Thermodynamics and Adsorption Isotherms of Copper Ions Removal from Solutions Using Synthetic Zeolite X

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The sorptive removal of copper ions from aqueous solutions using zeolite X has been studied by a batch technique. The impact of solute concentration and temperature on the process of sorption were examined. Using obtained experimental values thermodynamic parameters such as: ΔG^0, ΔH^0 and ΔS^0 were calculated.

Langmuir, Freundlich, Dubinin-Radushkevich and Sips isotherms were fitted to experimental data, and their goodness-of-fit were compared.

The isotherms that take into account some sort of heterogeneity were found to give a better fit to experimental data than Langmuir. An apparent free energy, calculated using Dubinin-Radushkevich isotherm, showed ion exchange type of spontaneous and endothermic sorption.

The results indicated that synthetic zeolite X can be used as an efficient ion exchange material for the removal of copper ions from wastewaters.

Key words:
Zeolite X, copper, isotherms, thermodynamics

Introduction

Copper is an essential trace mineral for the body's defence mechanisms, however, very large intakes of copper can cause liver and kidney damage, anaemia and even death. Drinking water that contains higher than normal levels of copper can lead to vomiting, diarrhoea, stomach cramps, and nausea. Therefore, copper ions represent a hazardous pollutant in wastewater and have to be removed.

Zeolites are an appropriate material for removing heavy metal ions from wastewater because of their relatively low price and harmlessness of their exchangeable ions.[1] Equilibrium uptake on zeolites has been studied for many cations, but relatively little is known about copper equilibrium in zeolite X.[1–7]

Zeolite X is a microporous, crystalline solid with a well defined three-dimensional silica-alumina structure and extra-framework exchangeable sodium cation. It is the synthetic form of naturally occurring aluminosilicate mineral faujasite. Its unit cell consists of 8 supercages, 8 sodalite cages and 16 hexagonal prisms. The supercages have a diameter of 1.3 nm, which are accessible through 12 member ring windows of 0.74 nm diameter tetrahedrally arranged around the supercage. This structure incorporates a high number of charge-compensating cations (sodium), which occupy a number of well-defined positions, limited by symmetry and charge conditions.[8] Zeolite X is widely used in different fields like heterogeneous catalysis, selective separation and adsorption, purification and drying, as well as ion exchange processes.[9–12]

Sorption isotherm data are measured to determine the capacity of sorbent, zeolite X, for metal ions. Various isotherm models, with two or three parameters, are available for modelling this equilibrium data.

In this study Langmuir, Freundlich and Dubinin-Radushkevich (two-parameter isotherm models) and Sips (three-parameter isotherm model) were used to fit the experimental equilibrium data.

Two-parameter isotherms are the most commonly used isotherms because of their simplicity and possibility of linearization. However, transformation of non-linear isotherm models to linear forms usually results in parameter estimation error.[13] Three-parameter isotherms have three adjustable parameters and cannot be estimated by linear regression. Therefore, the adjustable parameters of all isotherms were calculated using nonlinear regression analysis. The algorithm for nonlinear regression analysis was developed in MathCad.[14,15]

In order to describe the goodness-of-fit of the experimental data to the proposed models, the correlation coefficient (r^2), the residual root square error (RMSE) and chi-square test (χ^2) were also calculated and included in tables.[15,16,17]

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The goals of this work were to a) find thermodynamic parameters such as ΔG^0, ΔH^0 and ΔS^0, b) determine the type of sorption (physical or chemical) and c) make a comparison of different adsorption models that can describe the sorption of Cu on zeolite X by using nonlinear regression analysis.

Materials and methods

Zeolite X (NaX) (Sigma-Aldrich) with $r_{\mathrm{Si/Al}} = 1.23$ and BET specific surface area $s = 14.66$ m^2 g^{-1} was crushed and sieved to obtain a particle diameter, $d_{\mathrm{p}} = 0.06$–0.1 mm.

Solutions containing Cu^{2+} were prepared by dissolving the appropriate weight of $Cu(NO_3)_2 \cdot 3H_2O$ (Kemika) in distilled water. The initial concentrations in the range from $c_0 = 3.881$ mmol dm^{-3} to $c_0 = 39.983$ mmol dm^{-3} were checked by Perkin Elmer Lambada 201 UV/VIS spectrophotometer.

