Removal of ammonium and heavy metals by cost-effective zeolite synthesized from waste quartz sand and calcium fluoride sludge
Qian Zhang, Bing Lin, Junming Hong and Chang-Tang Chang

ABSTRACT
This study focuses on the effectiveness of zeolite (10% CF-Z [0.5]) hydrothermally synthesized from waste quartz sand and calcium fluoride (CF) for ammonium ion and heavy metal removal. Zeolite was characterized through powder X-ray diffraction, Fourier-transform infrared spectroscopy, micromeritics N2 adsorption/desorption analysis, and field emission scanning electron microscopy. The effects of CF addition, Si/Al ratio, initial ammonium concentration, solution pH, and temperature on the adsorption of ammonium on 10% CF-Z (0.5) were further examined. Results showed that 10% CF-Z (0.5) was a single-phase zeolite A with cubic-shaped crystals and 10% CF-Z (0.5) efficiently adsorbs ammonium and heavy metals. For instance, 91% ammonium (10 mg L$^{-1}$) and 93% lead (10 mg L$^{-1}$) are removed. The adsorption isotherm, kinetics, and thermodynamics of ammonium adsorption on 10% CF-Z (0.5) were also theoretically analyzed. The adsorption isotherm of ammonium and lead on 10% CF-Z (0.5) in single systems indicated that Freundlich model provides the best fit for the equilibrium data, whereas pseudo-second-order model best describes the adsorption kinetics. The adsorption degree of ions on 10% CF-Z (0.5) in mixed systems exhibits the following pattern: lead > ammonium > cadmium > chromium.

Key words | ammonium, calcium fluoride, heavy metals, waste quartz sand, zeolite

INTRODUCTION
Industrial chemical production processes often yield large amounts of wastewater discharged into soil and water. Wastewater usually contains many pollutants, such as ammonium and heavy metals, which elicit toxic effects on ecosystems. Thus, low-cost and efficient methods for industrial wastewater treatment should be established. Various methods for ammonium and heavy metal removal from wastewater have been developed, and biological treatments (Du et al. 2015) and adsorption (Kirbiyük et al. 2016) have been widely employed. However, biological treatments are affected by temperature, and biosorbent separation is difficult after adsorption occurs. Adsorption has been performed with cost-effective ion exchangers, such as zeolite.

Zeolites possess a porous structure that accommodates various cations, such as Na$^+$, K$^+$, Ca$^{2+}$, or Mg$^{2+}$. These ions can be readily exchanged for other ions in a contact solution (Cundy & Cox 2003). The adsorption performance of zeolite depends on its chemical structure. Compared with natural zeolite, synthetic zeolites are suitable for industrial applications. Ferronato et al. (2015) used static flow (A) and laminar flow (B) methods to evaluate the efficiency of clinoptilolite, which is a zeolite, in reducing the concentration of different contaminants in the outflow wastewater of an old municipal treatment plant in Bologna District, Northern Italy. Akhigbe et al. (2016) prepared silver-modified zeolite to remove *Escherichia coli* and metals. Yu et al. (2015) synthesized coal cinder-zeolite balls for ammonium nitrogen adsorption from low-pollutant-concentration wastewater. Despite the rapid advancements and utilization of zeolite, the preparation of synthetic zeolites from the chemical sources of silica remains costly. Electrolytic manganese residues (Li et al. 2015), rice husk (Yusof et al. 2010), kaolinite (Belviso et al. 2013), and coal fly (Izidoroa et al. 2012) have been used as silicon sources to prepare zeolite aluminosilicate materials, and wastes have been successfully fabricated to produce adsorbents. However,
the total equilibrium time is generally long, and synthetic zeolite products contain a significant amount of residual raw materials (Zhang et al. 2014). Consequently, the long equilibrium time limits the applicability of synthetic zeolite. Thus, effective and low-cost synthetic zeolites with short equilibrium time should be developed.

Waste quartz sand (WQS) is a by product of industrial silica production processes. The SiO₂ content of WQS can exceed 80%. Calcium fluoride (CF) sludge is a waste product of electroplating sludge treatment in semiconductor plants. Toxic hydrofluoric acid is produced when CF reacts with an acidic solution. At present, WQS is used as a material for floors, walls, and sidewalks, whereas CF is a material used for cements and ceramics. WQS and CF may also be recycled to synthesize materials as effective adsorbents for the removal of various pollutants, such as ammonium or heavy metals, from water.

