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Removal of copper and cobalt ions by fly ash-based geopolymer from solutions-equilibrium study

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ABSTRACT

Fly ash-based geopolymer was used for removal of copper and cobalt ions from aqueous solutions by a batch technique. The experimental data were obtained at constant geopolymer particles size (0.071–0.090 mm) for the different initial concentrations (in the range from 3.881 to 39.390 mmol L^{-1}) of copper and cobalt solutions, respectively, and at various temperatures (T = 298, 308 and 318 K). For characterization of synthesized geopolymer, before and after sorption of heavy metals, FTIR, XRD, and SEM/EDS analyses were used to confirm the dissolution of geopolymer structure. SEM/EDS analysis also confirmed that sorption process occurred, as well as the fact that Na ions are outgoing ions. Various types of isotherm models, two-parameter isotherms: Langmuir, Freundlich, Jovanovic, and Dubinin–Radushkevich and three-parameter isotherms: Hill, Redlich–Peterson, and Sips were fitted to the experimental data obtained. In order to calculate parameters of the isotherms a nonlinear regression method was used. According to the results obtained, the most appropriate models for describing equilibrium data were Langmuir, Jovanovic, Hill, and Redlich–Peterson isotherm models. Thermodynamic parameters indicated endothermic (positive values of ΔH°) and spontaneous nature (negative values of ΔG°) of sorption process.

Keywords: Geopolymer; Copper; Cobalt; Thermodynamics; Isotherm models

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1. Introduction

The heavy metals pollution represents an important environmental problem since heavy metals are used in every aspect of our modern culture; mainly in agriculture, different types of industries, power plants, and residential areas [1].

Heavy metals tend to accumulate in the different parts of the body so long-term exposure may result in various neurological diseases, allergies, and may even cause cancer [1].

Copper is extensively used in electronics, as building material, in agriculture, as well as cobalt, which is used in the glass manufacture industry, paint industry, etc. This all contributes to the loading of wastewater as well as groundwater with these heavy metals.

The toxicity of wastewaters from various sources, such as industrial, mining, and agricultural areas, is mainly caused by the pollution of heavy metals and metalloids [2], and its purification has been practiced for several decades now, using the most

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common physicochemical processes such as chemical precipitation, oxidation and reduction, filtration, adsorption and ion exchange, evaporation, reverse osmosis, and electrochemical treatment. Nowadays, there is a growing interest in using low-cost materials for the sorption of heavy metals. The term sorption is used to describe the capture of a substance from the external surface of materials as well as from the internal surface of porous materials and can be classified as physical sorption, chemical sorption, or electrostatic sorption (ion exchange) [3]. Geopolymers seemed to be an appropriate choice for it since they have proven to be an effective sorption material and can be synthesized from various waste material, most commonly fly ash [4–8].

In this paper, geopolymer, synthesized from Croatian fly ash class F [8], has been used as a sorption material. Langmuir, Freundlich, Jovanovic, Dubinin–Raduskhevich (two-parameter isotherm model), Hill, Redlich–Peterson, and Sips (three-parameter isotherm model) were used to fit the experimental equilibrium data of copper and cobalt sorption from solutions. In order to describe the goodness-of-fit of the experimental data to the proposed isotherm models, the correlation coefficient (r^2) and the residual root square error (RMSE) were calculated. The aims of this work were to determine thermodynamic parameters, the type of sorption, and to make a comparison of different isotherm models describing the sorption of copper and cobalt on fly ash-based geopolymer using nonlinear regression analysis.

2. Materials and Methods

2.1. Materials

Geopolymer, synthesized from fly ash class F (as defined in ASTM C618) from the Croatian power plant Plomin 2 (Plomin), was used as a sorbent material in this study. Detailed chemical analysis of the used fly ash, as well as thorough process of the geopolymer synthesis were published in previous works [8,9]. Sodium hydroxide solution (Kemika) and sodium silicate solution (a type S water glass) were used as alkaline activator. The composition of the initial mixture used for geopolymer synthesis was calculated on the basis of mole ratios between the main oxides and is presented in Table 1. The degree of reaction α is also presented in Table 1. Synthesized geopolymer was crushed and sieved to obtain particle diameter 0.071–0.090 mm for equilibrium sorption studies.

Solutions containing cobalt ions were prepared by dissolving the appropriate weight of $Co(NO_3)_2 \times 6H_2O$ (Prolabo) in distilled water.

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

2.2. Instrumentation

X-ray diffraction patterns of all samples were recorded using Shimadzu diffractometer XRD 6000 with Cu Kα radiation. Data were collected between 5 and 70° 2Θ in a step scan mode with steps of 0.02° and scan speed of 2°min^{-1} at current of 30 mA and voltage of 40 kV.

The FTIR spectra of geopolymers were made on KBr pastille on a Shimadzu IRAffinity-1 in the range from 4,500 to 450 cm^{-1}.

Surface morphology was observed using scanning electronic microscope (JEOL JSM-6510 LV). The samples were coated with a thin film of gold.

