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Removal of lead, copper, nickel, cobalt, and zinc from water by a cancrinite-type zeolite synthesized from fly ash

Wei Qiu, Ying Zheng*

Department of Chemical Engineering, University of New Brunswick, 15 Dineen Dr., Fredericton, New Brunswick E3B 5A3, Canada

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ABSTRACT

As a low Si/Al ratio zeolite, cancrinite received very scant study in previous studies on the adsorption removal of heavy metals from water. In this study, a cancrinite-type zeolite (ZFA) was synthesized from Class C fly ash via the molten-salt method. Adsorption equilibriums of Pb^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+} on ZFA were studied in aqueous solutions and were well represented by Langmuir isotherms. The increase of pH levels during the adsorption process suggests that the uptake of heavy metals on ZFA was subjected to an ion exchange mechanism. It is found that the maximum exchange level (MEL) follows the order: Pb^{2+} ($2.530\,mmol\,g^{-1}$) > Cu^{2+} ($2.081\,mmol\,g^{-1}$) > Zn^{2+} ($1.532\,mmol\,g^{-1}$) > Co^{2+} ($1.242\,mmol\,g^{-1}$) > Zn^{2+} ($1.154\,mmol\,g^{-1}$). Comparison with previous studies shows that the MEL of ZFA is higher than the commonly used natural zeolites; and it is also comparable to (or higher than) several synthetic zeolites and ion exchange resins. The high MEL of heavy metals on ZFA is attributed to the high cation exchange capacity (CEC) and proper pore size of cancrinite. The pseudo-first-order kinetics suggests that the ion exchange processes were diffusion-controlled.

1. Introduction

Heavy metals such as lead, copper, nickel, cobalt, and zinc are naturally occurring elements. Small amounts of these elements are common in our environment and they are actually necessary for our health. But large amounts of any of them may cause acute or chronic toxicity [1–3]. Heavy metals in human bodies tend to bioaccumulate, which may result in damaged or reduced mental and central nervous function, and damage to blood composition, lungs, kidneys and liver. The regulatory levels of health metals in drinking level are presented in Table 1 [4–6].

As many heavy metal salts have high solubility in water, many different treatment techniques such as chemical precipitation, coagulation–precipitation, adsorption and ion exchange have been developed to remove heavy metals from contaminated water [7–9]. Coagulation–flocculation and chemical precipitation are perhaps the most widely used, however they both have the drawbacks of difficult sludge disposal and more importantly the diminished effectiveness when treating water with low heavy metal levels [10]. Membrane filtration and reverse osmosis were also reported [11]. However, these methods usually involve expensive materials and high operation costs. Other methods such as electrodialysis, membrane electrolysis and electrochemical precipitation have also been investigated however their applications have been limited due to the high energy consumption [12]. On the other hand, as a cost-effective method ion exchange process normally involve low-cost materials and convenient operations, and they have been proved to be very effective for removing contaminants from water such as ammonia and heavy metals [12–14]. Moreover, ion exchange is particular effective for treating water with low concentration of heavy metals which is very common in practice [9].

The development of potential low-cost adsorbents with high exchanged levels is essential to facilitate the application of ion exchange processes for heavy metal removal. Various materials, including natural and synthetic zeolites, polymeric resins, have been studied for this purpose [15]. Zeolites are known excellent adsorbents that can readily adsorb and exchange metal cations with positive charges in their framework. Studies on heavy metal removal using natural and synthetic zeolites as ion exchangers have been reported [2,11,16]. Cancrinite-type zeolites received scant study for heavy metal removal in reported studies. In this study, we synthesized a cancrinite-type zeolite (ZFA) from Class C fly ash via a molten-salt method. The synthesized product, designated as ZFA, was used as an ion exchanger to remove Pb^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+} from water. The synthesized ZFA was expected to have high exchange levels for heavy metal cations due to its low Si/Al ratio [17]. The uptake of heavy metal cations on ZFA was studied for its mechanism, equilibrium and kinetics. The maximum exchange

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Abbreviations: ZFA, zeolite synthesized from fly ash; MEL, maximum exchange level ($mmol\,g^{-1}$); CEC, cation exchange capacity ($meq\,g^{-1}$).

