

Solid-state conversion of fly ash to effective adsorbents for Cu removal from wastewater

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Abstract

Solid-state conversion of fly ash to an amorphous aluminosilicate adsorbent (geopolymer) has been investigated under different conditions and the synthesised material has been tested for Cu²⁺ removal from aqueous solution. It has been found that higher reaction temperature and Na:FA ratio will make the adsorbents achieving higher removal efficiency. The adsorbent loading and Cu²⁺ initial concentration will also affect the removal efficiency while the adsorption capacity exhibits similarly at 30–40 °C. The adsorption capacity of the synthesised adsorbent shows much higher value than fly ash and natural zeolite. The capacity is 0.1, 3.5 and 92 mg/g, for fly ash, natural zeolite, and FA derived adsorbent, respectively. The kinetic studies indicate that the adsorption can be fitted by the second-order kinetic model. Langmuir and Freundlich isotherms also can fit to the adsorption isotherm.

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1. Introduction

Heavy metals are nowadays among the most important pollutants in source and treated water, and are becoming a severe public health problem. Elevated levels of Cu²⁺ in the environment can be attributed to a variety of sources, such as industrial effluents from metal cleaning and plating baths, paper, paperboard mills, wood-pulp production, tire manufacture, and fertiliser industries. Excessive intake of copper results in its accumulation in the liver, leading to copper poisoning and gastrointestinal problems. It is also toxic to aquatic organisms, even at very low concentration [1].

Since its first introduction for heavy metal removal, activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment applications throughout the world. However, activated carbon remains an expensive material due to its cost in production and regeneration. Attention has been focused on the various adsorbents, which have metal-binding capacities and are able to remove

unwanted heavy metals from contaminated water at low cost [2].

Fly ash is a waste substance from thermal power plants. In recent years, utilisation of fly ash has gained much attention in public and industry. Being readily available and inexpensive, fly ash is considered an economic alternative to conventional adsorbents such as activated carbon and ion-exchange resins. It has been reported that fly ash could be effective for removal of heavy metals, dyes, and organic matters from wastewater [2–4]. However, fly ash still shows lower adsorption capacity unless it is chemically treated or activated [4,5].

Conversion of fly ash to crystalline zeolite or amorphous geopolymers has been gaining much attention in the last a few years. Synthetic and natural zeolites gained a significant interest among scientist, mainly due to their valuable properties such as ion exchange capability. The most common method used for the conversion of fly ash into zeolites or geopolymers involves a hydrothermal process, whereby the fly ash is mixed with an alkali solution such as sodium hydroxide at different conditions of temperature, pressure and reaction time. Recently, a new process has been developed by introducing an alkaline fusion stage prior to the conventional zeolite synthesis, usually known as the fusion method. This significantly improved the

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zeolitisation process and the product is typically conformed by highly crystalline zeolites from faujasite group [6,7].

On the contrary, geopolymers are a diverse group of ceramic-like materials formed by a geosynthetic reaction of aluminosilicate minerals in the presence of an alkali solution at low temperatures (<100 °C) [8,9]. Geopolymers can best be viewed as the amorphous equivalent of certain synthetic zeolites. Fly ash-based geopolymers are growing in commercial potential due to their reliance on cheap and readily available waste fly ash as the main feedstock. In the last a few years, geopolymers have also been used to immobilise and stabilise low-level radioactive waste of pure or contaminated (mixed waste) forms as well as heavy metals [10,11].

Recently, several investigators have conducted investigations on fusion method to extract aluminosilicate from fly ash and using the supernatant to prepare mesoporous materials [12,13]. However, they did not investigate the properties of the residual after fly ash extraction. In the present study, we investigated the fusion solid-state reaction for fly ash conversion at different conditions and characterised the residual as geopolymer-based adsorbents and their application in heavy metal removal from aqueous solution. We will compare the adsorption capacity of the synthesised adsorbents with fly ash and natural zeolite and investigate the adsorption kinetics and isotherm for Cu ions.

