



Evaluation of zeolites synthesized from fly ash as potential adsorbents for wastewater containing heavy metals

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Abstract

The pure-form zeolites (A and X) were synthesized by applying a two-stage method during hydrothermal treatment of fly ash prepared initial Cu and Zn gel. The difference of adsorption capacity of both synthesized zeolites was assessed using Cu and Zn as target heavy metal ions. It was found that adsorption capacity of zeolite A showed much higher value than that of zeolite X. Thus, attention was focused on investigating the removal performance of heavy metal ions in aqueous solution on zeolite A, comparing with zeolite HS (hydroxyl-solidate) prepared from the residual fly ash (after synthesis of pure-form zeolite A from fly ash) and a commercial grade zeolite A. Batch method was used to study the influential parameters of the adsorption process. The equilibrium data were well fitted by the Langmuir model. The removal mechanism of metal ions followed adsorption and ion exchange processes. Attempts were also made to recover heavy metal ions and regenerate adsorbents.

Key words: fly ash; zeolite; heavy metal; adsorption; recovery

Introduction

It has been known that heavy metal ions are among the most important pollutants in several industrial wastewaters. The presence of the toxic metals generated by metal finishing or mineral processing industries in streams and lakes can result in major hazards to the environment and public health (Matis *et al.*, 1998). Thus, the tighter regulations established in many countries require to remove effectively toxic heavy metal ions from the wastewaters prior to discharge into natural water. During the last few years, the common methods available to remove heavy metal ions from wastewaters are including coagulation, chemical precipitation, ion-exchange, adsorption, and reverse osmosis. Most of these methods not only require highly capital and operational costs and large amount of chemical in actual application, but also produce a problem that how to deal with residual metal sludge. Ion exchange method is feasible for the full-scale application and resin can be used as an ion exchanger that has a high selectivity for heavy metal ions removal. Generally, the metal-saturated resin was incinerated to recover heavy metals. However, the cost of this recovery process can be never afforded in large-scale application. Among these processes, adsorption technique employing solid adsorbents are well established for treating industrial wastewaters containing heavy metals. Currently, activated

carbon, is the most popular adsorbents. However, activated carbon suffers from drawback of the cost in production and regeneration. Thus, there is a need to develop inexpensive and readily regenerative adsorbents for substituting activated carbon and resins to perform metals purification function.

Fly ash is a waste material generated from electric power plants and approximate 500 million tons of fly ash is discharged per year throughout the world. Because fly ash has a pozzolanic property after reacted with lime (Inada *et al.*, 2005), about 20% of fly ash is used as building materials. However, the remaining fly ash disposed in landfill still causes an increasing threat to the environment due to its fine structure and toxic elements. As one of economically viable solutions, the utilization of fly ash as inexpensive adsorbents has also been widely attempted for flue gas cleaning (Davini, 1995; Kastner *et al.*, 2002; Lu and Do, 1991) and removal of toxic metals (Ayala *et al.*, 1998; Bayat, 2002; Dasmahapatra *et al.*, 1996; Panday *et al.*, 1985), dyes (Gupta *et al.*, 2004; Mohan *et al.*, 2002), and organics (Aksu and Yener, 2001) from wastewaters. However, in those cases, the fly ash still exhibit low adsorption capacity.

Zeolites have been found widespread application in ion exchange, molecular sieve and adsorption due to their structural characteristics and valuable properties. Conversion of fly ash into zeolites becomes one important issue of waste management in the recent years (Hollman *et al.*, 1999; Hui and Chao, 2006; Molina and Poole, 2004;

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Park *et al.*, 2000; Tanaka *et al.*, 2002). The most common method used for zeolites synthesized from fly ash involves a hydrothermal process (Inada *et al.*, 2005; Park *et al.*, 2000), where fly ash is mixed with an alkali solution such as NaOH at the required conditions. A new synthesis process has been developed by introducing alkaline fusion stage prior to the conventional zeolites synthesis, usually known as the fusion method. This significantly improved the zeolitisation process and can obtain single-phase and high-crystalline zeolites such as zeolites A and X. Mishra and Tiwari (2006) compared the adsorption behavior of Cu^{2+} , Co^{2+} , and Ni^{2+} by fly ash and synthetic zeolite X. They found that the adsorption behavior of synthetic zeolite X was greater than fly ash. Wang *et al.* (2006) found that a pseudo second-order kinetics best fitted the dynamic adsorption of Cu^{2+} and Ni^{2+} in aqueous solution by the obtained zeolite P from modifying fly ash with NaOH solution. However, the synthetic products not only varied widely but also contained a significant amount of non-zeolitic phases. Moreover, zeolites Na-P1 and hydroxyl-solidate and non-zeolitic phases existing in the synthetic products hinder its potential applications owing to their more condensed structure (low pore volume). Hollman *et al.* (1999) first presented a two-stage method that enables to synthesize pure-form zeolites from high-Si solution extracted by NaOH solution from fly ash. This process has the advantage of synthesizing pure-form zeolites such as zeolites A and X (high pore volume), instead of blend zeolites/residual fly ash particles obtained from other methods (Hui and Chao, 2006; Park *et al.*, 2000). Hui *et al.* (2005) investigated the removal performance and the selectivity sequence of mixed heavy metal ions in aqueous solution on pure-form zeolite A prepared from fly ash, commercial grade zeolite A, and the residual products recycled from fly ash. They found that the equilibrium data were well fitted by the Langmuir model and showed the affinity order: $\text{Cu}^{2+} > \text{Cr}^{3+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+}$ (fly ash prepared and commercial grade zeolite A). However, there were no studies about recover heavy metals and regenerate the spent adsorbents. Knowledge on this topic could be useful in designing wastewater treatment systems using inexpensive adsorbents. In fact, after synthesis of pure-form zeolite A from fly ash, the residual fly ash from the process may also be potential adsorbents with further treatment and is worthy of a comprehensive study, especially considering few Si sources are left behind as residues in synthesis process.