* Corresponding author. Tel.: +1 506 447 3329; fax: +1 506 453 3591.
E-mail address: yzheng@unb.ca (Y. Zheng).

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Nomenclature

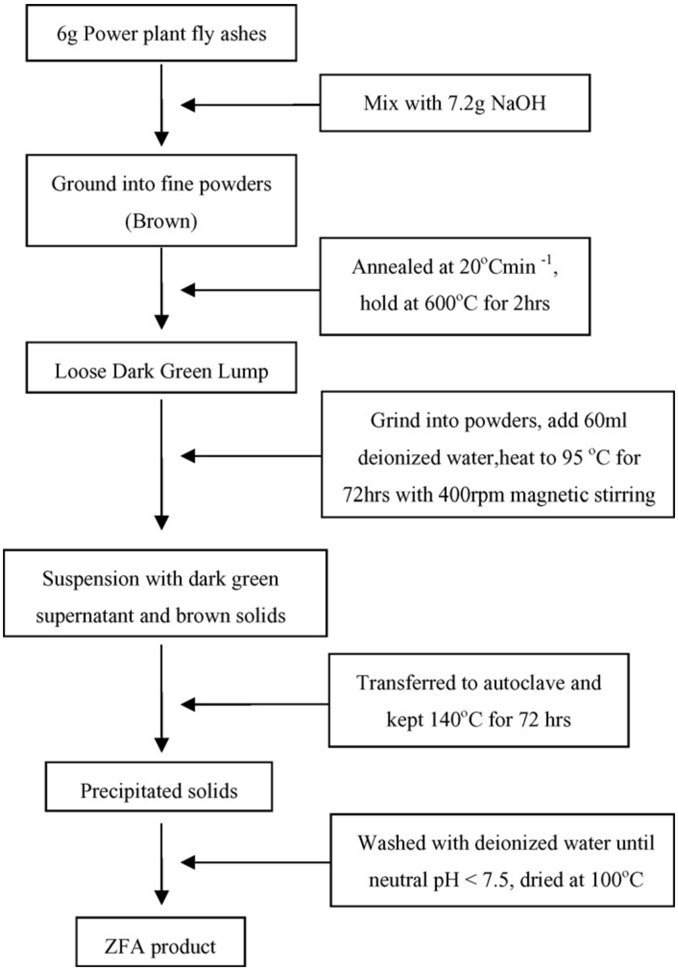
C	concentration of heavy metals (mmol l^{-1})
C_0	initial concentration of heavy metals (mmol l^{-1})
C_{eq}	concentration of heavy metals at equilibrium (mmol l^{-1})
d_c	charge density of cation (m^{-3})
k	kinetic constant of ion exchange process (s^{-1})
q_{eq}	exchanged cations at equilibrium on per mass of ZFA (mmol g^{-1})
Q	valence of cations
Q_0	maximum exchange level of cations on per mass of ZFA (mmol g^{-1})
r	diameter of cation (m)

level (MEL) for different heavy metal species was compared with reported results of other ion exchangers.

2. Experimental

2.1. Preparation and characterization of ZFA

Fly ashes were sampled from the Grand Lake Power Generation Plant (owned by N.B. Power Co.) in New Brunswick, Canada. The preparation of ZFA has been described in our previous work [18,19] and it is presented in the diagram below.



The crystal structure of ZFA was determined by powder X-ray diffraction (XRD) on a Bruker AXS D8 advance X-ray diffractometer. The specific surface area of ZFA was determined by nitrogen adsorption–desorption isotherms at 77 K on a Quantachrome Autosorb-1 Surface Area and Pore Size Analyzer. The BET specific surface area was determined by fitting the linear portion of the plot to the BET equation. Pore size distribution was calculated from the desorption plot of the adsorption–desorption isotherms using the Barrett–Joyner–Halenda (BJH) method.

