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Fly ash-based geopolymeric adsorbent for copper ion removal from wastewater

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ABSTRACT

The batch experiments were carried out to study the removal of copper ions from aqueous solutions by sorption process on geopolymer synthesized from fly ash (FA). The influence of solute concentration and temperature on the sorption process were examined at constant particle size and the sorption capacity of copper ions increases with the initial concentration and temperature. Several kinetic models were used to test the experimental kinetic data: Lagergren pseudo-first-order, the pseudo-second-order (Ho), and Elovich models were analyzed using nonlinear regression technique. A kinetic study has shown that the best fit is achieved when the Ho model was applied. The results obtained indicate that geopolymer synthesized from FA has excellent adsorption ability and could be used as an efficient material for the sorption of copper ions.

Keywords: Copper; Geopolymers; Kinetics

1. Introduction

Problem of heavy metals contamination and its immobilization is very significant due to the increasing environmental pollution and growing interest in sustainable development. Oxidized and soluble heavy metals are significant components of many industrial wastes, in particular wastes from the mining and metallurgical industries, and preventing their release into the ecosystem is of great interest [1]. Since these elements do not degrade and tend to accumulate in living organisms, causing intoxication, it is important to remove them from wastewater. Precipitation, solvent extraction, and sorption are the conventional methods for the heavy metals removal. Zeolites have been often reported to exhibit high sorption capacity for divalent cations for sorption applications. Erdem et al. reported that natural zeolites hold great potential for the sorption of several divalent metal cations and can be used as alternative for activated carbon [2].

Since geopolymers can best be viewed as the amorphous equivalent of certain synthetic zeolites and would generally have more or less the same chemical composition, they could also be used as sorption material.

Davidovits [3] proposed that geopolymers consists of a polymeric silicon–oxygen–aluminium framework, like that found in zeolites, with alternating silicon and aluminium tetrahedra joined together in three directions by sharing all the oxygen atoms. The fact is that aluminium is four coordinated with respect to oxygen that creates a negative charge imbalance and therefore

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the presence of cations such as K^+ and Na^+ is essential to maintain electric neutrality in the matrix.

Geopolymers are materials with unique properties such as quick compressive strength development, resistance to acid attack and fire, low permeability, and tendency in decreasing the mobility of most heavy metal ions contained within the structure [4–6]. Materials most often used for geopolymer synthesis are fly ash (FA), slag, and clay [1].

It was paid a great attention on usage of different sorts of FA and FA-based zeolite as a potential material for removal of Cd, Ni, Pb, Cu, phosphate, NO_x, boron, flouride, radionuclide of ^{137}Cs and ^{90}Sr, and dyes [7]. Recently, geopolymers have been also used as a potential material for removal. Li et al. studied the adsorption of methylene blue dye onto geopolymeric adsorbent based on FA [8]. Al-Zboon et al. have tested geopolymer as adsorbent for Pb removal [9]. Wang et al. also synthesized geopolymer that was tested for copper sorption, but geopolymer, used in this experiment, was synthesized in different conditions (lower temperature of synthesis, different raw materials were used). In this work, time needed for copper sorption on geopolymer was lower, approximately after 120 min, instead of ~50 h obtained by Wang et al. and, both, synthesis and sorption processes are more economically carried out [5].

In order to gain a better understanding of the sorption process, various kinetic models should be used to test the experimental data. The present work studies the influence of concentration and temperature on copper ion removal by geopolymeric material and makes a comparison of different kinetic models which can describe this process.

2. Materials and methods

2.1. Materials

A type F (as defined in ASTM C618) FA from the Croatian power plant Plomin 2 (Plomin) was used in the present study. The chemical analysis of FA is given elsewhere [10]. Technical-grade sodium silicate solution (a type S, water glass, $3Na_2O{\cdot}3SiO_2$) and NaOH, p. a. (Kemika) were used as alkaline activator.

Solutions containing copper ions were prepared by dissolving the appropriate weight of $Cu(NO_3)_2{\cdot}3H_2O$ (Kemika) in distilled water.

2.2. Geopolymer synthesis and analysis

Certain amounts of FA were mixed with 16 M sodium hydroxide solution and sodium silicate solution to prepare paste specimens. Solution/ash ratio was 0.40 and to provide good workability, extra water was added.