This study aimed to synthesize zeolite from WQS and CF via hydrothermal method. The effects of CF addition and Si/Al ratio on the properties of CF-Z were investigated. The adsorption capacity of CF-Z as a low-cost adsorbent for ammonium and heavy metals removal was examined. The effects of ammonium concentration and solution pH on the adsorption capacity of materials were also assessed. The isothermal, kinetic, and thermodynamic adsorption of ammonium and lead were analyzed and established.

EXPERIMENTAL AND METHODS

Raw materials and silicate extraction

WQS and CF were obtained from manufacturing wastes of Taiwan Semiconductor Manufacturing Company, Ltd and Taiwan United Microelectronics Corporation. The chemical composition of the waste quartz and CF is listed in Table 1. A total of 20 g of WQS powder, 20 g of solid sodium hydroxide, and 100 mL of deionized water were placed in a hydrothermal reactor and heated at 473 K for 4 h to extract the silicon. The liquid was then naturally cooled and filtered through gravitational flow. The concentrations of silicon and sodium in the filtrate as measured through microwave plasma-atomic emission spectrometer (MP-AES) method were 158,750 mg L⁻¹ and 14,750 mg L⁻¹.

Zeolite synthesis

Gel with a molar ratio of 3.5Na₂O: Al₂O₃: 2xSiO₂: 150H₂O (x = 0.5, 1, 1.5, and 2) was used for zeolite synthesis. The gel was prepared by adding sodium aluminate to an aqueous solution of sodium hydroxide followed by the addition of the high silica filtrate. The obtained gel was then stirred for 30 min at room temperature and mixed with the CF (a = 0%, 5%, 10%, 20%, and 40%) and stirred for another 12 h. The homogenized gel was then placed in a Teflon-lined stainless steel autoclave and hydrothermally treated for 24 h at 363 K. After the gel was filtered off and washed with deionized water, then air dried at 373 K for 24 h, CF-Z(x) was obtained.

Characterization

The amount of inorganic compounds in the WQS and CF were measured using an X-ray fluorescence spectrometer (XRF, Riguka, NEXCG) in the air. Identification of the species of the zeolites was carried out by powder X-ray diffraction (XRD, Rigaku Inc. Ultima IV, USA) with Cu Kα radiation (λ = 0.1541 nm). The surface functional structures of the zeolites were studied by Fourier-transform infrared spectra (FT-IR, Spectrum 100, USA). The FT-IR spectrum of each sample was scanned three times with a resolution of 4 cm⁻¹ over a range of 600 cm⁻¹ to 4,000 cm⁻¹. Surface area measurements were performed using a Micromeritics N₂ adsorption/desorption analyzer (model ASAP 2020N, USA) by adsorbing gaseous N₂ at the melting point of the nitrogen. The surface morphologies of zeolites were observed by field emission scanning electron microscope (FE-SEM, JSM-6701F, JEOL) at an extra-high tension voltage of 3 kV.

Batch experiments

Adsorption studies were carried out using batch contact adsorption mode with 10% CF-Z (0.5) as adsorbent of ammonium and heavy metals in aqueous solutions. The ammonium and heavy metal solutions were prepared from

<table>
<thead>
<tr>
<th>Components</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>SO₃</th>
<th>K₂O</th>
<th>CaO</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass% (WQS)</td>
<td>99.9</td>
<td>–</td>
<td>0.0069</td>
<td>0.0136</td>
<td>0.0067</td>
<td>0.0728</td>
</tr>
<tr>
<td>Mass% (CF)</td>
<td>29.9</td>
<td>3.35</td>
<td>4.95</td>
<td>0.076</td>
<td>60.5</td>
<td>–</td>
</tr>
</tbody>
</table>
standard lead, cadmium, and chromium solution (J.T. Baker Ltd and Merck Taiwan). The ammonium solutions were prepared from NH₄Cl (AR; Merck Taiwan). Before the reaction was initiated, blank adsorption experiments were conducted in 250 mL serum bottles, and the pH range of the solution was adjusted to 3–9 without adding zeolite. In blank experiments, the concentration of the ammonium and metal solution was maintained at stable levels for 30 min without adding zeolite.

