Adsorption of copper from aqueous solutions on synthetic zeolites produced from Greek fly ash: Equilibrium and kinetic studies

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Abstract

Lignite fly ash obtained from the thermoelectric power plant of Megalopolis (Peloponnese, Greece) was used for zeolite synthesis. Zeolites synthesis process by fusion treatment was performed by mixing NaOH pellets to fly ash with mass ratios of 1:1 and 1:1.5 at 600 °C for 1 h. The produced zeolite was crushed and mixed with distilled water, in a constant ratio of 20% w/v under stirring overnight. After incubation of the suspension, the solids which used as adsorbents were recovered by centrifugation and then dried. For the adsorption kinetic experiments stock aqueous solutions of different copper concentrations were prepared (50 to 200 mg·L^{-1}) from the corresponding salt of $Cu(NO_3)_2$ $3H_2O$ at constant ionic strength of NaCl 0.1 M. Equilibrium experiments were carried out using adsorbent concentration varying between 0.3 to 1.5 g·L^{-1}. The adsorption isotherm models of Langmuir and Freundlich were applied for the equilibrium study. Possible kinetic equations of copper adsorption on synthesized zeolites were derived and discussed. XRD and BET analyses were also carried out.

1. Introduction

The generation of electricity in Greece is strongly dependent (~73%) on the use of domestic lignite as combustion material. Annually, Greek power plants consume approximately 64 million tons of lignite producing nearly 13 million tons of fly ash as by-product [1]. In Greece the main lignite centers are Ptolemais-Amynteon and Megalopolis (located in North-western and Peloponnese, South Greece, respectively). Currently, fly ash disposal involves mainly landfilling at the open pits, ponds and/ or the sea. The emitted or disposed fly ash causes serious environmental pollution due to heavy metal accumulation at the disposal sites [2]. Only 10–20% of the fly ash produced in Greece, due to its pozzolanic properties, is used as construction material in concrete and cement industries [3]. However, different alternatives are under consideration, as a means of reducing the amount of fly ash that must be disposed of, mainly for the production of inorganic polymers andceramics, as soil amendment and for sewage sludge stabilization due to its high alkalinity, as raw material for the extraction of valuable metals and/ or synthesis of high cation exchange capacity zeolites [4-7]. Converting fly ash into zeolites not only partially solves the disposal problem but also converts a potentially hazardous material into a value-added, marketable product [8-10].

Zeolites are microporous, hydrated aluminosilicates containing alkali elements and alkaline earth metals (Na^+, K^+, Ca^{2+} or Mg^{2+}) [11]. Zeolites have been used as adsorbents, mainly because zeolite exchangeable ions are relatively nontoxic. Thus, they are considered suitable for removing toxic heavy metal ions (such as copper) from municipal, agricultural, mining and metallurgical wastewaters [12]. Nowadays adsorption is considered to be suitable for wastewater treatment due to its simplicity and cost effectiveness and zeolites prepared from coal fly ash may be used as adsorbents [8]. The aim of this work was to synthesize zeolites from lignite fly ash after fusion at varied experimental conditions and use them as adsorbents for the uptake of copper ions from aqueous solutions. The adsorption isotherms were determined and kinetic parameters were also calculated.

2. Material and Methods

Adsorbents. Lignite fly ash obtained from the Greek thermoelectric power plant of Megalopolis (FAM) (Peloponnese, Greece) was used for zeolite synthesis. Its chemical composition, derived through XRF analysis, showed that FAM contained $SiO_2+Al_2O_3+Fe_2O_3$ 73.64% and CaO 9.94%, thus it is classified as Class F. treatment involved heating of fly ash and ground NaOH pellets (N) using mass ratios of N to FAM of 1:1 (ZFAM7) and 1:1.5 (ZFAM15) at 600 °C for 1 h. The resulting material was crushed and mixed with distilled water (in a constant ratio of 20% w/v) under stirring overnight. After incubation of the suspension at low temperature of 30 °C for 4 days synthesized zeolites were obtained after centrifugation and then dried at 80 °C for 24 h [13]. Specific surface area was calculated by the BET single-point method by nitrogen adsorption (Quantachrome instruments). X-Ray Diffractometer (Siemens D500) was used to investigate the mineralogical structure of the synthesized zeolites. For the adsorption kinetic experiments stock aqueous solutions were prepared from the corresponding salt $Cu(NO_3)_2·3H_2O$ (Alfa Aesar) and different initial metal ion concentrations were tested (50 to 200 mg·L^{-1}) at constant ionic strength of NaCl 0.1 M and room temperature (20 ±1 °C). Batch experiments were performed in a series of conical flasks (250 mL operating volume) equipped with magnetic stirrers using different concentrations of zeolites as adsorbents (0.3 to 1.5 g·L^{-1}). The suspension was stirred at 600 rpm. The adsorption tests lasted up to 360 min until equilibrium was reached. At regular intervals aliquots

