

# Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash

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## Abstract

The removal performance and the selectivity sequence of mixed metal ions ( $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$ ) in aqueous solution were investigated by adsorption process on pure and chamfered-edge zeolite 4A prepared from coal fly ash (CFA), commercial grade zeolite 4A and the residual products recycled from CFA. The pure zeolite 4A (prepared from CFA) was synthesized under a novel temperature step-change method with reduced synthesis time. Batch method was employed to study the influential parameters such as initial metal ions concentration, adsorbent dose, contact time and initial pH of the solution on the adsorption process. The experimental data were well fitted by the pseudo-second-order kinetics model (for  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions) and the pseudo-first-order kinetics model (for  $\text{Ni}^{2+}$  ions). The equilibrium data were well fitted by the Langmuir model and showed the affinity order:  $\text{Cu}^{2+} > \text{Cr}^{3+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+}$  (CFA prepared and commercial grade zeolite 4A). The adsorption process was found to be pH and concentration dependent. The sorption rate and sorption capacity of metal ions could be significantly improved by increasing pH value. The removal mechanism of metal ions was by adsorption and ion exchange processes. Compared to commercial grade zeolite 4A, the CFA prepared adsorbents could be alternative materials for the treatment of wastewater.

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## 1. Introduction

Several industrial wastewater streams may contain heavy metals such as Sb, Cr, Cu, Pb, Zn, Co, Ni, etc. including the waste liquids generated by metal finishing or the mineral processing industries [1]. The toxic metals, probably existing in high concentrations (even up to  $500 \text{ mg l}^{-1}$ ), must be effectively treated/removed from the wastewaters. If the wastewaters were discharged directly into natural waters, it will constitute a great risk for the aquatic ecosystem, whilst the direct discharge into the sewerage system may affect negatively the subsequent biological wastewater treatment [2]. In recent years, the removal of toxic heavy metal ions from sewage, industrial and mining waste effluents has been widely

studied. Their presence in streams and lakes has been responsible for several types of health problems in animals, plants and human beings [3,4]. Among the many methods available to reduce heavy metal concentration from wastewater, the most common ones are chemical precipitation, ion-exchange, adsorption and reverse osmosis. Most of these methods suffer from some drawbacks such as high capital and operational costs and problem of disposal of residual metal sludge. Ion-exchange is feasible when an exchanger has a high selectivity for the metal to be removed and the concentrations of competing ions are low. The metal may then be recovered by incinerating the metal-saturated resin and the cost of such a process naturally limits its application to only the more valuable metals. In many cases, however, the heavy metals are not valuable enough to warrant the use of special selective exchangers/resins from an economic point of view. This has encouraged research into using low-cost adsorbent materials to purify water contaminated with metals.

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Coal fly ash was formed by combustion of coal in coal-fired power station as a waste product. The generation rate of coal fly ash for the whole world is approximately 500 million tons per year and is predicted to increase [5]. Efficient disposal of coal fly ash is a worldwide issue because of its massive volume and harmful effects on the environment [6,7]. As a technique for recycling coal fly ash, synthesis of zeolites from coal fly ash has attracted a great deal of attention [8]. However, the total conversion time was generally long (24–72 h) and the synthesis temperature was 90–225 °C. In addition, the obtained zeolites usually consisted of condensed structure (low pore volume) such as NaP1, sodalite and analcime in a mixture form with coal fly ash. Thus, the applicability of synthetic zeolites from coal fly ash has greatly been hindered. Recently, the authors [9] have successfully applied a temperature step change method in synthesizing pure zeolite 4A from coal fly ash with reduced synthesis time. This has enabled wider use of coal fly ash converted zeolite products in various industrial and environmental protection activities.

Among the different minerals which possess adsorbent properties, zeolite appears to be one of the most promising to perform metal purification function [10]. Zeolites have a three-dimensional structure constituted by (Si, Al)O<sub>4</sub> tetrahedra connected by all their oxygen vertices forming channels where H<sub>2</sub>O molecules and exchangeable cations counterbalance the negative charge generated from the isomorphous substitution. The advantage of zeolites over resins, apart from their much lower cost, is their ion selectivities. Owing to zeolite's structural characteristics and their adsorbent properties, they have been applied as chemical sieve, water softener and adsorbents [10–12]. Several researchers have studied the removal performance and selectivity sequence of heavy metal ions by natural zeolites (clinoptilolite and chabazite) [13–20] as well as synthetic zeolites [21–24]. Ouki and Kavannagh [15] studied the performance of natural zeolites (clinoptilolite and chabazite) on the treatment of mixed metal effluents (Pb<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cr<sup>3+</sup>, Ni<sup>2+</sup> and Co<sup>2+</sup>; concentration: 1–30 mg l<sup>-1</sup>); however, there were no data about kinetic modeling of the process. Panayotova and Velikov [19] found that a pseudo-first-order kinetic reaction best described the removal of mixed metal ions (Pb<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Ni<sup>2+</sup>) at a concentration of 50 mg l<sup>-1</sup> by natural zeolite (clinoptilolite). Álvarez-Ayuso et al. [23] studied the sorption behavior of Cr<sup>3+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> ions by natural (clinoptilolite) and synthetic (NaP1) zeolites. They found that the sorption capacity of synthetic NaP1 zeolite was 10 times greater than the natural zeolite. The general observation is that most of the authors dealt with solutions of single heavy metal ion under equilibrium condition. Conclusions drawn from such studies may not be valid when applying adsorption process to a mixed effluent is considered. Even less is known about the adsorption kinetics of multi-heavy metal ions by coal fly ash prepared, pure and chamfered-edge, zeolite 4A. Knowledge on this topic could be useful in designing wastewater treatment systems using low-cost adsorbent mate-

rials (coal fly ash based). In fact, in the synthesis of pure form zeolite using coal fly ash, the residues from the process may also be potential adsorbents and is worthy of a comprehensive study, especially considering that around 30% of the NaP1 zeolites are left behind as residues in the synthesis process.

The present work focused on utilizing a pure and chamfered-edge zeolite 4A prepared from coal fly ash to remove mixed heavy metal ions such as Cr<sup>3+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup> and Co<sup>2+</sup> in water. The kinetic of the process and the sorption capacity of the adsorbents were determined in relation to the effects of various factors on the adsorption process. The parameters in this study included initial concentration of the mixed heavy metal ions, contact time, initial pH of the solution and adsorbent dosage. Moreover, an attempt was made to investigate the removal capacity of mixed heavy metal ions by the treated coal fly ash (residual products after preparation of pure and single phase zeolite 4A from the coal fly ash). The heavy metal adsorption performances of the original coal fly ash and a commercial grade zeolite 4A were also studied for comparison.

## 2. Materials and methods

### 2.1. Adsorbate

All the compounds used to prepare the reagent solutions were of analytic reagent grade. The mixed heavy metal ions solutions containing 50, 100, 200 and 300 mg l<sup>-1</sup> each of Cr<sup>3+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup> and Co<sup>2+</sup> ions were prepared by dissolving a weighed quantity of the respective nitrate salts in deionized water. Before mixing the adsorbate with the adsorbents, the initial pH of each solution (pH=3 and 4) was adjusted to the required value by adding 0.1–10 M HNO<sub>3</sub> and 0.1–10 M NaOH solution [25,26]. It should be noted that nitrate anions are not forming precipitates or complexes with the corresponding metals at the test conditions and are considered to be inert [27]. In addition, at pH=3 and 4, the effect of complexing of the metal ions with hydroxide ion are not significant [28]. It is assumed that the impact of adjusting the initial solution pH with HNO<sub>3</sub> and NaOH solutions in terms of changing the chemistry of the solution is not significant.