2.2. Adsorption isotherms

The adsorption isotherms of heavy metals on ZFA were studied in a batch mode in an air-conditioned room with the temperature of 25.0 ± 2.1 °C as monitored by a digital wall-mounted thermometer (Cole-Parmer). Heavy metal nitrates were supplied from Aldrich (Reagent Grade) and used as received. Stock solutions of 4 mmol l^{-1} of $Pb(NO_3)_2$, $Zn(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, and $Cu(NO_3)_2{\cdot}2.5\ H_2O$ were prepared, respectively. Each solution was diluted to obtain a series of solutions containing 0.5–4 mmol l^{-1} heavy metals. Calculated amounts of $NaNO_3$ (99.0%, Aldrich) were added to keep a constant total exchange charge of 8 meq l^{-1} in the solutions, where 1 eq equals 1 mol positive charge. ZFA was added in each solution to give an adsorbent loading of 0.5 g l^{-1}. After adding ZFA, and drops of nitric acid (ACS grade, Fisher) were added to adjust the initial pH to 6.0 ± 0.2 for each solution. Polyethylene bottles containing 100 ml solution of each sample were sealed and shaken at 400 rpm for 72 h on an orbital shaker (KS-130, IKA). The pH was monitored by pH meter (Acumet 3000, Fisher) and re-adjusted to 6.0 ± 0.2 at set time intervals (t = 2, 24, 48, 72 h) to avoid the precipitation of heavy metal cations. The solution was filtered through a 0.45-μm nylon syringe filter (Cole-Parmer). The concentration of heavy metals in the filtration was determined by ICP-AES (inductively coupled plasma-atomic emission spectrometry, Spectro Ciros).

2.3. Adsorption kinetics

The amount of heavy metals exchanged with ZFA was studied as a function of time in batch experiments. A total amount of 500 ml solution with an initial concentration of 4 mmol l^{-1} heavy metal were mixed with 0.5 g ZFA and stirred at 400 rpm on a magnetic stirrer. The solution was acidified before adding the ZFA to avoid the cation precipitation caused by the pH increase. The pH of solution was examined and re-adjusted at the time intervals when samples were collected. Aliquots of samples (10 ml) were collected at set time intervals and immediately filtered by pushing through the 0.45-μm syringe filters. The concentration of heavy metal cations in the filtrate was determined by ICP-AES.

3. Result and discussion

3.1. Characterization of fly ash and ZFA

Fly ashes were sampled from the Grand Lake power generation plant, owned by N.B. Power Co. in New Brunswick, Canada. Fly ashes were used as received. The composition of fly ash has been determined in our previous study as: SiO_2: 31.6 wt.%; Al_2O_3: 27.8 wt.%; Na_2O: 27.7 wt.%; CaO: 6.4 wt.%; Fe_2O_3: 2.1 wt.%; P_2O_5: 1.5 wt.%; MgO: 1.4 wt.%; SO_3: 0.9 wt.%; other: 0.7 wt.% [18]. It can be categorized as Class C fly ash in terms of ASTM C618-99 specification.

The crystallographic structures of ZFA have been determined in our previous work [18]. The XRD pattern in Fig. 1 shows that the dominant phase in ZFA is carbonate cancrinite

Table 1
Drinking water limits of heavy metals

	Lead ($mg\,l^{-1}$)	Copper ($mg\,l^{-1}$)	Nickel ($mg\,l^{-1}$)	Cobalt ($mg\,l^{-1}$)	Zinc ($mg\,l^{-1}$)
EPA [4]	0.015	1.3	n.a.	0.002–0.107[a]	5.0
World Health Organization [5]	0.01	2.0	0.07	n.a.	n.a.
European Union [6]	0.01	2.0	0.02	n.a.	n.a.

[a] No regulatory level data available. Drinking water contains cobalt at an average concentration of 0.002 mg/L but values up to 0.107 mg/L have been reported.