The adsorbate concentration was determined by comparing absorbance to a calibration curve previously obtained. All experiments were duplicated and only the mean values were reported. The amount of adsorbate onto the adsorbent, \( q_e \) (mg g\(^{-1}\)), was calculated by Equation (1):

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]

where \( C_0 \) and \( C_e \) (mg L\(^{-1}\)) are the initial and equilibrium liquid-phase concentrations of adsorbate, respectively. \( V \) (L) is the volume of the solution and \( m \) (g) is the mass of dry adsorbent used. For batch kinetic studies, the same procedure was followed, but the aqueous samples were taken at preset time intervals. The concentrations of adsorbate were similarly measured. The amount of adsorbate onto the adsorbent at any given time, \( q_t \) (mg g\(^{-1}\)), was calculated by the following equation:

\[
q_t = \frac{(C_0 - C_t)V}{m}
\]

where \( C_t \) (mg L\(^{-1}\)) is the liquid-phase concentration of adsorbate at any given time. The normalized standard deviation, \( \Delta q_e(\%) \), was calculated by the following equation:

\[
\Delta q_e(\%) = 100\left(\frac{1}{N-1}\sum\left(\frac{q_{e,exp} - q_{e,cal}}{q_{e,exp}}\right)^2\right)
\]

where \( N \) is the number of data points and \( q_{e,exp} \) and \( q_{e,cal} \) (mg g\(^{-1}\)) are the experimental and calculated equilibrium adsorption capacity values, respectively.

**Adsorption of ammonium**

A total of 200 mL of solutions with various ammonium concentrations (5 to 80 mg L\(^{-1}\)) and temperatures (283 K to 303 K) was placed in different 250 mL serum bottles, and the pH range of the solution was adjusted to a desirable level (pH range 3–9). Approximately 2 g L\(^{-1}\) of adsorbent was added to each volumetric bottle, and the bottles were placed in a water bath isothermal shaker (Deng Yng Co., DKW-20) for 20 min at a shaker speed of 125 rpm to achieve equilibrium. The final concentration of the ammonium solution (using 0.45 \( \mu \)m membrane filters) in the flasks was determined using ion chromatography (IC, Metrohm 761 compact IC).

**Adsorption of heavy metal**

Heavy metal adsorption experiments were carried out using various single metal concentration (5 mg L\(^{-1}\) to 40 mg L\(^{-1}\)) and various kinds of metal (lead, chromium, and cadmium). Approximately 0.4 g of adsorbent was added to 200 mL of solution that contained lead, chromium, or cadmium, and the solution-containing flasks were placed in a water bath isothermal shaker (Deng Yng Co., DKW-20) for 110 min at a shaker speed of 125 rpm to achieve equilibrium. The final concentration of metal solution (using 0.45 \( \mu \)m membrane filters) in the flasks was determined using MP-AES (Agilent 4100, USA).

**Adsorption of ammonium and metal in binary systems**

Ammonium and metal adsorption experiments were conducted using various ammonium/lead concentration ratio (10 mg L\(^{-1}\)/20 mg L\(^{-1}\), 10 mg L\(^{-1}\)/10 mg L\(^{-1}\), 20 mg L\(^{-1}\)/10 mg L\(^{-1}\), and 40 mg L\(^{-1}\)/10 mg L\(^{-1}\)). Approximately 2 g L\(^{-1}\) of adsorbent was added to 200 mL of solutions that included ammonium and lead content, and the flasks containing the solution were placed in a water bath isothermal shaker for 110 min at a shaker speed of 125 rpm to achieve equilibrium. The final concentration of ammonium and metal solution (using 0.45 \( \mu \)m membrane filters) in the flasks was determined using IC and MP-AES.

