, 98.30%, 70.10%, and 99.99%, respectively, by HCZ. The selectivity of the removal efficiency of both LCZ and HCZ was Pb$^{2+}$ > Cu$^{2+}$ > Zn$^{2+}$ > Cd$^{2+}$. The crystal structure,
ionic hydration radius, and hydration free energy of the materials were the main factors in the selectivity (Hui et al. 2005). Panayotova (2001) found that as regards the covalent metal ions, the adsorption affinity increased with decreasing hydration radius and hydration free energy. In accordance with the size of hydrated radius, the selectivity should be Pb$^{2+}$(0.401 nm) > Cu$^{2+}$(0.410 nm) > Cd$^{2+}$(0.426 nm) > Zn$^{2+}$(0.430 nm). However, this order does not explain well the higher selectivity of Zn$^{2+}$ in comparison with that of Cd$^{2+}$. The higher selectivity could be attributed to the hydration free energy of Zn$^{2+}$ ($-2,044$ kJ·mol$^{-1}$) being lower than that of Cd$^{2+}$ ($-979$ kJ·mol$^{-1}$) (Volkov et al. 1997; Tansel 2012). In general, there is little difference in the removal efficiency of Zn$^{2+}$, Cu$^{2+}$, and Pb$^{2+}$ between LCZ and HCZ. In addition, LCZ is more effective for Cd$^{2+}$ removal. The difference in adsorption is probably because the calcium
ions are released from the synthesis of zeolite from HFA, which forms competitive adsorption with the heavy metal ions (Juan et al. 2009). Based on the integrated wastewater discharge standard in China (GB 8978-1996), the treated wastewater could reach Class I by using LCZ, when the adsorbent dosage is 2.5 g·L$^{-1}$/C$_0$ and by using HCZ at 5 g·L$^{-1}$/C$_0$ when the initial heavy metal concentration is 100 mg·L$^{-1}$.  

Effect of initial concentration of Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$

The uptake of Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$ by the synthesized zeolites was studied under different initial concentrations of heavy metal ions, ranging from 10 to 200 mg·L$^{-1}$. The results in Figure 6 show that with the increase in initial concentrations of Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$, the removal efficiency by both LCZ and HCZ decreased. For instance, the removal efficiency of Zn$^{2+}$ by LCZ decreased from 100.00% to 79.27% when the initial concentration increased from 10 to 200 mg·L$^{-1}$. The decrease in the removal efficiency can be explained by the adsorbents having limited sorption sites (Perego et al. 2013; Ivanova et al. 2014).

Adsorption kinetics

Pseudo-first-order (Lagergren 1898) (Equation (3)) and pseudo-second-order (Ho & McKay 1999) (Equation (4))
kinetic models were applied to simulate the sorption kinetic data:

\[
\ln \left( \frac{q_e}{C_0} - \frac{q_t}{C_0} \right) = \ln \frac{q_e}{C_0} - k_1 t
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e}
\]

where \( q_e \) and \( q_t \) are the amounts of heavy metals adsorbed on the zeolites (mg·g\(^{-1}\)) at equilibrium and at time \( t \), respectively. The values \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g·mg\(^{-1}\)·min\(^{-1}\)) are the rate constants of the pseudo-first-order and pseudo-second-order sorption, respectively. The fitting results are depicted in Figure 7, and the fitting parameters are summarized in Table 2. For the sorption of Zn\(^{2+}\), Cu\(^{2+}\), Cd\(^{2+}\), and Pb\(^{2+}\) by LCZ and HCZ, the coefficient of determination (\( R^2 \)) (\( R^2 = 0.999 \) for all instances) for the pseudo-second-order model was much higher than that obtained by using the pseudo-first-order model (\( R^2 = 0.978, 0.876, 0.899, \) and 0.970 for Zn\(^{2+}\), Cu\(^{2+}\), Cd\(^{2+}\), and Pb\(^{2+}\) removal by LCZ; and \( R^2 = 0.947, 0.989, 0.580, \) and 0.954 for HCZ). Therefore, the pseudo-second-order model explains the kinetic process better, suggesting that chemisorption is the rate-controlling step for the uptake process of Zn\(^{2+}\), Cu\(^{2+}\), Cd\(^{2+}\), and Pb\(^{2+}\) by synthesized zeolites (Ho & McKay 1999).

Adsorption isotherm

The commonly used Langmuir and Freundlich isotherm models were applied to fit the sorption isotherm data of Zn\(^{2+}\), Cu\(^{2+}\), Cd\(^{2+}\), and Pb\(^{2+}\) by LCZ and HCZ at 25 °C, respectively.