2. Experimental

2.1. Adsorbent materials and chemicals

A raw fly ash (FA) sample was obtained from Muja Power Station in Western Australia. The chemical compositions of the fly ash are SiO₂ (55%), Al₂O₃ (29%), Fe₂O₃ (8.8%), CaO (1.6%) and MgO (1.0%). This fly ash was sieved under different particle size and the section with particle size less than 45 μm was obtained and used for hydrothermal treatment. For the fusion method, the coal fly ash was treated with sodium hydroxide at different ratio and various temperatures for 1 h to obtain a fused mass, which was cooled to room temperature. The obtained fused fly ash powder was then mixed with water in a weight ratio of 1:4 and aged for 1 day at room temperature with agitation. After that, the slurry was filtrated, washed and dried at 110 °C overnight. A natural zeolite was obtained from the Zeolite Australia Ltd.

Cu²⁺ solutions were prepared using Cu(NO₃)₂ (AR, AJAX) in distilled water. A stock solution with concentration at 10⁻⁴ M was prepared and the solutions for adsorption tests were prepared from the stock solution to the various desired concentrations.

2.2. Characterisation of adsorbents

Power XRD patterns were measured by a Rigaku miniflex diffractometer with Co Kα radiations generated at 30 kV, 15 mA. Scattering patterns were collected from 1.5° to 80° with a scan time of 1 min per 2 steps.

Nitrogen adsorption–desorption isotherms were obtained using NOVA 1200 (USA) at the liquid nitrogen temperature (−196 °C). Powder samples were degassed to less than 5 mTorr

at 200 °C for 4 h prior to analysis. Surface area calculations were made using the BET equation. Pore size distributions were calculated from desorption branches of isotherms based on BJH methods.

2.3. Sorption test

The adsorption of Cu²⁺ was conducted in batch experiments. Typically, 100 ml of solution containing different concentrations of Cu²⁺ were poured into a 250 ml bottle with 0.015 g adsorbents, otherwise indicated, and set at 100 rpm and different temperatures (30 and 40 °C) for various time. After adsorption, solution was filtered and the concentrations of Cu²⁺ in solution were determined by an Atomic Adsorption Spectrometer (SpectrAA110, Varian). After preliminary test, the adsorption equilibrium can be achieved after 50 h and thus 72 h was selected as equilibrium time in all cases.

The removal efficiency (*E*) and amount of Cu²⁺ adsorbed on solids were defined as

$$E (\%) = \frac{C_0 - C_1}{C_0} \times 100 \quad (1)$$

$$Q_e = \frac{(C_0 - C_1)V}{W} \quad (2)$$

where *C*₀ and *C*₁ are the initial and equilibrium concentration of Cu²⁺ solution (mg/L), respectively, *V* the volume (L), and *W* is the weight (g) of adsorbent.

3. Results and discussion

3.1. Characterisation of adsorbents

The XRD patterns of fly ash, the fusion treated fly ash at 550 °C, and natural zeolite are presented in Fig. 1. As shown that three adsorbents exhibit different crystalline phases. For fly ash, major chemical phases are quartz and mullite, some minor phases such as hematite and magnetite are also existed. For natural zeolite, clinoptilolite is the major component with minor amounts of mordenite and quartz. For the treated fly ash,

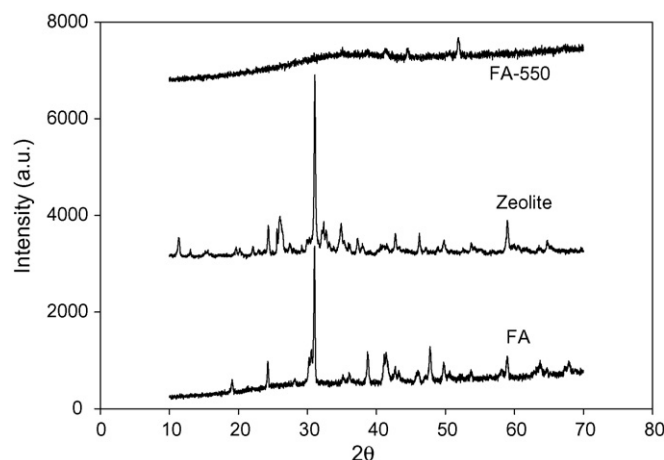


Fig. 1. XRD patterns of different adsorbents.