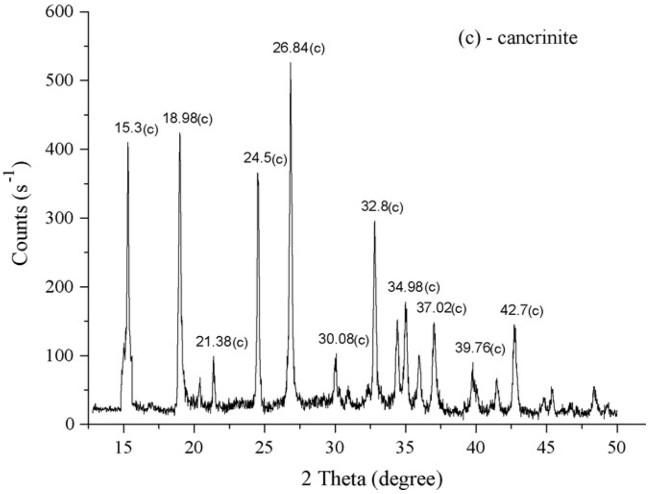


Fig. 1. XRD pattern of ZFA.

($Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2{\cdot}2H_2O$). A minor amount of calcium silicate hydroxide ($Ca_{4.5}Si_6O_{15}(OH)_3{\cdot}2H_2O$) is also found. The nitrogen adsorption–desorption isotherm of ZFA is shown in Fig. 2. The BET surface area of ZFA is 278.9 $m^2\,g^{-1}$. The Type IV adsorption isotherm of ZFA implies the mesoporous structure of materials. The pore size distribution confirms that the pore size of ZFA ranged from 20 Å (1 Å = 0.1 nm) to 200 Å. However, it should be noted that the pore sizes shown in Fig. 2 are of the secondary pores between the cancrinite crystals rather than the pores in the cancrinite framework. The mesoporous pore structure may be favourable for the ion exchange process as it provides easy accesses for sorbate cations to approach the inner micropores in the cancrinite framework since most heavy metal cations are below 5 Å, as shown in Section 3.3.

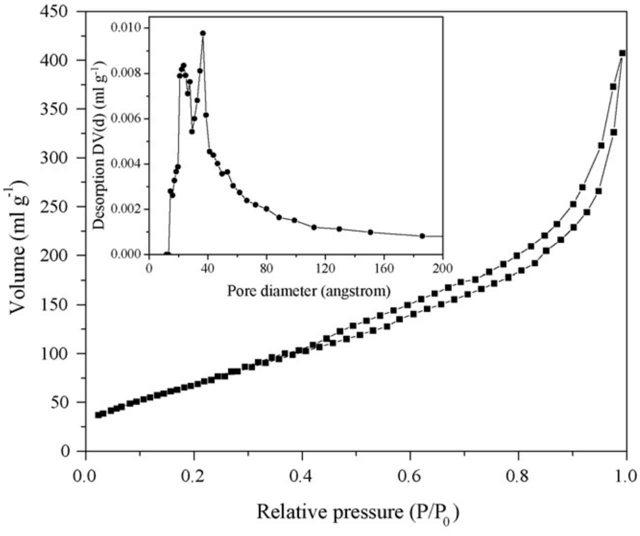


Fig. 2. Nitrogen adsorption–desorption isotherm of ZFA.

3.2. Adsorption mechanism

The uptake of heavy metal cations on zeolites has been extensively studied. Most studies considered it as a cation exchange process between metal cations presence in water and cations in the zeolite framework [2,11,17,20–28]. Researchers also proposed the adsorption of heavy metal cations was due to the surface reaction with terminal hydroxyl groups on zeolites and the combination of positive charges of metal cations and negative charges on zeolite surfaces [9,29,30]. The surface reaction can be described as:

$$n\text{Si–OH} + \text{M}^{n+} \leftrightarrow (\text{Si–O})_n\text{–M} + n\text{H}^+ \quad (1)$$

$$\text{SiO}^- + \text{MOH}^+ \rightarrow \text{SiOMOH} \quad (2)$$

$$n\text{SiO}^- + \text{M}^{n+} \leftrightarrow (\text{Si–O})_n\text{–M} \quad (3)$$

$$n\text{MOH}^+ + \text{M}'(\text{z}) \leftrightarrow \text{M}_n(\text{z}) + \text{M}'^{n+} + n\text{OH}^- \quad (4)$$

Eqs. (1)–(3) represent the surface reaction and charge combination mechanism, and Eq. (4) represents the ion exchange mechanism. M′(z) is the metal cation (mostly Na^+ or Ca^{2+}) in the zeolite framework. MOH^+ is the hydrolyzed divalent metal cation (M^{2+}) in aqueous solution.