### 2.2. Adsorbent

A commercial grade zeolite 4A (Valfor 100) from PQ Chemicals (Thailand) Limited and coal fly ash prepared pure and chamfered-edge zeolite 4A were used. The coal fly ash prepared pure zeolite 4A was synthesized by the effect of step-change of synthesis temperature during the hydrothermal treatment. Generally, a mixture of 30 g of fly ash and 300 ml of 2 M NaOH solution in a 1 L sealed PP bottle was kept in an oil bath at 100 °C for 2 h under stirred condition (300 rpm). Then, the solution was separated from the mixture by a filtration process. The molar

ratio  $\text{SiO}_2/\text{Al}_2\text{O}_3:\text{Na}_2\text{O}/\text{SiO}_2:\text{H}_2\text{O}/\text{Na}_2\text{O}$  in the solution was adjusted to 1.64:8.09:56.51 by adding 100 ml of aluminium solution. The purpose of the addition of 100 ml aluminum solution was to control the molar ratio of the solution for subsequent synthesis of pure zeolite 4A from coal fly ash extracted solution. In addition, with the addition of the aluminum solution, it was shown that pure, single phase and high crystalline zeolite 4A sample could be easily synthesized from coal fly ash. The solution was then stirred (500 rpm) for 30 min at room temperature (25 °C) and was synthesized at the first temperature of 90 °C for 1.5 h and subsequently at the second temperature of 95 °C for 2.5 h. The coal fly ash prepared zeolite 4A was then pretreated with 1 M NaCl for 24 h at 25 °C before the adsorption experiment. The purpose of the pretreatment was to bring the zeolite 4A to near homoionic form (Na-form) so as to increase its effectiveness in the uptake of the heavy metal ions. After the conversion of the coal fly ash into pure zeolite 4A process, it was observed that the residual fly ash was also converted into NaP1 zeolite. In order to recycle the coal fly ash completely, the residual fly ash was denoted as treated coal fly ash which was also used in the study of adsorption experiment. Treated coal fly ash labeled as TFA2 and TFA4.5 were used and they were formed by the treatment of 30 g of the coal fly ash and 300 ml of 2 M NaOH solution at 100 °C for 2 and 4.5 h respectively. Finally, in order to contrast the removal performance of the coal fly ash based adsorbents, the original coal fly ash was also used in the adsorption study. Detailed information about the synthesis and characterization of the adsorbents converted from the coal fly ash could be found in reference [9].

### 2.3. Characterization

Powder X-ray diffraction (XRD) patterns of the adsorbents were obtained using a powder diffractometer (Philips PW 1830) equipped with a Cu K $\alpha$  radiation. The accelerating voltage and current used were 40 kV and 20 mA, respectively. The chemical compositions of the adsorbents was determined by a JEOL X-ray reflective fluorescence spectrometer (XRF, JSX 3201Z). All metal concentrations were analyzed using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, Perkin-Elmer 3000 XL). The samples were usually diluted five times by deionized water. Therefore, the concentration of metal ion solutions should be in the range of 0–60 mg l<sup>-1</sup>. The calibration standards were prepared using the standard solutions which was certified by the supplier. Three calibration standards (20, 40 and 60 mg l<sup>-1</sup>) and blank solution were used to calibrate the equipment. A linear calibration curve was obtained after calibration. If the correlation coefficient  $R^2$  was less than 0.999, the machine was re-calibrated to ensure the accuracy of results. The samples were automatically measured three times in one aspiration. If the standard deviation of the test results were greater than 1%, the samples were measured again until the test results fulfilled the analysis requirement.

All the instrumental conditions were optimized for the maximum sensitivity as indicated by the manufacturer's manual. The pH values of the aqueous solutions were measured by a Mettler-Toledo meter (MP 120). Surface morphology of the adsorbents was analyzed by scanning electronic microscopy (SEM, JEOL 6300) coupled with energy dispersive X-ray analysis (EDAX). In the SEM analysis, the adsorbent samples were coated with a thin layer of gold and mounted on a copper stub using a double-stick tape. The particle size of the adsorbents was measured by laser beam scattering technique (Coulter LS 230). Nitrogen adsorption/desorption was carried out at 77 K using the Coulter SA3100 nitrogen physisorption apparatus. The volume of adsorbed nitrogen was normalized to standard temperature and pressure (STP). Prior to the experiments, the sample was dehydrated at 150 °C for 2 h.

### 2.4. Batch sorption experiment

The experiments were performed in a batch reactor (250 ml) at 25 ± 0.5 °C with continuous stirring at 600 rpm.

#### 2.4.1. Kinetics studies

The 0.1 g of pure zeolite 4A (coal fly ash prepared) was left in contact with 100 ml of mixed heavy metal ion solutions (50 and 100 mg l<sup>-1</sup>) at the initial pH values of 3 and 4. Aliquots of supernatant (0.5 ml) were withdrawn at different time intervals (from 5 to 240 min) and the total sampling volume did not exceed 5% of the total solution volume. The supernatants were filtered with 0.45  $\mu\text{m}$  filter. The filtrates were acidified with 2% HNO<sub>3</sub> to decrease the pH value to below 3 in order to avoid any precipitation before the ICP-AES measurement.

#### 2.4.2. Sorption capacity

The adsorbents (0.5 g) were left in contact with 100 ml of mixed heavy metal ions solution in the range of 50–300 mg l<sup>-1</sup> with the initial pH value of 3 for 240 min. The filtrates were filtered with 0.45  $\mu\text{m}$  filter and acidified with 2% HNO<sub>3</sub> to decrease the pH to below 3 before the ICP-AES measurement. In order to obtain the sorption capacity, the amount of ions adsorbed per unit mass of adsorbent ( $q_e$  in milligrams of metal ions per gram of adsorbent) was evaluated using the following expression:

$$q_e = \frac{C_o - C_e}{m} \times V \quad (1)$$

where  $C_o$  is the initial metal ion concentration (mg l<sup>-1</sup>),  $C_e$  the equilibrium metal ion concentration (mg l<sup>-1</sup>),  $V$  the volume of the aqueous phase (l), and  $m$  the amount of the adsorbent used (g). Removal efficiency of metal ions by the adsorbent is considered in percentage as:

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

Table 1  
Chemical composition of the adsorbents

Composition (wt%)	Coal fly ash	Treated coal fly ash		Zeolite 4A	
		TFA2	TFA4.5	Coal fly ash prepared	Commercial (Valfor 100)
SiO <sub>2</sub>	50.09	42.12	40.22	43.34	44.68
Al <sub>2</sub> O <sub>3</sub>	24.91	24.15	24.51	35.71	34.91
Na <sub>2</sub> O	0.14	11.91	16.62	19.75	20.12
CaO	11.77	11.32	10.61	0.02	0.02
Fe <sub>2</sub> O <sub>3</sub>	7.60	5.87	5.01	0.80	0.03
MgO	0.40	1.15	0.84	0.25	0.18
TiO <sub>2</sub>	1.17	1.13	1.18	0.02	0.01
K <sub>2</sub> O	1.19	0.46	0.34	0.07	0.05
MnO	0.10	0.20	0.16	0.03	0.00
Si/Al mole ratio zeolite 4A	1.70	1.44	1.57	1.32	1.32
Crystallinity (%)	n.a.	n.a.	n.a.	47.41	86.05
BET surface area (m <sup>2</sup> g <sup>-1</sup> )	1.38	18.49	22.20	54.82	71.41

n.a.: Not available.

### 3. Results and discussion

The effects of contact time, initial pH, initial mixed heavy metal ions concentration and adsorbent dosage on selectivity sequence and adsorption kinetic of heavy metal ions were investigated. A comparative study of the removal efficiencies of mixed metal ions by the coal fly ash based adsorbents (the original coal fly ash, the treated coal fly ash residues and pure zeolite 4A prepared from coal fly ash) and a commercial grade zeolite 4A was also conducted.