After adding all the components, geopolymer paste started to form. The mixture was mixed for 10–15 min and poured into polypropylene cylindrical containers (49.1 × 40 mm) along with constant stirring. Containers were hermetically sealed to prevent moisture evaporation. The fresh pastes were heat cured at 85°C for 24 h in an oven. After 24 h, the geopolymer samples were removed from the oven and kept at room temperature for 3 days.

Geopolymer bodies were washed at least three times with acetone to remove the excess alkaline activator solution and then crushed and sieved to obtain particle diameter 0.071–0.09 mm, used for sorption processes and to obtain particle diameter <0.045 mm used for geopolymer analysis. The FTIR spectra of geopolymers were made on KBr pastille on a Perkin–Elmer Spectrum One in the range from 4,000 to 450 cm^{-1}.

2.3. Batch experiments

The sorption of copper ions on FA-based geopolymer was studied by agitating 0.2 L of metal solution with 1.0 g of geopolymer in batch reactors. The mixture was agitated with a turbine impeller at 240 rpm. Different parameters were tested, Table 1, and the samples of solution were taken out from the system at the certain contact time. The concentration of the copper ions in the filtered sample was determinate by Perkin–Elmer Lambda EZ 201 UV/Vis spectrophotometer.

Sampling intervals are a consequence of sorption rate; sampling was done more often in the beginning and as the sorption slows down the frequency of sampling decreases.

The amount of copper retained on the geopolymer sample, q_t, was calculated by Eq. (1) as the difference between the amounts present in the initial copper solution and that remaining in the solution:

$$q_{\mathrm{t}} = \frac{(c_0 - c_t)V}{m} \tag{1}$$

Table 1
The various parameters tested on the sorption of copper ions on fly ash-based geopolymer

Parameter tested	Concentration (mmol L^{-1})	Temperature (K)
Concentration	5.915, 7.780, 9.898, 11.763	298
Temperature	11.763	298, 308, 318

where c_0 is the initial concentration of metal in solution (mmol L^{-1}), c_t is concentration of metal in solution at time t (mmol L^{-1}), V is the volume of solution (L), and m is the mass of the geopolymer (g) [11].

3. Results and discussion

3.1. FTIR analysis of geopolymer sample

The FTIR spectrum for geopolymer system, as well as, the spectrum for the original FA, are plotted in Fig. 1. These spectra reveal the differences between the original FA and geopolymeric material formed. The main broad band at 1,087.07 cm^{-1} in the original FA, corresponding to asymmetric stretching vibrations of Si–O–Si and Al–O–Si [12,13] becomes sharper and shifts towards lower frequencies (1,015.33 cm^{-1}) as a result of the formation of new reaction products associated with ongoing alkali activation.

The bands located at 798.40 and 460.97 cm^{-1} are ascribed to bending vibrations of Si–O–Si and O–Si–O bonds implying to the presence of quartz which is hardly affected by alkaline activation of FA [14,15]. The bands located at 691.41 cm^{-1} and 563.05 cm^{-1} are specifying the presence of mullite.

In all geopolymeric materials, new bands appeared in the regions of 1,653.01 cm^{-1} and 3,456.22 cm^{-1} that were attributed to bending vibrations (H–O–H) and stretching vibrations (–OH, H–O–H). Water is needful for process of geopolymerisation as it implicates the destruction of solid particles and the hydrolysis of dissolved Al^{3+} and Si^{4+} ions. Bond at 1,451.32 cm^{-1} assigned to the stretching vibrations of O–C–O bond occurred in all alkali activated fly ash (AAFA) samples implying to the presence of the sodium bicarbonate.

This observation of changes in the FTIR spectra of the AAFA materials indicate that the geopolymerisation reaction occurred leading to the formation of the main reaction product, an amorphous aluminosilicate gel in all samples examined.

3.2. Effect of initial concentration

The effect of the initial concentration was studied at four different initial concentrations and constant temperature (298 K), and particle size (0.071–0.09 mm). The results studied are shown in Fig. 2. It is evident that the increase of initial concentration results in slight increase of copper sorption as a result of increase in the driving force, which is concentration of the solution [16]. The shape of the curves in Fig. 2 shows that amount of copper ion sorbed sharply increases with the time in the initial stage and then gradually increases until the equilibrium is reached.