of suspensions were taken and filtered (0.45 μm PTFE, Chromafil) while metal concentration was determined by AAS (Analyst-100 of Perkin Elmer). The initial and final pH solution was also measured (4.7±0.4). PHREEQC simulations indicate that possible precipitation of $Cu(OH)_2$ may occur at pH values over 6. During adsorption experiments no precipitation occurred. The adsorption isotherm models of Langmuir and Freundlich were applied for the equilibrium study. Possible kinetic equations of copper adsorption on synthesized zeolites were derived and discussed.

Equilibrium studies. The adsorption capacity of zeolites was calculated by using Eq. 1. The degrees of adsorption (%AD) and regeneration (%RD) were calculated according to Eq. 2 and 3 [**14, 15**]. Experimental data were fitted to linear forms of Langmuir and Freundlich isotherm equation models, [**16, 17**].

$$q_t = \frac{V(C_0 - C_t)}{m} \qquad \text{Eq. 1}$$

$$\%AD = \frac{(C_0 - C_t)}{C_0}\% \qquad \text{Eq. 2}$$

$$\%RD = \frac{(C_e - C_t)}{C_e}\% \qquad \text{Eq. 3}$$

where: q_t is the mass of adsorbed metal ion per unit mass of adsorbent ($mg \cdot g^{-1}$), V is the volume of the aqueous phase (L), C_0 and C_t are the initial and final metal ion concentration ($mg \cdot L^{-1}$) respectively, and m is the mass of adsorbent used (g); C_e ($mg \cdot L^{-1}$) is the residual adsorbate concentration in solution at equilibrium.

Kinetic studies. Kinetic studies involve the determination of adsorption rate, residence time and mass transfer parameters such as external mass transfer coefficients and intraparticle diffusivity. These parameters are essential for the design and operation of any adsorption unit. Therefore, kinetic studies enable the evaluation of the suitability of any material as a potential adsorbent in removing pollutants from solution. The linearized kinetic models used in this study are the pseudo-first and pseudo-second order models according to previous studies [**16, 17**].

3. Results & Discussion

Synthetic zeolites. Physicochemical properties of the synthetic zeolites (ZFAM7 and ZFAM15) from fly ash were defined (**Table 1**). BET surface area was ~5.2 $m^2 \cdot g^{-1}$ (mean value). The range of particle size (Malvern Instruments) of the synthesized zeolites used in this study was <200 μm. The XRD spectra (**Fig. 1**) showed the significant presence of X- and A-type zeolites, sodium aluminium silicate hydrate and sodalite [**8**].

Table 1: Particle size (μm) and surface area ($m^2 \cdot g^{-1}$) of the synthesized zeolites (N:FAM mass ratio).