The initial concentrations of copper solutions (in range 3.881–39.390 mmol L^{-1}) and cobalt solutions (in range 4.080–39.182 mmol L^{-1}) were checked by Perkin Elmer Lambda EZ 201 UV/VIS spectrophotometer. Nitrate solutions of the selected heavy metals (Co and Cu) were used because these solutions are colored and the concentrations of these solutions can easily be determined using UV/VIS spectrophotometer.

Concentrations of Na (exchangeable ions) K, Ca, and Mg ions after equilibrium were measured by the 761 Compact IC, Metrohm, those of Si using the spectrophotometer and those of Al using the atomic spectrophotometer Analytic Jena. Also, using the HANNA instruments pH meter the pH value of the solutions before and after equilibrium was measured too for all the experiments conducted.

2.3. Equilibrium studies

Equilibrium studies of the heavy metals sorption on fly ash-based geopolymer were performed by agitating 0.2 L of metal solutions of various concentrations with 1.0 g of geopolymer in batch reactors at different temperatures (T = 298, 308, and 318 K). The mixture was agitated until the equilibrium was reached. The samples of solution were taken out from the system at the certain contact time in order to establish whether the equilibrium was reached. The equilibrium was reached after 24 h. The concentration of the remained heavy metal ions in the filtered sample was determinated by UV/Vis spectrophotometer.

The amount of the heavy metal (copper, cobalt) retained on the geopolymer sample, q_e, was calculated as the difference between initial and equilibrium heavy metal concentration according to Eq. (1):

Table 1
Composition of the initial mixes and molar ratios between the main oxides, as well as the degree of reaction α

SiO_2 (moles)	Al_2O_3 (moles)	Na_2O (moles)	SiO_2/Al_2O_3 (molar ratio)	Na_2O/Al_2O_3 (molar ratio)	Na_2O/SiO_2 (molar ratio)	H_2O/Na_2O (molar ratio)	Degree of reaction α (%)
1.06	0.23	0.16	4.61	0.69	0.15	11.19	65.90

$$q_e = \frac{(c_0 - c_e)V}{m} \qquad (1)$$

where c_0 is the initial concentration of metal in solution (mmol L^{-1}), c_e is concentration of metal in solution at equilibrium (mmol L^{-1}), V is the volume of solution (L), and m is the mass of geopolymer (g) [10].

3. Results and discussion

3.1. XRD, FTIR, and SEM/EDS analyses of geopolymer samples, before and after equilibrium study

The XRD pattern of geopolymer, before and after equilibrium study, is shown in Fig. 1. Geopolymer sample consists of quartz as major mineral and considerable amount of hematite and mullite. Anorthite and cristoballite are present in trace amounts. Crystalline components present in the geopolymer structure are due to the incomplete dissolution of fly ash particles during geopolymerization. Original fly ash consists of only 31.23% of reactive silica, as the part that reacts with alumina and the alkalis giving place to a cementitious material. Unreacted fly ash particles are encapsulated inside the amorphous geopolymer gel. The XRD patterns of geopolymer after sorption of heavy metal differ from the original geopolymer pattern revealing the dissolution of phases located in unreacted fly ash particles. The phases, such as anorthite and cristoballite, determinated in original geopolymer, dissolved in geopolymer after sorption of heavy metals. Dissolution of these phases was confirmed by analyzing the content of solutions after equilibrium was reached (Tables 2 and 3).

The FTIR spectrum for original geopolymer system as well as the spectra for geopolymer after sorption of heavy metals are plotted in Fig. 2. Bands of interest are marked on spectra and explained in previous work [8]. The main broad band, located in original geopolymer at 1,022.27 cm^{-1} corresponding to asymmetric stretching vibrations of Si–O–Si and Al–O–Si, is wider then in original geopolymer sample. The bands at 1,489.05 cm^{-1} and 1,454.33 cm^{-1}, assigned to the stretching vibrations of C–O–C bond, suggesting the presence of sodium bicarbonate or due to carbonation [9,11] disappear in geopolymer after sorption of copper.

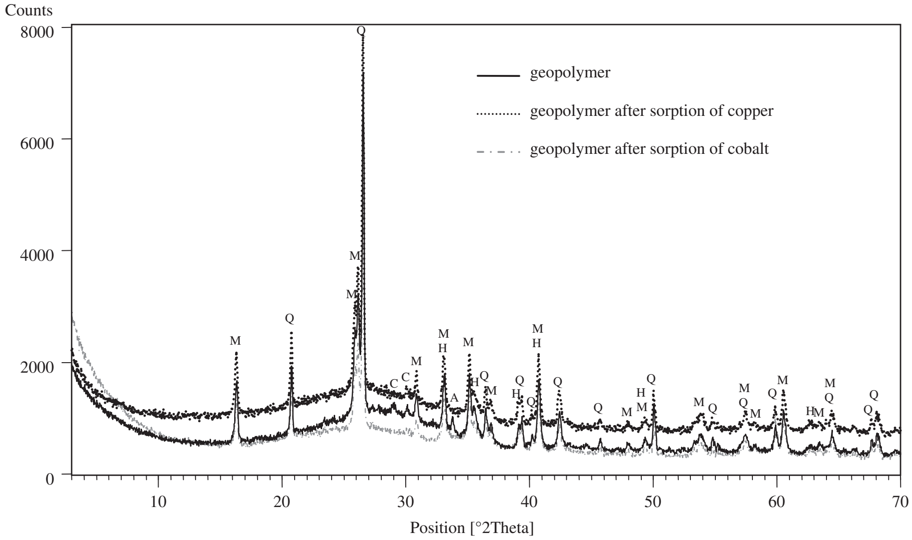

Fig. 1. XRD patterns of original geopolymer and geopolymers after sorption of heavy metals (Q—quartz, H—hematite, M—mullite, C—cristoballite, A—anorthite).