The Langmuir isotherm model is given in Equation (5):

\[
\frac{C_e}{q_e} = \frac{1}{b Q_m} + \left( \frac{1}{Q_m} \right) C_e
\]

where \( b \) is a constant related to the affinity of the binding sites and energy of the adsorption (L·mg\(^{-1}\)), \( Q_m \) is the maximum monolayer adsorption capacity (mg·g\(^{-1}\)), \( q_e \) is the heavy metal amount adsorbed on a unit mass of zeolites (mg·g\(^{-1}\)), and \( C_e \) is the heavy metal equilibrium concentration (mg·L\(^{-1}\)).

The fundamental characteristics and practicability of the Langmuir isotherm model can be defined by a dimensionless constant separation factor or equilibrium parameter \( R_L \) (Hall et al. 1966):

\[
R_L = \frac{1}{1 + b C_0}
\]

when \( R_L > 1 \), the sorption is unfavorable. When \( R_L = 1 \), adsorption is linear. When \( 0 < R_L < 1 \), adsorption is a favorable process, whereas \( R_L = 0 \) illustrates that the sorption process is irreversible.

The Langmuir isotherm fitting results are summarized in Figure 8 and Table 3. The Langmuir constants, \( Q_m \), of Zn\(^{2+}\), Cu\(^{2+}\), Cd\(^{2+}\), and Pb\(^{2+}\) removal by LCZ were 155.76, 197.86, 123.76, and 186.22 mg·g\(^{-1}\), respectively, which were higher than the experimental results (135.11, 121.95, 134.89, and 178.49 mg·g\(^{-1}\)). For HCZ, the \( Q_m \) values were 154.08, 183.15, 118.91, and 191.94 mg·g\(^{-1}\), respectively, which were similar to the experimental results (115.79, 127.45, 134.89, and 178.49 mg·g\(^{-1}\)).
Table 2 | Fitting parameters of pseudo-first-order and pseudo-second-order kinetic models for heavy metals removal by zeolites

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Synthetic zeolite</th>
<th>Pseudo-first-order</th>
<th>qe (mg·g⁻¹)</th>
<th>k₁ (min⁻¹)</th>
<th>R²</th>
<th>Pseudo-second-order</th>
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<tbody>
<tr>
<td>Zn</td>
<td>LCZ</td>
<td>0.162</td>
<td>86.88</td>
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<td></td>
<td>HCZ</td>
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<td>0.876</td>
<td></td>
<td>0.011</td>
</tr>
<tr>
<td></td>
<td>HCZ</td>
<td>0.202</td>
<td>95.92</td>
<td>0.989</td>
<td></td>
<td>0.019</td>
</tr>
<tr>
<td>Cd</td>
<td>LCZ</td>
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<td>74.27</td>
<td>0.899</td>
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<td>0.007</td>
</tr>
<tr>
<td></td>
<td>HCZ</td>
<td>0.213</td>
<td>70.60</td>
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<tr>
<td>Pb</td>
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<td>98.72</td>
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</tr>
<tr>
<td></td>
<td>HCZ</td>
<td>0.099</td>
<td>97.68</td>
<td>0.954</td>
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Figure 7 | Pseudo-first-order (a) and (b) and pseudo-second-order (c) and (d) kinetic model fitting of Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ removal by LCZ (a) and (c) and HCZ (b) and (d) (adsorbent dosage = 1.0 g·L⁻¹; pH = 6.0; T = 25 °C).
133.90, and 140.71 mg·g⁻¹). Based on the coefficient of determination values ($R^2$) (in the range 0.81–0.99), the sorption of Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ onto synthesized zeolites constituted the monolayer adsorption process. The range of $R_L$ was 0.0002 to 0.3924 (0 < $R_L$ < 1), suggesting that the uptake process was favorable.

