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 ($Na_6[AlSiO_4]_6 \cdot 4H_2O$), whereas LCZ mainly consists of faujasite-type zeolite. The optimum sorption conditions were pH = 6.0; adsorbent dosage = $1.0 \ g \cdot L^{-1}$; temperature = $25 \ ^\circ C$; contact time = 100 min; and initial heavy metal concentration = $100 \ mg \cdot L^{-1}$. 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 $186.22 \ mg \cdot g^{-1}$, respectively. For HCZ, the values were 154.08, 183.15, 118.91, and $191.94 \ mg \cdot g^{-1}$, respectively. The zeolites were regenerated by NaCl solution ($1 \ mol \cdot L^{-1}$) 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

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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; Kołodyńska *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 & Pavasant 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 & Pavasant 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-calcium and high-calcium 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$_2$,

Table 1 │ Chemical compositions of fly ash and synthesized zeolites

Chemical compositions	Content (%)								
	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	TiO$_2$	K$_2$O	MgO	MnO	Na$_2$O
LFA	53.30	16.98	8.57	3.14	0.60	0.97	0.91	0.10	0.08
LCZ	43.55	16.27	10.07	3.69	2.96	0.71	0.99	0.12	21.10
HFA	37.95	14.52	16.73	17.86	1.09	1.44	1.09	0.44	1.24
HCZ	33.65	12.62	11.70	15.00	0.79	0.46	0.70	0.31	23.16

LFA, low-calcium fly ash; LCZ, zeolites synthesized from LFA; HFA, high-calcium fly ash; HCZ, zeolites synthesized from HFA.

and PbCl$_2$ solids (analytical reagent grade) in distilled water, which were further diluted to the desired concentration by adding distilled water. All sorption experiments were carried out in 100 mL stoppered conical flasks, on a temperature-controlled shaker, with continuous stirring at 180 rpm. After the shaking process, the mixtures were centrifuged and filtered through a 0.45 μm cellulose acetate membrane. Finally, the Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ concentrations in the filtrate were measured by inductively coupled plasma optical emission spectroscopy (Plasma Quad 3, UK). All experiments were conducted three times.

The effect of the contact time on Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ removal by the synthesized zeolite was investigated from 0 to 360 min at 25 °C. The initial Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ concentrations were 100 mg·L⁻¹, respectively, and the adsorbent dosage was 1.0 g·L⁻¹. The initial pH was adjusted to 6.0, and the pH value was measured upon equilibrium.

The effect of pH was investigated in a pH range from 2.0 to 12.0 at 25 °C. The initial Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ concentration was 100 mg·L⁻¹ and the zeolite dosage was 1.0 g·L⁻¹. The initial pH of the suspensions was adjusted with 1 mol·L⁻¹ of HNO₃ solution or NaOH solution, and the pH was monitored with a pH meter (PHS-3C, China).

The effect of the zeolite dosage on the removal of cations was studied at a range of 0.5–5.0 g·L⁻¹ at 25 °C. The initial Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ concentrations were 100 mg·L⁻¹, respectively. The pH of the solutions was kept constant at 6.0.

The effect of the initial Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ concentrations was studied in the range 10 to 200 mg·L⁻¹ at 25 °C. The adsorbent dosage was 1.0 g·L⁻¹. The pH of the solutions was adjusted to 6.0.

Adsorption isotherm tests were conducted at 25 °C. The initial Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ concentrations ranged from 10 to 200 mg·L⁻¹. The dosage of the synthesized zeolite was 1.0 g·L⁻¹ and the equilibrium pH was adjusted to 6.0.

Calculation of adsorption capacity and removal efficiency

The sorption capacity and the removal efficiency of Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ by the synthesized zeolites (mg·g⁻¹) were calculated by Equations (1) and (2), respectively.

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

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

where C_o and C_e are the initial and equilibrium Zn²⁺, Cu²⁺, Cd²⁺ and Pb²⁺ 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 °C for 12 h and subsequently sieved through a 100 mesh for further work.

To evaluate the performance of the regenerated zeolites for Zn²⁺ Cu²⁺, Cd²⁺, and Pb²⁺ 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 53.30% SiO_2 and 16.98% Al_2O_3, while the HFA contained 37.95% SiO_2 and 14.52% Al_2O_3. The Fe_2O_3 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 ($SiO_2 + Al_2O_3 + Fe_2O_3 >$ 70%), whereas the HFA is Class C fly ash ($50\% < SiO_2 + Al_2O_3 + Fe_2O_3 < 70\%$). 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 Na_2O 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 ($Na_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 6H_2O$), and thermonatrite, whereas HCZ mainly consisted of the unnamed zeolite ($Na_6(AlSiO_4)_6 \cdot 4H_2O$) 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 $Cd(OH)(NO_3)$. This result illustrates that Cu^{2+} and Pb^{2+} have been exchanged with LCZ. In respect of $Cd(OH)(NO_3)$, the HNO_3 was used to adjust the pH of the heavy metal solution, and the pH value of LCZ was 8 to 9 ($Cd(NO_3)_2 + OH^- \rightarrow Cd(OH)(NO_3) + NO_3^-$). The XRD patterns of the saturated HCZ indicate that there were $Cu_4(PO_4)_2O$, $Cd(H_2PO_2)_2$, and $Zn_3(PO_4)_2$ after the reaction. The results illustrate that the removal of Zn^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+} 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 microparticles 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 SSAs were 0.07 $m^2 \cdot g^{-1}$ for both LFA and HFA, which dramatically increased to 3.26 $m^2 \cdot g^{-1}$ for LCZ and 8.36 $m^2 \cdot g^{-1}$ for HCZ.

