

Process optimization for copper sorption onto synthetic zeolite NaX

S. Svilović*, D. Rušić, R. Stipišić, N. Kuzmanić

*Department of Chemical Engineering, Faculty of Chemistry and Technology, University of Split,
Ruđera Bošković 35, 21000 Split, Croatia*

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Taguchi's approach to experimental design was applied to determine the effect of some process parameters on the sorption of copper ions onto zeolite NaX. The impact of solute concentration (c), temperature (T), contact time (t), impeller speed (n) and anion type (A) on the amount of copper retained on the zeolite, in a batch stirred reactor, was investigated. Optimum experimental conditions and influence of controllable factors were determined using larger-the-better approach. The applied method showed that the optimal copper removal is achieved at the lowest solute concentration, when sulphate anions were used, at the highest impeller speed and temperature used and after 45 min. The influence of controllable factors in descending order is $c > n > A > T > t$. Also, the impact of anion type, solute concentration and temperature on the process equilibrium was examined. The experimental data were modelled using Langmuir, Freundlich and Sips isotherms and their goodness-of-fit was analysed. Thermodynamic parameters such as ΔG^0 , ΔH^0 , and ΔS^0 were also determined. According to the thermodynamic parameters copper sorption on zeolite NaX was a spontaneous and endothermic process for all anions used.

Keywords: Taguchi method; zeolite NaX; isotherms; equilibrium; thermodynamic

INTRODUCTION

Zeolites are an appropriate material for removing heavy metal ions from wastewater and a very promising support for design and preparation of environmentally friendly catalysts. Copper-exchanged zeolites are also used as catalysts and, among others, are applied to selective ammonia oxidation, carbon monoxide oxidation at low temperatures, toluene removal, and wet peroxide oxidation of phenol [1–4]. Zeolite NaX after copper sorption also could be used as a catalyst [3, 4]. Cu-NaX zeolite can be prepared by sorption of copper ions on zeolite NaX from various copper solutions. In previous studies impact of a few parameters on copper sorption from nitrate solutions was studied [5–7]. Also the equilibrium of copper sorption from chloride and sulphate solution on NaX, synthesized from fly ash, was investigated [8]. In most studies all parameters but one are fixed at a certain level in order to determine the optimum conditions. This procedure requires a large number of experiments and that is why Taguchi method arises as an important tool for optimisation.

The Taguchi method uses a specifically designed orthogonal array consisting of controllable parameters and their variation levels in order to optimise experimental conditions. The advantage of Taguchi method is the assessment of optimal experimental conditions with the least number of experiments. This method has already been used for process optimization for heavy metal sorption [9-

13].

In this paper, along with process optimization using Taguchi method, equilibrium data for copper sorption on synthetic zeolite NaX using $\text{CuSO}_4 \times 5\text{H}_2\text{O}$, $\text{CuCl}_2 \times 2\text{H}_2\text{O}$ and $\text{C}_4\text{H}_6\text{CuO}_4 \times \text{H}_2\text{O}$ solutions were obtained.

The goals of this work were to: a) obtain optimum operating conditions to effectively use zeolite NaX for maximum copper removal; b) make a comparison of different adsorption models that can describe the sorption of Cu on zeolite NaX by using nonlinear regression analysis; c) find thermodynamic parameters such as ΔG^0 , ΔH^0 , and ΔS^0 ; d) compare obtained data to previous research in which copper nitrate solution was used.

MATERIALS AND METHODS

Materials

Zeolite NaX (Sigma-Aldrich) with $r\text{Si}/\text{Al} = 1.23$ was crushed and sieved to obtain particles smaller than 0.09 mm. Solutions containing Cu^{2+} were prepared by dissolving appropriate weights of $\text{Cu}(\text{NO}_3)_2 \times 3\text{H}_2\text{O}$; $\text{CuSO}_4 \times 5\text{H}_2\text{O}$, $\text{CuCl}_2 \times 2\text{H}_2\text{O}$ and $\text{C}_4\text{H}_6\text{CuO}_4 \times \text{H}_2\text{O}$ (Kemika), respectively, in distilled water. The initial concentrations were checked using a Perkin Elmer Lambda 25 UV/VIS spectrophotometer.

Taguchi's methodology

The Taguchi method applies an orthogonal array for experimental design and the signal to noise (S/N)

* To whom all correspondence should be sent:
E-mail: sandra@ktf-split.hr

ratio for quality assessment [9].