According to Eqs. (1)–(3), a pH decrease would be observed if the adsorption follows the surface reaction mechanism, while a preserved pH should be observed once the charge combination is dominated. This is not consistent with the pH measurements during the adsorption process. It was found that the pH of solution continuously increased during the adsorption process, from which we can imply that OH^- groups were generated in the process, which, in turn, supports the ion exchange mechanism in Eq. (4).

Due to the pH increase, it is necessary to adjust the pH of solution during the ion exchange process to avoid the precipitation of heavy metal cations and structural collapse of zeolite at high pH to investigate the ion exchange behaviour of heavy metals on ZFA. The precipitation pH for heavy metals are: Pb^{2+}(7-8), Cu^{2+}(7-14), Ni^{2+}(8-14), Co^{2+}(8-14), and Zn^{2+}(7-8). The initial pH of solution was adjusted to 6.0. The pH was measured at time intervals and adjusted back to 6.0 ± 0.2. It is necessary to ensure the same pH level at the equilibrium for a comparable basis because the negative charge density on zeolite is affected by the solution pH and there are more cation exchange sites on zeolite as higher pH levels [23].

3.3. Equilibrium isotherms

The ion exchange isotherm can be mathematically described by the Langmuir adsorption isotherm:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{Q_0 b} + \frac{C_{eq}}{Q_0} \quad (5)$$

where C_{eq} is the concentration of cations in the solution at equilibrium ($mmol\,l^{-1}$), q_{eq} is the amount of cations exchanged with ZFA at equilibrium ($mmol\,g^{-1}$), Q_0 and b are the parameters corresponding to the MEL ($mmol\,g^{-1}$) and adsorption energy ($g^{-1}\,l$), respectively. Fig. 3 presents the adsorption isotherm results. It is found that the amount of exchanged cations on ZFA (q_{eq}) increased with the equilibrium heavy metal concentrations (C_{eq}), which indicates that a

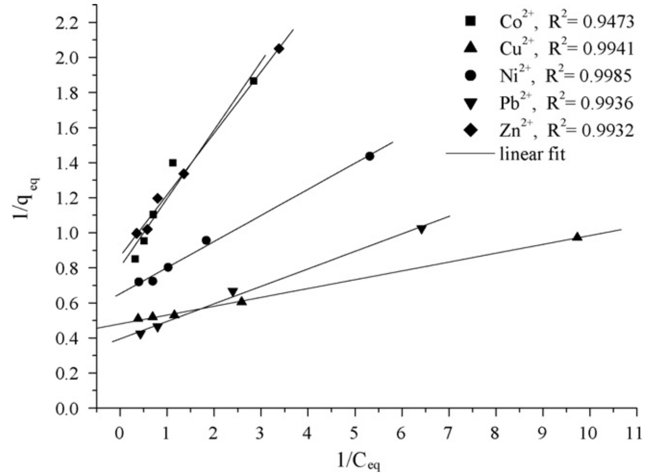


Fig. 3. Ion exchange equilibriums fitted with Langmuir isotherm (8.0 meq l^{-1}, 0.5 g l^{-1} ZFA, 72 h shaking, 400 rpm, 25 °C).

higher concentration of the cations enabled the ion exchange process at the less active exchangeable sites on ZFA. The parameters in the Langmuir equation were determined by fitting experimental results with the mathematical model. Results are shown in Table 2.