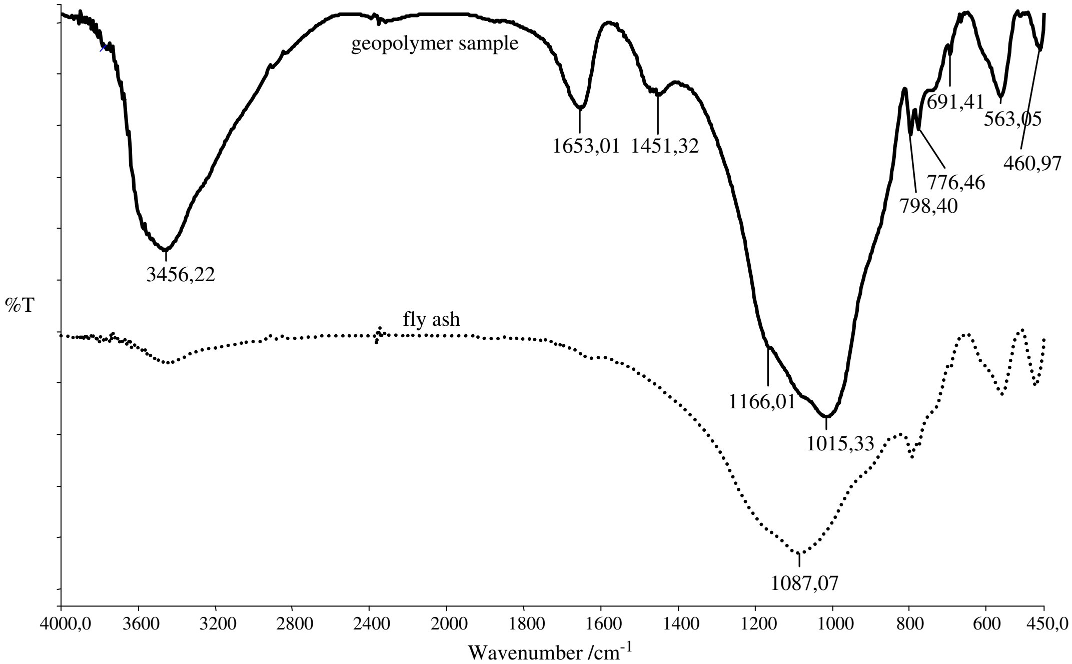

Fig. 1. FTIR spectra for the original FA and geopolymer sample. Wave numbers of interest are indicated.

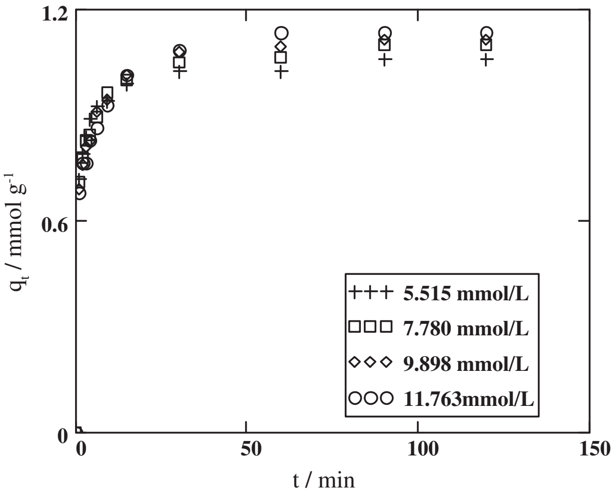

Fig. 2. Effect of initial concentration on the amount of copper ions sorbed on geopolymer.

3.3. Effect of temperature

Fig. 3 shows the variation of the amounts of copper ions sorbed at the different time, for the fixed initial ion concentration of 11.763 mmol L^{-1} and particle size of 0.071–0.09 mm at different sorption temperatures of 298, 308 and 318 K. At higher temperature copper ions are moving faster and become smaller, as their solvation is reduced and in the case of synthetic and natural zeolites, this reduction effect allows ions to diffuse into the smaller pores of zeolite [17,18]. Considering that geopolymer structure consists of different pores size the similar behaviour was expected [19]. The experimental data confirmed that expectation indicating that the amount of the sorbed copper ions increases with the increase of temperature.