In this study experiments were planned according to Taguchi's L16 orthogonal array, which has 16 rows corresponding to the number of experiments and five columns corresponding to the controllable factors, Table 1. Anion type, concentration, impeller speed, time and temperature were chosen as controllable factors and their impact on the amount of copper retained into the zeolite phase was studied. As it can be seen from Table 2, each factor used had four testing conditions – represented by levels 1, 2, 3 and 4.

In this work larger-the-better quality characteristic was used [9]:

$$S / N_{LB} = -10 \log \frac{\sum_{i=1}^n \frac{1}{(y)_i}}{n} \quad (1)$$

Table 1. Design of the experiments.

Test	Factor				
	A	C	n	t	T
1	1	1	1	1	1
2	1	2	2	2	2
3	1	3	3	3	3
4	1	4	4	4	4
5	2	1	2	3	4
6	2	2	1	4	3
7	2	3	4	1	2
8	2	4	3	2	1
9	3	1	3	4	2
10	3	2	4	3	1
11	3	3	1	2	4
12	3	4	2	1	3
13	4	1	4	2	3
14	4	2	3	1	4
15	4	3	2	4	1
16	4	4	1	3	2

where S/N_{LB} represents signal-to-noise ratio; subscript LB represents larger-the-better; n is the number of repetitions (four) under the same experimental conditions and y is a measurement result, i.e. sorption efficiency.

The sorption efficiency is presented as $R\%$ and it was calculated by eq. (2):

$$R\% = \frac{(c_0 - c_e)}{c_0} \cdot 100 \quad (2)$$

The next step in Taguchi method is the calculation of the average S/N_{LB} ratio of each controllable factor at level i , denoted as S/N_{FL} , to determine the optimal conditions:

$$S / N_{FL} = \frac{\sum_{j=1}^{n_{Fi}} [(S / N_{LB})_i^F]_j}{n_{Fi}} \quad (3)$$

where S/N_{FL} represents S/N_{LB} ratio for factor F on the level i , the superscript j is the j -th appearance of the i -th level [9]. For the 16 tests, each level for every factor appears 4 times.

Experimental procedure – Taguchi

Experiments for Taguchi method were carried out in stirred batch reactors. Each batch reactor was filled with $V = 0.2 \text{ dm}^3$ of metal solution and $m = 1 \text{ g}$ of zeolite NaX. The mixture was agitated with a turbine impeller. After a defined time, Table 2, samples were taken from the suspensions. Prior to the analysis with the UV/Vis spectrophotometer, all samples were centrifuged and filtrated.

Isotherms and thermodynamic parameters

The purpose of the sorption isotherms is to reveal the relation between equilibrium concentration of the heavy metal in the bulk and on the zeolite [14]. Their application is very useful for understanding the sorption mechanisms and the surface properties and affinities of the sorbent [12].

Table 2. Controllable factors and associated levels.

Factor	Level 1	Level 2	Level 3	Level 4
Anion; A	Cl^-	SO_4^{2-}	CH_3COO^-	NO_3^-
Concentration; C (mmol dm^{-3})	3	6	9	12
Impeller speed; n (rpm)	0	60	120	180
Time; t (min)	15	30	45	60
Temperature (K)	300	302	304	306

A number of isotherm models can be found in the literature but three more frequently used, Langmuir, Freundlich and Sips isotherm (Table 3), were chosen in this study [15–17]. The amount of copper retained in the zeolite phase, q_e , was calculated by eq (4) as the difference between the amount present in the initial copper solution and that remaining in the solution after equilibrium [5]:

$$q_e = \frac{(c_0 - c_e) V}{m} \quad (4)$$

where c_0 and c_e are the initial and equilibrium concentrations of metal in solutions, V is the volume of solution, and m is the mass of the zeolite NaX.

Table 3. Isotherm models [15–17]

	Isotherm models	
Langmuir	$q_e = \frac{K c_e q_{max}}{(1 + K c_e)}$	(5)
Freundlich	$q_e = K c_e^\beta$	(6)
Sips	$q_e = \frac{K^\beta c_e^\beta q_{max}}{1 + K^\beta c_e^\beta}$	(7)

* q_{max} is maximum sorption capacity (mmol g⁻¹), K is constant, β is constant.

The amount of copper ions exchanged for all equilibrium experiments was used to obtain the thermodynamic parameters. These parameters were calculated using the following equations [5, 18]:

$$K_d = \frac{q_e}{c_e} \quad (8)$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R T} \quad (9)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (10)$$

where K_d is the distribution coefficient, T is temperature (K), R is gas constant (J mol⁻¹ K⁻¹), ΔH^0 is the molar enthalpy change (J mol⁻¹), ΔS^0 is the molar entropy change (J mol⁻¹ K⁻¹) and ΔG^0 is Gibbs free energy of change (J mol⁻¹).