#### 3.1. Characteristics of adsorbents

Elemental composition data for the coal fly ash, treated coal fly ash residues, coal fly ash prepared zeolite 4A and commercial zeolite 4A were shown in Table 1. The amount of amorphous SiO<sub>2</sub> in the coal fly ash was 46.2 wt% assayed by a quantitative X-ray diffraction (XRD) method [29]. After the zeolite 4A synthesis process, the treated coal fly ash residues (TFA2 and TFA4.5) were incorporated with significant amount of Na after they were treated with NaOH solution. The amount of Na element incorporated in the treated coal fly ash residues increased with the treatment time. Fig. 1 shows the morphology of the various adsorbents. The coal fly ash consisted of smooth spheres (0.04–600 μm, with a mean diameter of 20.7 μm). These particles were formed from the cooling of molten products after the combustion of clay compounds in the original coal [29]. By contrast, the morphology of the treated coal fly ash residues (TFA2 and TFA4.5) was rough (1–10 μm, with a mean diameter of 3 μm), appearing as aggregates of small plates. This was because zeolite crystals (mainly NaP1) were precipitated out on the surface of the coal fly ash particles. The morphology of zeolite 4A (coal fly ash prepared and commercial grade) was chamfered-edged cubes (well developed {1 1 0} faces). The chamfered-edged cube morphology was due to the initial SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> concentration used in the synthesis process [30]. The particle size of the coal fly ash prepared zeolite 4A and commercial (Val-

for 100) zeolite 4A were 1–4 μm with a mean diameter of 2.7 μm and 1–3 μm with a mean diameter of 2 μm, respectively. Table 1 also includes data on the specific surface area of the samples. The surface area of TFA2 and TFA4.5 has increased 13- and 16-fold. This increase in surface area is due to the crystallization of the many zeolite crystals on the originally smooth fly ash spheres. Compared to coal fly ash prepared zeolite, the larger surface area of commercial zeolite may be due to the smaller particle size of the sample. From the XRD patterns of the adsorbents (not shown), the primary crystalline species in the coal fly ash sample were quartz (SiO<sub>2</sub>), mullite (3Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>) and calcite (CaCO<sub>3</sub>) as identified by the sharp peaks, while the presence of the amorphous phases of SiO<sub>2</sub> were identified by the presence of a broad diffraction peak (near 2θ = 24°). Quartz and mullite were produced during the thermal decomposition of clay minerals such as kaolinite during combustion. Treated coal fly ash residues (TFA2 and TFA4.5) were identified as a mixture of NaP1 zeolite (JCPDS card 39-0219) and calcite (CaCO<sub>3</sub>, JCPDS card 05-0586). Coal fly ash prepared zeolite and commercial zeolite were identified as a single-phase zeolite 4A (JCPDS card 43-0142).

#### 3.2. Sorption kinetics

There are essentially three stages in the adsorption process by porous adsorbents [31]: (1) solute transfer from the bulk solution to the external surface of the sorbent through a liquid boundary layer (film resistance); (2) solute transfer from the sorbent surface to the intraparticle active sites (intraparticle resistance); and (3) interactions of the solute with the available sites on both the external and internal surfaces of the sorbent (reaction resistance). One or more of the above-mentioned stages may control the rate at which the solute is adsorbed and the amount of solute that is adsorbed onto the sorbent. In this study, the kinetics of sorption that defines the efficiency of sorption of mixed metal ions was checked by the pseudo-first-order and pseudo-second-order equations.

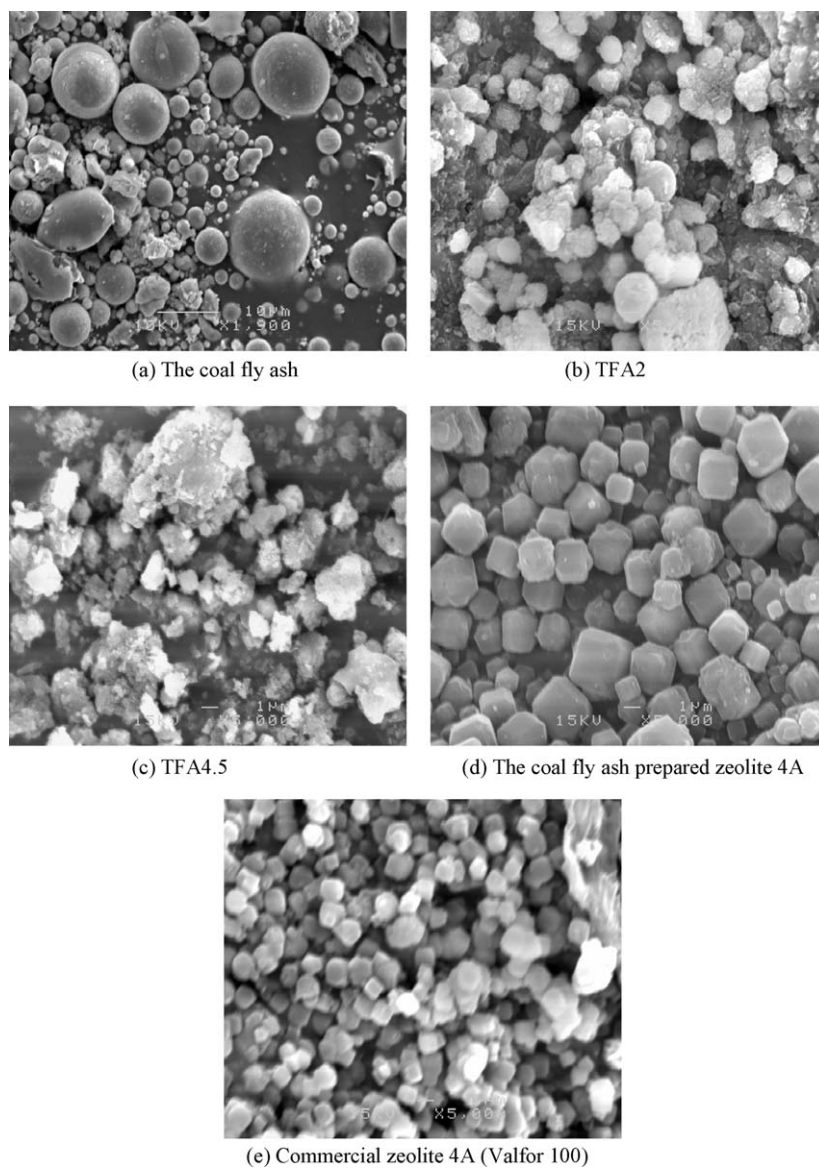


Fig. 1. SEM pictures of the coal fly ash and the adsorbents.

### 3.2.1. Pseudo-first-order kinetics model

In 1898, Lagergren [32] suggested a pseudo-first-order equation for the sorption of liquid/solid system based on solid capacity. It assumes that the rate of change of sorbate uptake with time is directly proportional to the difference in the saturation concentration and the amount of solid uptake with time. The Lagergren equation is the most widely used rate equation in liquid phase sorption. The general equation is expressed as:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \quad (3)$$

where  $q_e$  and  $q_t$  are the amounts of metal ions adsorbed onto the adsorbents ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$ , respectively.  $k_1$  is the rate constant of first order ( $\text{min}^{-1}$ ). By plotting  $\log(q_e - q_t)$  versus  $t$ , the first-order constant  $k_1$  and

the equilibrium capacity  $q_e$  can be obtained from the slope and intercept, respectively.