Table 1
Textural properties of fly ash and zeolite samples

Sample	S_{BET} (m^2/g)	V (cm^3/g)
FA	8.4	0.010
FA-100	31.8	0.054
FA-200	36.0	0.091
FA-250	44.1	0.12
FA-350	38.9	0.097
FA-450	41.4	0.10
FA-550	56.0	0.14
Zeolite	16.0	0.039

most crystalline phases disappeared and an amorphous phase occurred, which correspondences to geopolymer.

The BET surface areas and pore volumes of fly ash and derived adsorbents treated at different temperatures were obtained from N_2 adsorption and are given in Table 1. It is seen that FA has the lowest surface area and pore volume. Natural zeolite exhibits higher surface area and pore volume than FA. Solid-state conversion of fly ash produces the materials with even higher surface area and pore volume. Reaction temperature shows strong effect on the variation of textural properties. Higher temperature treatment resulted in higher surface area and pore volume. The FA-550 can give surface area and pore volume of $56 \text{ m}^2/\text{g}$ and $0.14 \text{ cm}^3/\text{g}$, respectively.

The pore size distributions of fly ash, natural zeolite and FA-550 are presented in Fig. 2. As shown that fly ash is nonporous material while natural zeolite and FA-550 present porous structure. Only one sharp peak occurs in the range of $30\text{--}50 \text{ \AA}$ on natural zeolite while FA-550 shows a sharp peak at $30\text{--}50 \text{ \AA}$, similar to natural zeolite, and a broad peak at $50\text{--}100 \text{ \AA}$, which makes the FA-550 having larger pores for adsorption.

3.2. Cu^{2+} adsorption studies

3.2.1. Comparison of adsorption with different adsorbents

Fig. 3 gives a comparison of adsorption capacity of three adsorbents, fly ash, natural zeolite and FA-550. As shown that fly ash produces little adsorption capacity for Cu^{2+} and natural

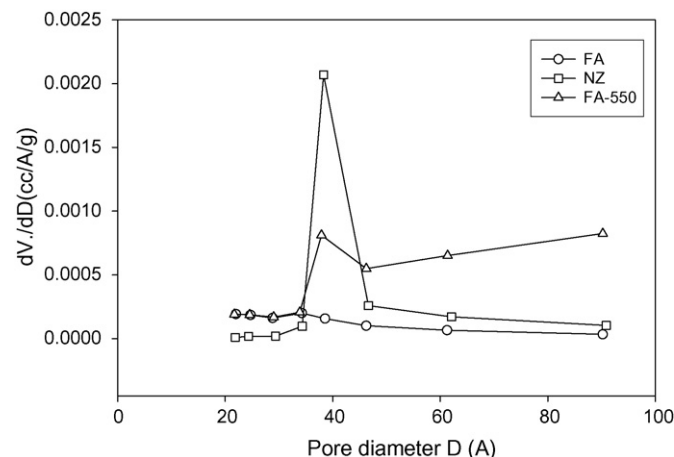


Fig. 2. Pore size distribution of various adsorbents.

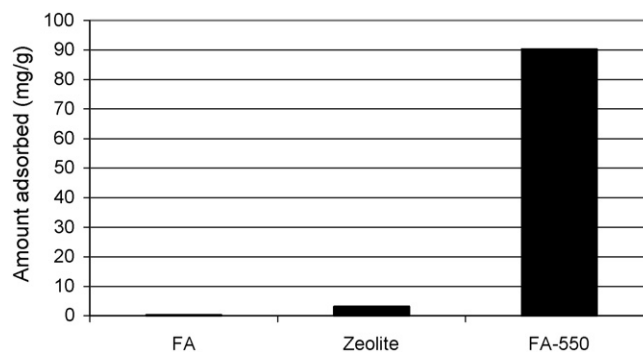


Fig. 3. Adsorption capacity of Cu^{2+} on various adsorbents. Adsorption conditions: adsorbent weight = 0.20 g, $[\text{Cu}^{2+}]_0 = 50 \text{ ppm}$, $T = 30 \text{ }^\circ\text{C}$, $\text{pH} = 6.2$.