Table 2
Concentration of ions in equilibrium—copper

Concentration (mmol L^{-1})								
Initial copper solution	Copper retained	Copper sorbed	Na	Si	Al	K	Ca	Mg
298 K								
3.881	0.000	3.881	8.615	0.723	0.000	0.204	0.000	0.000
7.780	2.271	5.509	8.684	0.697	0.000	0.159	0.019	0.000
11.763	5.915	5.848	11.089	0.646	0.000	0.393	0.000	0.000
19.305	13.712	5.593	10.420	0.575	0.000	0.393	0.000	0.000
30.576	25.153	5.423	10.094	0.607	0.000	0.350	0.248	0.000
39.390	33.966	5.424	10.437	0.839	0.000	0.390	0.000	0.000
308 K								
3.881	0.000	3.881	8.615	0.678	0.000	0.204	0.000	0.000
7.780	2.102	5.678	9.149	0.762	0.000	0.221	0.155	0.000
11.763	5.407	6.356	10.729	0.729	0.000	0.520	0.415	0.000
19.305	13.488	5.817	10.791	0.689	0.000	0.526	0.429	0.000
30.576	24.729	5.847	10.786	0.588	0.000	1.060	0.383	0.000
39.390	33.542	5.848	10.761	0.710	0.000	0.544	0.363	0.000
318 K								
3.881	0.000	3.881	9.193	0.665	0.000	0.199	0.000	0.000
7.780	2.017	5.763	11.004	0.871	0.000	0.423	0.745	0.071
11.763	4.983	6.780	11.530	1.279	0.000	0.558	0.640	0.583
19.305	13.373	5.932	11.581	1.292	0.000	2.815	0.000	1.114
30.576	24.644	5.932	11.330	1.060	0.000	0.663	0.655	0.000
39.390	33.458	5.932	11.886	1.125	0.000	0.649	0.644	0.080

Table 3
Concentration of ions in equilibrium—cobalt

Concentration (mmol L^{-1})								
Initial cobalt solution	Cobalt retained	Cobalt sorbed	Na	Si	Al	K	Ca	Mg
298 K								
4.080	0.202	3.878	8.150	0.434	0.002	0.165	0.000	0.000
7.753	3.467	4.286	9.954	0.115	0.004	0.315	0.207	0.000
12.039	7.549	4.490	9.691	0.059	0.011	0.314	0.222	0.000
19.794	15.508	4.286	10.567	0.143	0.020	0.286	0.271	0.000
28.978	24.692	4.286	10.369	0.132	0.031	0.349	0.298	0.074
39.182	34.896	4.286	10.816	0.138	0.040	0.335	0.338	0.074
308 K								
4.080	0.202	3.878	8.359	0.582	0.000	0.392	0.027	0.000
7.753	3.059	4.694	10.263	0.331	0.002	0.359	0.224	0.000
12.039	6.937	5.102	10.404	0.331	0.009	0.381	0.284	0.052
19.794	14.896	4.898	10.378	0.132	0.021	0.357	0.018	0.016
28.978	24.080	4.898	10.803	0.389	0.030	0.383	0.320	0.051
39.182	34.284	4.898	10.486	0.582	0.000	0.422	0.327	0.073
318 K								
4.080	0.406	3.674	9.222	0.958	0.000	0.272	0.000	0.000
7.753	2.855	4.898	9.778	0.402	0.005	0.485	0.154	0.000
12.039	6.325	5.714	11.040	0.640	0.009	0.463	0.391	0.000
19.794	14.284	5.510	10.932	0.620	0.018	0.493	0.399	0.000
28.978	23.467	5.511	10.891	0.646	0.030	0.441	0.494	0.084
39.182	33.672	5.510	11.321	0.842	0.040	0.530	0.708	0.096