### 3.2.2. Pseudo-second-order kinetic model

Ho and McKay developed a pseudo-second-order equation based on the amount of sorbed sorbate on the sorbent [33]. If the rate of sorption is a second-order mechanism, the pseudo-second-order chemisorption kinetics rate equation is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

For the boundary conditions  $t=0$  to  $t=t$  and  $q_t=0$  to  $q_t=q_t$ , the integrated form of Eq. (4) becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2t \quad (5)$$

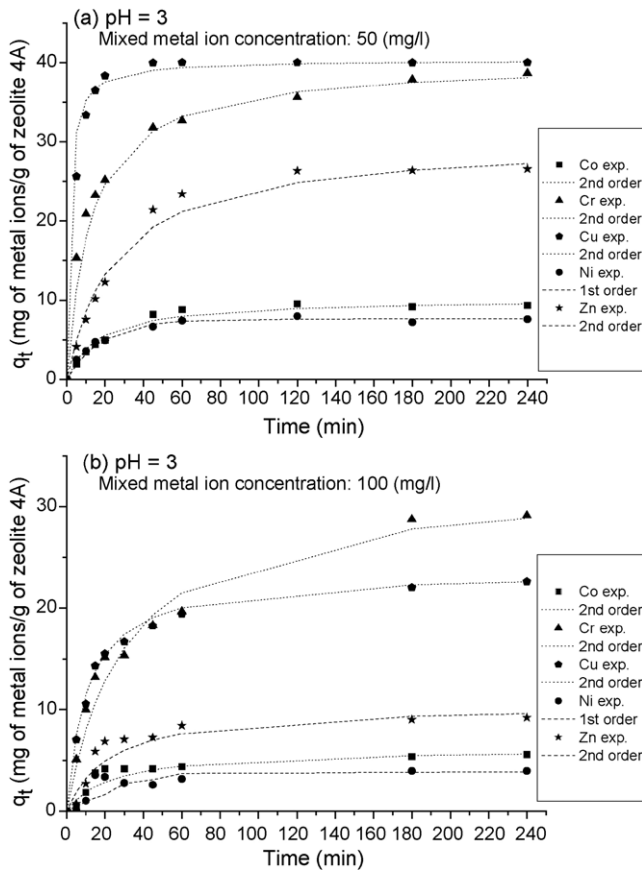


Fig. 2. Comparison between the measured and modelled time profiles for adsorption of mixed heavy metal ions at pH 3 ( $T$ , 25 °C; stirring speed, 600 rpm;  $V$ , 100 ml;  $m$ , 0.1 g of zeolite 4A (coal fly ash prepared)).

which is the integrated rate law for a pseudo-second-order reaction. Eq. (5) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

The constants can be determined by plotting  $t/q_t$  versus  $t$ . The second-order sorption rate constant  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) and  $q_e$  ( $\text{mg g}^{-1}$ ) can be determined from the intercept and the slope of the plot. This model is based on the assumption that the rate limiting step may be a chemical sorption involving valence forces through sharing or exchange of electrons between the adsorbent and the adsorbate [34].

Figs. 2 and 3 show the kinetics of metal ions adsorption onto the coal fly ash prepared zeolite 4A. It was observed that the pseudo-first-order model fitted well for  $\text{Ni}^{2+}$  ions and the pseudo-second-order model fitted well for  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions in the tested sorption system. The model selected for fitting the experimental data was based on the tendency of the model to estimate the quantity of metal ions removed at the initial and the final state of adsorption. At pH=3, it was seen that all the metal ions were rapidly removed by the zeolite 4A (coal fly ash prepared) within 120 min, except  $\text{Cr}^{3+}$ . In addition, the results demonstrated that around 90% of the metal ions were removed in the first

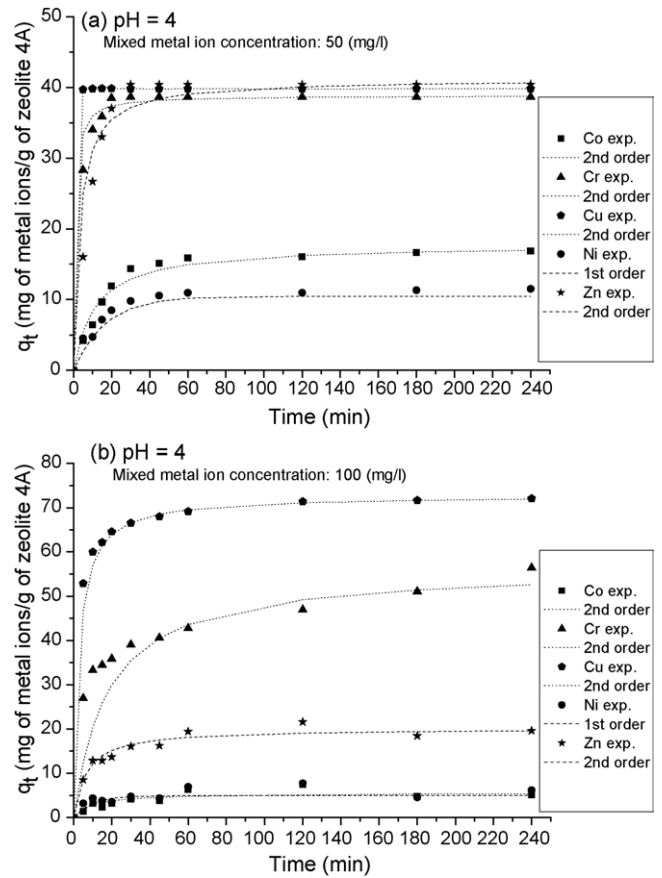


Fig. 3. Comparison between the measured and modelled time profiles for adsorption of mixed heavy metal ions at pH 4 ( $T$ , 25 °C; stirring speed, 600 rpm;  $V$ , 100 ml;  $m$ , 0.1 g of zeolite 4A (coal fly ash prepared)).

60 min. Similarly, at pH=4, all mixed metal ions were rapidly removed by zeolite 4A within 60 min and around 90% of the removal of the metal ions was achieved in the first 30 min, except  $\text{Cr}^{3+}$  at higher concentrations ( $100 \text{ mg l}^{-1}$ ). It was because at higher values of pH, the  $\text{H}_3\text{O}^+$  ions competed less with the metal ions for the exchange sites in zeolite. It was observed that under all the experimental sites in zeolite, no significant adsorption was seen after 240 min of stirring. For subsequent experiments, the contact time was thus maintained for 240 min to ensure that equilibrium could be achieved. It showed that ions removal was highly dependent on the initial metal ion concentration. While increasing the initial concentration of the mixed metal ions, a significant decrease in the sorption of  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions was observed which could be attributed to the higher selectivity to  $\text{Cu}^{2+}$  and  $\text{Cr}^{3+}$  ions by zeolite 4A. The competition for zeolite 4A adsorption sites in the presence of  $\text{Cu}^{2+}$  and  $\text{Cr}^{3+}$  led to a decrease in the uptake of other metal ions. Similar results were reported by Panatotova and Velikov [19]. The increase in loading capacity of zeolite 4A when increasing the initial concentration of mixed heavy metal ions was probably due to a high driving force for mass transfer. Similar observations were reported in the removal of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  by sawdust [34]. The observed selectivity series could be the