As seen from Table 2, the MEL follows the order: $Pb^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}$. The MEL of zeolites generally depends on: (1) the charge density of cations, (2) the exchangeable sites and pore size on the zeolite framework, (3) the equilibrium temperature. Since the ion exchange was conducted at the same condition for each heavy metal species, the different MEL of cations was ascribed to the different charge density of cations. The charge density is described by the following relationship between the electrovalence and the size of cations [31]:

$$d_c = \frac{3Q}{4\pi r^3} \tag{6}$$

d_c is the charge density of cation. Q and r represent the charge of cation expressed in Coulombs and the radius of the cation in meters, respectively. Since the cations are of the same valence (+2) in our study, the order of charge density was determined by the cation size. It has been well established that water was attracted to the positively charged cations due to its dipolar nature and the attracted water molecules created a shell around the cation where the hydrated cation was formed. Erdem et al. reported that [11] heavy metal cations are present as hexaaqua complex ions with six surrounding water molecules in water solution. These cations moved through the pores of ZFA in this form and replace the exchangeable cations. The cation radii and hydrated cation radii are shown in Table 2. The order of charge density generally follows the reverse order of hydrated cation radii except for Cu^{2+} and Ni^{2+}. This discrepancy may be ascribed to the different solubility of $Cu(NO_3)_2$ and $Ni(NO_3)_2$. At 25 °C, they have a solubility of 59.2 g (0.46 mol) and 99.2 g (0.62 mol) in 100 g water, respectively [32]. It was suggested that the solubility was an influencing factor on MEL since a lower solubility of sorbate in water would enable a higher affinity to the adsorbent [9].

Table 3 shows the comparison of the MEL of ZFA and other ion exchangers reported in previous studies. A direct comparison between Tables 2 and 3 shows that ZFA had an exceptionally high MEL than natural zeolites (clinoptilolite and scolecite), and a higher or comparable MEL than several synthetic zeolites including zeolite P_1, zeolite NaY, zeolite A, and ion exchange resins. For some ion exchangers, the experimental values of cation exchange capacity (CEC) are also shown in Table 3. Table 4 compares of the properties of cancrinite and other zeolite-type ion exchangers including the Si/Al ratio, pore size, and CEC. The theoretical CEC gives the maximum capacity of an ion exchanger to accommodate foreign cations, which is determined by the Si/Al ratio and molecule weight of zeolite. It should be noted that the theoretical values of CEC were higher than the experimental data shown in Table 3 due to the fact that some cations located in the small cages may be only exchanged at favourable conditions such as higher temperature, or smaller cations. It could also be ascribed to the unavoidable presence of impurities in the ion exchangers, particularly in the natural zeolites. It is clear that carbonate cancrinite has the highest CEC (theoretical CEC: 9.19 meq g^{-1}) among the zeolite-type ion exchanges. Furthermore, the pore size (5.9 Å) of cancrinite ensures the access for hydrated heavy metal cations to approach exchangeable cations in ZFA framework. For zeolite with relatively small pore sizes such as zeolite P_1 (2.6 Å), Na–A (4.2 Å), clinoptilolite (4.0 Å), and scolecite (3.9 Å), some of the water molecules involved in metal hydration have to be removed in order to accommodate the metal ions within the zeolite channel [26], which eventually hinder the ion exchange process. In addition, the carbonate cancrinite was reported to have a self-buffer ability under acidic solution due to the presence of carbonate anions, and it can undertake a broader pH than other low Si/Al ratio zeolites such as zeolite A and zeolite X [36].

3.4. Ion exchange kinetics

Fig. 4 shows the kinetics plots of residual concentration fraction (C/C_0) versus time. The experimental results have been fitted by first-order kinetics which can be expressed as the equation below,

$$\ln\left(\frac{C}{C_0}\right) = -kt \tag{7}$$

where k is kinetic constant and t is time. The first-order kinetics suggests that the ion exchange process is diffusion-controlled and the rate-determining step is the diffusion of exchangeable ions within the zeolite pore network [24]. Ion exchange equilibriums were attained within 3 h for all cation species. The fast kinetics can be attributed to the relatively large surface area (278.9 $m^2\ g^{-1}$), the mesoporous secondary structure, and the proper pore size of ZFA.