Sample code	N:FAM	Particle size (μm)	Surface area ($m^2 \cdot g^{-1}$)
ZFAM07	1:1	<191.5	5.68
ZFAM15	1:1.5	<117.7	4.75
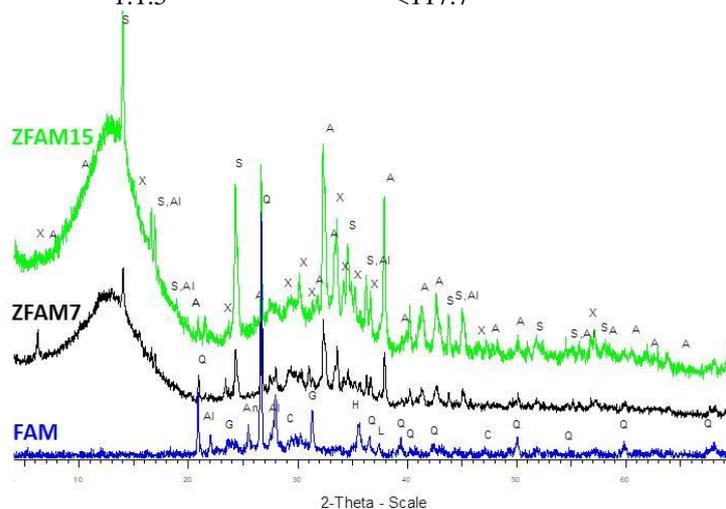
Fig. 1: Diffractograms of synthesized zeolites, ZFAM7, ZFAM15 and raw material, FAM. Q: Quartz, SiO_2 (078-2315); Al: Albite, $NaAlSi_3O_8$ (071-1154); G: Gehlenite, $Ca_2Al_2SiO_7$ (073-2041); An: Anhydrite, $CaSO_4$ (072-0916); H: Hematite, Fe_2O_3 (073-0603); L: Lime, CaO (082-1691); C: Calcite, $CaCO_3$ (086-2339); X: Zeolite X, $NaAlSi_{1.23}O_{4.46} \cdot 3.07H_2O$ (39-0218); A: Zeolite A, $NaAlSi_{1.1}O_{4.2} \cdot 2.25H_2O$ (43-0142); S,Al: Sodium aluminium silicate hydrate, $Na_6Al_6Si_{10}O_{32} \cdot 12H_2O$ (039-0219); S: Sodalite, $Na_8Al_6Si_6O_{24}Cl_2$ (089-9099).

Equilibrium isotherms. The adsorption isotherms of copper ions by synthesized zeolites (0.5 g·L^{-1}) are depicted in **Fig. 2**. For both synthesized zeolites, ZFAM7 and ZFA15, the Langmuir model represents a better fit to the experimental data compared to the Freundlich model. The good agreement of the Langmuir model with the experimental data suggests that a monolayer of metal ions is formed on the surface of the adsorbent. The values of q_m and k_l obtained from these plots and, k_f and n from the Freundlich parameters and correlation coefficients, R^2 are listed in **Table 2**. The correlation coefficients for Langmuir isotherms was as high as 0.99.. The equilibrium sorption capacity q_m, obtained for ZFAM7 was 310.6 mg·g^{-1} while the respective value for ZFAM15 was 295.9 mg·g^{-1}. In comparison to previous study [18] the adsorption capacity for Cu(II) onto synthetic pure-form zeolite A from fly ash was equal to 82.7 mg·g^{-1} (with high adsorbent dosage of 5 g·L^{-1}) that was lower to our study results (~300 mg·g^{-1}, mean value with 0.5 g·L^{-1}) In Langmuir theory the equilibrium parameter, R_L (dimensionless constant) shows the nature of adsorption [14]. According to experimental data copper ions adsorption was efficient, (R_L~0.005 for both synthesized zeolites).
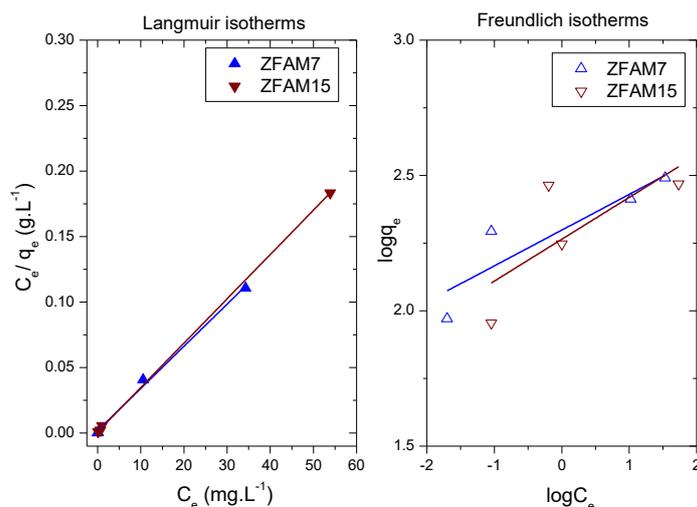
Fig. 2: Experimental and modelled Cu^{2+} adsorption isotherms of synthetic zeolites, ZFAM7 and ZFAM15 using Langmuir and Freundlich equations (Cu^{2+} concentration of 50 to 200 mg·L^{-1}, adsorbent concentration 0.5 g·L^{-1}; θ 25 °C; stirring speed 600 rpm; time 60 min; pH 4.4).