**RESULTS AND DISCUSSION**

**Characterization of zeolites**

The XRD patterns are shown in Figure 1. As can be seen, when the Si/Al molar ratio was 2, a mixture of zeolite A and zeolite X (PDF 73-2340 and PDF 38-0237) was crystallized. By using the lower molar ratio (Si/Al < 2), the XRD pattern of the samples was demonstrated to be that of zeolite A. In Figure 1(a)–1(c), there are no detected peaks of impurities, indicating the formation of single-phase zeolite A. A similar phenomenon was also observed in a study by Fotovat et al. (2009).
Scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS) images of zeolites are presented in Figure 2. As seen in Figure 2(a)–2(c), results show that cubic-shaped crystals were formed at a lower molar ratio (Si/Al < 2). A molar ratio of Si/Al = 2 yielded crystals that were sharp and irregularly shaped because of the mixture of zeolite A and zeolite X. However, substances with irregular morphology were seen in the SEM images of the zeolites, and the EDS spectra images show the presence of Ca, which should contribute to the addition of CF.

The different effects of CF addition and varying Si/Al molar ratio on zeolites were analyzed through N2 adsorption/desorption technique. The results are presented in Table 2. The results show that the addition of CF can increase the Brunauer–Emmett–Teller (BET) or N2-sorption surface areas of the zeolites, which in turn may affect the zeolite reactivity on adsorption (Perraki et al. 2010). Furthermore, the BET surface areas of the zeolites increases from 2.27 m² g⁻¹ to 305 m² g⁻¹ when the Si/Al molar ratio of the reaction mixture decreases from 2 to 0.5. However, the pore sizes of zeolites decrease from 13.0 nm to 3.41 nm when Si/Al molar ratio is from 0.5 to 2.

The FT-IR spectra images of zeolites with different Si/Al molar ratio are shown in Figure 3. The band at approximately 3,435 cm⁻¹ corresponds to OH stretching of water molecules present in the zeolite channels (Chen et al. 2012). The band at approximately 1,647 cm⁻¹ is ascribed to H₂O deformation mode because of incomplete dehydration. The sample exhibits a strong vibrational band at 1,006 cm⁻¹ corresponding to T-O-Tsym (T refer to Si or Al atom) stretching (Purnomo et al. 2012). The presence of zeolite X (Figure 3(d)) is indicated by a peak at approximately 748 cm⁻¹, typical of O-T-Osym stretching vibrations (Loshe et al. 1995). The presence of zeolite A (Figure 3) is indicated by the peaks at approximately 665(T-O), 560, and 465(T-O-Na) cm⁻¹. FT-IR results are consistent with the XRD results.
All the characteristic FT-IR bands of zeolite A and zeolite X are similar to those of A- and X-type zeolites synthesized from Kaolinite (Belviso et al. 2013).

**Ammonium removal in a single system**

**Effect of CF addition and Si/Al ratio**

The effect of CF addition and the Si/Al ratio on ammonium adsorption by zeolites is shown in Figures 4 and 5.

The results indicate that ammonium removal decreases from 89.9% to 49.4% when CF addition increases from 0% to 40%. Ammonium significantly decreases when the CF addition increases from 10% to 20%. It is proposed that the surface of zeolites with CF is covered by particles which probably block pores or cavities as the amount of CF added increases (Table 2). In conclusion, although CF addition slightly affects the zeolite adsorption of ammonium ions, particularly when CF addition is lower than 10%, the ammonium removal remains very high at 84.1%.

The effect of the Si/Al ratio on ammonium adsorption by zeolites is shown in Figure 5. The maximum ammonium removal is 91.5% at 0.5 Si/Al. This is likely because the 0.5 Si/Al ratio in the framework produces more negative charge. The framework needs more sodium to compensate for the excess negative charge and because more exchangeable sodium exists in the zeolite structure (Inglezakis 2005).

**Effect of initial ammonium concentration**

Initial ammonium concentrations varying from 10 mg L$^{-1}$ to 80 mg L$^{-1}$ were treated with 2 g L$^{-1}$ of 10% CF-Z (0.5). Figure 6 shows the effect of initial ammonium concentration on the adsorption performance of 10% CF-Z (0.5). With the increase of initial ammonium concentration, ammonium removal decreased from 91.5% to 85.0%, but the adsorption capacity of 10% CF-Z (0.5) increased from 4.62 mg g$^{-1}$ to 25.7 mg g$^{-1}$. This is attributed to the increase in the driving force to the vacant active pores of the adsorbent (Zhang et al. 2011). The ammonium adsorption rate gradually reduces as it approaches equilibrium within 20 min (results are not shown in Figure 6). Table 3 shows ammonium adsorption capacity of zeolites at 80 mg L$^{-1}$ ammonium concentration (Zhao et al. 2010; Widiastuti et al. 2011; Malekian et al. 2011; Lin et al. 2013; Liu et al. 2013; Alshameri et al.)
The 10% CF-Z (0.5) is the most effective adsorbent for ammonium among all zeolites.