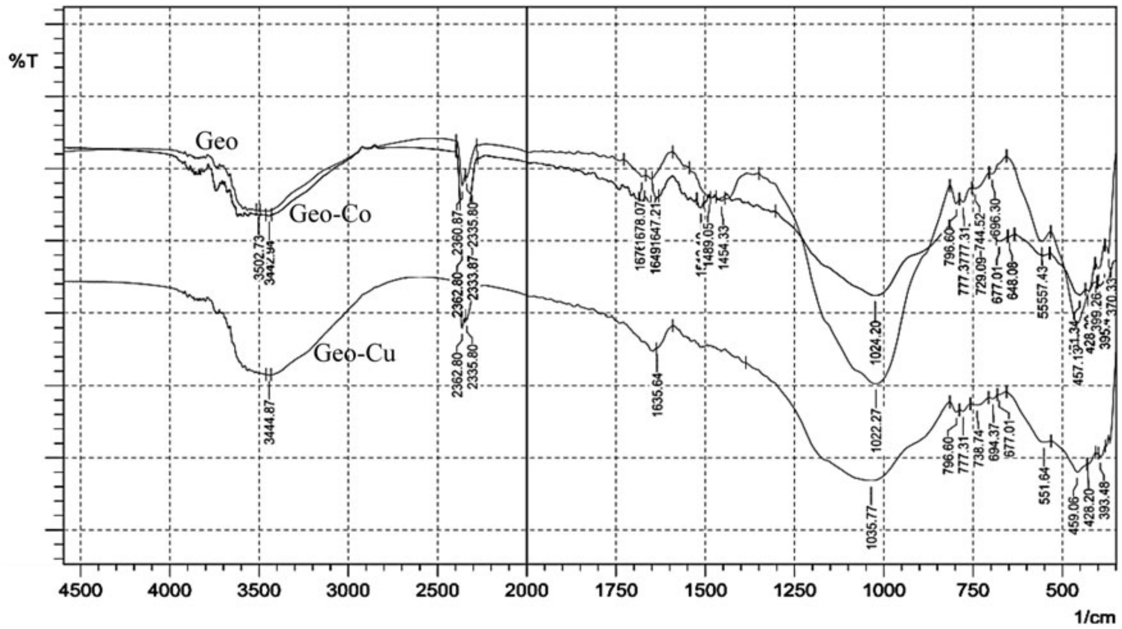

Fig. 2. FTIR spectra of original geopolymer (Geo) and geopolymers after sorption of heavy metals, copper (Geo–Cu), and cobalt (Geo–Co).

SEM micrographs (Fig. 3) were made on original geopolymer sample and on geopolymer after sorption in copper solution (11.763 mmol L^{-1}) and cobalt solution (12.039 mmol L^{-1}) at the temperature of 298 K. It is evident that original geopolymer structure consists of unreacted fly ash sphere surrounded by amorphous geopolymer gel. Differences are noticeable on the surface of geopolymer after the sorption of heavy metals. The surface is covered with heavy metals, copper, and cobalt. These findings were confirmed by EDS analysis. EDS analysis showed the decrease in concentration of sodium indicating that sodium is outgoing ion within the geopolymer matrix. Presence of the used heavy metals, determined by EDS analysis, indicates that the sorption process occurred confirming the results obtained by analyzing the equilibrium solutions after sorption of copper and cobalt.

3.2. *Equilibrium of heavy metal uptake—effect of initial concentration and temperature*

A series of experiments were carried out with different initial concentrations of heavy metal used at three different temperatures ($T = 298$, 308, and 318 K). The results are given in Fig. 4. The equilibrium amount of copper and cobalt ions, sorbed on geopolymer, increases for the first three initial concentrations used, then slightly decreases until it reaches its constant value. This decrease in maximum equilibrium value is due to the degradation of geopolymer structure at both higher and lower pH values [12]. This is evident from the concentrations of Si, Al, Mg, Ca, and K ions determined in liquid phase after sorption (Tables 2 and 3) for copper and cobalt solutions, respectively. In copper solutions, the concentration of Si was approximately the same for all the initial copper concentration at 298 and 308 K, while at the highest temperature (318 K), concentration of Si was higher at higher initial copper concentration, i.e. for lower initial and equilibrium pH values (Tables 2 and 3; Figs. 5 and 6). The Al ions were not detected in the remaining solution after sorption of copper on synthesized geopolymer. Nevertheless, a small concentration of Al ions was detected in remaining solution after cobalt sorption on geopolymer. Also, Mg ions were detected in remaining solutions after sorption of copper only at the highest temperature used. It seems that dissolution of geopolymer is more intense at that temperature than at other temperatures tested. For cobalt sorption, effect of initial concentration has a bigger impact on geopolymer dissolution than the impact of the temperature.

As for the impact of temperature on equilibrium uptake of heavy metals, in most cases, sorption increases with the increase in temperature [10]. The sorption of copper and cobalt on the geopolymer is also affected by the temperature. With the rise of temperature, the amount of heavy metal sorbed on