Equilibrium studies

Batch sorption studies of copper ions on zeolite X were performed at different temperatures ($T = 298$, 308 and 318 K) to obtain the equilibrium isotherms. The experiments took place in 0.35 dm^3 batch reactors. Each batch reactor was filled with $V = 0.2$ dm^3 of metal solution and $m = 1$ g of zeolite X. The mixture was agitated with a turbine impeller for 48 hours. The samples, taken from suspension in equilibrium, were filtrated and the concentration of the copper ions in the filtrate was determinate by UV/VIS spectrophotometer.

The pH value in all experiments was measured before and after equilibrium but solution was not buffered (in order to simulate the real situation in wastewater i.e. the variable pH). The pH ranged from 4.56 to 6.68 and there was no evidence of metal precipitation.

The amount of copper retained in the zeolite phase, q_e, was calculated by eq. (1) as the difference between the amounts present in the initial copper solution and that remaining in the solution after equilibrium[18]

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

where c_0 and c_e are the initial and equilibrium concentrations of metal in solutions (mmol dm^{-3}), V is the volume of solution (dm^3), and m is the mass of the zeolite X (g).

The distribution coefficient K_d was calculated using the following equation[18]

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

Results and discussion

Effect of initial concentration

It was observed that the amount of copper sorbed increase from $q_e = 0.761$ mmol g^{-1} to $q_e = 1.668$ mmol g^{-1}, $q_e = 0.761$ mmol g^{-1} to $q_e = 1.744$ mmol g^{-1} and $q_e = 0.761$ mmol g^{-1} to $q_e = 1.777$ mmol g^{-1} with an increase in the initial concentration from $c_0 = 3.881$ mmol dm^{-3} to $c_0 = 39.983$ mmol dm^{-3} for $T = 298$ K, 308 K and 318 K, respectively. However, the efficiency of removal decreased with the increased initial concentration, which may be explained by the saturation of accessible exchangeable sites in zeolite.[19]

Effect of temperature

Temperature is an important factor influencing heavy metal sorption on zeolite. In most cases, sorption increases with increasing temperature.[4,16] The equilibrium uptake of copper by zeolite X was also affected by temperature. As can be seen from Fig. 1, which shows the equilibrium sorption capacity, q_e, as a function of equilibrium concentration of copper in solution, c_e, for various temperatures, the highest temperature, $T = 318$ K, provides the best sorption of copper on zeolite X. An increase in equilibrium content with increasing temperature is a consequence of the reduced effective size of ions caused by a decrease of the ion hydration shell. This effect allows ions to diffuse in the inner part of the pore system of the zeolite.[20,21] This increase indicates the endothermic nature of the process.[4]

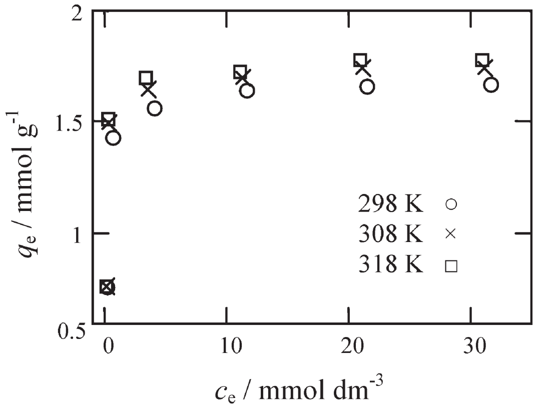

Fig. 1 – *Experimental equilibrium data*

Thermodynamic parameters

The thermodynamic parameters, ΔH^0 and ΔS^0, were calculated from the slope and intercept of a plot of $\ln(K_d)$ against $1/T$, Fig. 2, using equation:[22]

$$\ln(K_d) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{3}$$

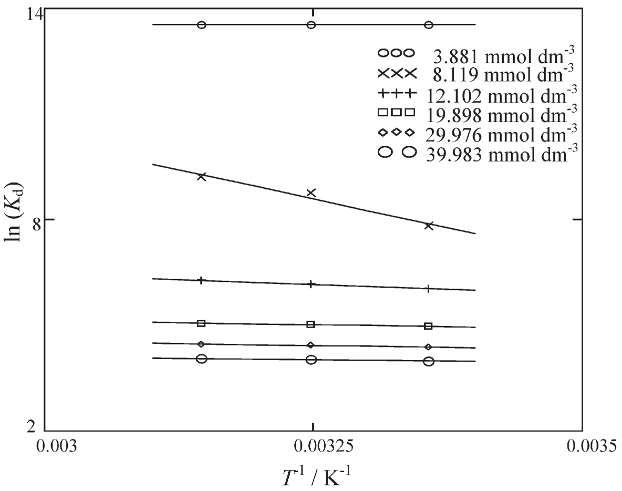

Fig. 2 – *Estimation of thermodynamic parameters (eq. (3))*

where T is temperature (K), R is gas constant (J mol^{-1} K^{-1}), ΔH^0 is the molar enthalpy change (J mol^{-1}) and ΔS^0 is the molar entropy change (J mol^{-1} K^{-1}).