The present work was performed to explore a possibility of utilizing the synthetic pure-form zeolites from fly ash to remove and recover heavy metal ions. Copper and zinc ions were chosen as target metal ions for the adsorption studies. The removal performance of heavy metal ions on both synthetic pure-form zeolites (A and X) were investigated, and the influencing factors were studied. Moreover, an attempt was made to investigate the removal performance of heavy metal ions on the modified residual fly ash. In order to develop an industrial application, heavy metal ions recovery and adsorbents regeneration were also investigated.

1 Materials and methods

1.1 Fly ash

Raw fly ash was obtained from a power plant located in Henan Province of China using electrostatic precipitators. The chemical composition of raw fly ash was determined by XRF (ARL9800XP+, Sweden) and is shown in Table 1. The average diameter of raw fly ash particles determined by a particle size analyzer (Malvern Instrument, UK) is $1.44 \mu\text{m}$ and the surface area calculated from N_2 isotherms at -196°C is $2.44 \text{ m}^2/\text{g}$.

Before synthesis, raw fly ash was pretreated by acid-washing process performed on a mixture of hydrochloric acid solution (10%) and fly ash (ratio, 25:1 (mL/g)) in a beaker. The beaker was kept in a water bath at 80°C for 1 h and stirred constantly (300 r/min). Then, fly ash was filtered off, washed repeatedly with distilled water and dried at 100°C for 24 h for further use. Table 1 also shows the three major composition of fly ash (involved composition for zeolitic adsorbents synthesis) obtained after acid-washing process.

1.2 Adsorbents

The pure-form zeolites were synthesized from fly ash by a two-step method. Generally, Si source of fly ash was extracted by an extraction process performed on a mixture of NaOH solution and fly ash with NaOH concentrations of 1.67 and 3.33 mol/L, respectively. The beaker was placed in a water bath at 80°C for 2 h with stirring constantly (300 r/min). The solution was separated from the mixture by a filtration for further use. The volume obtained in the solution was about 90 mL and the Si concentration was 21.66 and 29.85 mg/L, respectively. Then, 2.4 g and 1 g of NaAlO_2 (Shanghai Chemical Reagents, China) was mixed respectively with 30 mL of 1.67 mol/L NaOH solution to prepare NaOH- NaAlO_2 solution. The NaOH- NaAlO_2 solution was poured into the solution to form initial gel, then about 120 mL of initial gel was stirred intensely at 25°C for 30 min. Afterward, 120 mL of initial gel was transferred into specially designed stainless alloy autoclaves with thin walls which allow a fast heat transfer and were kept in oven at 100°C and autogenous pressure. After a desired crystallization times (5.5, 24 h), the solids were filtered, washed repeatedly with distilled water until the pH of washing water reach 7, dried at 100°C and kept in powder form for further use. The synthesis conditions

Table 1 Chemical composition of raw and pretreated fly ash

Component	Percentage (wt.%)	Component	Percentage (wt.%)
Raw fly ash			
SiO_2	49.29	CaO	2.05
Al_2O_3	33.07	MgO	0.27
Fe_2O_3	5.76	Na_2O	2.22
K_2O	2.58	MnO	0.13
TiO_2	1.18		
Pretreated fly ash			
SiO_2	59.62	Fe_2O_3	1.40
Al_2O_3	30.95		

of both pure-form zeolites (A and X) are summarized in Table 2. Before the adsorption test, the synthetic pure-form zeolites were pretreated by 1 mol/L NaCl solution to near Na-form to increase its effective adsorption capacity. In order to recycle fly ash completely, the residual fly ash was treated by NaOH fusion for adsorption test. The treatment process comprises two stages. First, 9 g of residual fly ash was mixed with 11.7 g of NaOH to obtain a homogeneous mixture; then heated in a nickel crucible in air at 600°C for 90 min. Second, the fusion product was ground and dissolved in 120 mL of distilled water, followed by an ageing process with vigorous agitation at 25°C for 24 h. The mixture was then crystallized at 100°C for 48 h. At the end of the process the solid is separated by filtration, wash with distilled water (until the filtrate pH reached to 7), dried at 100°C and kept in powder form for further use. The commercial grade zeolites purchased from Luoyang Jianlong Chemical Co., Ltd., China were also used in the adsorption study for comparing.

1.3 Characterization

The XRD pattern was recorded on a Bruker D8 Advance X-ray diffraction instrument (Cu, K_α), the diffraction angle (2θ) in the range 2–50° was scanned (Bruker, Germany). SEM images were obtained using JEOL JSM-6380LV electron microscope (JEOLJSM-6380LV, Japan). Cation exchange capacity (CEC) values were determined using the ammonium acetate method (Molina and Poole, 2004). The results were expressed as milliequivalents per 100 g of solids.

1.4 Adsorption experiments

Two heavy metal ion solutions (Cu^{2+} and Zn^{2+} , 300 mg/L for each) were prepared using $\text{Cu}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$ of analytical reagent grade in distilled water, respectively. The initial pH of the solutions was adjusted to the desired value by adding 2% HNO_3 and 1 mol/L NaOH solution.

The adsorption experiments of Cu^{2+} and Zn^{2+} were carried out from 100 mL of the solution containing different concentrations with 0.5 g adsorbents in a 250-mL stoppered conical flask. All adsorption experiments were carried out on a shaker at 150 r/min. After adsorption, the solution was filtered and pH was adjusted to 3 with 2% HNO_3 for avoiding any precipitation. The Cu^{2+} and Zn^{2+} concentration in solution were measured by an atomic adsorption spectrometer (AA320CRT, Shanghai, China). After preliminary experiment, the equilibrium time of all adsorption experiments was set as 4 h.