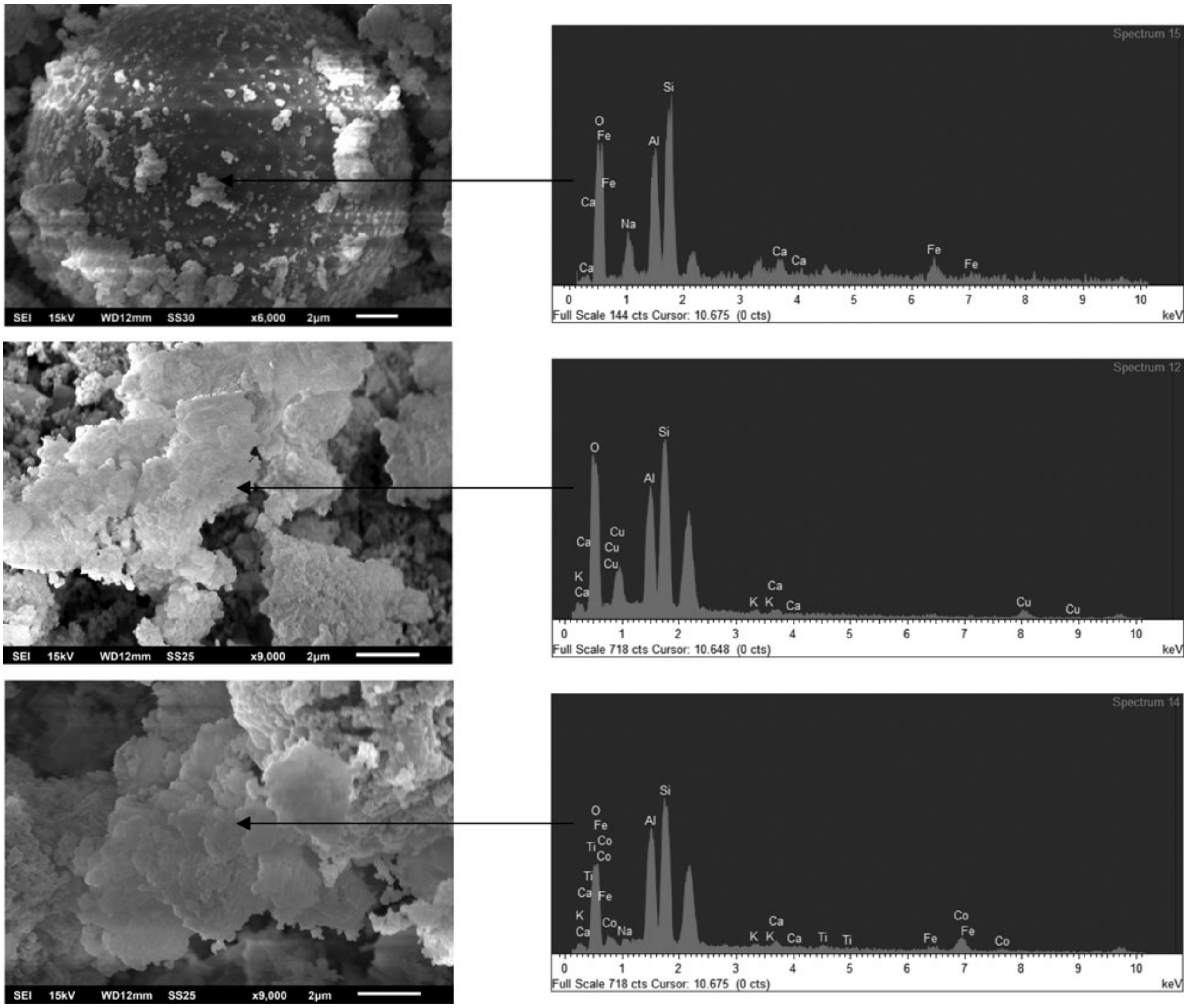

Fig. 3. SEM/EDS analysis of original geopolymer and geopolymers after sorption of heavy metals (spectrum 15—original geopolymer, spectrum 12—geopolymer after copper sorption, spectrum 14—geopolymer after cobalt sorption).

geopolymer rises, which is a consequence of the hydrated radius reduction in metal ions sorbed. This effect is more noticeable for cobalt than for copper ions.

The balance between the outgoing and ingoing ionic charge from and in the geopolymer matrix shows that the removal of heavy metals from aqueous solutions by geopolymer is a complex process consisting of ion exchange and adsorption. The total quantity of ingoing heavy metal cations is higher than the total quantity of outgoing Na cations, taking into account that the concentration of Na ions must be two times higher than the concentration of heavy metal ion because they exchange in a way two Na ions regarding to one ion of heavy metal (Tables 2 and 3). In some cases, for example, for the initial concentration of copper solution of 3.881 mmol L^{-1} at 298 K, it seems that the concentration of outgoing cation is higher. This can be explained by taking the pH value into account (Figs. 5 and 6). Hydrogen cation can also exchange original Na cation from the geopolymer matrix. The fact that the structure of geopolymer consists of geopolymer gel and unreacted fly ash spheres results in geopolymer degradation [13,14]. This contributes to the higher amount of outgoing cations in the solution for both copper and cobalt, respectively. The concentrations of Al, Si, Mg, Ca, and K ions, detected and measured from geopolymer structure, confirmed these findings (Tables 2 and 3).