The CEC values of LFA and HFA were 1.20 and 0.94 $mEq \cdot g^{-1}$, respectively, while the synthesized zeolites increased to 3.06 and 3.56 $mEq \cdot g^{-1}$, 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 Zn^{2+} Cu^{2+}, Cd^{2+}, and Pb^{2+} 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 Zn^{2+} Cu^{2+}, Cd^{2+}, and Pb^{2+} 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 Zn^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+} 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 $Cd^{2+} > Zn^{2+} > Cu^{2+} > Pb^{2+}$. 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, 2011a; 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 Zn^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+} removal. The increase in the dosage of LCZ and HCZ from 0.5 to 5.0 $g \cdot L^{-1}$ resulted in an enhanced removal efficiency of the four cations; however, the adsorbent
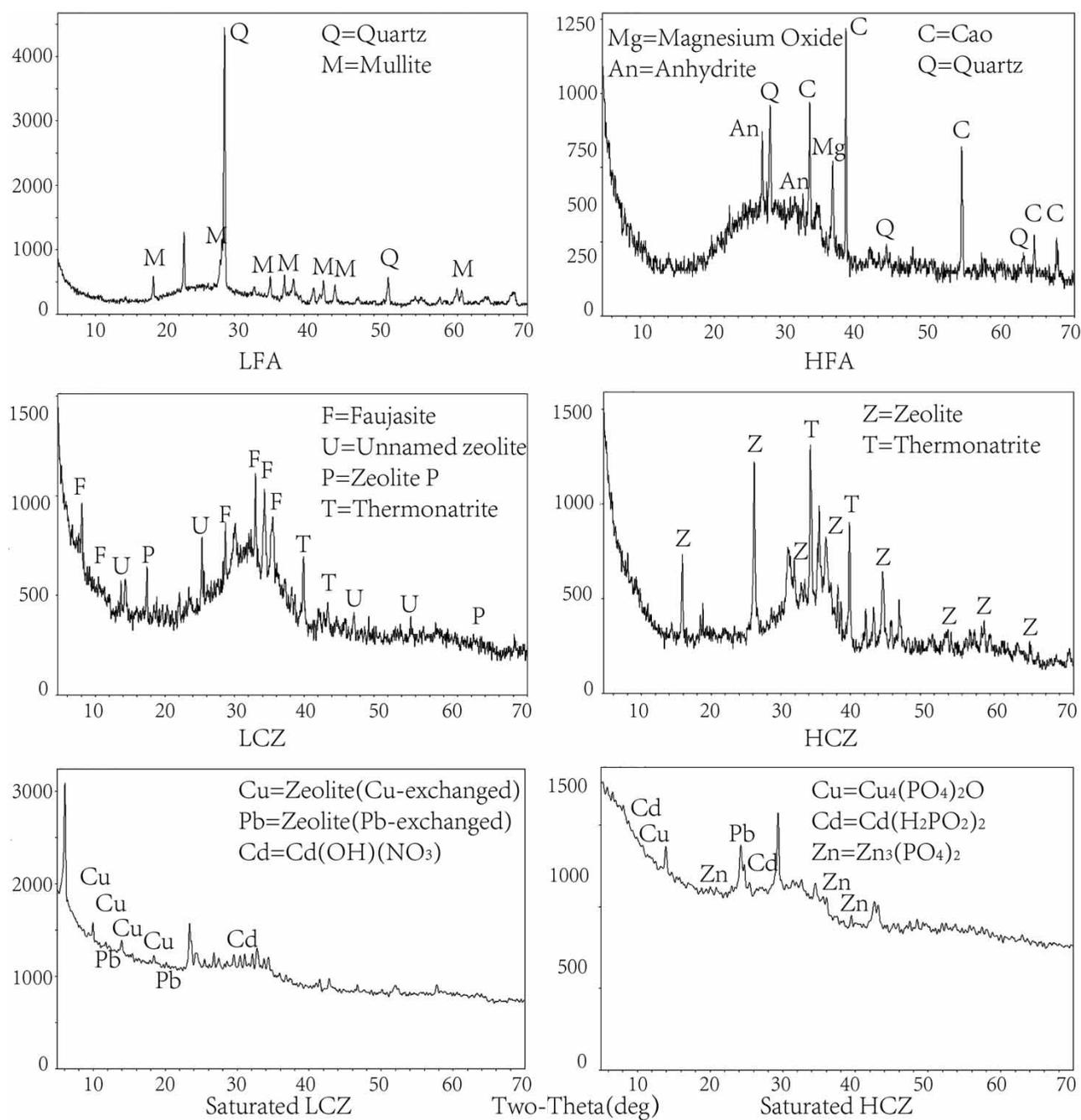
Figure 1 | XRD patterns of fly ash, synthesized zeolites, and adsorption saturated zeolites.

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 $g \cdot L^{-1}$. The maximum removal efficiency occurs at an adsorbent dosage of 2.5 $mg \cdot L^{-1}$. However, the Zn^{2+} adsorption capacity decreases from 121.95 to 19.99 $mg \cdot g^{-1}$. 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 $mg \cdot L^{-1}$. 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,
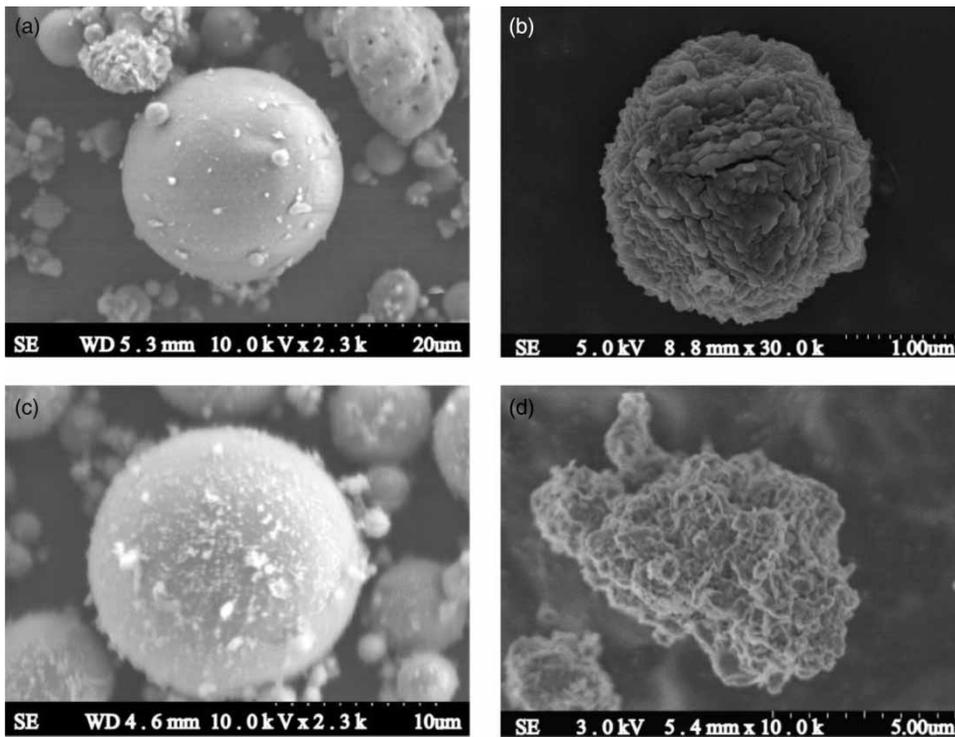
Figure 2 │ SEM images of (a) LFA, (b) LCZ, (c) HFA, and (d) HCZ.