zeolite also gives low adsorption capacity of 3.4 mg/g while the FA-550 exhibits much high adsorption around 90 mg/g . This variation in adsorption capacity is as the same as the surface area and pore volume, suggesting that pore structure is important for adsorption. Solid-state fusion conversion of fly ash to amorphous geopolymer produces larger pore structure favourable to Cu^{2+} adsorption.

Several investigators have employed fly ash for Cu^{2+} adsorption and found that fly ash showed varying capacity depending on the sources. Table 2 presents the results. As seen that fly ash usually exhibits low adsorption capacity and our work is quite similar to the previous reports. The extreme high adsorption on fly ash reported by Apak et al. is probably due the high content of CaO (42%) in the fly ash sample, leading Cu^{2+} precipitation on fly ash surface [14].

3.2.2. Effect of the fusion temperature

Fig. 4 presents the variation of removal efficiency at equilibrium on fly ash derived adsorbents synthesised at different temperatures. One can see that the Cu^{2+} removal efficiency generally increases with the increasing fusion temperature up to $350 \text{ }^\circ\text{C}$ and then the removal efficiency will keep constant. The surface area and pore volume of treated fly ash shows that the higher temperature will produce solids with more porous structure, resulting in higher surface area and pore volume, which will promote the adsorption of Cu^{2+} .

Table 2
Comparison of Cu adsorption on fly ash and its derivatives

Adsorbent	Adsorption (mg/g)	References
Fly ash	1.39	[15]
Fly ash + wollastonite	1.18	[15]
Fly ash	1.7–8.1	[16]
Fly ash (I)	0.34–1.35	[17]
Fly ash (II)	0.09–1.25	[17]
Fly ash	0.63–0.81	[18]
Fly ash	207.3	[14]
Fly ash-washed	205.8	[14]
Fly ash-acid	198.5	[14]
Fly ash	0.1	This work
Natural zeolite	3.4	This work
FA derived geopolymer	90	This work

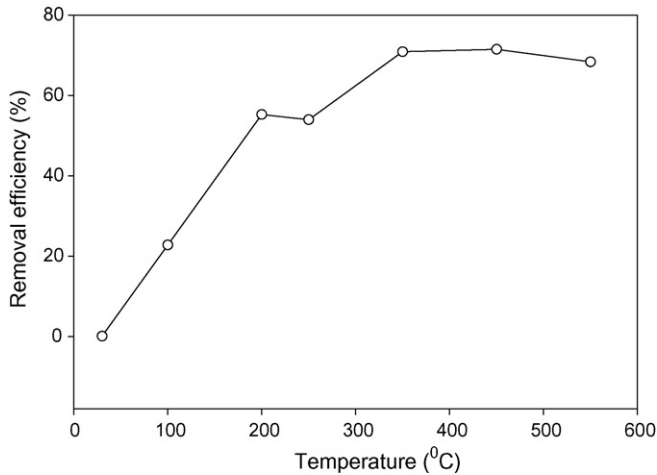


Fig. 4. Effect of treated temperature on Cu^{2+} removal efficiency. Adsorption conditions: adsorbent weight = 0.15 g, $[\text{Cu}^{2+}]_0 = 201$ ppm, $T = 30^\circ\text{C}$, pH 6.2.

3.2.3. Effect of fly ash: NaOH ratio

Fig. 5 shows the effect of ratio Na:FA on the Cu^{2+} removal efficiency at equilibrium. As shown that higher ratio of Na:FA will result in high removal efficiency. However, the improvement is not significant, suggested that the concentration of NaOH is not an important factor. The removal efficiency can only change from 65% to 75% when the ratio is increased from 0.8 to 1.6.