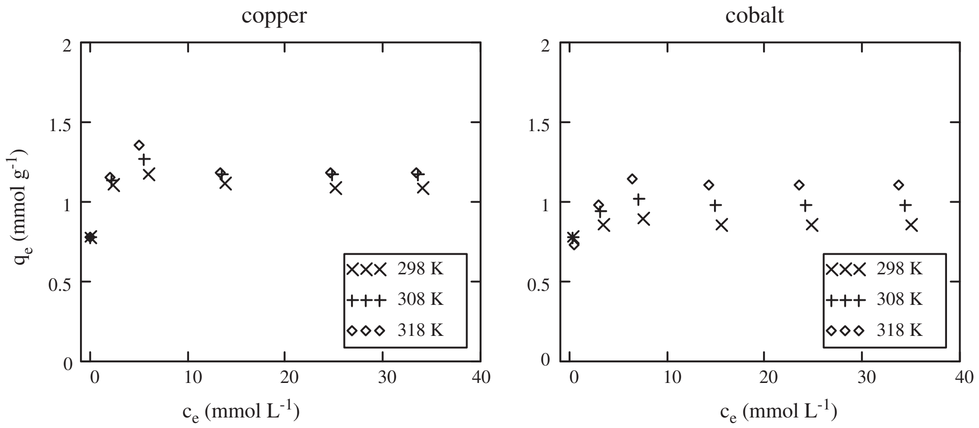

Fig. 4. Experimental equilibrium data for the copper and cobalt sorption on synthesized geopolymer at various initial concentrations of heavy metals used and various temperatures.

3.3. Thermodynamic parameters

Thermodynamics of heavy metal sorption on geopolymer were investigated at different temperatures using various initial concentrations of heavy metals.

The distribution coefficient K_d was calculated using the following equation:

$$K_d = \frac{q_e}{c_e} \tag{2}$$

The thermodynamic parameters, ΔH° and ΔS°, were calculated from the slope and intercept of a plot of ln (K_d) against $1/T$, Fig. 7 using equation:

$$\ln\,(K_d) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{3}$$

where T is temperature (K), R is gas constant (J mol^{-1} K^{-1}), ΔH° is the molar enthalpy change (J mol^{-1}), and ΔS° is the molar entropy change (J mol^{-1} K^{-1}) [15].

ΔG° was calculated using the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{4}$$

where ΔG° is Gibbs free energy (J mol^{-1}) [16].

The goodness-of-fit, for thermodynamic parameters, was tested using coefficient of determination, R^2.

The calculated thermodynamic parameters, as well as R^2, are presented in Tables 4 and 5. The positive values of ΔH° show that the sorption process is endothermic which may be due to the removal of water molecules from the solid/solution interface and from the sorbing ion [17]. The positive values also indicate that the entropy of the system increases after sorption process. When sorption of heavy metal cations on geopolymer occurs, the hydrated water

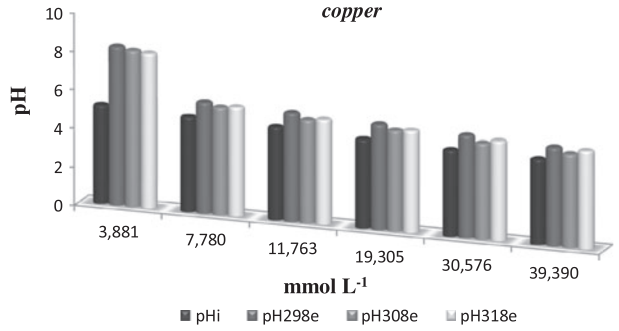

Fig. 5. Initial and equilibrium pH values for sorption of copper ions on geopolymer at 298, 308, and 318 K.

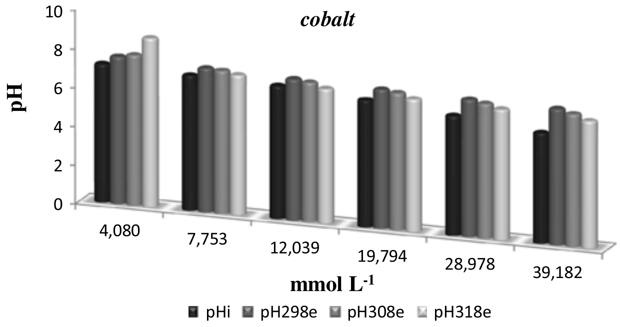

Fig. 6. Initial and equilibrium pH values for sorption of cobalt ions on geopolymer at 298, 308, and 318 K.

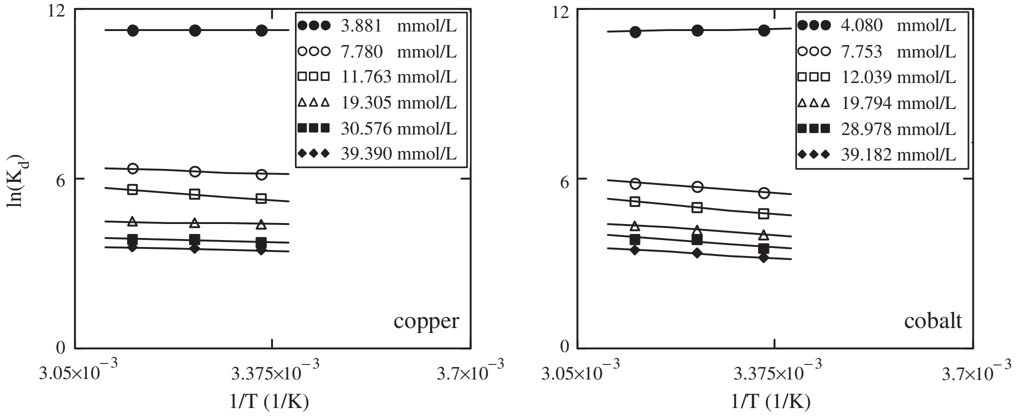

Fig. 7. Estimation of thermodynamic parameters (Eq. (3)) for copper and cobalt sorption on synthesized geopolymer.