**Effect of pH**

pH affects the amount of ammonium removed by the zeolite because pH influences the characteristics of ammonium ion and zeolite itself (Wang & Peng 2014). Figure 7 shows that pH significantly affects ammonium removal. The optimal pH by which 10% CF-Z (0.5) can remove ammonium was 5.0. Further, as the pH increased, the amount of ammonium removed decreased. The minimum ammonium removed was 79.2% at pH 9 because at pH levels higher than 6, ammonium forms ammonia, which cannot be removed through adsorption. Similar trends were also observed in the adsorption of ammonium through natural zeolite (Widiastuti et al. 2014). Wang & Peng (2014) found that the zeolites adsorb ammonium mainly through ion exchange, and sodium concentration in the solution increased with the increasing ammonium removal, which is inconsistent with our study results at pH = 3. We attributed this to the intensified competition for exchange sites of hydrogen ion (Wu et al. 2006).

**Adsorption isotherm**

Analysis of isotherm data by fitting it to different isotherm models is an important step in finding a suitable model for design purposes. In this study, the isotherm data were fitted to the Langmuir, Freundlich, and Tempkin isotherms.

The Langmuir equation is expressed as Equation (4):

$$q_e = \frac{Q_m K_L C_e}{(1 + K_L C_e)}$$

where $C_e$ is the equilibrium liquid-phase concentrations of adsorbate (mg L$^{-1}$) and $Q_m$ and $K_L$ are maximum adsorption capacity and Langmuir constant, respectively.

The Freundlich equation is expressed as Equation (5):

$$q_e = K_F C_e^{1/n}$$

where $K_F$ is the Freundlich adsorbent capacity and then parameter, known as the heterogeneity factor, can be used to indicate the partition between the two phases.

The Temkin equation is expressed as Equation (6):

$$q_e = \frac{RT}{b_T} \ln(k_T C_e)$$

where, $b_T$ and $k_T$ are Temkin constants, $R$ (8.314 J mol$^{-1}$ K$^{-1}$) and $T$ (K) are the gas constant and the absolute temperature, respectively.

**Table 3 | Ammonium adsorption capacity on zeolites at 80 mg L$^{-1}$ ammonium concentration**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Capacity (mg g$^{-1}$)</th>
<th>Temperature (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chinese natural zeolite</td>
<td>4.6</td>
<td>298</td>
<td>Lin et al. (2013)</td>
</tr>
<tr>
<td>Australian natural zeolite</td>
<td>6–7</td>
<td>298</td>
<td>Widiastuti et al. (2011)</td>
</tr>
<tr>
<td>Iranian natural zeolite</td>
<td>2.5</td>
<td>298</td>
<td>Malekian et al. (2011)</td>
</tr>
<tr>
<td>Chinese natural zeolite</td>
<td>7–8</td>
<td>298</td>
<td>Alshameri et al. (2014)</td>
</tr>
<tr>
<td>Modified zeolite</td>
<td>9–10</td>
<td>298</td>
<td>Alshameri et al. (2014)</td>
</tr>
<tr>
<td>Synthesized zeolite from fly ash</td>
<td>10–15</td>
<td>298</td>
<td>Zhang et al. (2011)</td>
</tr>
<tr>
<td>Synthesized zeolite A from halloysite mineral</td>
<td>10–15</td>
<td>288</td>
<td>Zhao et al. (2010)</td>
</tr>
<tr>
<td>Synthesized zeolite A from metakalin</td>
<td>10.4–19.3</td>
<td>–</td>
<td>Liu et al. (2015)</td>
</tr>
<tr>
<td>Magnetic zeolite A</td>
<td>10.4–18.7</td>
<td>–</td>
<td>Liu et al. (2015)</td>
</tr>
<tr>
<td>Synthesized zeolite A from WQS and CF</td>
<td>25.7</td>
<td>303</td>
<td>This work</td>
</tr>
</tbody>
</table>
The proposed equations revealed that all of the isotherm models could obtain analytical solutions for the Ce series profiles of the maximum adsorption capacity ($Q_m$). $K_L$, $K_F$, $n$, $b_T$, and $k_T$ can be calculated from the slope and intercept of the linear equations. The correlation coefficient $R^2$ of the linear equations is the parameter related to the fitting of predicted and experimental values. The values of the maximum adsorption amount, correlation coefficient, and the other parameters for all the isotherms are shown in Table 4.