3.2.4. Dynamic adsorption and kinetics

The dynamic Cu^{2+} removal on FA derived zeolite (FA-550) with the contact time is illustrated in Fig. 6. As seen that the adsorption of Cu^{2+} increases with the contact time and reaches equilibrium at about 30 h. The first-order rate expression given by Lagergren [19] and the pseudo second-order rate model [20] can be used for the description of the kinetics of Cu^{2+} adsorption on FA-550, listed as below:

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

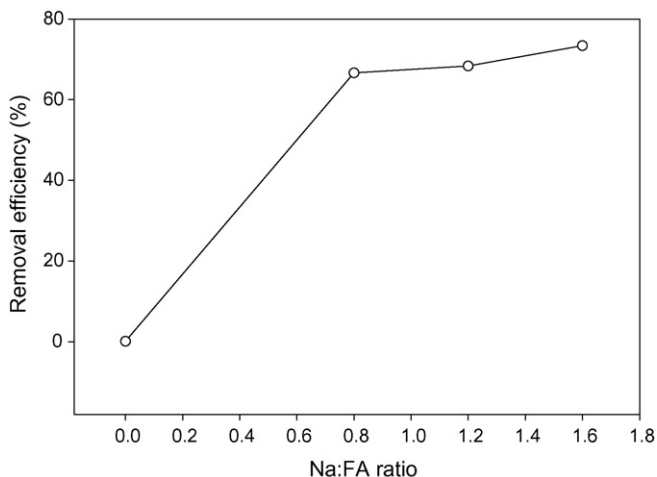


Fig. 5. Effect of Na:FA ratio on Cu^{2+} removal efficiency. Adsorption conditions: adsorbent weight = 0.15 g, $[\text{Cu}^{2+}]_0 = 201$ ppm, $T = 30^\circ\text{C}$, pH 6.2.

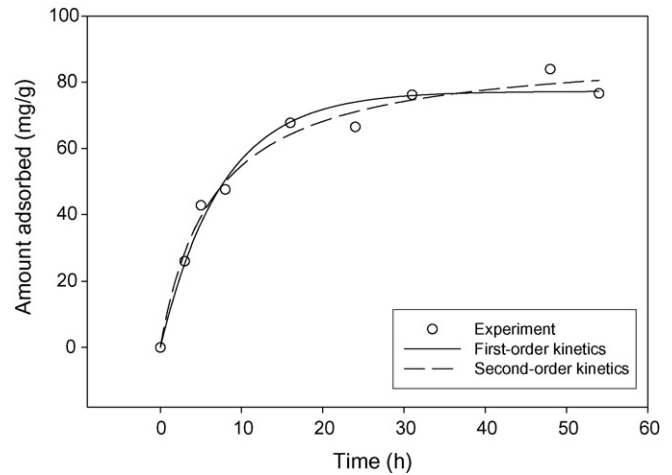


Fig. 6. Dynamic adsorption of Cu^{2+} on FA-550 and kinetic modelling. Adsorption conditions: adsorbent weight = 0.15 g, $[\text{Cu}^{2+}]_0 = 201$ ppm, $T = 30^\circ\text{C}$, pH 6.2.

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

where k_1 , k_2 , are the pseudo-first-order and pseudo-second-order rate constant, respectively, q_e the amount of solute sorbed (mg/g) at equilibrium and q_t is the amount of solute on the surface of the sorbent (mg/g) at any time t . Eq. (3) can be transformed to the following formula:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (5)$$

Fig. 6 presents the model simulation to the experimental data and the kinetic parameters are given in Table 3. One can see that both models fit well to the experiment with good correlation coefficients. The equilibrium capacity for the second-order kinetic model is higher than that obtained from the first-order kinetics.

3.2.5. Effect of Cu^{2+} initial concentration

Fig. 7 presents the effect of Cu^{2+} initial concentration on the removal efficiency. It is seen that the removal efficiency will remain high level at lower initial concentration and then decreases as the initial concentration is further increased from 100 mg/L. The efficiency can change from 90% at 100 mg/L to 30% at 250 mg/L. A lot of investigations have shown that the removal efficiency of heavy metals is concentration dependent. The removal efficiency shows a decreasing trend with the increasing initial concentration, which is similar to the results of this investigation [15,17].