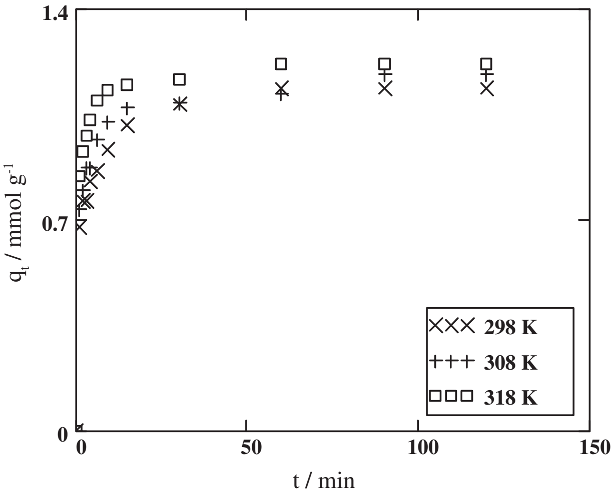

Fig. 3. Effect of contact time on the amount of copper ions sorbed on geopolymer at different temperatures.

Maximum amount of copper ions sorbed on geopolymer (1.217 mmol g^{-1} at 318 K) is higher than those gained on FA (249.1 mg g^{-1} at 333 K) or modified FA (137.1 mg g^{-1} at 333 K) used by Hsu et al. [20] or 92 mg g^{-1} gained at 313 K on geopolymer synthesized by Wang et al. [5].

3.4. Sorption kinetics models

In order to investigate the mechanism of sorption process, various kinetic models have been used to test experimental data. The parameters of all models used were calculated using nonlinear regression analysis. The algorithm for nonlinear regression analysis was developed in Mathcad 14. In order to describe the goodness of fit of the experimental data to the proposed models, the correlation coefficients (R^2) were calculated and included into the tables.

First model used was proposed by Elovich for the chemisorption of gas on the solids but it was also used, successfully, for the sorption kinetics in liquid–solid system [21,22] (Fig. 4):

$$\frac{dq_t}{dt} = A\exp(-Bq_t) \tag{2}$$

After integration, Eq. (2) becomes:

$$q_t = \frac{1}{B}\ln(1 + ABt) \tag{3}$$

where q_t is amount of copper ions sorbed after time t (mmol g^{-1}), t is time (min) and A and B are constants.

The data presented in Tables 2 and 3 show that constants A and B decreased with increase in initial concentration, unlike the increase of constants along with the temperature increase. The correlation coefficients show values higher then 0.896, which shows good agreement with experimental data. Although Elovich equation is useful in describing the chemical sorption on heterogeneous systems, no definite mechanism for this process could be suggested.

Lagergren pseudo-first-order model is one of the most widely used procedures for the sorption of the solute from aqueous solution.

The Lagergren model is expressed as [23]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{4}$$

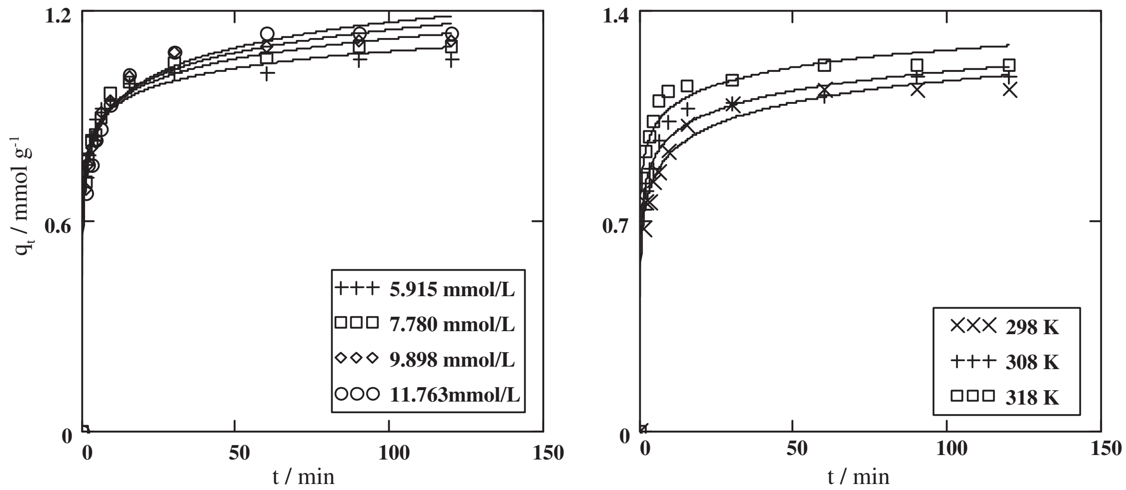

Fig. 4. Elovich plots for copper ions sorption on geopolymer for various initial concentrations and various temperatures.