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+} (0.419 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
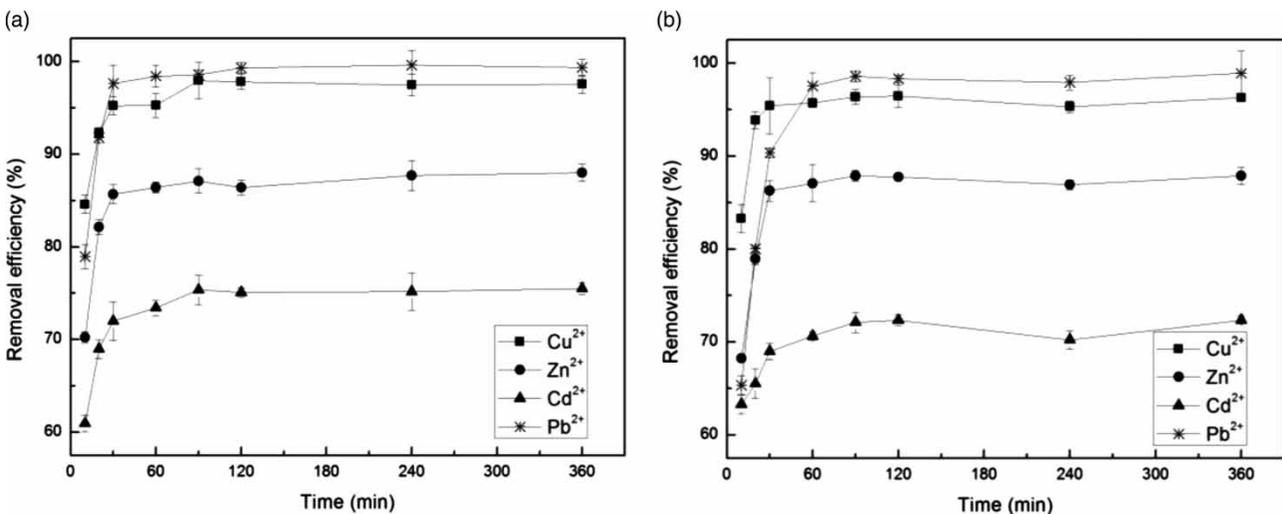
**Figure 3** │ Effect of contact time on Zn^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+} removal by (a) LCZ and (b) HCZ ($C_0 = 100$ mg·L^{-1}; adsorbent dosage = 1.0 g·L^{-1}; T = 25 °C).
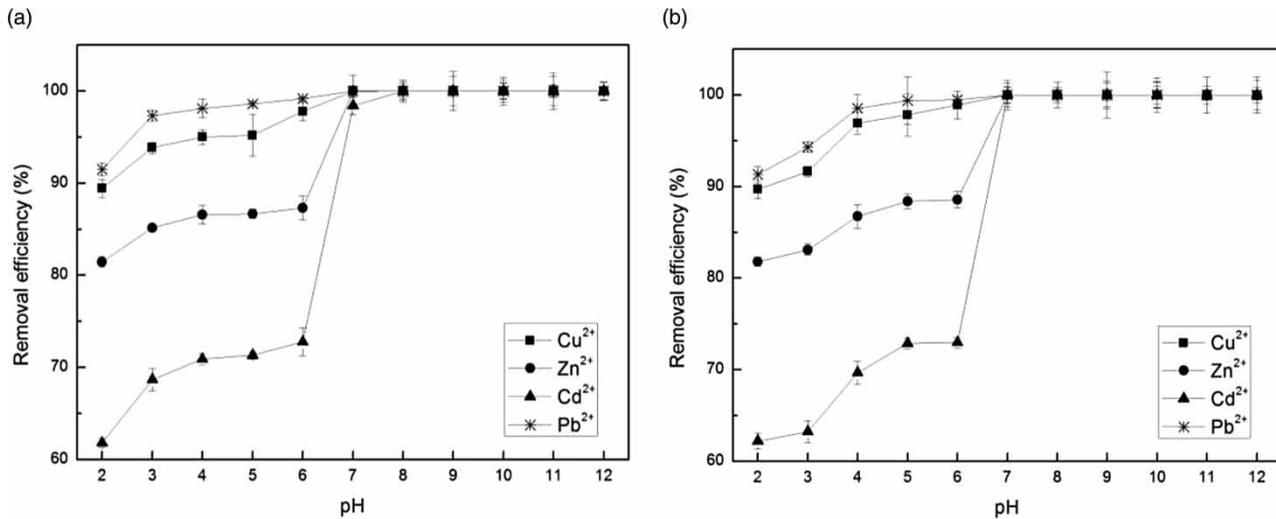
Figure 4 | Effect of pH on Zn^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+} removal by (a) LCZ and (b) HCZ ($C_0 = 100$ mg·L^{-1}; adsorbent dosage $= 1.0$ g·L^{-1}; T $= 25$ °C).