Table 2  
The pseudo-first(second)-order rate constants

pH	Initial conc. (mg l <sup>-1</sup> )	Metal ions	$q_{e, \text{exp}}$ (mg g <sup>-1</sup> )	Pseudo-first(second)-order kinetic model			
				$q_{e, \text{cal}}$		Rate constant	$R^2$
				(mg g <sup>-1</sup> )	(mmol g <sup>-1</sup> )		
3	50	Co <sup>2+a</sup>	9.34	10.15	0.17	0.006	0.998
		Cr <sup>3+a</sup>	38.69	40.11	0.77	0.002	1.000
		Cu <sup>2+a</sup>	40.01	40.34	0.63	0.017	1.000
		Ni <sup>2+b</sup>	7.59	7.63	0.13	0.054	0.963
		Zn <sup>2+a</sup>	26.58	30.14	0.46	0.001	0.997
	100	Co <sup>2+a</sup>	5.57	6.17	0.10	0.007	0.968
		Cr <sup>3+a</sup>	29.12	32.52	0.63	0.001	0.996
		Cu <sup>2+a</sup>	22.59	23.58	0.37	0.004	0.999
		Ni <sup>2+b</sup>	3.98	3.87	0.07	0.027	0.942
		Zn <sup>2+a</sup>	9.22	10.54	0.16	0.004	0.975
4	50	Co <sup>2+a</sup>	16.84	17.75	0.30	0.005	0.999
		Cr <sup>3+a</sup>	38.66	38.85	0.75	0.032	1.000
		Cu <sup>2+a</sup>	39.80	39.81	0.63	4.948	1.000
		Ni <sup>2+b</sup>	11.51	10.49	0.18	0.059	0.956
		Zn <sup>2+a</sup>	40.38	41.17	0.63	0.008	1.000
	100	Co <sup>2+a</sup>	5.15	5.50	0.09	0.020	0.978
		Cr <sup>3+a</sup>	56.41	56.47	1.09	0.001	0.996
		Cu <sup>2+a</sup>	72.04	72.73	1.14	0.005	1.000
		Ni <sup>2+b</sup>	6.14	4.95	0.08	0.102	0.989
		Zn <sup>2+a</sup>	19.59	20.10	0.31	0.008	0.997

$R^2$  is the correlation coefficient ( $T$ , 25 °C; stirring speed, 600 rpm; pH, 3, 4; time, 0–240 min;  $V$ , 100 ml;  $m$ , 0.1 g of zeolite 4A (coal fly ash prepared)).

<sup>a</sup> Values were determined by the pseudo-second-order kinetic model. Unit of rate constant  $k_2$  is g mg<sup>-1</sup> min<sup>-1</sup>.

<sup>b</sup> Values were determined by the pseudo-first-order kinetic model. Unit of rate constant  $k_1$  is min<sup>-1</sup>.

result of various factors, such as framework structure of zeolite, hydrated size and hydration free energy of metal ions. These effects will be discussed in Section 3.3. It should be noted that adsorption mechanism of multi-metal ions by an adsorbent is complicated. The behaviour of each metal ion in a multi-metal ions system depends strongly on the concentration and the properties of the other ions present, pH of the solution, and the physical and chemical properties of both the adsorbent and adsorbate. The shape and coefficients of the adsorption kinetics of the system were affected by both the interaction and competition effects among the multi-metal ions. Table 2 lists the results obtained from the pseudo-first-order and the pseudo-first-order kinetics models. It showed that the calculated  $q_e$  agreed well with the experimental data. The characteristic time for the pseudo kinetics models was found to be in the range of 1–2 orders of magnitude of minute.

### 3.3. Sorption isotherms

The analysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes. In order to investigate the sorption isotherm, two equilibrium models were analyzed: Langmuir and Freundlich isotherm equations. These two isotherm models were first derived and used for gas adsorption by microporous adsorbents, and then extended to solute adsorption from aqueous solutions [35,36]. The Langmuir model is obtained under the ideal assumption of a totally

homogeneous adsorption surface, whereas the Freundlich isotherm is suitable for a highly heterogeneous surface.

#### 3.3.1. Langmuir isotherm

The Langmuir sorption isotherm is the best known of all isotherms describing sorption [37] and it has been successfully applied to many sorption processes [23,38–40]. It is represented as:

$$q_e = q_m \frac{bC_e}{1 + bC_e} \quad (7)$$

where  $C_e$  is the equilibrium aqueous metal ions concentration (mg l<sup>-1</sup>),  $q_e$  the amount of metal ions adsorbed per gram of adsorbent at equilibrium (mg g<sup>-1</sup>),  $q_m$  and  $b$  are the Langmuir constants related to the maximum adsorption capacity and energy of adsorption, respectively. The values of  $q_m$  (mg g<sup>-1</sup>) and  $b$  (mg<sup>-1</sup>) can be determined from the linear plot of  $C_e/q_e$  versus  $C_e$ .

#### 3.3.2. Freundlich isotherm

The Freundlich isotherm is most frequently used to describe the adsorption of inorganic and organic components in solution [41,42]. This fairly satisfactory empirical isotherm can be used for a non-ideal sorption that involves heterogeneous sorption and is expressed as:

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (8)$$

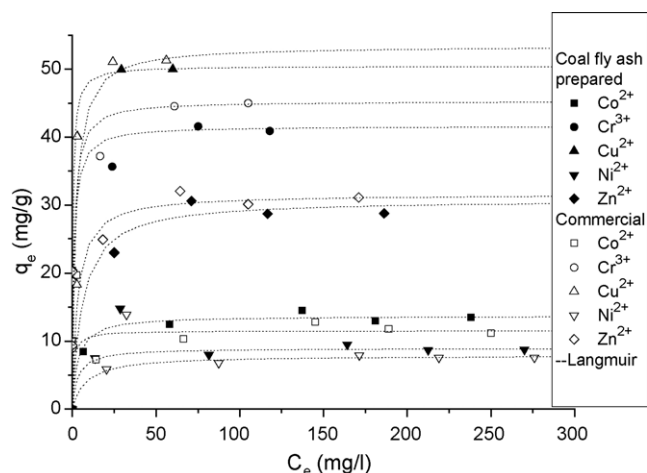


Fig. 4. Experimental metal adsorption isotherms of coal fly ash prepared and commercial zeolite 4A and modelled results using Langmuir equation ( $T$ , 25 °C; stirring speed, 600 rpm; time, 240 min; pH, 3;  $V$ , 100 ml;  $m$ , 0.5 g).

where  $K$  is roughly an indicator of the adsorption capacity and  $1/n$  the adsorption intensity. The magnitude of the exponent  $1/n$  gives an indication of the favorability of adsorption. Values of  $n$ , where  $n > 1$  represent favorable adsorption condition. By plotting  $\log q_e$  versus  $\log C_e$ , values of  $K$  and  $n$  can be determined from the slope and intercept of the plot.

For all cases, the Langmuir model represents a better fit to the experimental data than the Freundlich model. The adsorption isotherms of metal ions by coal fly ash prepared and commercial zeolite 4A are shown in Fig. 4. The good agreement of the Langmuir plots with the experimental data suggests a monolayer coverage of metal ions on the outer surface of the adsorbent. The values  $q_m$  and  $b$  obtained from these plots are listed in Table 3. The Freundlich parameters  $K$  and  $1/n$  are also presented in Table 3. For coal fly ash prepared zeolite 4A, the greatest equilibrium sorption capacity  $q_m$  was obtained for  $\text{Cu}^{2+}$ , i.e. 50.45  $\text{mg g}^{-1}$ , which decreased to 41.61  $\text{mg g}^{-1}$  for  $\text{Cr}^{3+}$ , 30.80  $\text{mg g}^{-1}$  for  $\text{Zn}^{2+}$ , 13.72  $\text{mg g}^{-1}$  for  $\text{Co}^{2+}$ , and 8.96  $\text{mg g}^{-1}$  for  $\text{Ni}^{2+}$ . Similarly, for commercial zeolite 4A, the greatest equilibrium sorption capacity  $q_m$  was obtained for  $\text{Cu}^{2+}$ , i.e. 53.45  $\text{mg g}^{-1}$ ,