Table 3
Kinetic parameters for Cu^{2+} adsorption on FA-550

Model	Experimental q_e (mg/g)	q_e (mg/g)	K	R^2
First-order	80	77	0.13 h^{-1}	0.98
Second-order	80	90	$1.7 \times 10^{-3} \text{ g/mg h}$	0.99

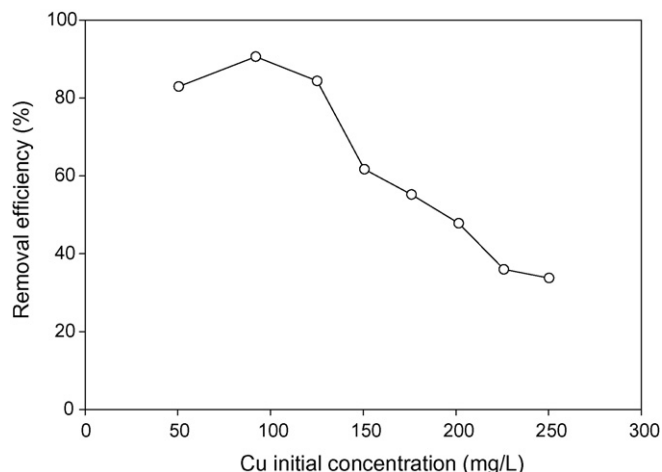


Fig. 7. Effect of Cu^{2+} initial concentration on removal efficiency. Adsorption conditions: adsorbent weight = 0.20 g, $T = 30^\circ\text{C}$, pH 6.2.

3.2.6. Effect of adsorbent loading

The dependence of Cu^{2+} sorption on adsorbent dose was also studied by varying the amount of FA-550 from 0.2 to 2.0 g/L, while keeping other parameters (pH, agitation speed, and contact time) constant. Fig. 8 presents the Cu^{2+} removal efficiency for FA-550. As can be seen that removal efficiency of FA-550 generally improved with increasing dose. This is because of more active sites available for adsorption with high amount of adsorbent in solution.

3.2.7. Effect of adsorption temperature

Fig. 9 presents the adsorption isotherm of Cu^{2+} adsorption on FA-550 at different temperatures. As shown that Cu^{2+} adsorption is increases with the increasing equilibrium concentration. However, the adsorption capacity is much similar at different temperatures. From the results, it is seen also that the adsorption capacity of FA-550 for Cu^{2+} is around 90 mg/g. Agrawal et al. [1] conducted a comparative adsorption study of copper on various industrial solid wastes including sea nodule residue, fly ash, and red mud. They found that there was no appreciable effect of

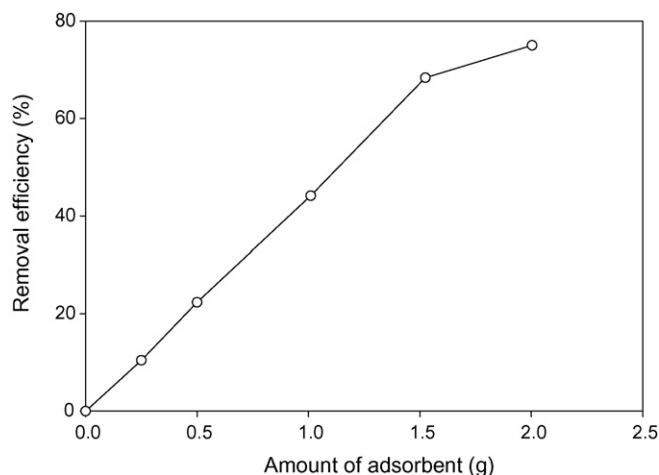


Fig. 8. Effect of adsorbent dose on Cu^{2+} removal efficiency. Adsorption conditions: $[\text{Cu}^{2+}]_0 = 201$ ppm, $T = 30^\circ\text{C}$, pH 6.2.