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} and by using HCZ at 5 g·L^{-1} 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))
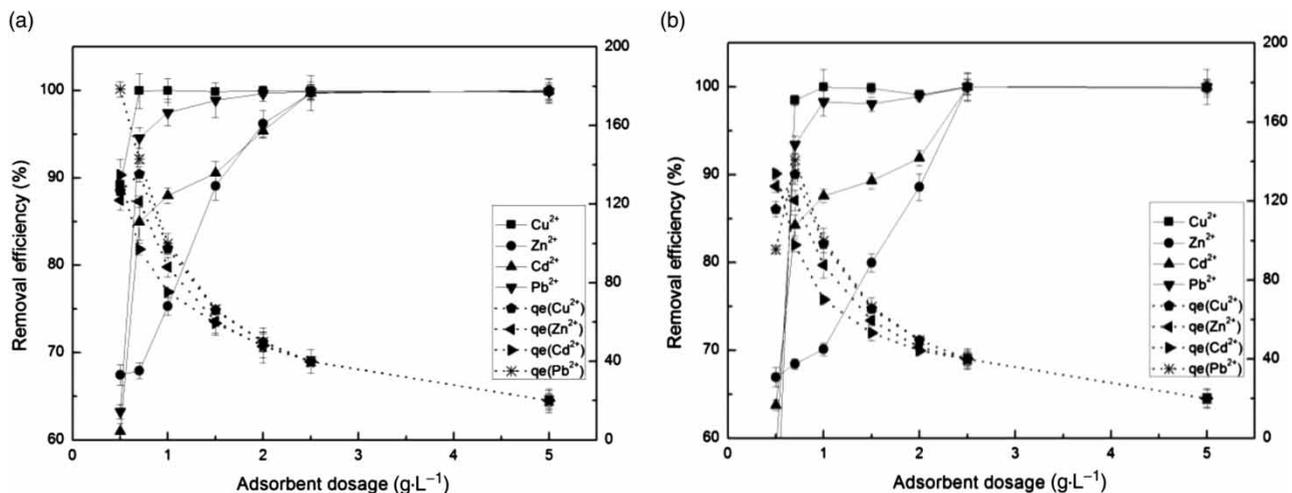

Figure 5 | Effect of (a) LCZ and (b) HCZ dosage on the Zn^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+} removal efficiency and adsorption capacity ($C_0 = 100$ mg·L^{-1}; pH $= 6.0$; T $= 25$ °C).
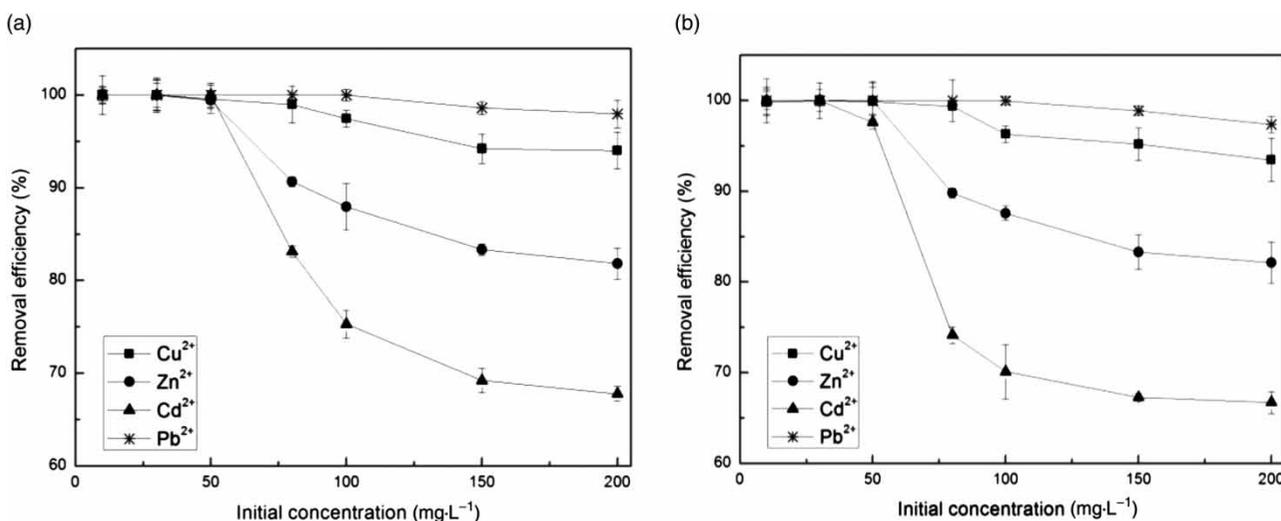
Figure 6 | Effect of initial concentration on the Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ removal efficiency by (a) LCZ and (b) HCZ (adsorbent dosage = 1.0 g·L⁻¹; pH = 6.0; T = 25 °C).

kinetic models were applied to simulate the sorption kinetic data:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

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 Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ 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 Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ 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 Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ 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 Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ by LCZ and HCZ at 25 °C, respectively.

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

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \left(\frac{1}{Q_m}\right)C_e \qquad (5)$$