Table 3 | Fitted parameters for Langmuir and Freundlich sorption isotherm models (adsorbent dosage = 1.0 g·L⁻¹; pH = 6.0; T = 25 °C)

<table>
<thead>
<tr>
<th>Heavy metal ions</th>
<th>Synthetic zeolites</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
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<td></td>
<td>Q_m (mg·g⁻¹)</td>
<td>b (L·mg⁻¹)</td>
<td>R²</td>
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<tr>
<td>Zn</td>
<td>LCZ</td>
<td>155.76</td>
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<td>HCZ</td>
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<td>HCZ</td>
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<tr>
<td></td>
<td>HCZ</td>
<td>191.94</td>
<td>16.52</td>
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</table>

Figure 8 | Langmuir isotherm model (a) and (b) and Freundlich isotherm model (c) and (d) of Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ removal by LCZ (a) and (c) and HCZ (b) and (d) (adsorbent dosage = 1.0 g·L⁻¹; pH = 6.0; T = 25 °C).
The Freundlich isotherm model is given as follows:

\[
\log q_e = \log K_f + n_f \log C_e
\]

where \(K_f\) and \(n_f\) are the Freundlich constant and adsorption intensity, respectively. The Freundlich constants are obtained by plotting the graph of \(\log q_e\) versus \(\log C_e\). The results are listed in Figure 8 and Table 3. The obtained \(K_f\) values were 58.28, 72.33, 52.29, and 130.69 mg·g\(^{-1}\), respectively. For HCZ, the \(K_f\) values were 60.99, 83.0, 43.13, and 130.07 mg·g\(^{-1}\), respectively. The range of \(n_f\) was 0.17–0.34. When the value of \(n_f\) is in the range 0.1–1, the adsorption is favorable. These results are consistent with those from the Langmuir sorption isotherm model. The coefficient of determination (\(R^2\)) was of the range 0.35–0.83, which is lower than the values obtained by the Langmuir model, indicating that the adsorption process fitted better with the Langmuir sorption isotherm model.

A comparison of the adsorption capacity of these four cations by different adsorbents is shown in Table 4. The synthetic zeolites in this study showed significant higher sorption capacity in comparison with various other materials.

**Heavy metals recovery and adsorbent regeneration**

The heavy metals adsorbed by zeolites were recovered by using NaCl solution (1 mol·L\(^{-1}\)) and the recovery efficiency was calculated by using the following equation:

\[
\text{Recovery efficiency (\%) = } \frac{C_M V}{q_e W} \times 100
\]

where \(C_M\) is the heavy metal ion concentration existing in 5% NaCl solution after recovery (mg·L\(^{-1}\)), \(V\) is the volume of 5% NaCl solution (L), \(q_e\) is the amount of metal ions adsorbed on the adsorbents (mg·g\(^{-1}\)), and \(W\) is the amount of adsorbents (g).

For HCZ, the recovery efficiency of \(\text{Zn}^{2+}\), \(\text{Cu}^{2+}\), \(\text{Cd}^{2+}\), and \(\text{Pb}^{2+}\) was 81.57%, 69.30%, 83.98, and 79.28%, respectively. For LCZ, the recovery efficiency was 83.24%, 72.19%, 84.15, and 79.44%, respectively. This indicated that the regenerative synthesized zeolite still contained heavy metal ions.

The adsorption capacity of regenerated zeolites was determined to further investigate the reusability of HCZ and LCZ. Figure 9 shows a comparison of the uptake of the four heavy metal ions on the original and regenerative adsorbents (the adsorbent dosage was 1.0 g·L\(^{-1}\)). The second application resulted in a reduction in the removal efficiency of \(\text{Pb}^{2+}\), \(\text{Cu}^{2+}\), \(\text{Zn}^{2+}\), and \(\text{Cd}^{2+}\) by 13.60%, 15.57%, 17.46%, and 16.49%, respectively, for LCZ and 19.79% 21.80%, 26.17%, and 30.60%, respectively, for HCZ when the adsorbent dosage was 1.0 g·L\(^{-1}\).

The decrease in adsorption capacity of regenerated adsorbents during one cycle can be explained by the fact that heavy metals adsorbed to the original zeolites were not fully released during the regeneration process. However, the regenerated zeolites still had a high removal efficiency. Consequently, the synthesized zeolites can be recycled and utilized for heavy metal removal. Owing to the high cost and loss in the regeneration process, the use of activated carbon and commercial grade zeolites as