Experimental procedure – Equilibrium

Equilibrium studies were performed in the same batch reactors as experiments for Taguchi analysis. The reactors were filled with $V = 0.2$ dm³ of metal solution and $m = 1$ g of zeolite NaX. The impeller speed for this investigation was fixed at 180 rpm and the time at 24 hours. The pH value was not buffered in order to compare results with previous research [5].

Prior to the analysis with the UV/Vis spectrophotometer, all samples were centrifuged and filtrated.

RESULTS AND DISCUSSION

Process optimization

One of the goals of this investigation was to find the optimum experimental conditions which provide the highest copper removal using larger-the-better quality characteristic. The results for S/N_{LB} ratios, calculated by Eq. (1), along with the sorption efficiency i.e. removal (%), the average removal (average of four repeated experiments denoted as R1, R2, R3 and R4) and standard deviation are shown in the Table 4. The results show that average removal is in the range from 32.081% to 100% and S/N_{LB} ratio in the range from 30.125 to 40.000 depending of the controllable factors.

Along with S/N_{FL} ratios of each controllable factor, range for every controllable factor was calculated (Table 5). Range was used to determine the impact of the controllable factors on the amount of copper removed from solution. It was calculated as the difference between highest and lowest signal-to-noise ratio of the factor. The largest range implied the most effective factor. In this study, according to range, concentration was found to be the most effective factor and it is followed by impeller speed and anion type whereas temperature and contact time were less effective.

From these S/N_{LB} ratios related S/N_{FL} (Eq. 3) ratios of each controllable factor were calculated and shown in Fig. 1 and Table 5. It could be seen that within increase of the concentration there are a significant decrease in efficiency of removal which may be explained by the saturation of available sorption sites [19].

The impact of impeller speed could be explained through the effect of film diffusion on the sorption, i.e. sorption kinetics since it is known that agitation speed affects the thickness of film around the particle, but, also, it could be that complete suspension is achieved only at maximum impeller speed used. The effect of anion, in the presence of acetate solution, might be explained by loss of sorption sites. It is found that in the presence of acetate ions dealumination and desilication of zeolite X occur and the increase in initial copper acetate concentration leads toward mild increase of Si/Al ratio [20]. When nitrate solution is used the Si/Al ratio remains unchanged and in the presence of chloride ions the Si/Al ratio after ion exchange is lower in comparison with pure NaX [21, 22].

It could be also observed that, for temperature, the difference for the S/N_{LB} ratios for the first three levels was only 0.154. Slightly larger impact of the temperature on the process was observed only for the highest temperature used. For the experimental

conditions used the final range for contact time was 0.193. This value indicates that the larger part of the copper is exchanged up to the first contact time level regardless of the slowest process, meaning that for high impeller speed equilibrium is reached fast and that for slower impeller speed, when the film diffusion affects the process, the differences between exchanges after 15 and 60 min are not significant.

Also, an evaluation of factor importance was made in statistical sense using sum of squares (SS), mean squares (MS) and percentage of contribution (pC), Table 5. Comparing these results with the range results it could be seen that the previously obtained order of significance is confirmed. So, every controllable factor, considering the obtained range, SS, MS and PC, was associated with rank. The factor which has a rank 1 should be utilized first and so on. From Table 5 the optimum operating

conditions could be evaluated and for the present study these conditions are: A2; C1; n4; t3; T4; that is solution of $\text{CuSO}_4 \times 5\text{H}_2\text{O}$, concentration 3 mmol dm^{-3} , 180 rpm impeller speed, 45 min contact time and temperature of 306 K.

Effect of process parameters on equilibrium

The effect of anion type was studied using chloride, sulphate and acetate solutions (Fig. 2). Data obtained in this work were also compared with data from a previous study and it is evident that the changes in the sorption capacity due to anion type are noticeable on the synthetic zeolite NaX while the sorption on NaX zeolite synthesized from coal fly ash showed negligible capacity differences for chloride and sulphate solutions (around 1%) [5, 8].