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):

$$R_L = \frac{1}{1 + bC_0}$$

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 Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ 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,
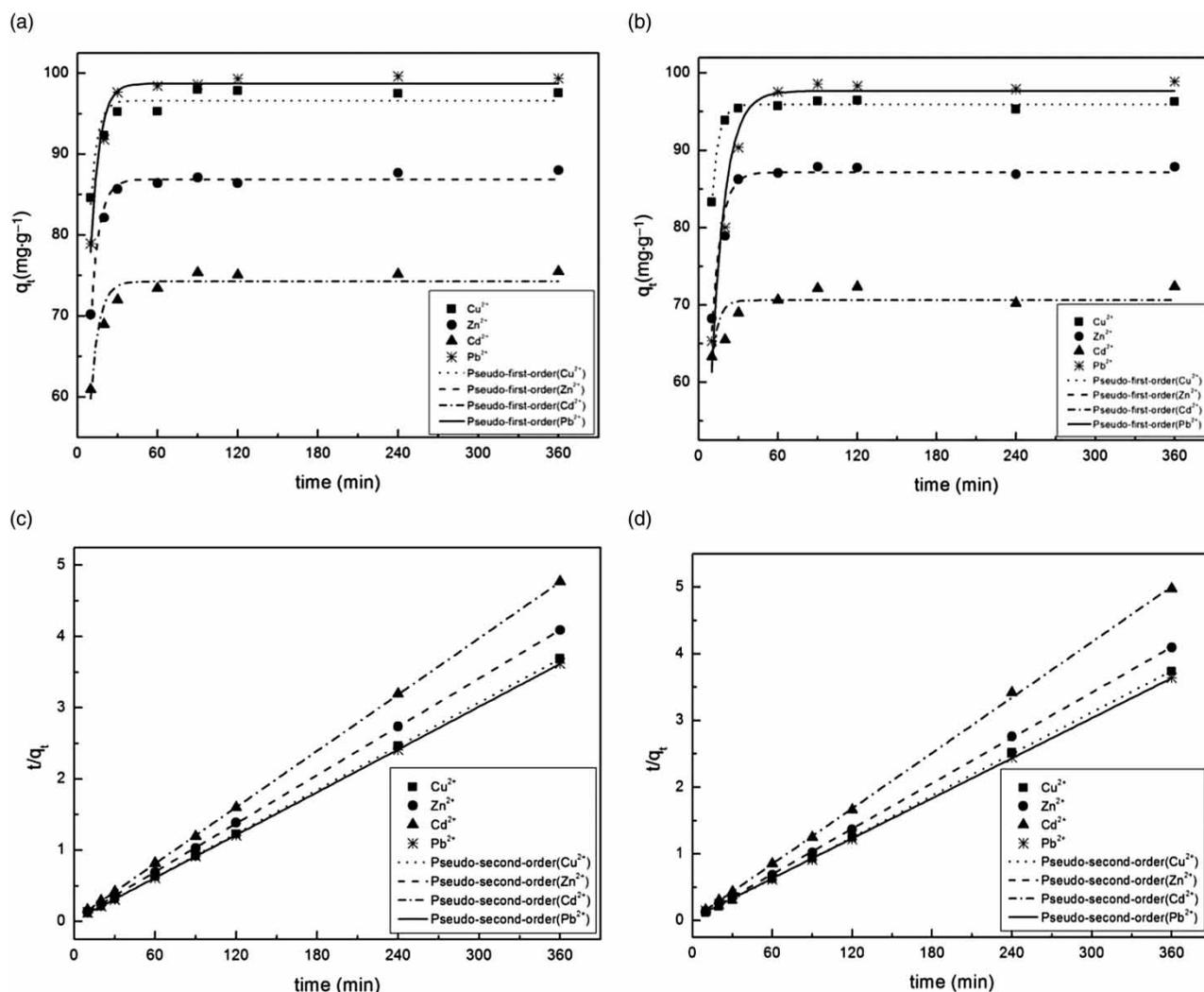
Figure 7 | Pseudo-first-order (a) and (b) and pseudo-second-order (c) and (d) kinetic model fitting of Zn^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+} removal by LCZ (a) and (c) and HCZ (b) and (d) (adsorbent dosage = 1.0 g·L^{-1}; pH = 6.0; T = 25 °C).

Table 2 | Fitting parameters of pseudo-first-order and pseudo-second-order kinetic models for heavy metals removal by zeolites