ΔG^0 was calculated using the following equation:[23]

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0 \tag{4}$$

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 Table 1.

The positive value of ΔH^0 shows that the sorption process is endothermic. The endothermicity of the sorption process may be due to the removal of water molecules from the solid/solution interface and from the sorbing cation.[24] The ΔG^0 is negative and decreases with increasing temperature, implying that the reaction is spontaneous and favoured by higher temperature. The ΔG^0 increases with increasing initial concentration of copper ions, indicating reduction in spontaneity with an increase in the amount of copper ions sorbed by zeolite: the same was observed by Singh *et al.* on WBAP.[24]

Adsorption isotherms

Two-parameter isotherm models

Langmuir isotherm (L) – The Langmuir isotherm was developed originally to describe the gas-solid phase adsorption, but its use was extended to liquid-solid adsorption.[17] The basic assumptions of the Langmuir isotherm are: surface is homogeneous, adsorption on surface is localized (atoms or molecules are adsorbed at definite, localized site), each site can accommodate only one molecule or atom.[25]

The Langmuir isotherm is defined as:

$$q_e = K\,c_e q_{\max}/(1 + K\,c_e) \tag{5}$$

where q_e is equilibrium amount of copper adsorbed per gram of zeolite (mmol g^{-1}), c_e is equilibrium concentration of metal in solution (mmol dm^{-3}), K is Langmuir constant related to the affinity of binding sites (dm^3 mmol^{-1}), and $q_{\max}$ is also Langmuir constant, maximum sorption capacity, which represents monolayer coverage of sorbent by the sorbate (mmol g^{-1}).

The essential features of the Langmuir isotherm may be expressed in terms of the dimensionless constant separation factor R_L which is defined by the following relationship:

$$R_L = \frac{1}{1 + K\,c_0} \tag{6}$$

The range of R_L values, as well as values of K, $q_{\max}$ and r^2, RMSE and χ^2 for all temperatures examined are presented in Table 2. The values of R_L are in the range of 0–1 which indicates favourable sorption. Also, the values of R_L indicate that sorption is more favourable at higher temperatures.[26] Langmuir constants $q_{\max}$ and K increase with temperature, indi-

Table 1 – *Thermodynamic parameters for the sorption of copper ions on zeolite X*

Concentration	ΔS^0 kJ mol^{-1} K^{-1}	ΔH^0 kJ mol^{-1}	ΔG^0_{298} kJ mol^{-1}	ΔG^0_{308} kJ mol^{-1}	ΔG^0_{318} kJ mol^{-1}	R^2
3.881 mmol dm^{-3}	0.112	$3.8 \cdot 10^{-11}$	–33.55	–34.67	–35.8	0.989
8.119 mmol dm^{-3}	0.249	54.784	–19.52	–22.01	–24.5	0.968
12.102 mmol dm^{-3}	0.08	9.099	–14.97	–15.77	–16.58	1
19.898 mmol dm^{-3}	0.052	3.437	–12.059	–12.579	–13.099	0.985
29.976 mmol dm^{-3}	0.049	3.350	–10.828	–11.304	–11.78	0.996
39.983 mmol dm^{-3}	0.042	2.882	–9.850	–10.227	–10.704	0.971