Table 2
Calculated parameters of Langmuir isotherm and cation sizes

Cations	Q_0 (mmol g^{-1})	b (l g^{-1})	R^2	Ionic radii in crystals[a] (nm)	Hydrated cation radii[b] (nm)	Width of hydration shell[c] (nm)
Pb^{2+}	2.130	3.962	0.992	0.119	0.401	0.143
Cu^{2+}	2.081	9.546	0.998	0.073	0.419	0.224
Ni^{2+}	1.532	4.384	0.994	0.049	0.404	0.233
Co^{2+}	1.242	2.063	0.947	0.065	0.423	0.220
Zn^{2+}	1.154	2.472	0.993	0.074	0.430	0.220

[a] Lide, 2006 [32]. Data are for ions with coordination number of six.
[b] Nightingale, E.R. Jr., 1959 [33]. The hydrated cation radii were determined at 25 °C.
[c] Marcus, Y., 1991 [34]. The hydration shell widths were determined at 25 °C.

Table 3
Comparison of MEL with other ion exchangers

Metal	Ion exchanger	Composition	CEC[a] (meq g^{-1})	MEL (mmol g^{-1})	Literature
Pb^{2+}	Natural clinoptilolite	$Na_{3.6}K_{1.5}Ca_{2.8}(Al_{7.8}Si_{27.4}O_{72})\cdot 27.8H_2O$	n.a.	0.42	[25]
	Na-Clinoptilolite	$Na_{7.3}Si_{29}Al_7O_{72}\cdot 23.9H_2O$	2.22	0.82	[18]
	Na-P_1 (synthesized from fly ash)	$Na_6Al_4Si_4O_{24}\cdot 4H_2O$	1.66	0.34	[21]
	Na-Y	$Na_{58}Al_{58}Si_{134}O_{384}\cdot 260H_2O$	n.a.	0.50	[16]
	Ca-alginate based ion exchange resin	n.a.	n.a.	2.01	[35]
Cu^{2+}	Natural clinoptilolite	$Na_{0.1}K_{8.57}Ba_{0.04}(Al_{9.3}Si_{26.83}O_{72})\cdot 19.56H_2O$	0.74	0.14	[8]
	Na-Clinoptilolite	$Na_{7.3}Si_{29}Al_7O_{72}\cdot 23.9H_2O$	2.22	0.74	[18]
	Na-Y	$Na_{58}Al_{58}Si_{134}O_{384}\cdot 260H_2O$	n.a.	2.04	[17]
	Zeolite 4A	$Na_{12}Al_{12}Si_{12}O_{48}\cdot 27.4H_2O$	5.44	2.25	[20]
Ni^{2+}	Natural scolecite	$Na_{2.6}Ca_{9.5}Al_{21}Si_{30}O_{100}\cdot 3H_2O$	5.2	1.19	[22]
	Zeolite 4A	$Na_{12}Al_{12}Si_{12}O_{48}\cdot 27.4H_2O$	5.44	1.36	[20]
	Na-Y	$Na_{58}Al_{58}Si_{134}O_{384}\cdot 260H_2O$	n.a.	1.57	[17]
	IRN 77	Polystyrene DVB gel with sulfonic acid	2.38	1.06	[13]
Co^{2+}	Natural clinoptilolite	$Na_{0.1}K_{8.57}Ba_{0.04}(Al_{9.3}Si_{26.83}O_{72})\cdot 19.56H_2O$	0.74	0.24	[8]
	Na-Y	$Na_{58}Al_{58}Si_{134}O_{384}\cdot 260H_2O$	n.a.	1	[19]
	Na-A (synthesized from fly ash)	$Na_{12}Al_{12}Si_{12}O_{48}\cdot 24H_2O$	n.a.	≤1.36	[14]
	IRN 77	Polystyrene DVB gel with sulfonic acid	2.38	1.28	[3]
	SKN 1	n.a.	~1.7	1.02	[3]
Zn^{2+}	Natural clinoptilolite	$Na_{3.6}K_{1.5}Ca_{2.8}(Al_{7.8}Si_{27.4}O_{72})\cdot 27.8H_2O$	n.a.	0.21	[25]
	Natural clinoptilolite	$K_2Ca_{1.3}Al_{5.2}Si_{30.8}O_{72}\cdot xH_2O$	1.47	0.75	[24]
	Na-Clinoptilolite	$Na_{7.3}Si_{29}Al_7O_{72}\cdot 23.9H_2O$	2.22	0.60	[18]
	Zeolite A	$Na_2Al_2Si_{1.85}O_{7.7}\cdot 5.1H_2O$	5.45	2.53	[23]

[a] Experimental data from the literature.