Heavy metals	Synthetic zeolite	Pseudo-first-order			Pseudo-second-order		
		k_1 (min^{-1})	q_e (mg·g^{-1})	R^2	k_2 (g·mg^{-1}·min^{-1})	q_e (mg·g^{-1})	R^2
Zn	LCZ	0.162	86.88	0.978	0.007	88.42	0.999
	HCZ	0.145	87.14	0.947	0.008	88.11	0.999
Cu	LCZ	0.202	96.61	0.876	0.011	97.94	0.999
	HCZ	0.202	95.92	0.989	0.019	96.25	0.999
Cd	LCZ	0.163	74.27	0.899	0.007	75.87	0.999
	HCZ	0.213	70.60	0.580	0.010	72.15	0.999
Pb	LCZ	0.155	98.72	0.970	0.007	99.90	0.999
	HCZ	0.099	97.68	0.954	0.003	99.80	0.999
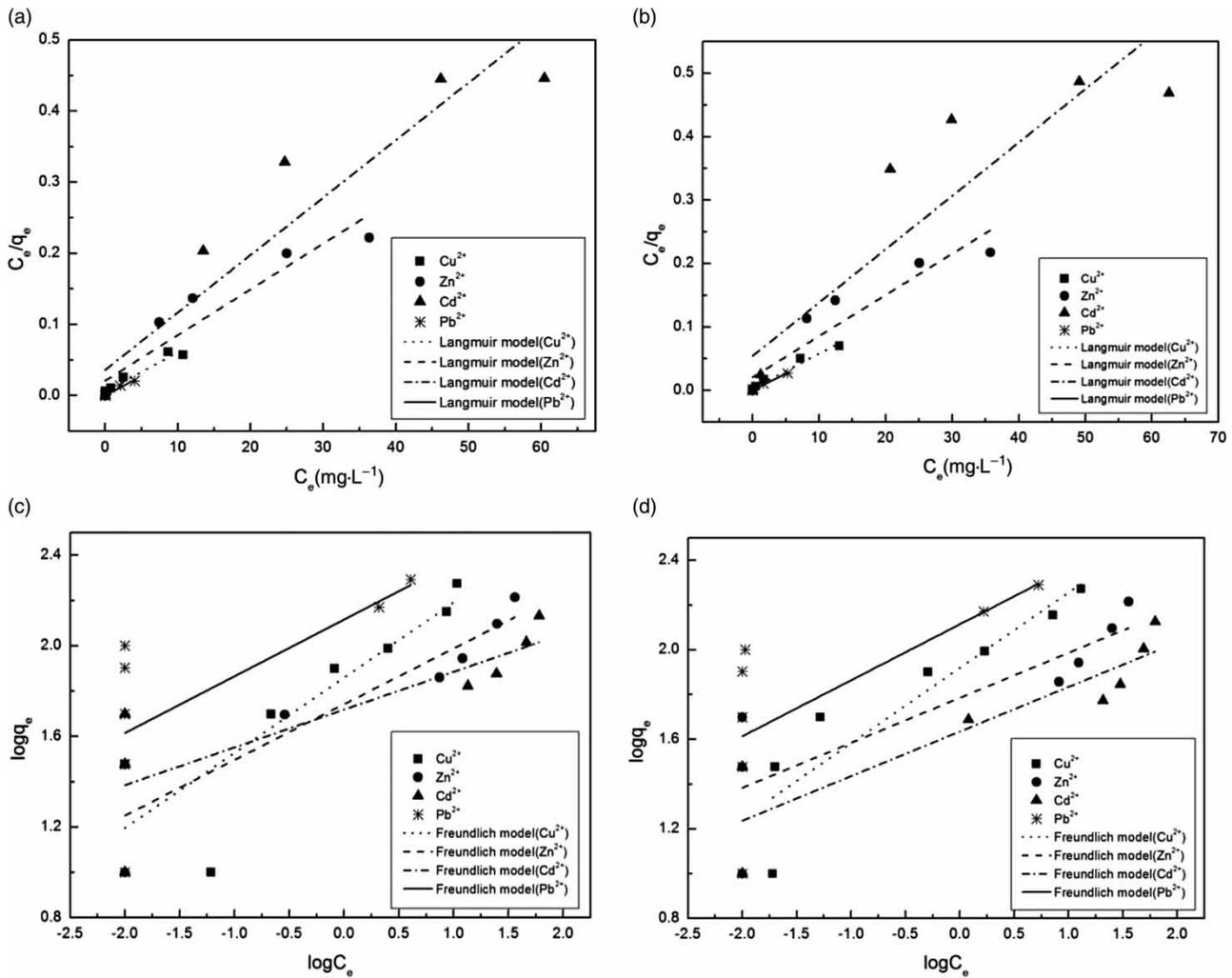
Figure 8 | Langmuir isotherm model (a) and (b) and Freundlich isotherm model (c) and (d) of Zn^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+} removal by LCZ (a) and (c) and HCZ (b) and (d) (adsorbent dosage = 1.0 g·L^{-1}; pH = 6.0; T = 25 °C).

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 Zn^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+} 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)

Heavy metal ions	Synthetic zeolites	Langmuir model			Freundlich model		
		Q_m (mg·g^{-1})	b (L·mg^{-1})	R^2	K_f (mg·g^{-1})	n_f	R^2
Zn	LCZ	155.76	0.31	0.89	58.28	0.25	0.83
	HCZ	154.08	0.31	0.87	60.99	0.20	0.66
Cu	LCZ	197.86	1.05	0.94	72.33	0.33	0.68
	HCZ	183.15	1.60	0.98	83.0	0.34	0.81
Cd	LCZ	123.76	0.22	0.81	52.29	0.17	0.61
	HCZ	118.91	0.15	0.82	43.13	0.20	0.78
Pb	LCZ	186.22	20.83	0.98	130.69	0.25	0.35
	HCZ	191.94	16.52	0.99	130.07	0.25	0.36

The Freundlich isotherm model is given as follows:

$$\log q_e = \log K_f + n_f \log C_e \qquad (6)$$

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 of Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ removal by LCZ 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:

$$\text{Recovery efficiency (\%)} = \frac{C_M V}{q_e W} \times 100 \qquad (7)$$

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 Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ 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 Pb²⁺, Cu²⁺, Zn²⁺, and Cd²⁺ 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

| Adsorbent	Maximum sorption capacity (mg·g⁻¹)	Heavy metal ions	System	References
Zeolite-based geopolymer	26.25	Cd²⁺	Single ion	Javadian *et al.* (2015)
Modified zeolite X	91.52, 97.44, 420.21	Cu²⁺, Cd²⁺, Pb²⁺	Single ion	Apiratikul & Pavasant (2008)
Multi-carboxyl-functionalized silica gel	39.96, 47.07, 41.48, 30.80	Zn²⁺, Cu²⁺, Cd²⁺, Ni²⁺	Single ion	Li *et al.* (2014)
Synthesized hydroxy-sodalite zeolite	40.10, 60.10	Zn²⁺, Cd²⁺	Single ion	Izidoro *et al.* (2012)
Synthesized zeolite material ZCET40	69.93, 96.15, 14.20, 238.10, 23.59	Zn²⁺, Cu²⁺, Cd²⁺, Pb²⁺, Ni²⁺	Mixed ions	Visa (2016)
Synthesized zeolite material ZDs40	6.35, 20.83, 14.21, 185.19, 9.95	Zn²⁺, Cu²⁺, Cd²⁺, Pb²⁺, Ni²⁺	Mixed ions	Visa (2016)
LCZ	155.76, 197.86, 123.76, 186.22	Zn²⁺, Cu²⁺, Cd²⁺, Pb²⁺	Mixed ions	This study
HCZ	154.08, 183.15, 118.91, 191.94	Zn²⁺, Cu²⁺, Cd²⁺, Pb²⁺	Mixed ions	This study
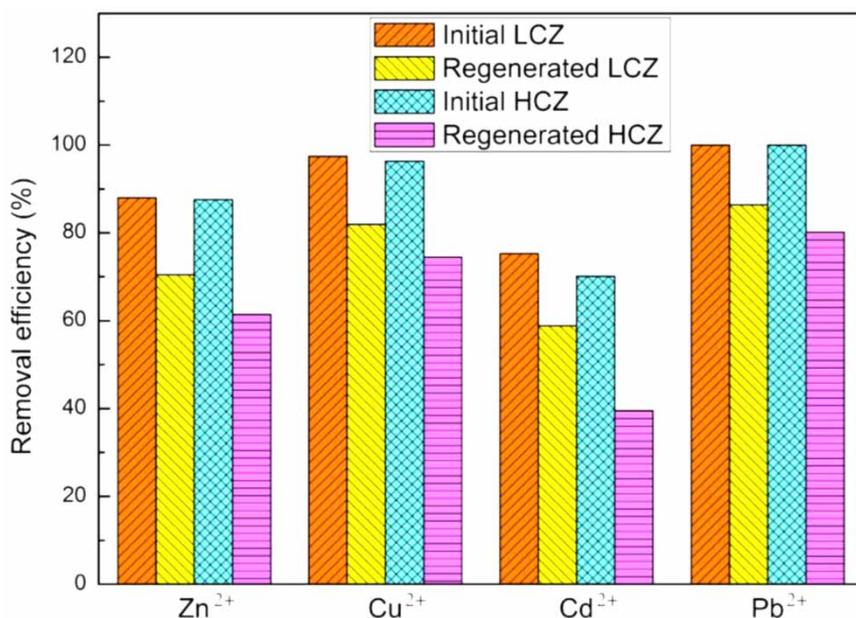
Figure 9 | Comparison of the removal ability for Zn²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ of initial zeolites and regenerated zeolites (adsorbent dosage = 1.0 g·L⁻¹).