Table 2: Calculated equilibrium adsorption isotherm constants.

	Langmuir isotherm				Freundlich isotherm		
	q_m	k_l	R^2	R_L	k_f	n	R^2
	mg·g^{-1}	L·mg^{-1}			g·L^{-1}		
ZFAM7	310.6	1.7	0.994	0.0052	198.7	7.5	0.725
ZFAM15	295.9	3.4	0.999	0.0049	152.2	5.6	0.904

Kinetic studies.

Effect of initial copper concentration. Different initial Cu^{2+} solution concentrations were prepared (45 to 200 mg·L^{-1}) and the adsorption capacity of each synthesized zeolite was determined (**Fig. 3**). An increase in initial adsorbent concentration results in an increase in the amount of copper adsorbed but the rate of adsorption decreases. For ZFAM7 the adsorption degree was 100% at lower initial copper concentration (45 and 100 mg·L^{-1}). For ZFAM15 the adsorption degree was 100% up to 140 mg·L^{-1}. The adsorption degree for ZFAM7 and ZFAM15 reached 82 and 73%, respectively at initial copper solution concentration of 200 mg·L^{-1}, respectively. The adsorption efficiency decrease with an increase in initial copper concentration until the system reaches a saturation point, at which further increase of the adsorbent concentration does not result in any significant increase in the metal amount adsorbed.
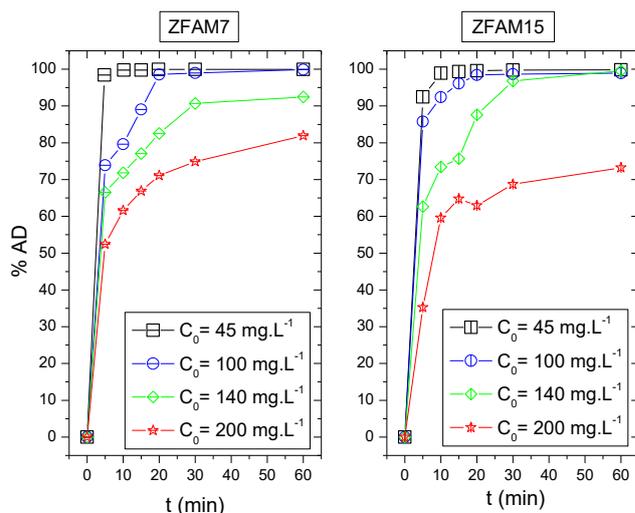
Fig. 3: Effect of initial Cu^{2+} concentration on the adsorption capacity of ZFAM7 and ZFAM15 (dosage of 0.5 g·L^{-1}, pH 4.4).

Effect of the adsorbent dosage. A series of kinetic experiments with various dosage of zeolite (0.3, 0.5, 1 and 1.5 g·L^{-1}) were conducted at constant initial Cu^{2+} concentration of 140 mg·L^{-1} (**Fig. 4**). The increase of adsorbent dosage resulted into the increase of adsorption degree due to the increase of the number of available adsorption sites. At low dosage (0.3 g·L^{-1}) the adsorption degree of ZFAM7 decreased by 45% compared to the adsorption capacity at higher dosage of ZFAM7 of 0.5 g·L^{-1}.
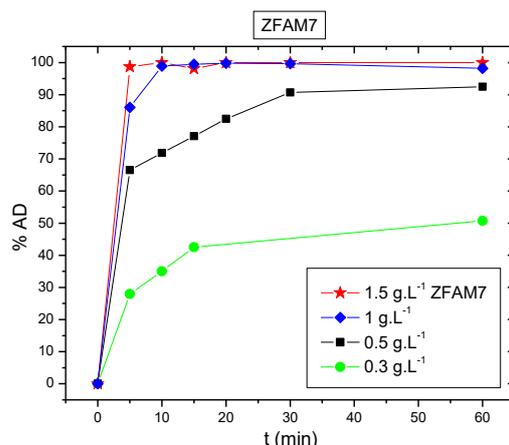
Figure 4: Effect of adsorbent dosage (g·L^{-1}) on the adsorption efficiency of ZFAM7 zeolite (initial Cu^{2+} concentration of 140 mg·L^{-1}; pH 4.4).