**Table 4 | Comparison of maximum sorption capacity of the removal of heavy metal ions by different adsorbents**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Maximum sorption capacity (mg·g(^{-1}))</th>
<th>Heavy metal ions</th>
<th>System</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite-based geopolymer</td>
<td>26.25</td>
<td>(\text{Cd}^{2+})</td>
<td>Single ion</td>
<td>Javadian et al. (2015)</td>
</tr>
<tr>
<td>Modified zeolite X</td>
<td>91.52, 97.44, 420.21</td>
<td>(\text{Cu}^{2+}), (\text{Cd}^{2+}), (\text{Pb}^{2+})</td>
<td>Single ion</td>
<td>Apiratikul &amp; Pavasant (2008)</td>
</tr>
<tr>
<td>Multi-carboxyl-functionalized silica gel</td>
<td>39.96, 47.07, 41.48, 30.80</td>
<td>(\text{Zn}^{2+}), (\text{Cu}^{2+}), (\text{Cd}^{2+}), (\text{Ni}^{2+})</td>
<td>Single ion</td>
<td>Li et al. (2014)</td>
</tr>
<tr>
<td>Synthesized hydroxy-sodalite zeolite</td>
<td>40.10, 60.10</td>
<td>(\text{Zn}^{2+}), (\text{Cd}^{2+})</td>
<td>Single ion</td>
<td>Izidoro et al. (2012)</td>
</tr>
<tr>
<td>Synthesized zeolite material ZCET40</td>
<td>69.93, 96.15, 14.20, 238.10, 23.59</td>
<td>(\text{Zn}^{2+}), (\text{Cu}^{2+}), (\text{Cd}^{2+}), (\text{Pb}^{2+}), (\text{Ni}^{2+})</td>
<td>Mixed ions</td>
<td>Visa (2016)</td>
</tr>
<tr>
<td>Synthesized zeolite material ZDs40</td>
<td>6.35, 20.83, 14.21, 185.19, 9.95</td>
<td>(\text{Zn}^{2+}), (\text{Cu}^{2+}), (\text{Cd}^{2+}), (\text{Pb}^{2+}), (\text{Ni}^{2+})</td>
<td>Mixed ions</td>
<td>Visa (2016)</td>
</tr>
<tr>
<td>LCZ</td>
<td>155.76, 197.86, 123.76, 186.22</td>
<td>(\text{Zn}^{2+}), (\text{Cu}^{2+}), (\text{Cd}^{2+}), (\text{Pb}^{2+})</td>
<td>Mixed ions</td>
<td>This study</td>
</tr>
<tr>
<td>HCZ</td>
<td>154.08, 183.15, 118.91, 191.94</td>
<td>(\text{Zn}^{2+}), (\text{Cu}^{2+}), (\text{Cd}^{2+}), (\text{Pb}^{2+})</td>
<td>Mixed ions</td>
<td>This study</td>
</tr>
</tbody>
</table>
conventional adsorbents would probably not be an economical way to treat wastewater compared with the application of zeolites converted from fly ash. Furthermore, converting fly ash into zeolitic adsorbents could relieve or even eliminate the problems associated with disposing huge quantities of fly ash that are generated by thermal power plants annually.

CONCLUSION

This study proved that fly-ash-based adsorbents (LCZ and HCZ) have the potential to act as effective adsorbents for simultaneous removal of Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$ from aqueous solution. We studied the influential parameters, namely, contact time, pH value, adsorbent dosage, and initial concentrations of heavy metals to determine the removal performance of heavy metal ions on these adsorbents. Generally, the removal efficiency was enhanced with an increase of the adsorbent dosage, and decreased with the increase of the initial heavy metal concentration. The removal efficiency of the four cations improved with an increase in pH from 2.0 to 6.0; moreover, the removal efficiency of the four cations was 100% by both LCZ and HCZ when the pH $\geq$ 7. The highest removal efficiency was obtained for the four heavy metal ions when the following parameters were used: pH value of 6.0, adsorbent dosage of 1.0 g·L$^{-1}$, adsorption temperature of 25°C, and initial heavy metal concentration of 100 mg·L$^{-1}$. The sorption kinetics of the four ions on both LCZ and HCZ followed a pseudo-second-order kinetic model. The adsorption isotherm data fitted the Langmuir isotherm model well. As regards LCZ, the maximum adsorption capacities of Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$ were 155.76, 197.86, 123.76, and 186.22 mg·g$^{-1}$, respectively. In respect of HCZ, the values were 154.08, 183.15, 118.91, and 191.94 mg·g$^{-1}$, respectively. Finally, quantitative recovery of metal ions could be achieved by using NaCl solution (1 mol·L$^{-1}$) and the adsorbents could be recycled after the regeneration process. The study shows that zeolites produced from fly ash are inexpensive alternative adsorbents for the removal of heavy metals from industrial wastewater. Furthermore, the synthesized zeolites were a way to achieve fly ash resource reutilization.

ACKNOWLEDGEMENTS

This work was supported by the Fundamental Research Funds for the Central Universities (No. 2015ZCQ-SB-01, No. 2016JX04).

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First received 6 March 2017; accepted in revised form 2 June 2017. Available online 24 June 2017