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 ≥ 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.

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REFERENCES

Albuquerque, C. F., Luna-Finkler, C. L., Rufino, R. D., Luna, J. M., Menezes, C. T. B. & Santos, V. A. 2012 Evaluation of biosurfactants for removal of heavy metal ions from aqueous

effluent using flotation techniques. *International Review of Chemical Engineering – Rapid Communication* **4** (2), 156–161.

Alloway, B. J. 1990 *Heavy Metals in Soils.* Springer Netherlands, Berlin, Germany.

Amrhein, C., Haghnia, G. H., Kim, T. S., Mosher, P. A., Gagajena, R. C., Amanios, T. & Torre, L. D. L. 1996 Synthesis and properties of zeolites from coal fly ash. *Environmental Science & Technology* **30** (3), 735–742.

Apiratikul, R. & Pavasant, P. 2008 Sorption of Cu^{2+}, Cd^{2+}, and Pb^{2+} using modified zeolite from coal fly ash. *Chemical Engineering Journal* **144** (2), 245–258.

Blissett, R. S. & Rowson, N. A. 2012 A review of the multi-component utilisation of coal fly ash. *Fuel* **97** (7), 1–23.

Chang, H. L. & Shih, W. H. 1998 A general method for the conversion of fly ash into zeolites as ion exchangers for cesium. *Industrial & Engineering Chemistry Research* **37** (1), S188–S189.

Chen, Q. Y., Zhou, L., Hills, C., Gang, X. & Tyrer, M. 2009 Precipitation of heavy metals from wastewater using simulated flue gas: sequent additions of fly ash, lime and carbon dioxide. *Water Research* **43** (10), 2605–2614.

Cui, L., Wu, J. & Ju, H. 2015 Electrochemical sensing of heavy metal ions with inorganic, organic and bio-materials. *Biosensors & Bioelectronics* **63** (63), 276–286.

El Samrani, A. G., Lartiges, B. S. & Villiéras, F. 2008 Chemical coagulation of combined sewer overflow: heavy metal removal and treatment optimization. *Water Research* **42** (4–5), 951–960.

Hall, K. R., Eagleton, L. C., Acrivos, A. & Vermeulen, T. 1966 Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. *Industrial & Engineering Chemistry Fundamentals* **5** (2), 587–594.

He, K., Chen, Y., Tang, Z. & Hu, Y. 2016 Removal of heavy metal ions from aqueous solution by zeolite synthesized from fly ash. *Environmental Science and Pollution Research* **23** (3), 1–11.

Ho, Y. S. & McKay, G. 1999 Pseudo-second order model for sorption processes. *Process Biochemistry* **34** (5), 451–465.

Hollman, G. G., Steenbruggen, G. & Janssen-Jurkovičová, M. 1999 A two-step process for the synthesis of zeolites from coal fly ash. *Fuel* **78** (10), 1225–1230.

Hui, K. S., Chao, C. Y. H. & Kot, S. C. 2005 Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash. *Journal of Hazardous Materials* **127** (1–3), 89–101.

Ivanova, I. I., Kasyanov, I. A., Maerle, A. A. & Zaikovskii, V. I. 2014 Mechanistic study of zeolites recrystallization into micro-mesoporous materials. *Microporous and Mesoporous Materials* **189**, 163–172.

Izidoro, J. d. C., Fungaro, D. A. & Wang, S. 2012 Zeolite synthesis from Brazilian coal fly ash for removal of Zn^{2+} and Cd^{2+} from water. *Advanced Materials Research* **356–360**, 1900–1908.

Izidoro, J. d. C., Fungaro, D. A., Abbott, J. E. & Wang, S. 2013 Synthesis of zeolites X and A from fly ashes for cadmium and zinc removal from aqueous solutions in single and binary ion systems. *Fuel* **103**, 827–834.

Javadian, H., Ghorbani, F., Tayebi, H.-A. & Asl, S. H. 2015 Study of the adsorption of Cd (II) from aqueous solution using zeolite-based geopolymer, synthesized from coal fly ash; kinetic, isotherm and thermodynamic studies. *Arabian Journal of Chemistry* **8** (6), 837–849.

Juan, R., Hernández, S., Andrés, J. M. & Ruiz, C. 2009 Ion exchange uptake of ammonium in wastewater from a sewage treatment plant by zeolitic materials from fly ash. *Journal of Hazardous Materials* **161** (2–3), 781–786.

Jusoh, A., Shiung, L. S., Ali, N. A. & Noor, M. J. M. M. 2007 A simulation study of the removal efficiency of granular activated carbon on cadmium and lead. *Desalination* **206** (1), 9–16.