Table 2
The calculated parameters of the Elovich, Lagergren, and Ho models for copper ions sorbed on geopolymer for various concentrations

Model	Parameter	Concentration (mmol L^{-1})			
		5.915	7.780	9.898	11.763
	q_e experimental (mmol g^{-1})	1.058	1.099	1.114	1.136
Elovich					
	A	4,024.0	616.599	202.362	75.907
	B	14.357	12.070	10.729	9.590
	R^2	0.926	0.963	0.958	0.967
Lagergren pseudo-first-order	q_e (mmol g^{-1})	0.982	1.002	1.021	1.032
	k_1 (min^{-1})	1.008	0.854	0.721	0.638
	R^2	0.949	0.920	0.909	0.885
Ho pseudo-second-order	q_e (mmol g^{-1})	1.031	1.061	1.084	1.100
	k_{2h} (g $mmol^{-1}$ min^{-1})	1.776	1.358	1.111	0.933
	R^2	0.991	0.980	0.976	0.963

Table 3
The calculated parameters of the Elovich, Lagergren, and Ho models for copper ions sorbed on geopolymer for various temperatures

Model	Parameter	Temperature (K)		
		298	308	318
	q_e experimental (mmol g^{-1})	1.136	1.183	1.217
Elovich	A	75.907	347.877	3343.0
	B	9.590	10.704	11.974
	R^2	0.967	0.951	0.896
Lagergren pseudo-first-order	q_e (mmol g^{-1})	1.032	1.072	1.144
	k_1 (min^{-1})	0.638	0.761	1.026
	R^2	0.885	0.918	0.955
Ho pseudo-second-order	q_e (mmol g^{-1})	1.100	1.135	1.200
	k_{2h} (g$mmol^{-1}$ min^{-1})	0.933	1.146	1.600
	R^2	0.963	0.979	0.993

where q_e is maximum amount of copper retained on geopolymer (mmol g^{-1}) and k_1 is the Lagergren rate constant (min^{-1}).

By integrating, Eq. (4) gives:

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

The rate constants, k_1, were found to be in the range of 1.008–0.638 min^{-1} for the initial copper concentration values of 5.915–11.763 mmol L^{-1} (Table 2) that is 0.638–1.026 min^{-1} for the temperature values of 298–318 K (Table 3). The data presented in these tables also demonstrate the decrease of rate constant values with initial concentration and increase with temperature. As can be seen from Fig. 5, equilibrium sorption capacity, q_e, increased with both, initial concentration and temperature. The correlation coefficients of the plots have values higher then 0.885 but the q_e calculated values are not in agreement with q_e experimental for all the sorption processes studied. Values of q_e calculated are lower than q_e experimental values.

The pseudo-second-order kinetic model (Ho) is based on the sorption capacity of the solid phase. The Ho model is usually presented as [24,25]:

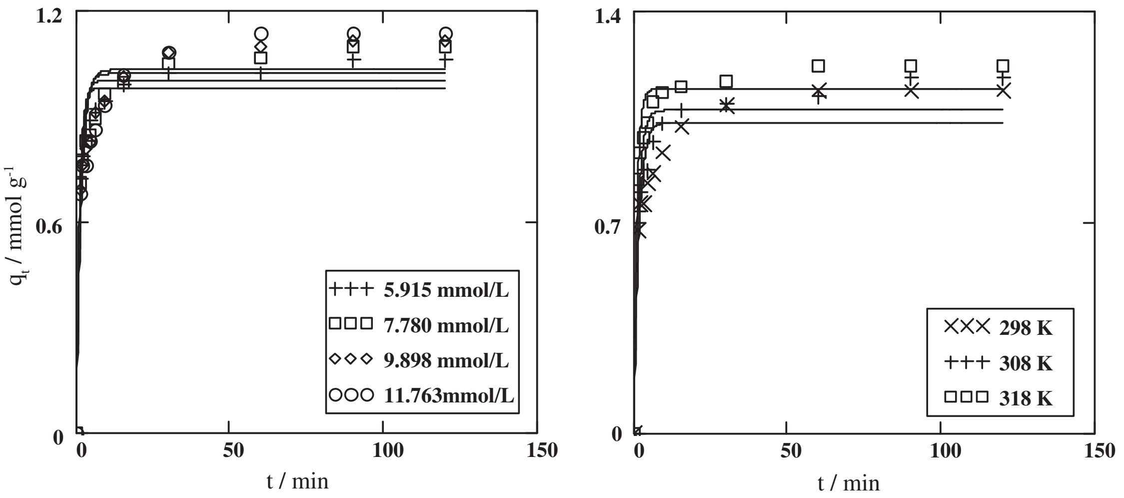

Fig. 5. Lagergren plots for copper ions sorption on geopolymer for various initial concentrations and various temperatures.

$$\frac{dq_t}{dt} = k_{2h}(q_e - q_t)^2 \tag{6}$$

where k_{2h} is the rate constant of the Ho model (g mmol^{-1} min^{-1}).

After integration, Eq. (6) becomes:

$$q_t = \frac{t}{1/k_{2h}q_e^2 + t/q_e} \tag{7}$$

The data presented in Tables 2 and 3 demonstrate that the rate constant decreased with increase of initial concentration which indicates that in a system with lower initial concentration equilibrium is established faster.

Equilibrium sorption capacity, q_e, increased with initial concentration (Fig. 6). Values of the calculated equilibrium sorption capacity are not only higher of those calculated by Lagergren pseudo-first-order but also show better agreement with experimental values. The values of correlation coefficients are also higher than values calculated for the Lagergren pseudo-first-order (R^2 >0.963) suggesting that the sorption of copper ions on geopolymer is a second-order reaction.

3.5. Prediction model: sorption vs. initial copper concentration

The values of q_e and k_{2h} were correlated with the initial copper concentration to obtain expressions for these values in terms of c_0.

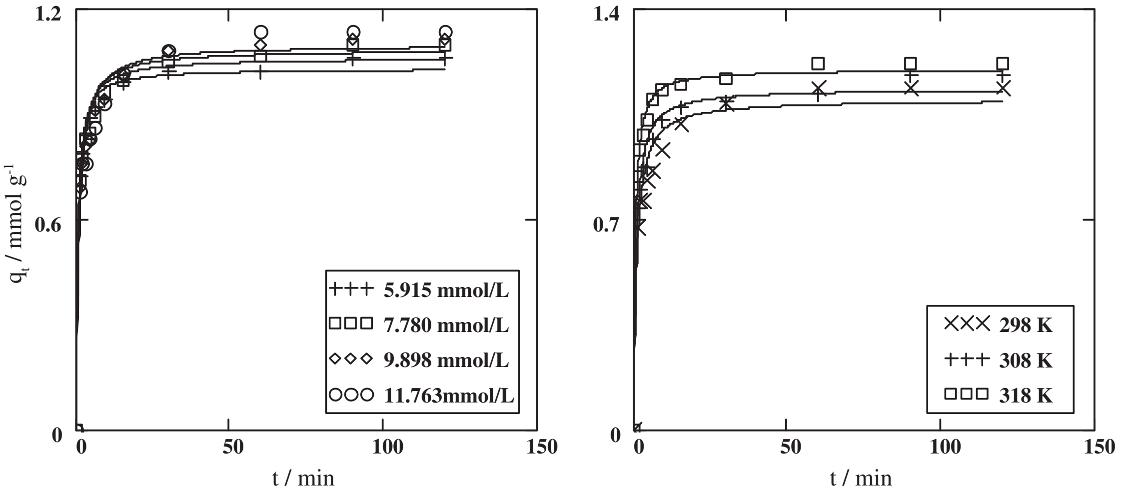

Fig. 6. Ho plots for copper ions sorption on geopolymer for various initial concentrations and various temperatures.