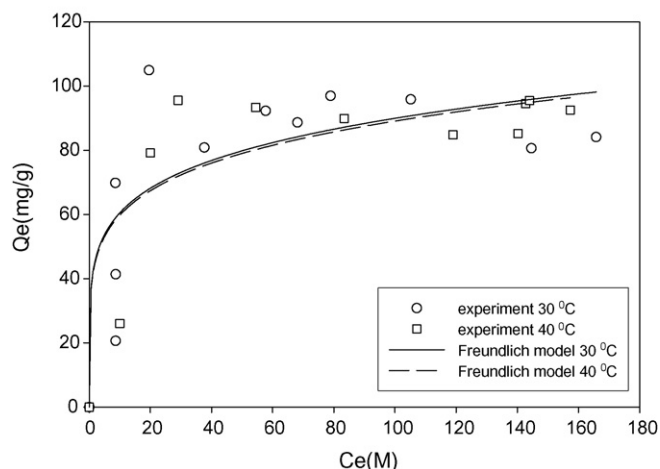
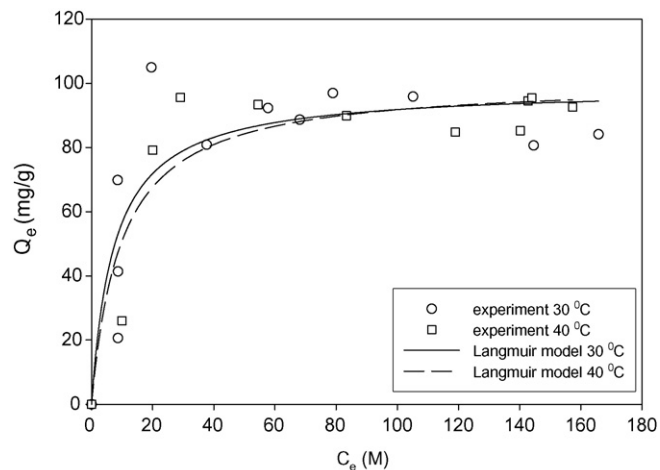


Fig. 9. Adsorption isotherms of Cu^{2+} on FA-550 at different temperature.

temperature on the metal removal on fly ash and red mud. However, other investigations showed that Cu^{2+} adsorption on fly ash increased with increasing temperature from 20 to 40°C [15].

Two adsorption isotherms, the Langmuir and Freundlich models, have been used for the fitting of the experiment data. These two models are listed in following equations:

$$q_e = \frac{K_L q_{\max} C_e}{1 + K_L C_e} \quad (6)$$

$$q_e = K_F C_e^{1/n} \quad (7)$$

Fig. 9 shows the fitted curves for two isotherms and the isotherm parameters are given in Table 4. As seen from Fig. 9 that both isotherms can fit the data well even though the correlation coefficients are not so high. While it seems from the table that the Langmuir isotherm would be better than the Freundlich model in data fitting. In addition, the parameters obtained from

Table 4
Isotherm parameters for Cu^{2+} adsorption on FA-550

Temperature ($^\circ\text{C}$)	Langmuir isotherm			Freundlich isotherm		
	K_L	q_{\max} (mg/g)	R^2	K_F (mg/g)	$1/n$	R^2
30	0.13	99	0.75	41	0.17	0.67
40	0.10	101	0.87	40	0.17	0.79

both isotherms are much close for different temperatures, confirming that the temperature has little effect on adsorption in this case.

4. Conclusion

Fly ash and natural zeolite are not good adsorbent for Cu^{2+} removal. Solid-state fusion reaction using NaOH can produce porous aluminosilicate adsorbent, geopolymer, enhancing the surface area, pore volume, and adsorption capacity for Cu^{2+} in aqueous solution. The preparation temperature and NaOH amount will significantly influence the adsorbent capacity for Cu^{2+} adsorption. In addition, Cu^{2+} initial concentration and adsorbent dose will also affect the Cu removal efficiency while the adsorption seems similar at 30–40 °C. Kinetic studies show that the adsorption process can be better fitted by the second-order rate model. Langmuir isotherm will exhibit better result in simulation of the adsorption isotherm.

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