which decreased to 45.29  $\text{mg g}^{-1}$  for  $\text{Cr}^{3+}$ , 31.58  $\text{mg g}^{-1}$  for  $\text{Zn}^{2+}$ , 11.52  $\text{mg g}^{-1}$  for  $\text{Co}^{2+}$ , and 7.90  $\text{mg g}^{-1}$  for  $\text{Ni}^{2+}$ . The sorption sequence of metal ions on zeolite 4A (coal fly ash prepared and commercial grade) was the same and was as follows:  $\text{Cu}^{2+} > \text{Cr}^{3+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+}$ . Factors such as crystal structure of zeolite 4A, free energy of hydration and hydrated radii of the metal ions may be responsible for the observed selectivity. Zeolites, in general, are weakly acidic in nature and therefore sodium form exchangers are selective for hydrogen ( $\text{R-Na} + \text{H}_2\text{O} \rightleftharpoons \text{RH} + \text{Na}^+ + \text{OH}^-$ ). This leads to high pH values when the exchanger is equilibrated with a relatively dilute electrolyte solution [43], making feasible the metal hydroxide precipitation. The crystal structure of zeolite 4A contains large cages having a near spherical shape and free diameter of 11.4 Å. Each of these cages is connected with six neighbouring cages via eight-membered rings (8-MR) having a crystallographic diameter of 4.1 Å. The effective pore width of zeolite 4A is 4 Å. A common factor preventing a group of metal ions from being adsorbed by zeolite 4A is the size of the hydrated ion. If the hydrated ion size is greater than that of the pore, the species may be excluded or some of the waters of hydration must be stripped from the solvated ions to enable them to enter the pores of the zeolite. According to the size of hydrated radii of ions in Table 4 [44], the selectivity sequence of the hydrated ions is as follows:  $\text{Ni}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Cr}^{3+}$ . Also, from the same table, the metal with the highest free energy of hydration should therefore prefer to remain in the solution phase. Thus, according to the free energy of hydration, the selectivity sequence is  $\text{Co}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+}$ . However, both selectivity sequences do not explain well the high selectivity of  $\text{Cu}^{2+}$  and  $\text{Cr}^{3+}$  ions and the observed sequences. It was postulated that the main mechanism involved in the sorption of  $\text{Cu}^{2+}$  and  $\text{Cr}^{3+}$  ions was based on precipitation of metal hydroxides on the surface of zeolite or inside the pore walls. A similar observation was reported on adsorption of  $\text{Cu}^{2+}$  and  $\text{Cr}^{3+}$  ions on NaP1 [23]. In comparison with  $\text{Ni}^{2+}$  ions, the high adsorption of  $\text{Co}^{2+}$  ions may be due to the accommodation of tetrahedral Co aquacomplexes to the zeolite framework [26].

Table 3  
Langmuir and Freundlich parameters for adsorption of mixed metal ions on zeolite 4A

Adsorbent	Metal	Langmuir model			Freundlich model		
		$q_m$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{l mg}^{-1}$ )	$R^2$	$K$ ( $(\text{mg g}^{-1})(\text{mg l}^{-1})^n$ )	$1/n$	$R^2$
Coal fly ash prepared zeolite 4A	$\text{Co}^{2+}$	13.72	0.32	0.998	6.66	0.145	0.959
	$\text{Cr}^{3+}$	41.61	0.98	0.998	28.47	0.076	0.850
	$\text{Cu}^{2+}$	50.45	2.16	1.000	37.11	0.079	0.974
	$\text{Ni}^{2+}$	8.96	0.32	0.997	6.27	0.066	0.834
	$\text{Zn}^{2+}$	30.80	0.17	0.995	18.47	0.089	0.623
Commercial zeolite 4A	$\text{Co}^{2+}$	11.52	1.15	0.997	4.79	0.17	0.911
	$\text{Cr}^{3+}$	45.29	0.93	0.999	27.54	0.11	0.971
	$\text{Cu}^{2+}$	53.45	0.49	0.997	36.85	0.09	0.965
	$\text{Ni}^{2+}$	7.90	0.13	0.998	4.24	0.11	0.946
	$\text{Zn}^{2+}$	31.58	0.33	0.997	17.61	0.13	0.871

$R^2$  is the correlation coefficient ( $T$ , 25 °C; stirring speed, 600 rpm; time, 240 min; pH, 3;  $V$ , 100 ml;  $m$ , 0.5 g of zeolite 4A).



Table 4  
Radii and hydration energies of different metal ions

Metal ions	Hydrated radius (Å)	Unhydrated radius (Å)	Free energy of hydration (kcal g <sup>-1</sup> -ion)
Co <sup>2+</sup>	4.23	0.82	-479.5
Cr <sup>3+</sup>	4.61	0.65	-
Cu <sup>2+</sup>	4.19	0.82	-498.7
Ni <sup>2+</sup>	4.04	0.72	-494.2
Zn <sup>2+</sup>	4.3	0.83	-484.6

Several selectivity sequences have been reported in the literature (mainly conducted in a single solution, except references [15,18,20] for natural clinoptilolite and Na-clinoptilolite: Ba<sup>2+</sup> > Pb<sup>2+</sup> > Cd<sup>2+</sup> > Zn<sup>2+</sup> > Cu<sup>2+</sup> [44], Pb<sup>2+</sup> > NH<sub>4</sub><sup>+</sup> > Cu<sup>2+</sup> ≈ Cd<sup>2+</sup> > Zn<sup>2+</sup> ≈ Co<sup>2+</sup> > Ni<sup>2+</sup> > Hg<sup>2+</sup> [13], Pb<sup>2+</sup> > Cu<sup>2+</sup> > Cd<sup>2+</sup> > Zn<sup>2+</sup> > Cr<sup>3+</sup> > Co<sup>2+</sup> > Ni<sup>2+</sup> [15], Pb<sup>2+</sup> > Cu<sup>2+</sup> > Cr<sup>3+</sup> [45], Pb<sup>2+</sup> > Cr<sup>3+</sup> > Fe<sup>3+</sup> > Cu<sup>2+</sup> [18], Pb<sup>2+</sup> > Fe<sup>3+</sup> > Cu<sup>2+</sup> > Cr<sup>3+</sup> [20]. For NaP1: Ba<sup>2+</sup> > Cu<sup>2+</sup> > Cd<sup>2+</sup> ≈ Zn<sup>2+</sup> > Co<sup>2+</sup> > Ni<sup>2+</sup> [46] and Cr<sup>3+</sup> > Cu<sup>2+</sup> > Zn<sup>2+</sup> > Cd<sup>2+</sup> > Ni<sup>2+</sup> [23]. For zeolite 4A: Cu<sup>2+</sup> > Co<sup>2+</sup> > Mn<sup>2+</sup> > Zn<sup>2+</sup> > Cd<sup>2+</sup> > Ni<sup>2+</sup> [26]. The observed differences were considered to be due to the specifics of the adsorbents and to the differences in the experimental techniques used. Moreover, there is less data relating to the selectivity of pure and chamfered-edge zeolite 4A prepared from coal fly ash. From the results obtained, it was inferred that the selectivity sequence of zeolite 4A (coal fly ash prepared and commercial grade) may be system specific which depended on the properties of the adsorbent and the experimental set-up used. It is also expected that the coal fly ash prepared zeolite could be considered for usage of purifying mixed heavy metal waste.

### 3.4. Effect of initial pH value on removal of heavy metal ions

The pH of the aqueous solution is an important controlling parameter in the sorption process [47] and metal removal typically increases with increasing pH values [48]. The pH may affect the ionization degree of the sorbate and the surface property of the sorbent [49]. Chemically, the solution pH influences metal speciation. For instance, heavy metal ions may form complexes with inorganic ligands such as OH<sup>-</sup>. The extent of the complex formation varies with pH, the ionic composition and the particular metal concerned. The exact speciation of a metal has a significant impact on the removal efficiency of the zeolites. The selectivity of metal ion by zeolites is also influenced by the character of the metal complex that predominates at a particular solution pH [15]. Exposure of the zeolite surface to water causes the ionization of surface hydroxyl groups (Si-OH and Al-OH). The degree of ionization depends on pH, and the acid/base reaction occurring at the hydroxyl groups may result in surface charge development [50]. Zeolites are not only influenced by pH but in turn are capable of affecting solution pH especially in batch system [43] and zeolites tend to have a higher internal pH. In addition, the zeolite surface may be influenced by the ambient pH which is not equal to the external solution pH value

and precipitation within the channels of zeolites and at the surface of zeolites may occur.