In order to investigate the adsorption capacity, removal efficiency (R_{em} , %) of metal ions on the adsorbents and

the amount of metal ions adsorbed on the adsorbents (q_e , mg/g) were calculated by Eqs. (1) and (2), respectively.

$$R_{\text{em}} = ((C_0 - C_e)/C_0) \times 100\% \quad (1)$$

$$q_e = V(C_0 - C_e) \times 10^{-3}/W \quad (2)$$

where, C_0 and C_e (mg/L) are the initial and equilibrium heavy metal ion concentration of the test solution, respectively. V (L) is the test solution volume, and W (g) is the amounts of adsorbents.

1.5 Heavy metals recovery and adsorbents regeneration

It is important to recover the valuable heavy metals from adsorbents and regenerate the spent adsorbents. The experiments were carried out by using NaCl solution to elute the metal-saturated adsorbents. The metal-saturated adsorbents (3 g original adsorbents reach to saturation at the initial pH 3.0) and 100 mL of 5% NaCl solution were mixed in a 250-mL stoppered conical flask and was shaken (150 r/min) at 25°C for 1 h. Then the solid was separated by filtration, dried at 100°C. The subsequent processes were the same as the above cycle, i.e., the obtained regenerative adsorbents reached to saturation again and were eluted by 5% NaCl solution to recover heavy metal ions, filtered and dried for further use. The recovery efficiency (R_{ec} , %) of metal ions was considered as Eq. (3):

$$R_{\text{ec}} = (C_M \times V)/q_e W \times 100\% \quad (3)$$

where, C_M (mg/L) is heavy metal ion concentration existing in 5% NaCl solution after recovery, V (L) is the 5% NaCl solution volume, q_e (mg/g) is the amount of metal ions adsorbed on the adsorbents, and W (g) is the amounts of zeolitic adsorbents.

The adsorption of heavy metal ions on regenerative adsorbents obtained at each cycle was conducted by the batch experiments at different temperature (15–40°C) and adsorbents dosage (0.5–2 g).

2 Results and discussion

2.1 Characterization of adsorbents

The XRD patterns in Fig. 1 illustrate that both synthetic products from fly ash were identified as pure-form and high-crystalline zeolites A (PDF card No.39-0222) and X (PDF card No.39-1380), respectively. It has been known that they are synthesized from initial gel differing essentially in $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios (higher for zeolite X) (Weitkamp and Puppe, 1999). For both prepared initial gel, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios were adjusted to 2.22 and 7.36

Table 2 Synthesis conditions of both pure-form zeolites (zeolites A and X)

Zeolite	Formation of initial gel				Crystallization conditions	
	Filtrate		NaOH-NaAlO ₂ solution		Temperature (°C)	Time (h)
	Fly ash (g)	NaOH solution	NaAlO ₂ (g)	NaOH solution		
Zeolite A	9	90 mL of 1.67 mol/L	2.4	30 mL of 1.67 mol/L	100	5.5
Zeolite X	9	90 mL of 3.33 mol/L	1	30 mL of 1.67 mol/L	100	24

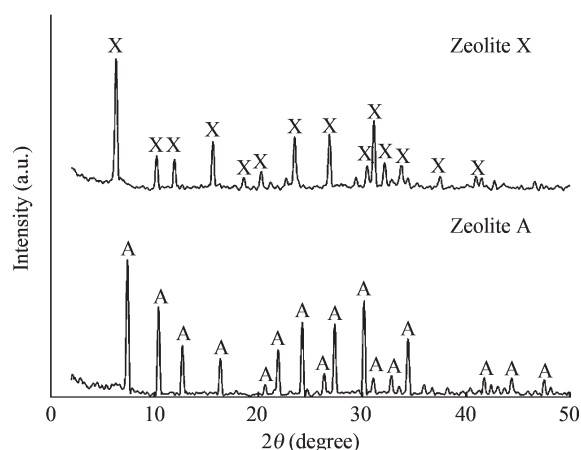


Fig. 1 XRD patterns of synthetic pure-form zeolites A and X.

by adding Al source to favor the formation of zeolites A and X, respectively. It is also worth noting the difference in crystallization time required for both zeolites (Table 2). The structural formation of zeolite X requires longer crystallization time due to its more complex and larger polymeric silicate units (D6R, double six rings) and sparser structure (Petrovic *et al.*, 1993). Morphological analysis of zeolites A and X performed by SEM is shown in Fig. 2. It was observed that zeolite A was in the formation of chamfered-edged cubes and the morphology of zeolite X generally exhibits to octahedral particles. Moreover, XRD patterns in Fig. 1 proved that crystalline particles with lattice fringe that can be assigned to (110) face of the cubic structure of zeolite A (Valentin *et al.*, 2005) and the crystallographic planes (111) was reflected to the structure of zeolite X (Breck, 1974). The particle size of zeolites A and X were in the range 1–5 μm with an average diameter of 2.5 μm and 1–4 μm with an average diameter of 2.7 μm , respectively. It has been demonstrated that the synthetic zeolites from pure chemicals result in no hazards to the environment and public health (Christophliemk *et al.*, 1992; Gloxhuber *et al.*, 1983). To understand whether there was any toxic element existing in the synthetic zeolites from fly ash, a comparative study of elemental composition between the synthetic zeolites from fly ash and commercial grade zeolites were conducted. Table 3 lists various trace elements of the synthetic zeolites and commercial grade zeolites. The results show that the synthetic zeolites do not pose any serious threat to environment and public health when compare with commercial grade zeolite. Apparently,

the presence of these elements, such as Fe, Mn, Mg, Ti, Ca and K, existing in the synthetic zeolites A may be due to the dissolution of these elements of fly ash under alkaline conditions, and may then be incorporated into framework structure of zeolites during hydrothermal treatment.