Table 4
Thermodynamic parameters for the sorption of copper ions on geopolymer

Concentration (mmol L^{-1})	ΔS° (kJ mol^{-1} K^{-1})	ΔH° (kJ mol^{-1})	ΔG°_{298} (kJ mol^{-1})	ΔG°_{308} (kJ mol^{-1})	ΔG°_{318} (kJ mol^{-1})	R^2
3.881	0.094	1.813×10^{-11}	−33.552	−34.678	−35.804	1.000
7.780	0.073	6.477	−15.339	−16.071	−16.803	0.974
11.763	0.086	12.607	−13.104	−13.967	−14.830	0.999
19.305	0.048	3.292	−10.920	−11.397	−11.874	0.947
30.576	0.048	4.341	−9.838	−10.314	−10.790	0.882
39.390	0.043	4.128	−8.609	−9.036	−9.464	0.880

Table 5
Thermodynamic parameters for the sorption of cobalt ions on geopolymer

Concentration (mmol L^{-1})	ΔS° (kJ mol^{-1} K^{-1})	ΔH° (kJ mol^{-1})	ΔG°_{298} (kJ mol^{-1})	ΔG°_{308} (kJ mol^{-1})	ΔG°_{318} (kJ mol^{-1})	R^2
4.080	0.087	2.115	−23.690	−24.555	−25.421	1.000
7.753	0.090	12.974	−13.689	−14.584	−15.479	0.974
12.039	0.095	16.469	−11.837	−12.786	−13.736	1.000
19.794	0.074	12.032	−10.000	−10.740	−11.479	0.998
28.978	0.074	12.995	−8.900	−9.635	−10.369	0.806
39.182	0.065	11.314	−7.934	−8.580	−9.226	1.000

molecules are separated from the cation before they attach to external and/or internal geopolymer surface. This effect increases the disorder of the system and thus increases its entropy [7]. The ΔG° is negative and decreases with the increase in temperature, implying that the reaction is spontaneous and favorable at higher temperature. The ΔG° values are higher if the initial concentration of heavy metal ions is higher, indicating the decrease in spontaneity of sorption process with an increase in the amount of heavy metal ions sorbed on geopolymer. The positive values of ΔS° also confirm the endothermic nature of the sorption process [7].

3.4. Testing of adsorption isotherms

A sorption isotherm represents the amount of material bound at the surface as a function of the material present in the solution or in the gas phase. Sorption isotherms are often used as empirical models, providing some insight into the sorption mechanism, the surface properties, and affinity of the sorbent [18].

Table 6
Isotherm models [19–22]

Two-parameter isotherm models		
Langmuir	$q_e = \frac{K_L c_e q_{max}}{(1+K_L c_e)}$	(5)
Freundlich	$q_e = K_F c_e^{\beta}$	(6)
Jovanovic	$q_e = q_{max}\left(1 - e^{-k_J c_e}\right)$	(7)
Dubinin–Radushkevich	$q_e = q_{max}\left\{-\frac{\left[RT\ln\left(1+\frac{1}{c_e}\right)\right]^2}{2E^2}\right\}$	(8)
Three-parameter isotherm models		
Hill	$q_e = \frac{q_{max} c_e^{b_H}}{a_H + c_e^{b_H}}$	(9)
Redlich–Peterson	$q_e = \frac{K_{RP} c_e q_{max}}{1+(K_{RP} c_e)^{\beta}}$	(10)
Sips	$q_e = \frac{(K_S c_e)^{\beta} q_{max}}{1+(K_S c_e)^{\beta}}$	(11)

In this paper, various types of isotherm models: Langmuir, Freundlich, Jovanovic, Dubinin–Raduskhevich, Hill, Redlich–Peterson, and Sips (Table 6) were used to fit equilibrium data of copper and cobalt sorption from solutions using nonlinear regression analysis.

The results obtained show that Langmuir and Jovanovic isotherms are in good agreement with experimental data which can be seen from the calculated values of r^2 and RMSE (Table 7) for the sorption of both heavy metals used. These findings were expected because the Jovanovic model is very similar to the Langmuir's considering a monolayer sorption and no lateral interactions [19,23].

By fitting three-parameter isotherm models to the experimental data, it could be concluded that Hill