Table 4. Results of experimental part of Taguchi design, S/ N_{LB} ratios and standard deviation

Test	Removal (%)				Average removal (%)	STD	S/N _{LB} ratio
	R1	R2	R3	R4			
1	76.212	77.080	76.416	76.212	76.480	0.356	37.671
2	74.251	74.118	74.188	73.378	73.966	0.344	37.380
3	70.562	71.431	70.562	72.300	71.214	0.720	37.050
4	61.652	61.720	61.720	61.533	61.656	0.077	35.800
5	91.999	91.754	91.509	91.754	91.754	0.173	39.252
6	73.523	73.262	73.138	73.400	73.331	0.145	37.306
7	78.420	78.508	78.409	77.950	78.322	0.218	37.878
8	58.081	58.016	58.147	57.680	57.981	0.180	35.266
9	91.682	92.090	92.090	91.810	91.918	0.178	39.268
10	90.129	90.223	90.129	90.050	90.133	0.061	39.098
11	41.146	41.304	41.191	41.225	41.217	0.057	32.301
12	32.020	32.079	32.112	32.112	32.081	0.038	30.125
13	100.00	100.00	100.00	100.00	100.00	0.000	40.000
14	96.848	97.135	96.991	96.562	96.884	0.212	39.725
15	44.919	45.014	44.919	45.109	44.991	0.079	33.062
16	32.861	32.790	32.790	32.790	32.808	0.031	30.320

Table 5. S/N_{FL} ratios and contribution of each controllable factor.

Factor	A	C	N	t	T
Level 1	36.975	39.048	34.399	36.350	36.274
Level 2	37.425	38.377	34.955	36.237	36.211
Level 3	35.198	35.073	37.827	36.430	36.120
Level 4	35.777	32.877	38.194	36.359	36.770
Range	2.288	6.171	3.795	0.193	0.650
SS	12.813	100.308	45.330	0.077	1.014
MS	4.2711	33.4359	15.1099	0.0255	0.3381
pC (%)	8.03	62.87	24.41	0.050	0.64
Rank	3	1	2	5	4

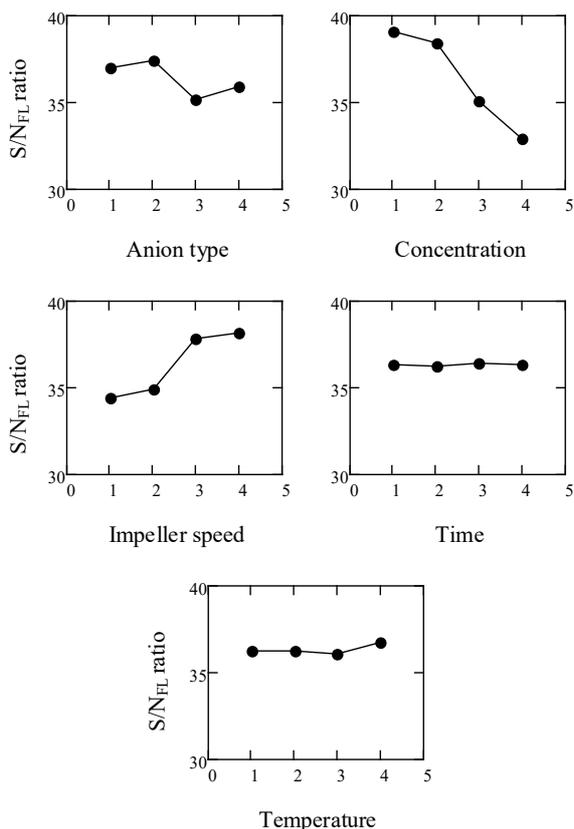


Figure 1. Response distribution of S/N_{FL} ratios.

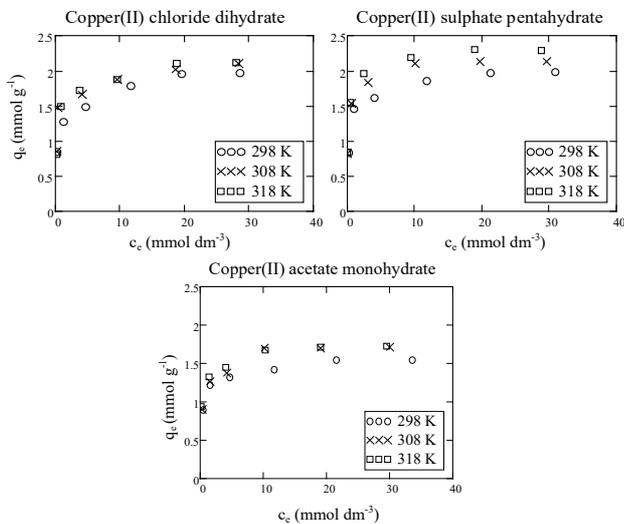


Figure 2. Experimental equilibrium data

Following sorption capacities were achieved for 298 K: for acetate solution 1.555 mmol g⁻¹, for nitrate solution 1.668 mmol g⁻¹, for chloride solution 1.975 mmol g⁻¹ and for sulphate solution 1.986 mmol g⁻¹. Kyziol-Komosińska *et al.* also found that the maximum sorption capacity was achieved for a sulphate solution [8]. These results are in correlation with the observation in the Process optimisation

chapter of this work.