According to Fig. 3, it is evident that acid-washing process prior to synthesis contributes to improve the CEC values of the products. The CEC values in zeolites A and X increased about 38% and 35%, respectively. The percentage of the CEC values of the zeolites A and X reached 95.84% and 97.06%, respectively, compared to the commercial zeolites. This behavior can be explained in the light of the synthesis processes. Iron oxides bearing composition in fly ash can be dissolved by NaOH solution, and then form the precipitates (insoluble iron

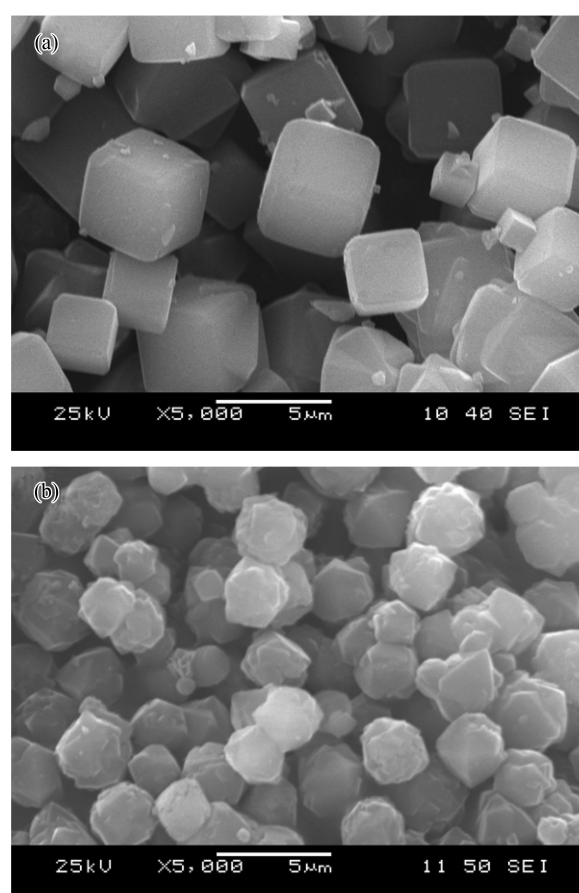


Fig. 2 SEM images of synthetic pure-form zeolites. (a) zeolite A; (b) zeolite X.

Table 3 Comparison of elemental composition of both synthetic pure-form zeolites and the commercial grade zeolites (wt.%)

Composition (wt.%)	Zeolite A		Zeolite X	
	Fly ash synthesized	Commercial	Fly ash synthesized	Commercial
SiO ₂	42.66	44.88	44.14	49.17
Al ₂ O ₃	35.27	34.72	33.62	34.72
Na ₂ O	19.89	20.37	19.01	18.87
Fe ₂ O ₃	0.36	0.32	0.79	0.50
K ₂ O	0.35	0.15	0.47	0.30
TiO ₂	1.15	nda	0.68	nda
CaO	0.41	0.62	0.28	0.48
MgO	1.02	0.93	0.85	1.03
MnO	nd	0.23	0.43	0.32

nd: Not detected.

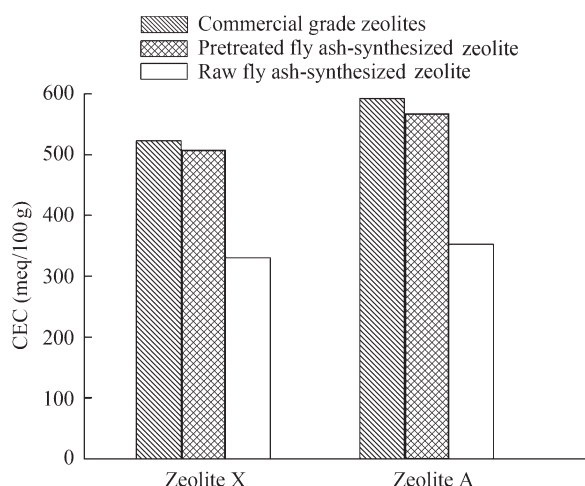


Fig. 3 Comparison of the CEC values of synthetic pure-form zeolites from raw and pretreated fly ash and the commercial grade zeolites.

hydroxides) (Weitkamp and Puppe, 1999). This yields not only a brownish tinge (Rayalu *et al.*, 2001) but also the undesirable products which have a deleterious effect on the CEC values.

Since acid-washing process clearly demonstrated a benefit effect on synthesis, only the synthetic pure-form zeolites from pretreated fly ash was used for subsequent comparative studies.

2.2 Removal performance of heavy metal ions on both synthetic pure-form zeolites

Figure 4 presents the comparative results of the adsorption capacity of zeolites A and X for heavy metal ions. It showed that zeolite A had a higher removal efficiency than zeolite X. For zeolite A, the amount of Cu^{2+} ion adsorbed is 37.99 mg/g, and 29.68 mg/g for Zn^{2+} . For zeolite X, the amount of Cu^{2+} adsorbed is 28.88 mg/g, and 22.44 mg/g for Zn^{2+} . The observed adsorption behavior may be explained by that: (1) the nature of metals, such as hydrated size, ionic potential and hydrolysis constant (K_h); (2) framework structure of zeolites, such as the effective pore size and the amount of exchangeable Na^+ bonded to zeolites framework (Chang and Shih, 1998, 2000). Zeolites

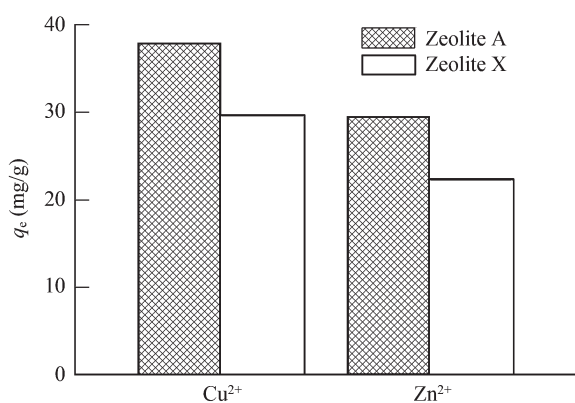


Fig. 4 Comparison of adsorption capacity of synthetic pure-form zeolites. Adsorption conditions: adsorbents dosage 0.5 g; C_0 200 mg/L; 25°C; pH 3.0.