Kinetic modelling. Kinetic modelling was carried out to investigate the rate determining step in the removal of copper ions from solution. Models were selected to fit experimental data in order to estimate the amount of metal ion removed from aqueous solutions through adsorption. The models used in this investigation are the pseudo-first and pseudo-second order kinetic models (**Table 3**). **Fig. 5** shows the pseudo-first (**Fig. 5A, B**) and pseudo-second order (**Fig. 5C, D**) kinetics of Cu^{2+} adsorption onto ZFAM7 and ZFAM15 zeolites. It was observed that the pseudo-second-order model fitted well the experimental data of Cu^{2+} ions adsorption indicating that the reaction rate depends on the number of active sites available on the adsorbent surface [**17**]. These results are consistent with previous studies [**14, 15**]. However, in our case the adsorption capacity (196 and 176 mg·g^{-1}, respectively) was higher at lower adsorbent dosage (0.5 g·L^{-1} ZFAM7 and ZFAM15) compared to a previous study ($40\text{-}70 \text{ mg·g}^{-1}$ with 1 g·L^{-1} zeolite A) [**16**]. The calculated $q_{e,cal}$ agreed well with the experimental data ($q_{e, exp.}$). The rate constant, k_2, was not constant for different initial concentrations of Cu^{2+} ions. This lack of consistency proves that even though the results gave a good fit to the kinetic model, surface diffusion instead of chemisorption of Cu^{2+} ions at the adsorption sites of synthetic zeolites is the rate determining step.
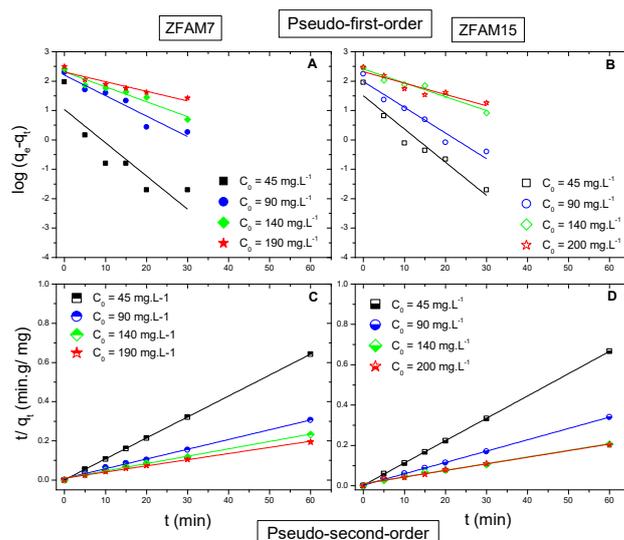
Figure 5: Pseudo-first and pseudo-second-order adsorption of Cu^{2+} onto ZFAM7 (A, C) and ZFA15 (B, D) synthesized zeolites.

Table 3. The pseudo-first and second-order rate constants.