Also it can be seen that for all anions used the copper sorption was favoured by an increase in temperature. This is probably a consequence of the reduced effective size of ions caused by a decrease of the ion hydration shell, which allows ions to diffuse in the inner part of the pore system of the zeolite [5]. This increase indicates the endothermic nature of the process.

Comparison of the isotherms

Values for experimental maximum sorption capacity, q_{max} , statistical comparison values, and the other parameters of all isotherms are shown in Table 6. For all the equilibrium experiments Freundlich or/and Sips isotherms work better than Langmuir isotherm. Like in the previous study [5] the isotherm models that take into account some sort of heterogeneity, seem to have an advantage over the Langmuir isotherm in explaining the equilibrium relations. Also, the β values calculated from the Freundlich and Sips isotherm were less than 1, confirming this statement.

In the study of sorption equilibrium from copper nitrate solution on zeolite NaX all isotherms showed the same trend in the changes of the parameter values [5]. In this study q_{max} , increases with increased temperature for all isotherms. For other parameters, in few calculations, there was a deviation from the trend. In the presence of chloride and sulphate ions β decreases as temperature increases while in acetate solution this trend for Freundlich isotherm was not observed. For the K constant in the presence of the sulphate ions for Langmuir isotherm and in the presence of acetate ions for Sips isotherm the trend was not observed. For all other calculations K increases with the temperature, like q_{max} , this indicates that the sorption was more favourable at the higher temperature.

Thermodynamic parameters

Calculated thermodynamic parameters along with the coefficient of determination are presented in Table 7. According to the obtained results the sorption process is endothermic ($\Delta H^0 > 0$) and spontaneous ($\Delta G^0 < 0$) regardless of anion type and temperature used. ΔG^0 becomes more negative with increasing temperature and less negative with increasing initial concentration. This shows that spontaneity grows with an increase in temperature and reduces with an increase in initial concentration, the same was observed for the sorption from a nitrate solution [5].

Table 6. Adsorption isotherm parameters and statistical comparison values.

Isotherm parameters for copper (II) chloride dihydrate				
Isotherm	Parameter	Temperature		
		298 K	308 K	318 K
	q_{\max} experimental (mmol g ⁻¹)	1.975	2.107	2.113
Langmuir	K	5.067	5.550	5.944
	q_{\max}	1.799	1.934	1.972
	r^2	0.790	0.905	0.915
	RMSE	0.228	0.167	0.164
	χ^2	0.144	0.072	0.068
Freundlich	K	1.214	1.335	1.373
	β	0.153	0.144	0.140
	r^2	0.991	0.953	0.940
	RMSE	0.047	0.117	0.132
	χ^2	5.58×10^{-3}	0.047	0.058
Sips	K	1.757	2.212	2.861
	q_{\max}	2.003	2.249	2.380
	β	0.659	0.570	0.454
	r^2	0.938	0.979	0.991
	RMSE	0.189	0.110	0.074
	χ^2	0.209	0.047	0.014
Isotherm parameters for copper (II) sulphate pentahydrate				
Isotherm	Parameter	Temperature		
		298 K	308 K	318 K
	q_{\max} experimental (mmol g ⁻¹)	1.986	2.131	2.295
Langmuir	K	7.892	7.676	31.375
	q_{\max}	1.858	2.054	2.103
	r^2	0.892	0.935	0.794
	RMSE	0.164	0.152	0.271
	χ^2	0.067	0.065	0.156
Freundlich	K	1.334	1.478	1.622
	β	0.128	0.127	0.120
	r^2	0.951	0.913	0.965
	RMSE	0.109	0.17	0.136
	χ^2	0.039	0.083	0.049
Sips	K	4.921	5.100	55.247
	q_{\max}	2.037	2.304	2.328
	β	0.694	0.535	0.490
	r^2	0.964	0.997	0.924
	RMSE	0.117	0.032	0.268
	χ^2	0.042	2.04×10^{-3}	0.180