A and X, in general, have the effective pore size of 0.42 and 0.74 nm, respectively. A common factor preventing metal ions from being adsorbed on zeolites is the size of hydrated ion. According to hydrated radii reported for Cu^{2+} and Zn^{2+} ions, i.e., 0.419 and 0.43 nm (Semmens and Seyfarth, 1978), the hydrated ion size is greater than that of the effective pore size of zeolites A and X. Thus, the metal ions may be excluded or the waters of hydration must be stripped from the solvated ion to enable them enter the pores of zeolites (Hui *et al.*, 2005). According to the effective pore sizes of zeolites A and X, the amount of metal ions adsorbed on zeolite X should exhibit more than zeolite A. However, the effective pore sizes of zeolites A and X do not be explained well the high adsorption capacity of the synthetic zeolite A. It is speculated that the main mechanism involved in the sorption of metal ions is based on cation exchange reaction of zeolites. It is known that the Si/Al molar ratio of zeolite A (from 1 to 1.2) is lower than that of zeolite X (from 1 to 1.5). The smaller Si/Al molar ratio in the zeolite framework produces more charge deficiency. Thus, the framework needs more Na^+ to compensate the excess negative charge and more exchangeable Na^+ exist in the zeolite structure. In other words, the amount of exchangeable Na^+ is inversely proportional to the Si/Al molar ratio in the framework of the zeolite structure (Breck, 1974). A similar result was obtained for the CEC (NH_4^+) values of zeolites A and X from fly ash in this study. Thus, the amount of exchangeable Na^+ bonded to zeolites framework play an important role in the removal performance of heavy metal ions.

It is also observed from Fig. 4 that the amount of Cu^{2+} was evidently higher than that of Zn^{2+} . The difference is influenced by not only the size of hydrated ion but also the ionic potential and hydrolysis constant (K_h) value of the metal ions in aqueous solution (Mishra and Tiwari, 2006). Cu^{2+} has a low $\text{p}K_h$ (8.00) value in comparison to Zn^{2+} (9.20) (Perrin and Dempsey, 1974). Generally, zeolites have high adsorption capacity for metal ion with low ionic potential and low $\text{p}K_h$ value. The similar results were reported by Hui *et al.* (2005) and Alvarez-Ayuso *et al.* (2003), for the adsorption of Cu^{2+} on zeolites A and NaP1, respectively. They considered that the main mechanism of Cu^{2+} removal was based on precipitation of metal hydroxides on the surface of zeolites or inside the pore wall. In addition, Hui *et al.* (2005) found that there were exchangeable ions (Si^{4+} , Al^{3+} , and Na^+) leached from zeolite framework at acid condition during adsorption process. The leaching of Si- and Al-species may be due to the effect of H^+ on the aluminosilicate framework of zeolites, which initially causes a rupture of the Al-O bond and further detachment of Si- and Al-species through hydrolysis reactions (Filippidis *et al.*, 1996). By investigating the ratio of exchanged Na^+ to total adsorbed metal ions, it was concluded that the adsorption of metal ions depended on the common function of cation exchange reaction of zeolites and precipitation of metal hydroxides (Hui *et al.*, 2005). From the results obtained, it is expected that the synthetic pure-form zeolite A from fly ash could

be considered for usage of purifying heavy metal ions wastewater.

2.3 NaOH fusion treatment of residual fly ash

Figure 5a shows the XRD pattern of the fused residual fly ash, indicating that the main components were sodium silicate and sodium aluminosilicate, which indicated that the major crystalline phases quartz and mullite in the residual fly ash were converted into sodium silicate and sodium aluminosilicate. After hydrothermal treatment of the fused residual fly ash, shows the major produced phase in Fig. 5b is identified as single-phase and high-crystalline zeolite hydroxyl-solite (PDF card No.37-0476). Zeolite hydroxyl-solite ($\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$) has a small pore size of 0.23 nm. The sodium silicate is easily soluble in water, while sodium aluminosilicate is soluble in alkaline solution. It is considered that aluminate ions and silicate ions are condensed during alkaline dissolving process of the fused residual fly ash to form an aluminosilicate gel which can be used as zeolites precursor and crystallization of zeolites. Inada *et al.* (2005) found that the Si-lean residual fly ash has a tendency to form hydroxyl-solite with the small $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio.

2.4 Adsorption studies of heavy metal ions

The labeling of the synthetic pure-form zeolite A from fly ash, zeolite HS (hydroxyl-solite) prepared from the residual fly ash (after synthesis of pure-form zeolite A from fly ash) and a commercial grade zeolite A was denoted as FA-ZA, RFA-ZHS and C-ZA in this study, respectively. The effect of initial pH value, adsorbents dosage and adsorption temperature on removal performance of Cu^{2+} and Zn^{2+} by the three zedites was studied.

2.4.1 Effect of initial pH value, adsorbents dosage and adsorption temperature on different adsorbents

Figure 6a shows that the removal efficiency for Cu^{2+} and Zn^{2+} increased with the initial pH value. The lower pH value cause an increase of H^+ ion concentration which competed with metal ions for exchange sites in zeolitic adsorbents (Hui *et al.*, 2005; Shriver *et al.*, 1990). Moreover, a decrease of the removal efficiency of Cu^{2+} and Zn^{2+} ion can be ascribed to the partial destruction of zeolite

framework at lower pH value. The higher pH value can lead to more precipitation of metal hydroxides that make a predominant contribution to the metal ions removal.