Kang, S.-Y., Lee, J.-U., Moon, S.-H. & Kim, K.-W. 2004 Competitive adsorption characteristics of Co^{2+}, Ni^{2+}, and Cr^{3+} by IRN-77 cation exchange resin in synthesized wastewater. *Chemosphere* **56** (2), 141–147.

Kang, K. C., Kim, S. S., Choi, J. W. & Kwon, S. H. 2008 Sorption of Cu^{2+} and Cd^{2+} onto acid- and base-pretreated granular activated carbon and activated carbon fiber samples. *Journal of Industrial and Engineering Chemistry* **14** (1), 131–135.

Kołodyńska, D., Krukowska-Bąk, J., Kazmierczak-Razna, J. & Pietrzak, R. 2017 Uptake of heavy metal ions from aqueous solutions by sorbents obtained from the spent ion exchange resins. *Microporous & Mesoporous Materials* **244**, 127–136.

Ku, Y. & Jung, I.-L. 2001 Photocatalytic reduction of Cr(VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide. *Water Research* **35** (1), 135–142.

Lagergren, S. 1898 About the theory of so called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakademiens Handlingar* **24**, 1–39.

Li, M., Li, M.-Y., Feng, C.-G. & Zeng, Q.-X. 2014 Preparation and characterization of multi-carboxyl-functionalized silica gel for removal of Cu (II), Cd (II), Ni (II) and Zn (II) from aqueous solution. *Applied Surface Science* **314**, 1063–1069.

Panayotova, M. I. 2001 Kinetics and thermodynamics of copper ions removal from wastewater by use of zeolite. *Waste Management* **21** (7), 671–676.

Perego, C., Bagatin, R., Tagliabue, M. & Vignola, R. 2013 Zeolites and related mesoporous materials for multi-talented environmental solutions. *Microporous and Mesoporous Materials* **166**, 37–49.

Polat, H. & Erdogan, D. 2007 Heavy metal removal from waste waters by ion flotation. *Journal of Hazardous Materials* **148** (1–2), 267–273.

Querol, X., Moreno, N., Umaña, J. C., Alastuey, A., Hernández, E., López-Soler, A. & Plana, F. 2002 Synthesis of zeolites from coal fly ash: an overview. *International Journal of Coal Geology* **50** (1–4), 413–423.

Shigomoto, N., Hayashi, H. & Miyaura, K. 1993 Selective formation of Na–X zeolite from coal fly ash by fusion with sodium hydroxide prior to hydrothermal reaction. *Journal of Materials Science* **28** (17), 4781–4786.

Tansel, B. 2012 Significance of thermodynamic and physical characteristics on permeation of ions during membrane separation: hydrated radius, hydration free energy and viscous effects. *Separation and Purification Technology* **86**, 119–126.

Teh, C. Y., Budiman, P. M., Shak, K. P. Y. & Wu, T. Y. 2016 Recent advancement of coagulation–flocculation and its application in wastewater treatment. *Industrial & Engineering Chemistry Research* **55** (16), 4363–4389.

Visa, M. 2016 Synthesis and characterization of new zeolite materials obtained from fly ash for heavy metals removal in advanced wastewater treatment. *Powder Technology* **294**, 338–347.

Volkov, A. G., Paula, S. & Deamer, D. W. 1997 Two mechanisms of permeation of small neutral molecules and hydrated ions across phospholipid bilayers. *Bioelectrochemistry and Bioenergetics* **42** (2), 153–160.

Wang, S. 2008 Application of solid ash based catalysts in heterogeneous catalysis. *Environmental Science & Technology* **42** (49), 7055–7063.

Wang, H., Zhou, A., Peng, F., Yu, H. & Yang, J. 2007a Mechanism study on adsorption of acidified multiwalled carbon nanotubes to Pb(II). *Journal of Colloid and Interface Science* **316** (2), 277–283.

Wang, L. K., Hung, Y.-T. & Shammas, N. K. 2007b *Advanced Physicochemical Treatment Technologies*. Humana Press, Totowa, NJ, USA.

Wang, C., Li, J., Sun, X., Wang, L. & Sun, X. 2009a Evaluation of zeolites synthesized from fly ash as potential adsorbents for wastewater containing heavy metals. *Journal of Environmental Sciences* **21** (1), 127–136.

Wang, C., Li, J., Wang, L., Sun, X. & Huang, J. 2009b Adsorption of dye from wastewater by zeolites synthesized from fly ash: kinetic and equilibrium studies. *Chinese Journal of Chemical Engineering* **17** (3), 513–521.

Wang, P., Du, M., Zhu, H., Bao, S., Yang, T. & Zou, M. 2015 Structure regulation of silica nanotubes and their adsorption behaviors for heavy metal ions: pH effect, kinetics, isotherms and mechanism. *Journal of Hazardous Materials* **286**, 533–544.

Yusof, A. M., Keat, L. K., Ibrahim, Z., Majid, Z. A. & Nizam, N. Z. 2010 Kinetic and equilibrium studies of the removal of ammonium ions from aqueous solution by rice husk ash-synthesized zeolite Y and powdered and granulated forms of mordenite. *Journal of Hazardous Materials* **174** (1–3), 380–385.

Zhang, B.-H., Wu, D.-Y., Wang, C., He, S.-B., Zhang, Z.-J. & Kong, H.-N. 2007 Simultaneous removal of ammonium and phosphate by zeolite synthesized from coal fly ash as influenced by acid treatment. *Journal of Environmental Sciences* **19** (5), 540–545.

Zhang, M., Zhang, H., Xu, D., Han, L., Niu, D., Tian, B., Zhang, J., Zhang, L. & Wu, W. 2011a Removal of ammonium from aqueous solutions using zeolite synthesized from fly ash by a fusion method. *Desalination* **271** (1–3), 111–121.

Zhang, M., Zhang, H., Xu, D., Han, L., Niu, D., Zhang, L., Wu, W. & Tian, B. 2011b Ammonium removal from aqueous solution by zeolites synthesized from low-calcium and high-calcium fly ashes. *Desalination* **277** (1–3), 46–53.