Table 7
Adsorption isotherms and statistical comparison values

Isotherm model	Parameter	Copper			Cobalt		
		Temperature					
		298 K	308 K	318 K	298 K	308 K	318 K
	q_e (mmol g^{-1})	1.085	1.169	1.186	0.857	0.980	1.102
Langmuir	K_L	457.954	21.24	36.972	42.286	18.089	4.580
	q_{max} (mmol g^{-1})	1.112	1.192	1.219	0.867	0.987	1.118
	r^2	0.951	0.931	0.859	0.824	0.930	0.937
	RMSE	0.390	0.391	0.396	0.019	0.026	0.043
Freundlich	K_F	1.107	1.188	1.208	0.821	0.872	0.875
	β	2.038×10^{-5}	1.465×10^{-5}	1.880×10^{-5}	0.019	0.044	0.081
	r^2	0.951	0.929	0.859	0.567	0.766	0.765
	RMSE	0.390	0.391	0.396	0.030	0.047	0.083
Jovanovic	K_J	1.982	1.451	1.421	11.248	7.773	2.776
	q_{max} (mmol g^{-1})	1.115	1.194	1.228	0.865	0.980	1.086
	r^2	0.952	0.939	0.872	0.831	0.913	0.871
	RMSE	0.390	0.391	0.395	0.018	0.029	0.062
Dubinin–Radushkevich	q_{max} (mmol g^{-1})	1.120	1.193	1.225	0.896	1.020	1.163
	E (kJ mol^{-1})	3.704	3.726	3.885	1.174	1.247	1.036
	r^2	0.950	0.934	0.863	0.820	0.947	0.961
	RMSE	0.390	0.391	0.396	0.391	0.391	0.372
Hill	q_{max} (mmol g^{-1})	1.112	1.183	1.213	0.865	0.994	1.134
	a_H	0.002	4.113×10^{-4}	1.484×10^{-4}	0.0052	0.080	0.839
	b_H	1.823	0.24	0.684	1.935	0.785	0.258
	r^2	0.951	0.929	0.859	0.832	0.933	0.940
	RMSE	0.390	0.391	0.396	0.018	0.025	0.042
Redlich–Peterson	K_{RP}	52.063	1.437	0.974	27.836	18.805	4.850
	q_{max} (mmol g^{-1})	1.229	1.642	1.878	0.929	0.977	1.096
	β	1.015	1.089	1.135	1.011	0.998	0.996
	r^2	0.957	0.955	0.911	0.859	0.930	0.937
	RMSE	0.389	0.389	0.391	0.017	0.026	0.043
Sips	K_S	460.177	364.843	244.538	5.357	19.526	1.857
	q_{max} (mmol g^{-1})	1.417	1.513	1.215	1.586	1.473	1.601
	β	0.152	0.155	0.921	0.041	0.123	0.238
	r^2	0.930	0.920	0.859	0.580	0.806	0.828
	RMSE	0.393	0.394	0.396	0.029	0.043	0.071

isotherm model, as well as Redlich–Peterson isotherm model, shows better agreement than Sips isotherm, which was also expected. Hill isotherm model also describes the sorption of sorbate on homogeneous sorbents as Langmuir isotherm model [24]. When the value of β constant of Redlich–Peterson isotherm model is closer to 1, Redlich–Peterson model is based on the assumptions of the Langmuir isotherm model [19].

4. Conclusions

These results show that geopolymer synthesized from fly ash class F is an effective sorbent for the removal of cobalt and copper ions from aqueous solutions. The equilibrium between heavy metal and geopolymer was achieved in approximately 24 h. The statistical parameters used (r^2 and RMSE) showed that Langmuir, Jovanovic, Hill, and Redlich–Peterson models give a better fit of experimental data than Dubinin–Radushkevich, Freundlich, and Sips isotherms. XRD and FTIR analyses confirmed the dissolution of unreacted fly ash particles inside the geopolymer structure due to the change in pH values of solution. SEM/EDS analysis confirmed that sorption process occurred, as well as the fact that Na ions are outgoing ions. The analysis of the remaining solution, after equilibrium was reached, showed the concentration of various ions (Al, Si, Ca, K, Mg, and Na), confirming that the dissolution of unreacted fly ash particles occurred. Finally, the negative values of ΔG° indicate the spontaneous nature of sorption process which is favored by the increase in temperature. Positive values of ΔH° showed that the process of sorption of the heavy metals on geopolymer is endothermic.

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Nomenclature

c_0	—	initial concentration of metal in solution (mmol L^{-1})
c_e	—	equilibrium concentration of metal in solution (mmol L^{-1})
m	—	mass of the geopolymer (g)
q_e	—	amount of copper and cobalt ions sorbed at equilibrium (equilibrium capacity) (mmol g^{-1})
T	—	temperature (K)
t	—	time (min)
V	—	volume of solution (L)
R	—	gas constant (J mol^{-1} K^{-1})
ΔH°	—	molar enthalpy change (J mol^{-1})
ΔS°	—	molar entropy change (J mol^{-1} K^{-1})
ΔG°	—	Gibbs free energy (J mol^{-1})
$q_{\max}$	—	maximum sorption capacity (mmol g^{-1})
K_L	—	Langmuir constant
K_F	—	Freundlich constant
β	—	Freundlich isotherm parameter
k_J	—	Jovanovic isotherm constant
a_H	—	Hill isotherm constant
b_H	—	Hill cooperativity coefficient of the binding interaction
K_S	—	Sips constant
K_{RP}	—	Redlich–Peterson constant
K_d	—	distribution coefficient
pHi	—	initial pH value
pHe	—	equilibrium pH value
r^2	—	correlation coefficient
R^2	—	coefficient of determination
E	—	mean free energy of sorption of Dubinin–Radushkevich isotherm model (J mol^{-1})
RMSE	—	residual root square error
H	—	hematite
Q	—	quartz
M	—	mullite
C	—	cristoballite
A	—	anorthite

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