The results for the removal efficiency of Cu^{2+} and Zn^{2+} with varying the amount of adsorbents from 0.5 to 2 g are given in Fig. 6b. An increasing of adsorbents dosage favor Cu^{2+} and Zn^{2+} removal. The significant enhancement in the removal efficiency of Cu^{2+} and Zn^{2+} on adsorbent RFA-ZHS was obtained when dosage is 1.5 and 1 g, respectively. This is because more exchangeable sites of zeolitic adsorbents exist in solution. In addition, zeolitic adsorbents are not only influenced by pH of solution but in turn can affect pH of solution. The alkaline cations (Ca, Mg, and Fe etc.) existing in zeolitic adsorbents may consume H^+ of solution by neutralization reaction so as to increase the final pH value of solution, which contributes to metal ions removal. As shown in Fig. 6c, a gradually increase in the removal efficiency of Cu^{2+} and Zn^{2+} with temperature increases from 15 to 40°C. The high temperature provides a large amount of heat energy required for dehydration of metal ions, which make metal ions enter the pores of zeolites from the channel freely. The increase in temperature also causes the decrease of viscosity of the solution, which contribute to metal ions enter into the interior surface of adsorbent particles. It is indicated that the adsorption of Cu^{2+} and Zn^{2+} on adsorbents is the endothermic nature. However, the removal efficiency shows a decrease at 60°C. It is possible that further increasing temperature favor desorption over adsorption in the solid-liquid system.

On the basis of the experimental results, it is concluded that adsorbent FA-ZA had the similar removal efficiency of Cu^{2+} and Zn^{2+} ion to adsorbent C-ZA. Besides, it was interesting that adsorbent RFA-ZHS had a relative removal efficiency of Cu^{2+} and Zn^{2+} ion. Adsorbents FA-ZA and RFA-ZHS could both be applied for treatment of wastewaters.

2.4.2 Adsorption isotherms

The Langmuir isotherm is obtained under an assumption that the adsorption occurs at a specific homogeneous surface of the adsorbent (Langmuir, 1918). It is represented

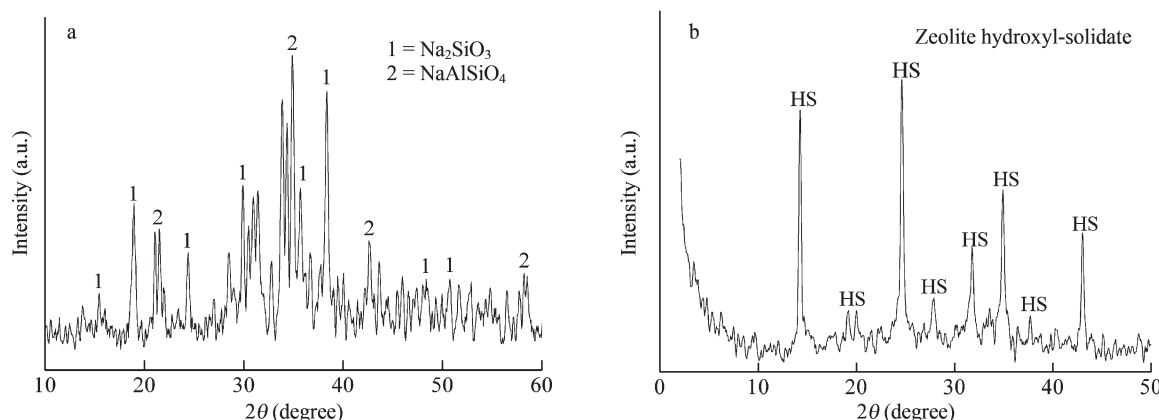


Fig. 5 XRD patterns of the residual fly ash after fused (a) and hydrothermal (b) treatment.