The fitting of Langmuir, Freundlich, and Temkin isotherm to the experimental data is shown in Figure 8. Freundlich isotherm model yields the best fit with the highest correlation coefficient ($R^2 = 0.995$) and lower $\Delta q_e$ (5.02%) than Langmuir and Temkin isotherm models.

**Kinetic adsorption**

The kinetic adsorption data can provide valuable information on the dynamics of the adsorption reactions for the efficiency and mechanism of the adsorption process. The three most commonly used models to describe the adsorption behavior of pollutants solid surfaces are the pseudo-first-order, pseudo-second-order and Elovich models.

The pseudo-first-order equation is expressed as Equation (7):

$$q_t = q_e (1 - e^{-kt})$$

The pseudo-second-order equation is expressed as Equation (8):

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$$

The Elovich equation is expressed as Equation (9):

$$q_t = \frac{RT}{\beta} \ln (\alpha \beta C_e)$$
where \( q_t \), \( k_1 \), \( k_2 \), \( k_{id} \), \( \alpha \) and \( C \) \( (\beta) \) are the amount of ammonium adsorbed onto 10% CF-Z (0.5), rate constant, and constant, respectively.

The kinetic parameters, including correlation coefficients \( (R^2) \), \( k_1 \), \( k_2 \), \( \alpha \), \( \beta \), and calculated \( q_e \), are determined through linear regression \( (Table \ 5) \). \( R^2 \) \( (\geq 1) \) of pseudo-second-order model is significantly higher than that of pseudo-first-order model and Elovich model. Therefore, adsorption is controlled by chemisorption, which involves valence forces by inducing the exchange of electrons between an adsorbent and an adsorbate \( (Biškup \ & \ Subotić \ 2004) \).

**Adsorption thermodynamic**

Changes in free energy, enthalpy, and entropy have been calculated on the basis of Langmuir equilibrium constant for ammonium adsorption. The thermodynamic equilibrium constant in Gibbs energy change is unitless, whereas the Langmuir equilibrium constant is in liters per mole. Therefore, Langmuir equilibrium constant can be reasonably used for determination of \( \Delta G^0 \). Liu \( (2009) \) demonstrated that Langmuir equilibrium constant can be reasonably used to determine \( \Delta G^0 \) for neutral adsorbates with weak charges. For charged adsorbates, determining \( \Delta G^0 \) is reasonable only for a dilute solution. In this research, Langmuir equilibrium constant can be reasonably used to identify \( \Delta G^0 \) because ammonium is a weak charged adsorbate and not a multivalent ion. The thermodynamics of ammonium adsorption on 10% CF-Z (0.5) and the thermodynamic constants, such as enthalpy change \( \Delta H \), free energy change \( \Delta G \), and entropy change \( \Delta S \), were calculated using Equation (10):

\[
\Delta G = -RT \ln K_C
\]

\( K_C \) \( (L \ g^{-1}) \) is the standard thermodynamic equilibrium constant.

The thermodynamic parameters obtained are summarized in \( Table \ 6 \). All \( \Delta G \) values are negative, indicating that ammonium adsorption by 10% CF-Z (0.5) was spontaneous. A positive \( \Delta H^0 \) implies that adsorption is an endothermic and physical adsorption process, whereas a negative \( \Delta H^0 \) indicates an exothermic and chemical adsorption \( (Liu \ 2009) \). Thus, the negative adsorption enthalpy \( (\Delta H = -13.1 \ kJ \ mol^{-1}) \) and entropy \( (\Delta S = -87.7953.7 \ J \ mol^{-1}) \) in \( Table \ 6 \) show that adsorption was exothermic \( (Liu \ 2009; \ Auta \ & \ Hameed \ 2012) \) and entropy did not change significantly during adsorption \( (Liu \ 2009) \).