The effect of pH (from 3 to 5) on the adsorption of mixed metal ions by zeolite 4A was examined. Based on the solubility products of the metal hydroxides [51], the pH of precipitation at the test concentrations was computed, as shown in Table 5. Precipitation occurred when the initial pH of the solutions were adjusted to 5. As a result, only the removal efficiency of metal ions by zeolite 4A (coal fly ash prepared) at pH 3 and 4 were reported. As shown in Fig. 5, the removal efficiency of metal ions generally increased when the initial pH was increased. This was because zeolites were highly selective for H<sub>3</sub>O<sup>+</sup> ions when the H<sub>3</sub>O<sup>+</sup> ions concentration was high. Thus, at lower pH values the H<sub>3</sub>O<sup>+</sup> ions competed with metal ions for the exchange sites in zeolite [52]. Moreover, surface functional groups of zeolite may dissociate at higher pH values leaving more anionic surface sites that may make a significant contribution to the metal removal [53]. Besides, it was reported that the isoelectric point of zeolite 4A was around pH = 8 [54]. So, the zeolite surface is positively charged when the pH of solution is lower than 8. The reduced removal of metal ions as the pH decreases can be ascribed to this increase in positive charge on zeolite surface. The results

Table 5  
pH value when precipitation occurred at the tested concentrations

Initial concentration (mg l <sup>-1</sup> )	Metal ions	pH when precipitation occurred
50	Co <sup>2+</sup>	8.09
	Cr <sup>3+</sup>	5.07
	Cu <sup>2+</sup>	5.89
	Ni <sup>2+</sup>	7.92
	Zn <sup>2+</sup>	7.80
100	Co <sup>2+</sup>	7.94
	Cr <sup>3+</sup>	4.97
	Cu <sup>2+</sup>	5.74
	Ni <sup>2+</sup>	7.77
	Zn <sup>2+</sup>	7.65
200	Co <sup>2+</sup>	7.79
	Cr <sup>3+</sup>	4.87
	Cu <sup>2+</sup>	5.59
	Ni <sup>2+</sup>	7.62
	Zn <sup>2+</sup>	7.50
300	Co <sup>2+</sup>	7.70
	Cr <sup>3+</sup>	4.81
	Cu <sup>2+</sup>	5.50
	Ni <sup>2+</sup>	7.53
	Zn <sup>2+</sup>	7.41

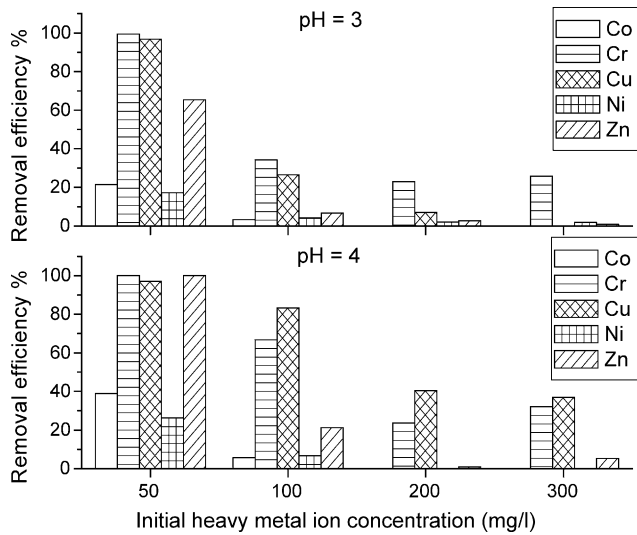


Fig. 5. Effect of pH on removal efficiency of metal ions ( $T$ , 25 °C; stirring speed, 600 rpm; time, 240 min;  $V$ , 100 ml;  $m$ , 0.1 g of zeolite 4A (coal fly ash prepared)).

also showed that the removal efficiency of  $\text{Cu}^{2+}$  was higher than  $\text{Cr}^{3+}$  when the initial pH value was increased. This variation underlined that the sorption of metal ions on zeolite 4A was dependent on pH value. Similar observations have been pointed out in the study of selectivity of  $\text{Cu}^{2+}$  and  $\text{Cr}^{3+}$  ions by natural clinoptilolite [20]. Regarding metals adsorption on zeolite 4A, the impact of pH on the surface chemistry of zeolite was not investigated in this study; however, investigation of pH influence on the distribution constants of metals adsorption on zeolite 4A can be found in Majdan et al. work [26].

### 3.5. Exchangeable ions passed into the heavy metal ions solution

In order to investigate if there was any exchangeable ions leached from the zeolite 4A (coal fly ash prepared and commercial grade) after the removal process, a study of the differences between the initial and the final ions concentrations

of the solutions was conducted. After the removal process (240 min), elements (such as Al, Si, K, Na, Sb, As, Cd, Ca, Mg, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Se, Ag, Tl, Zn and Ti) in the solutions were examined by ICP–AES. Table 6 shows the concentrations of exchangeable ions passed into the solutions from the zeolitic framework. It is seen that only  $\text{Si}^{4+}$ ,  $\text{Al}^{3+}$  and  $\text{Na}^{+}$  ions passed into the solutions. The leaching of Si- and Al-species may be due to the effect of the hydrogen ions on the aluminosilicate framework of the zeolite, which initially causes a rupture of the Al–O bonds and further detachment of Al- and Si-species through hydrolysis reactions [55]. The results showed that both the adsorption of total heavy metal ions and the CEC of zeolite increased with increasing concentration of the ions in the solution. Similar observations were obtained in the study of removal of  $\text{NH}_4^{4+}$  ion by zeolite [56]. Table 6 also shows, in the test conditions, the ratio of exchanged  $\text{Na}^{+}$  ions to total adsorbed metal ions is from 24 to 31%. It is shown that the removal mechanism of heavy metal ions was by the adsorption and ion exchange processes. However, compared to the total metal ions removed in the tests, the amount of metal ions removed by the ion exchange process could not be quantified in this study.

Sodium ion, being the sixth most abundant metallic ion in the earth's crust, is a natural constituent of both water and food. In water, sodium is found by several sources such as dissolution of underground sodium salt deposits, sea water and natural ion exchange in soils. In seawater, the average concentration of sodium ions is around  $10,760 \text{ mg l}^{-1}$ . Besides, water purification and bacterial control in water supplies are accomplished by adding sodium hypochlorite. In addition, softening water in municipal water treatment plants requires the addition of sodium carbonate (lime-soda method). In typical tannery wastewater [39] and tannery effluent after the precipitation treatment [50], the average concentration of sodium ions is around  $12,500$  and  $22,029 \text{ mg l}^{-1}$ , respectively. It is postulated that the impact of the leached sodium ions from ion exchange process ( $69$ – $218 \text{ mg l}^{-1}$ ) on the treatment of wastewater may not be significant. According to the studies by the Water Quality Association (WQA), the disposal of waste brine do not harm the leach fields [57]. However, when

Table 6  
Variation of concentrations of exchangeable ions with initial heavy metal ion concentrations