Table 4
Properties of different types of ion exchangers

Zeolite	Main composition	Si/Al	Pore size (Å)	Theoretical CEC (meq g^{-1})
Cancrinite	$Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2\cdot 2H_2O$	~1	5.9	9.19
Na-Clinoptilolite	$Na_4Al_4Si_{15}O_{36}\cdot 12H_2O$	4.14	4.0	2.83
Scolecite	$Ca_2Al_2Si_3O_{10}\cdot 3H_2O$	1.42	3.9	5.10
Na-P_1	$Na_6Al_4Si_4O_{24}\cdot 4H_2O$	~1	2.6	7.37
Na-Y	$Na_{58}Al_{58}Si_{134}O_{384}\cdot 260H_2O$	2.3	7.4	4.53
Na-A	$Na_{12}Al_{12}Si_{12}O_{48}\cdot 24H_2O$	1.21	4.2	5.62

The kinetic constants are calculated based on the model fitting results. It is found that the order of kinetic constants agrees with the order of MEL ($k_{Pb} = 8.849 \times 10^{-4}\,s^{-1}$, $k_{Cu} = 4.777 \times 10^{-4}\,s^{-1}$, $k_{Ni} = 2.607 \times 10^{-4}\,s^{-1}$, $k_{Co} = 2.200 \times 10^{-4}\,s^{-1}$, $k_{Zn} = 1.876 \times 10^{-4}\,s^{-1}$). Also, it is shown that the time required to reach equilibrium for each heavy metal solution generally conforms to reverse order of the hydrated cation radii, which proves that a smaller size of cation enables it to move through the pores and channels of ZFA more easily (faster diffusion rate) and have more accesses to the exchangeable sites in ZFA (larger MEL).

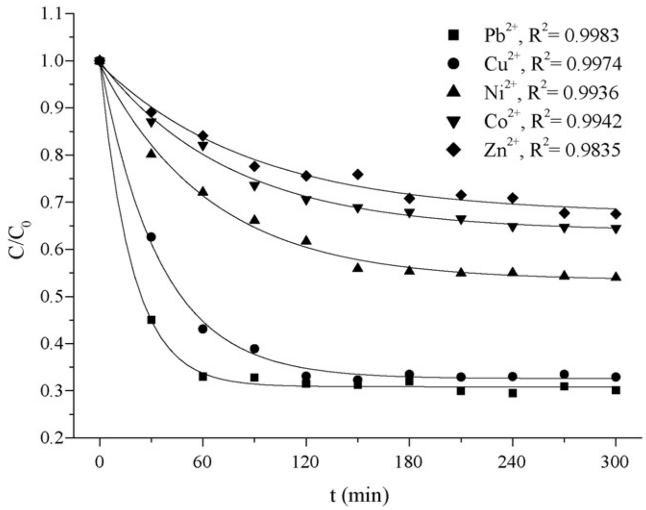


Fig. 4. Kinetics plots fitted with pseudo-first-order kinetics model (4.0 mmol l^{-1}, 1.0 g l^{-1} ZFA, 72 h shaking, 400 rpm, 25 °C).

4. Conclusion

(1) The cancrinite-type ZFA synthesized from fly ash by molten method can be used as an alternative ion exchanger for the heavy metal removal from water.
(2) For the removal of lead, copper, nickel, cobalt, and zinc, the synthesized ZFA has a higher MEL than natural zeolites (clinoptilolite and scolecite). It also shows a higher or comparable MEL than several synthetic zeolites (zeolite NaP_1, NaY, zeolite A), and ion exchange resins (IRN 77, SKN 1, Ca-alginate based resin). The high MEL of ZFA was attributed to the low Si/Al ratio and proper pore size of cancrinite.
(3) The ion exchange showed a pseudo-first-order kinetics, which suggests the ion exchange process is diffusion-controlled. The relatively large specific area (278.9 m^2 g^{-1}) and mesoporous secondary pore structure of ZFA are favourable for the diffusion of heavy metal cations into the ZFA pores.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2008.05.001.

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