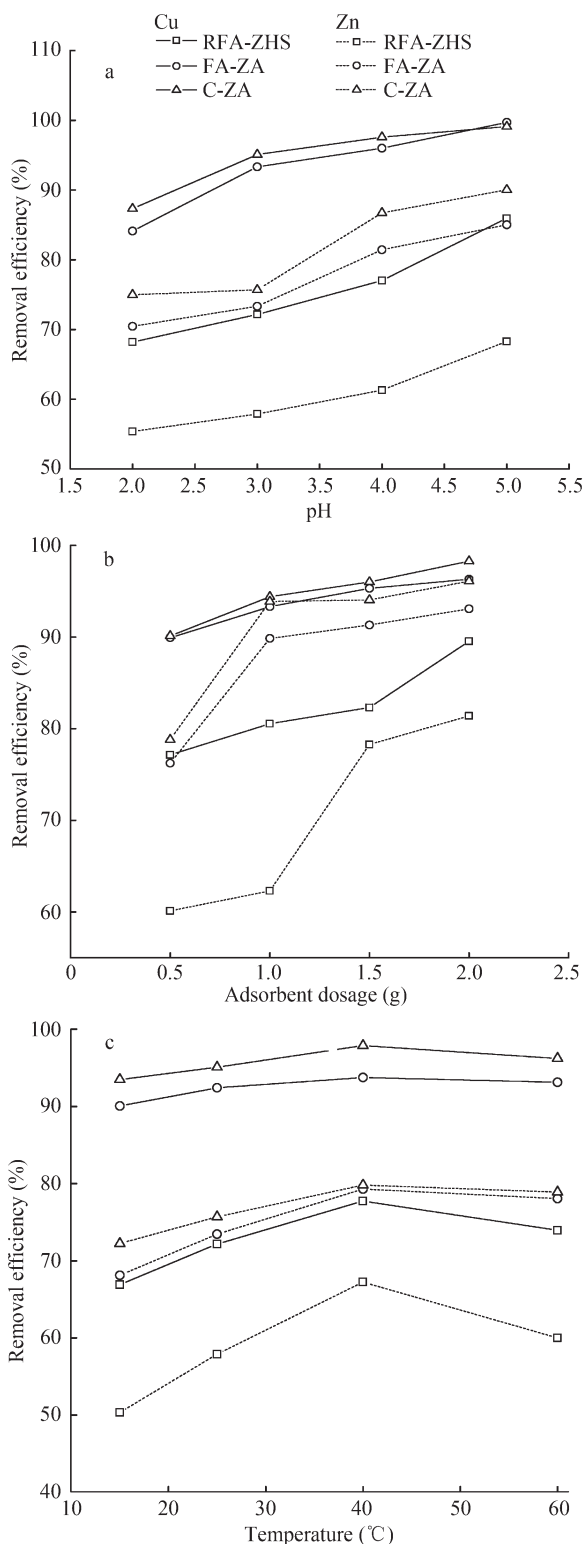


Fig. 6 Effect of initial pH (a), adsorbents dosage (b), and adsorption temperature (c) on the adsorption. Adsorption conditions for (a): dosage 0.5 g; C_0 50 mg/L; temperature 25°C, for (b): C_0 200 mg/L; temperature 25°C; pH 3.0, and for (c): dosage 0.5 g; C_0 50 mg/L; pH 3.0.

in Eq. (4):

$$q_e = (bq_m C_e) / (1 + bC_e) \quad (4)$$

where, q_e (mg/g) is the amount of metal ions adsorbed on adsorbents, b is binding constant, q_m (mg/g) is monolayer adsorption capacity, and C_e (mg/L) is equilibrium concen-

tration of metal ions in solution.

In this study, the linearly transformed Langmuir isotherm is used to fit the adsorption data and is expressed as Eq. (5):

$$C_e/q_e = C_e/q_m + 1/(q_m b) \quad (5)$$

The Freundlich isotherm is an empirical equation which is used for the heterogeneous systems and is expressed as Eq. (6) (Namasivayam *et al.*, 1994, 2003):

$$\log q_e = (1/n) \log C_e + \log K_F \quad (6)$$

where, K_F is the indicative of the extent of the adsorption, and n is the adsorption intensity.

The model parameters from all isotherms obtained are given in Table 4. Figure 7 shows the linearized Langmuir and Freundlich adsorption isotherms of adsorbent FA-ZA for Cu^{2+} and Zn^{2+} . It is seen from correlation coefficient (R^2) that the Langmuir model is better than Freundlich model in simulation of the adsorption isotherm. The agreement of the Langmuir model with the experimental results suggests that a monolayer coverage of Cu^{2+} and Zn^{2+} ions on the outer surface of adsorbent FA-ZA. The greatest equilibrium adsorption capacity obtained for Cu^{2+} and Zn^{2+} is 82.74 and 47.34 mg/g, respectively. The apparent equilibrium constant (K_a) determined by the product of b and q_m can be used as relative indicators of the affinity of adsorbent towards adsorbate. It is indicated from both K_a values that the affinity of adsorbent FA-ZA for Cu^{2+} is quite higher in comparison of Zn^{2+} .

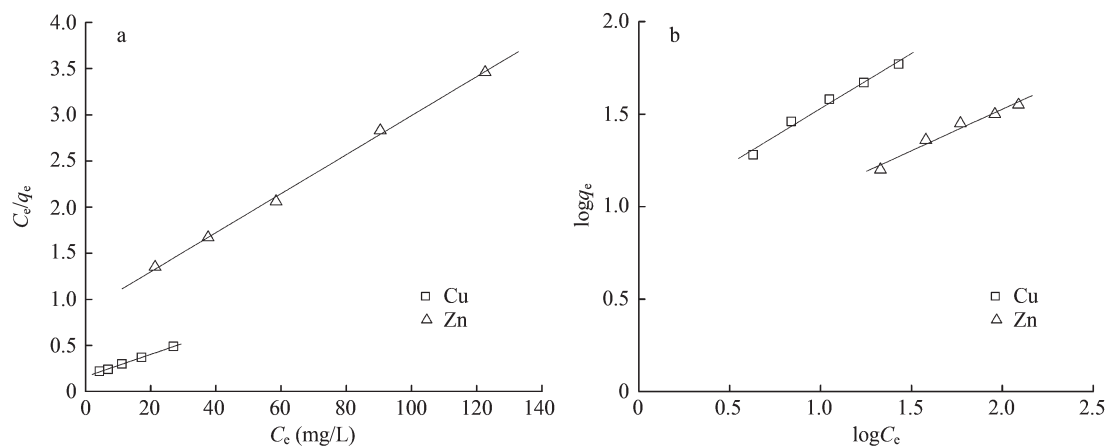
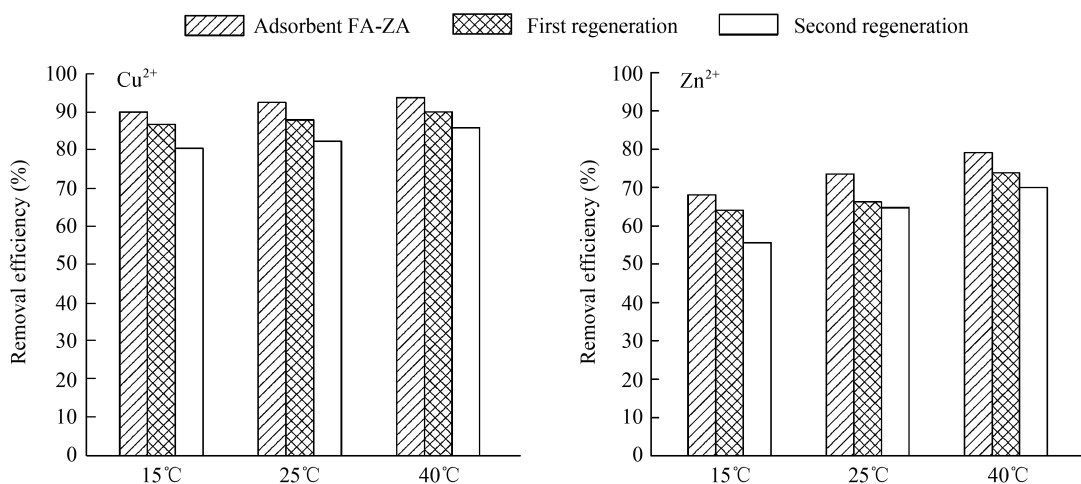
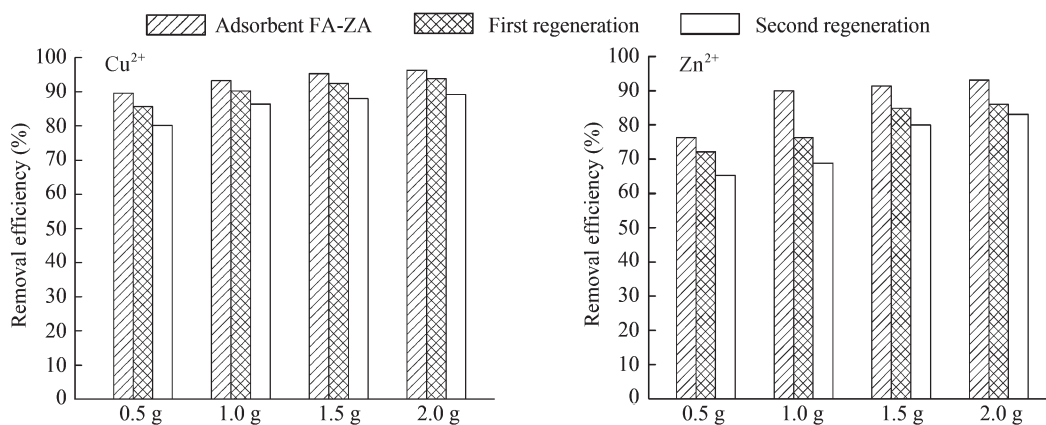
2.5 Heavy metal ions recovery and adsorbents regeneration