Initial conc. ( $\text{mg l}^{-1}$ )	Adsorbent	Exchangeable ions ( $\text{mg l}^{-1}$ )			Capacity ( $\text{mg g}^{-1}$ )		Ratio of exchanged $\text{Na}^{+}$ ions to total adsorbed metal ions (%)	CEC ( $\text{meq g}^{-1}$ )
		$\text{Si}^{4+}$	$\text{Al}^{3+}$	$\text{Na}^{+}$	Total adsorbed metal ions	Exchanged $\text{Na}^{+}$ ions		
50	Zeolite 4A	8.12	0.78	69.40	48.09	13.86	28.82	0.6
	Valfor 100	10.72	0.68	75.20	47.98	14.98	31.22	0.65
100	Zeolite 4A	9.78	0.74	115.60	93.54	23.04	24.63	1
	Valfor 100	11.23	0.70	124.08	91.07	24.54	26.95	1.07
200	Zeolite 4A	9.34	1.92	145.74	130.35	31.66	24.29	1.37
	Valfor 100	10.52	1.82	154.16	130.04	33.46	25.73	1.45
300	Zeolite 4A	17.20	2.24	208.20	140.85	41.46	29.44	1.8
	Valfor 100	22.20	2.62	218.08	140.14	43.55	31.08	1.89

$T$ , 25 °C; stirring speed, 600 rpm; time, 240 min; pH, 3;  $V$ , 100 ml;  $m$ , 0.5 g.

Table 7  
Equilibrium sorption capacity and removal efficiency of mixed metal ions by different adsorbents

Initial conc. (mg l <sup>-1</sup> )	Adsorbent	Equilibrium sorption capacity <sup>a</sup> (removal efficiency, %)					Equilibrium pH
		Co <sup>2+</sup>	Cr <sup>3+</sup>	Cu <sup>2+</sup>	Ni <sup>2+</sup>	Zn <sup>2+</sup>	
200	Coal fly	0.87	10.91	18.64	0.87	3.52	3.99
	Ash	(1.96)	(26.73)	(45.74)	(1.92)	(7.64)	
	TFA2	12.63	40.75	40.12	12.76	38.15	5.90
		(28.27)	(100)	(98.55)	(28.53)	(82.92)	
	TFA4.5	11.17	40.80	40.16	11.73	36.80	6.02
		(25.2)	(100)	(98.53)	(25.96)	(79.91)	
	Zeolite 4A	14.51	35.63	40.11	9.51	30.59	5.62
	(Coal fly ash)	(32.75)	(87.33)	(98.42)	(21.06)	(66.42)	
Valfor 100	12.81	37.17	40.08	7.94	32.04	5.75	
	(28.92)	(91.19)	(98.44)	(17.6)	(69.62)		
300	Coal fly	1.20	10.00	15.19	2.00	4.00	3.79
	Ash	(1.96)	(17.61)	(27.14)	(3.18)	(6.21)	
	TFA2	8.79	48.72	54.96	9.19	30.33	4.84
		(14.38)	(85.85)	(98.22)	(14.65)	(47.14)	
	TFA4.5	6.39	50.66	54.20	6.39	27.51	4.71
		(10.46)	(89.37)	(96.97)	(10.46)	(42.8)	
	Zeolite 4A	13.54	41.58	49.94	8.76	27.04	4.73
	(Coal fly ash)	(22.22)	(73.52)	(89.57)	(14.01)	(42.17)	
Valfor 100	11.18	44.53	51.08	7.59	25.76	4.89	
	(18.3)	(78.52)	(91.36)	(12.1)	(40.06)		

T, 25 °C; stirring speed, 600 rpm; time, 240 min; pH, 3; V, 100 ml; m, 0.5 g.

<sup>a</sup> Unit of equilibrium sorption capacity: mg g<sup>-1</sup>.

the treated effluent is discharged onto open land, into fresh water bodies such as ponds and streams, proper treatment on the high concentration of sodium ions solution should be undertaken. It is reported that a significant degradation in the quality of the groundwater in the area is indicated by the high concentrations of Na<sup>+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, and HCO<sup>3-</sup> ions in samples from dug wells and bore wells located in the vicinity of the effluent-disposal sites [58].

### 3.6. Comparative study of the removal efficiency of metal ions by the coal fly ash, treated fly ash residues (TFA2 and TFA4.5) and zeolite 4A (coal fly ash prepared and commercial grade)

It was observed that the removal efficiency of metal ions increased with increasing the mass of zeolite 4A (coal fly ash prepared and commercial grade) which could be attributed to the increase in the available surface area per unit volume of solution for adsorption with zeolite. Table 7 lists the equilibrium sorption capacity and the removal efficiency of metal ions by different adsorbents. The original coal fly ash had the lowest removal efficiency and equilibrium sorption capacity of the metal ions at the tested concentrations. Besides, it was interesting that the treated fly ash residues (TFA2 and TFA4.5) had a relatively high removal efficiency and equilibrium sorption capacity of the metal ions (except Co<sup>2+</sup> ions) than zeolite 4A (coal fly ash prepared and commercial grade). The high removal efficiency of metal ions by TFA2 and TFA4.5 may be caused by the existence of NaP1 zeolite on the surface of the treated fly ash particles. It was believed that the main mechanisms of removal of metal ions

by TFA2 and TFA4.5 were due to adsorption and precipitation formation. For adsorbents TFA2 and TFA4.5, it was observed that the selectivity sequence of Cr<sup>3+</sup> and Cu<sup>2+</sup> metal ions was dependent on initial concentration of the solution. Based on the experimental results obtained, it was concluded that the coal fly ash prepared zeolite 4A and the treated fly ash residues (TFA2 and TFA4.5) could both be applied for treatment of wastewaters.

Adsorption at solid–solution interfaces is an important means for controlling the extent of pollution due to industrial or landfill effluents [49]. Due to its high cost and loss in regeneration, the use of activated carbon or zeolite as conventional adsorbents may not be an economical way of treating wastewater compared to the use of zeolite products and residues converted from coal fly ash. Furthermore, converting coal fly ash into adsorbents could relieve or eliminate the problems regarding the disposal of huge quantities of coal fly ash generated by thermal power plants every year.

## 4. Conclusion

The present study showed that the coal fly ash based adsorbents were effective in removing mixed heavy metal ions from aqueous solutions compared to the commercial zeolite 4A. It showed that the selectivity sequence of metal ions by the adsorbents was dependent on the system employed, and was mainly dependent on the initial concentrations of the metal ions and the initial pH of the solution. Generally, at the tested concentration of 300 mg l<sup>-1</sup>, it was Cu<sup>2+</sup> > Cr<sup>3+</sup> > Zn<sup>2+</sup> > Co<sup>2+</sup> > Ni<sup>2+</sup>

(coal fly ash prepared and commercial zeolite 4A),  $\text{Cu}^{2+} > \text{Cr}^{3+} > \text{Zn}^{2+} > \text{Co}^{2+} \approx \text{Ni}^{2+}$  (treated fly ash residues: TFA2 and TFA4.5) and  $\text{Cu}^{2+} > \text{Cr}^{3+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+}$  (the coal fly ash). The sorption kinetics of  $\text{Ni}^{2+}$  ions could be best described by pseudo-first-order model and ions such as  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$  could be best described by pseudo-second-order model. The effect of pH of the solution could significantly improve the sorption rate and sorption capacity of metal ions. Adsorption isotherms of metal ions could be best modeled by Langmuir equation. The sorption capacity of coal fly ash prepared zeolite 4A is similar to that of the commercial one (Valfor 100). It is also observed that the removal mechanism of heavy metal ions was by adsorption and ion exchange processes.

The coal fly ash based adsorbents may be an alternative to more costly adsorbents such as activated carbon and commercial zeolites for the treatment of aqueous wastes containing mixed metal ions. Moreover, the rapid sorption rates of metal ions, especially at pH 4, allows the consideration of removal of metal ions by column filled setup which generally has a short contact time between the metal solution and the adsorbent during the sorption process.

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