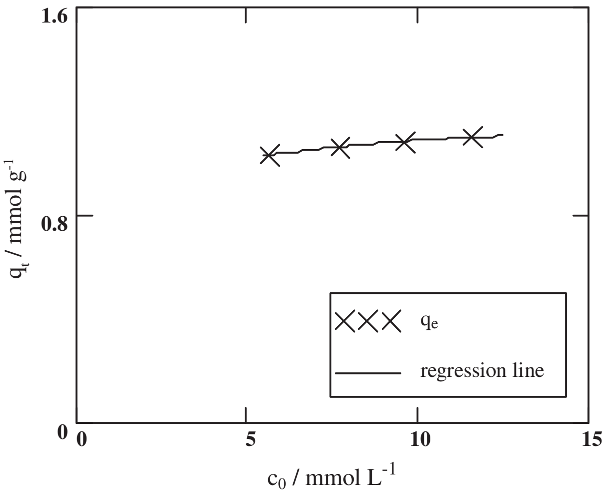

Fig. 7. Equilibrium capacity vs. initial concentration.

Equilibrium capacity increased with an increase in concentration as shown in the Fig. 7 showing a relationship in form:

$$q_e = \frac{-10.475}{51.122 + c_0^2} + 1.157 \tag{8}$$

Ho second-order constant decreased with an increase in concentration as shown in the Fig. 8 giving relationship in form:

$$k_{2h} = \frac{38.448}{c_0^2} + 0.693 \tag{9}$$

Incorporating Eq. (8) and (9) into Ho model the following equation is gained:

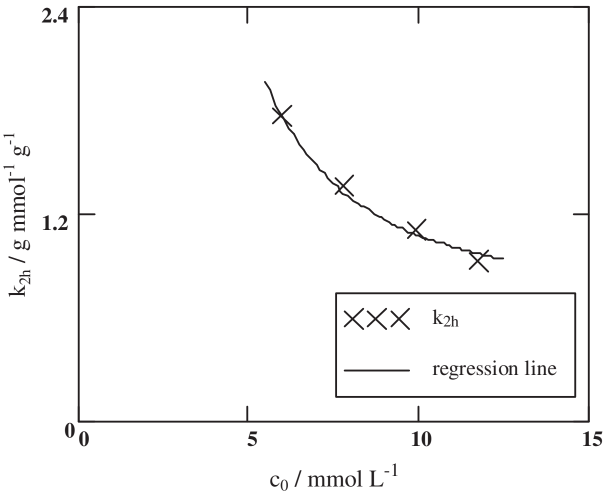

Fig. 8. Ho second-order constant vs. initial concentration.

$$q_t = \frac{t}{\frac{1}{\left(\frac{38.448}{c_0^2}+0.693\right)\left(\frac{-10.475}{51.122+c_0^2}+1.157\right)^2} + \frac{t}{\left(\frac{-10.475}{51.122+c_0^2}+1.157\right)}} \tag{10}$$

This equation can be used for prediction of amount of copper sorbed on geopolymer used for any given initial concentration and contact time.

4. Conclusions

FA-based geopolymer has been successfully synthesized by alkali activation of Class F FA with water glass solution and NaOH solution and tested for the removal of copper ions from aqueous solutions.

Sorption of copper ions on the geopolymer is affected by temperature and initial concentration, which is evident from the experimental and calculated results obtained.

The sorption capacity is favored by both, initial concentration and temperature, while the rate constant increases with temperature and decreases with increase of initial concentration.

The results obtained indicate that FA-based geopolymer has excellent adsorption ability making geopolymer a potential material for heavy metal removal.

The experimental kinetics data were analyzed using reaction based kinetic models. The correlation coefficients of the Ho model were higher than in all other models tested indicating that the sorption of copper ions on geopolymer is a second-order reaction.

Nomenclature

A — constant
B — constant
c_0 — initial concentration of metal in solution, mmol L^{-1}
c_t — concentration of metal in solution at time t, mmol L^{-1}
k_1 — Lagergren rate constant, min^{-1}
k_{2h} — is the rate constant of the Ho model, g mmol^{-1} min^{-1}
m — mass of the geopolymer, g
q_e — amount of copper ions sorbed at equilibrium (equilibrium capacity), mmol g^{-1}
q_t — amount of copper ions sorbed after time t, mmol g^{-1}
T — temperature, K
t — time, min
V — volume of solution, L

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