Isotherm parameters for copper (II) acetate monohydrate				
Isotherm	Parameter	Temperature		
		298 K	308 K	318 K
	q_{\max} experimental (mmol g ⁻¹)	1.555	1.707	1.720
Langmuir	K	3.019	3.929	4.721
	q_{\max}	1.511	1.646	1.660
	r^2	0.944	0.849	0.839
	RMSE	0.066	0.143	0.110
	χ^2	0.013	0.059	0.034
Freundlich	K	1.085	1.161	1.213
	β	0.122	0.129	0.118
	r^2	0.932	0.938	0.967
	RMSE	0.072	0.091	0.075
	χ^2	0.019	0.022	0.002
Sips	K	3.157	3.878	3.112
	q_{\max}	1.673	1.822	2.014
	β	0.542	0.513	0.417
	r^2	0.982	0.953	0.981
	RMSE	0.038	0.086	0.034
	χ^2	4.29×10 ⁻³	0.019	2.99×10 ⁻³

Table 7. Thermodynamic parameters for the sorption of copper ions on zeolite NaX.

Thermodynamic parameters for copper (II) chloride dihydrate						
Concentration	ΔS^0	ΔH^0	ΔG^0_{298}	ΔG^0_{308}	ΔG^0_{318}	R^2
mmol dm ⁻³	kJ mol ⁻¹ K ⁻¹	kJ mol ⁻¹	kJ mol ⁻¹	kJ mol ⁻¹	kJ mol ⁻¹	
4.121	0.127	16.385	-21.598	-22.872	-24.147	0.823
8.121	0.133	22.267	-17.508	-18.843	-20.178	0.835
12.299	0.094	13.521	-14.372	15.307	16.244	0.975
18.933	0.074	9.581	-12.567	-13.309	-14.052	0.777
29.381	0.052	3.924	-11.443	-11.959	-12.474	0.953
38.843	0.047	3.352	-10.519	-10.984	-11.450	0.860

Thermodynamic parameters for copper (II) sulphate pentahydrate						
Concentration	ΔS^0	ΔH^0	ΔG^0_{298}	ΔG^0_{308}	ΔG^0_{318}	R^2
mmol dm ⁻³	kJ mol ⁻¹ K ⁻¹	kJ mol ⁻¹	kJ mol ⁻¹	kJ mol ⁻¹	kJ mol ⁻¹	
4.210	0.185	32.464	-22.620	-24.468	-26.317	0.924
8.311	0.150	26.532	-18.219	-19.721	-21.222	0.995
12.262	0.141	27.032	-14.888	-16.294	-17.770	0.996
20.500	0.092	14.890	-12.605	-13.527	-14.450	0.931
30.344	0.073	10.04	-11.241	-11.971	-12.700	0.997
38.843	0.062	8.209	-10.321	-10.943	-11.564	1.000

Thermodynamic parameters for copper (II) acetate monohydrate						
Concentration	ΔS^0	ΔH^0	ΔG^0_{298}	ΔG^0_{308}	ΔG^0_{318}	R^2
mmol dm ⁻³	kJ mol ⁻¹ K ⁻¹	kJ mol ⁻¹	kJ mol ⁻¹	kJ mol ⁻¹	kJ mol ⁻¹	
4.275	0.155	27.024	-19.057	-20.604	-22.149	0.858
7.888	0.081	7.643	-16.414	-17.220	-18.028	1
11.168	0.079	9.339	-13.994	-14.776	-15.559	1
18.733	0.078	11.296	-12.026	-12.809	-13.591	0.769
29.256	0.066	9.078	-10.669	-11.331	-11.994	0.814
38.537	0.063	9.088	-9.569	-10.195	-10.821	0.840

CONCLUSION

The objectives of this study were to investigate the optimum process parameters and equilibrium data of copper ions sorption on zeolite NaX in an agitated and temperature-controlled batch reactor. Impact of five process parameters was investigated in this study. The parameters were combined using Taguchi's design of experiments which led to 16 experiments. As a result, it could be concluded that concentration has a very significant role, followed by impeller speed and anion type while other process parameters are less significant.

All isotherms used can be fitted to the experimental equilibrium data but isotherms that took surface heterogeneity into account, Freundlich and Sips isotherm, showed better agreement with the experimental data.

Thermodynamic parameters indicate that copper sorption on zeolite NaX from all solutions used was a spontaneous and endothermic process.

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