**Heavy metals removal in single system**

**Adsorption of single and mix heavy metals**

The effects of initial single metal concentration on the 10% CF-Z (0.5) performance in single and triple systems are shown in \( Figures \ 9 \) and \( 10 \). At a heavy metal concentration of 5 mg L\(^{-1}\), lead, chromium, and cadmium were completely removed. As the initial heavy metal concentration increased

\( Table \ 5 \) | Pseudo-first, pseudo-second-order and Elovich models parameters for ammonium and lead adsorption on 10% CF-Z (0.5)

<table>
<thead>
<tr>
<th>Adsorption kinetic models</th>
<th>10 mg L(^{-1})</th>
<th>20 mg L(^{-1})</th>
<th>40 mg L(^{-1})</th>
<th>80 mg L(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium adsorption</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pseudo-first-order</td>
<td>( K_1 ) 0.119</td>
<td>0.101</td>
<td>0.102</td>
<td>0.102</td>
</tr>
<tr>
<td></td>
<td>( R^2 ) 0.710</td>
<td>0.932</td>
<td>0.763</td>
<td>0.809</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>( K_2 ) 5.80</td>
<td>0.854</td>
<td>0.934</td>
<td>0.341</td>
</tr>
<tr>
<td></td>
<td>( q_e ) 4.61</td>
<td>8.86</td>
<td>15.6</td>
<td>25.5</td>
</tr>
<tr>
<td></td>
<td>( R^2 ) 1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Elovich</td>
<td>( \alpha ) 2.29 \times 10^{-37}</td>
<td>8.44 \times 10^{-35}</td>
<td>1.98 \times 10^{-37}</td>
<td>1.10 \times 10^{-23}</td>
</tr>
<tr>
<td></td>
<td>( \beta ) 17.3</td>
<td>16.1</td>
<td>17.4</td>
<td>19.8</td>
</tr>
<tr>
<td></td>
<td>( R^2 ) 0.897</td>
<td>0.794</td>
<td>0.896</td>
<td>0.977</td>
</tr>
<tr>
<td>Lead adsorption</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pseudo-first-order</td>
<td>( K_1 ) 0.108</td>
<td>0.0728</td>
<td>0.0380</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>( R^2 ) 0.994</td>
<td>0.781</td>
<td>0.904</td>
<td>–</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>( K_2 ) 0.448</td>
<td>0.226</td>
<td>0.565</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>( q_e ) 4.66</td>
<td>10.2</td>
<td>17.0</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>( R^2 ) 1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>–</td>
</tr>
<tr>
<td>Elovich</td>
<td>( A ) 8.55 \times 10^9</td>
<td>1.91 \times 10^5</td>
<td>7.55 \times 10^7</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>( B ) 6.15</td>
<td>1.56</td>
<td>8.05</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>( R^2 ) 0.965</td>
<td>0.883</td>
<td>0.925</td>
<td>–</td>
</tr>
</tbody>
</table>
Figure 9 | Effect of initial single heavy metal concentration on the 10% CF-Z (0.5) performance in single ion systems.

Figure 10 | Effect of initial single heavy metal concentration on the 10% CF-Z (0.5) performance in triplet ion systems.

Figure 11 | Langmuir, Freundlich and Temkin isotherms for lead adsorption on 10% CF-Z (0.5).

Table 6 | Thermodynamics parameters for ammonium adsorption on 10% CF-Z (0.5)

<table>
<thead>
<tr>
<th>$\Delta H$ (kJ mol$^{-1}$)</th>
<th>$\Delta S$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>288 K</th>
<th>293 K</th>
<th>298 K</th>
<th>303 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>–13.1</td>
<td>–33.7</td>
<td>–3.43</td>
<td>–3.18</td>
<td>–3.03</td>
<td>–2.92</td>
</tr>
</tbody>
</table>

(5–40 mg L$^{-1}$), lead removal decreased from 100% to 85.2%, the chromium removal decreased from 100% to 11.7%, and the cadmium removal decreased from 100% to 33.1%.

Figures 9 and 10 show that the adsorption sequence of metal ions on 10% CF-Z (0.5) was as follows: lead > cadmium > chromium. This order is obtained because heavy metal concentration influences ionic exchange in zeolites; therefore, metals with high hydration free energy likely remain desorbed in the solution phase (Ouki & Kavannagh 1997). This result is consistent with the adsorption sequence of metal ions on zeolite P (pumice lapillus prepared) (Catalfamo et al. 2006).