The heavy metal ions adsorbed was recovered using 5% NaCl solution (100 mL) to elute the metal-saturated adsorbent FA-ZA. The recovery efficiency of metal ions was calculated using Eq. (3). It was found that the recovery efficiency reach to 92.56% and 88.86% for Cu^{2+} ; 85.56% and 79.19% for Zn^{2+} at first and second cycle, respectively. In order to check the adsorption capacity, regenerative adsorbents for each cycle are reloaded with metal ion solution of known concentrations at different temperature (15–40°C) and adsorbents dosage (0.05–0.2 g) (Figs. 8 and 9). The expected fall in adsorption capacity of regenerative adsorbents was observed during first and second cycle. This may be due to the partial destruction of the structure of zeolitic adsorbents at acid condition. However, the obtained data for recovery and regeneration allows the consideration of column filled setup for the treatment of wastewaters containing dye metal ions.

Because of its high cost and loss in regeneration, the use of activated carbon and commercial grade zeolites as conventional adsorbents may not be an economical way of treating wastewater compared to the use of zeolite products converted from fly ash. Furthermore, completely converting fly ash into zeolitic adsorbents could relieve or eliminate the problems regarding the disposal of huge quantities of fly ash generated by thermal power plants every year.

Table 4 Langmuir and Freundlich parameters for adsorption of Cu^{2+} and Zn^{2+} on adsorbent FA-ZA

Metal ion	Langmuir isotherm				Freundlich isotherm		
	b (L/mg)	q_m (mg/g)	R^2	K	K_F (mg/g)	$1/n$	R^2
Cu^{2+}	0.0741	82.74	0.998	6.13	8.564	0.60	0.992
Zn^{2+}	0.0241	47.34	0.999	1.14	4.066	0.46	0.986

**Fig. 7** Adsorption isotherms of adsorbent FA-ZA for Langmuir (a) and Freundlich (b). Conditions adsorption: dosage 0.5 g, 25°C, pH 3.0.**Fig. 8** Comparison of adsorption of original and regenerative adsorbent FA-ZA at different temperatures. Conditions: dosage 0.5 g; C_0 50 mg/L; pH 3.0.**Fig. 9** Comparison of adsorption of original and regenerative adsorbent FA-ZA at different adsorbent dosages. Conditions: C_0 200 mg/L; 25°C; pH 3.0.

3 Conclusions

The two pure-form zeolites (A and X) were synthesized. The comparative studies showed that zeolite A was more effective in removing metal ions (Cu^{2+} and Zn^{2+}) compared to zeolite X. The influential parameters were studied for the removal performance of metal ions on adsorbents FA-ZA, RFA-ZHS and C-ZA, all adsorbents showed effective adsorption with higher capacity for Cu^{2+} than Zn^{2+} . For the three adsorbents the greatest removal efficiency was obtained for Cu^{2+} (99.73%, 89.56% and 99.12%), compare to Zn^{2+} (93.16%, 81.45%, and 96.09%). Adsorption isotherms (adsorbent FA-ZA) studies showed that the adsorption process could be best fitted by the Langmuir equation. Recovery of metal ions could be achieved using 5% NaCl solution as eluent and adsorbents (adsorbent FA-ZA) can be recycled after the regeneration process. The present study showed that fly ash based adsorbents is proposed as an alternative to more expensive adsorbents such as activated carbon for removal of heavy metals from wastewaters.

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