	*Experimental		Pseudo-first order			Pseudo-second order		
	C_0	$q_{e, exp}$	$q_{e, cal}$	k_1	R^2	$q_{e, cal}$	k_2	R^2
	$mg \cdot L^{-1}$	$mg \cdot g^{-1}$	$mg \cdot g-1$	$1 \cdot min^{-1}$		$mg \cdot g^{-1}$	$g \cdot mg^{-1} \cdot min^{-1}$	
ZFAM7	47	93.49	10.72	0.260	0.721	93.54	0.3516	1.000
	98	196.41	158.74	0.160	0.905	137	0.0107	0.997
	140	258.69	204.87	0.117	0.930	265.96	0.0017	0.995
	190	309.70	202.44	0.075	0.878	318.47	0.0011	0.994
ZFAM15	45	90.08	31.43	0.260	0.918	90.33	0.0756	0.999
	90	176.54	95.52	0.201	0.929	177.94	0.0122	0.999
	145	290.79	255.81	0.108	0.946	302.11	0.0011	0.991
	200	294.01	206.82	0.089	0.847	305.81	0.0011	0.991

*dosage 0.5 $g \cdot L^{-1}$; θ 25 °C; stirring speed 600 rpm; time 60 min; pH 4.4.

Regeneration experiments. Regeneration experiments of ZFAM15 was performed by using Na_2-EDTA solution 0.05 M at constant ionic strength 0.1 M NaCl, pH 4.4 [**14**]. Prior to regeneration, adsorption experiments were conducted at high initial copper concentration of 1000 $mg \cdot L^{-1}$ and adsorbent dosage of 5 $g \cdot L^{-1}$. After adsorption zeolite was filtered, dried (at 80 °C overnight) and subjected to regeneration experiments. The adsorption degree of Cu(II) onto ZFAM15 increased rapidly to 40% in 10 min and became constant, 100% indicating that the removal of Cu(II) mainly occurred within 30 min (**Fig. 6**). The regeneration degree was 20% in 10 min and became constant to zero indicating that Cu(II) was removed from ZFAM15 into Na2-EDTA solution within 20 min. The adsorption and desorption efficiency of ZFAM15 was 100%. Hence, ZFAM15 was successfully regenerated by Na_2EDTA solution. Additional number of cycles (adsorption-regeneration) needs to be done in order to define the zeolite recovery and removal efficiency.
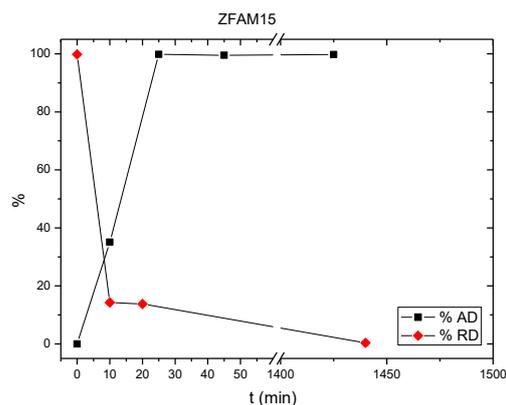
Figure 6: Adsorption (%AD) with NaCl 0.1 M and, regeneration degree (%RD) with 0.05 M Na₂EDTA and 0.1 M NaCl of Cu(II) by ZFAM15 during adsorption at dosage 0.5 g·L⁻¹; θ 25 °C; stirring speed 600 rpm; pH 4.4.

4. Conclusions

The adsorption of copper ions from aqueous solutions on synthesized zeolites ZFAM7 and ZFAM15 produced after fusion of fly ash and NaOH followed by hydro-activation takes place efficiently. It is the most efficient at low concentrations of copper ions (up to 100 mg·L⁻¹) and dosage of synthesized zeolites of 0.5 g·L⁻¹, at constant 25 °C and pH 4.4. The adsorption kinetics is reasonably fast within 30 min. This means that ~70% of Cu^{2+} ions, at high initial concentration of 200 mg·L⁻¹ Cu^{2+}, are removed from aqueous solutions. Both ZFAM7 and ZFAM15 zeolites exhibited high removal efficiency (100%). Equilibrium studies show that adsorption of copper ions strongly depends on the initial concentration in solution. The experimental data fit well the pseudo-second order kinetic model. The rate constant k_2, however, depended on the initial concentration of Cu^{2+} ions in solution, indicating that the rate determining step is surface diffusion. Synthesized zeolites from fly ash are considered very good alternative adsorbents compared to the high-cost adsorbents of activated carbon and commercial zeolites for the treatment of wastewaters containing copper metal ions. Synthetic zeolite was successfully regenerated by Na₂EDTA solution.

Acknowledgments

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