**Adsorption isotherm and kinetic of lead**

The values of the maximum amount adsorbed, correlation coefficient, and other parameters for all the isotherms are shown in Table 4. Fitting of the Langmuir, Freundlich, and Temkin isotherm to the experimental data is shown in Figure 11. The Freundlich correlation coefficient ($R^2 = 0.999$) and $\Delta q_e$ (2.46%) shows that the experimental data agree best with Freundlich model. The adsorption process was favorable ($n > 1$), and there was a high possibility of multilayer adsorption of lead on the active heterogeneous surface ($0 < 1/n < 1$) sites of 10% CF-Z (0.5) (Auta & Hameed 2015). The results of fitting the experimental data with pseudo-first-order, pseudo-second-order and Elovich models for adsorption of lead onto 10% CF-Z (0.5) are presented in Table 5. As can be seen, the correlation coefficients ($R^2$) are 1.00 for the pseudo-second-order model, indicating a better fit with pseudo-second-order model. Pseudo-second-order sorption model is predominant, and the overall rate constant of each ion exchange process appears to be controlled by the chemical sorption process (Biškup & Subotić 2004).

**Ammonium and metal removal in binary systems**

Ammonium or heavy metal adsorption by zeolites has been extensively studied. However, these investigations focused on
the performance of zeolites for a single ion. This work included adsorption using binary ammonium metal (lead) mixtures (Figure 12) considered because the wastewater of some industries contain these two types of pollutants, namely, ammonium and heavy metals. Figure 12(a) shows that the presence of lead (10 mg L\(^{-1}\)) significantly affects the adsorption of ammonium. Ammonium removal decreased from 91.5%, 86.1%, and 78.6% to 41.4%, 38.0%, and 27.9%, at 10, 20, and 40 mg L\(^{-1}\) ammonium concentration, respectively. However, the presence of ammonium has little effect on the adsorption of lead. When ammonium concentration was increased (10–40 mg L\(^{-1}\)), lead removal decreased from 93.9% to 91.9%, 88.5%, and 84.0%, respectively. In conclusion, the adsorption sequence on 10% CF-Z (0.5) was as follows: lead > ammonium > cadmium > chromium in Figures 9, 10, and 12.

In this research, the alternative Si source used to synthesize a zeolite is the same source that enables industries to fabricate valuable adsorption materials from WQS and CF at low costs. Zeolite can be used as an adsorbent for ammonium and metals. Zeolite is a very useful adsorbent in terms of cost efficiency and recyclability. Future zeolite applications may include garbage leachate and electroplating wastewater treatment. The adsorption capacity of waste-prepared zeolite is much higher than that of other adsorbents, such as clinoptilolite, natural bentonite, and vermiculite. Therefore, waste-prepared zeolite can be used as an adsorbent for metal ions.

### CONCLUSION

Pure and single-phase zeolite A (10% CF-Z [0.5]) was successfully synthesized from CF and WSQ through hydrothermal method. The addition of CF improves the BET surface areas of zeolites, but slightly affects ammonium removal. Ammonium adsorption capacity of 10% CF-Z (0.5) increases as the initial ammonium concentration increases because of the increasing drive force. However, the ammonium adsorption capacity of 10% CF-Z (0.5) decreases as the solution temperature increases because it is an exothermic adsorption process. At pH 5, 10% CF-Z (0.5) has high ammonium adsorption capacity when ammonium was the predominant species.

The best-fit adsorption isotherm was achieved with Freundlich model for the adsorption of ammonium and lead onto 10% CF-Z (0.5) in a single system. Furthermore, pseudo-second-order kinetic model was in line with the dynamical behavior for the adsorption of ammonium and lead onto 10% CF-Z (0.5) in a single system. This finding suggests that the overall rate constant of ammonium and lead adsorption is controlled by the chemical sorption process. The adsorption sequence of ions on 10% CF-Z (0.5) was as follows: lead > ammonium > cadmium > chromium. Our results indicate that the cost-effective 10% CF-Z (0.5) efficiently removes ammonium and lead.

### ACKNOWLEDGEMENTS

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