Table 2 – *Adsorption isotherm constants and statistical comparison values*

Two-parameter isotherms				
isotherm	parameter	temperature		
		298 K	308 K	318 K
Langmuir	K	10.618	28.104	40.903
	$q_{\max}$	1.652	1.714	1.750
	R_L range; c_0 = 3.881–39.983 mmol dm^{-3}	0.015–0.003	0.006–0.001	0.004–0.0008
	r^2	0.915	0.880	0.984
	RMSE	0.034	0.041	0.036
	χ^2	0.002	0.003	0.001
Freundlich	K	1.471	1.571	1.613
	β	0.04	0.032	0.031
	r^2	0.973	0.992	0.987
	RMSE	0.019	0.011	0.018
	χ^2	0.001	0.001	0.001
Dubinin-Radushkevich	$q_{\max}$	1.597	1.682	1.786
	E	25.398	25.65	26.29
	r^2	0.947	0.963	0.988
	RMSE	0.154	0.079	0.062
	χ^2	0.06	0.015	0.001
Sips	K	54.616	131.7	211.1
	$q_{\max}$	1.734	1.762	1.793
	β	0.536	0.482	0.472
	r^2	0.987	0.956	0.987
	RMSE	0.004	0.027	0.022
	χ^2	0.044	0.001	0.001

cating that the sorption capacity and intensity of sorption are enhanced at higher temperatures.

Freundlich isotherm (F) – Adsorbents that follow the Freundlich isotherm equation are assumed to have a heterogeneous surface consisting of sites with different adsorption potentials, and each type of site is assumed to adsorb molecules.[27] The Freundlich isotherm may be represented by the following equation:[27,28]

$$q_e = K\, c_e^{\beta} \tag{7}$$

K and β are Freundlich isotherm constants. K is roughly an indicator of sorption capacity and β of sorption favourability.[27]

Calculated data for this isotherm are reported in Table 2. The values of β are in the range of 0–1 which indicates favourable sorption.[27] Freundlich constant β decreases and K increases with increased temperature, indicating that sorption is more favourable at higher temperatures. The highest r^2 values are obtained for this isotherm.

Dubinin-Radushkevich isotherm (DR) – The experimental data were also modelled by the Dubinin-Radushkevich (6) isotherm to determine the type of sorption (physical or chemical).[22]

Dubinin-Radushkevich isotherm may be represented by the following equation:[19]

$$q_e = q_{\max} \exp\left(-\frac{(R\,T \ln(1+1/c_e))^2}{2\,E^2}\right) \tag{8}$$

where $q_{\max}$ is the maximum sorption capacity and E is apparent free energy (kJ mol^{-1}). The magnitude of E is related to the reaction mechanism. The value of E is smaller than 8 kJ mol^{-1} for physical sorption and higher than 8 kJ mol^{-1} for chemical sorption (ion exchange).[4,22]

Calculated data for this isotherm are reported in Table 2. The values of E estimated from the Dubinin-Radushkevich isotherm range from 25.398 to 26.29 kJ mol^{-1}. Calculated energy values are comparable to that of general ion exchange or chemisorptions that could reach the value of 40 kJ mol^{-1}.[29] The positive value of E indicates the endothermic nature of the process.

All two-parameter isotherms are presented in Fig. 3.

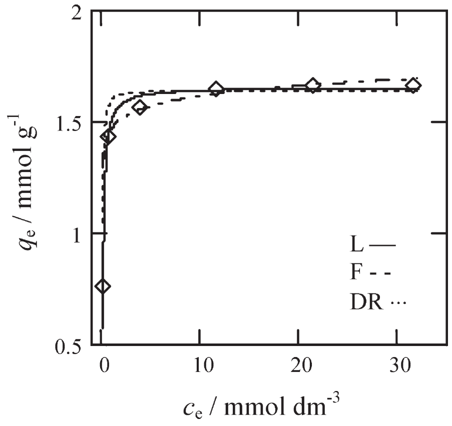

Fig. 3 – *Two-parameter isotherms of copper ions sorbed on zeolite X at T = 298 K*

Three-parameter isotherm

Sips isotherm (S) – Sips isotherm is a combination of the Langmuir and Freundlich isotherms. At low sorbate concentration it reduces to the Freundlich isotherm, while at high sorbate concentration it predicts a monolayer sorption capacity characteristic of the Langmuir isotherm.[19] Sips isotherm may be represented by the following equation:

$$q_e = \frac{(K\,c_e)^{\beta}\,q_{\max}}{1+(K\,c_e)^{\beta}} \tag{9}$$

where K is constant, $q_{\max}$ represents maximum sorption capacity (mmol g^{-1}) and β is degree of heterogeneity.

The data calculated by Sips isotherm are reported in Table 2. Degree of heterogeneity, β, decreases with increased temperature and its values are less than one. This fact indicates that some kind of heterogeneity in the surface or pore of zeolite X will play a role in the metal ion sorption. Unlike β, Sips constants $q_{\max}$ and K increase with temperature.

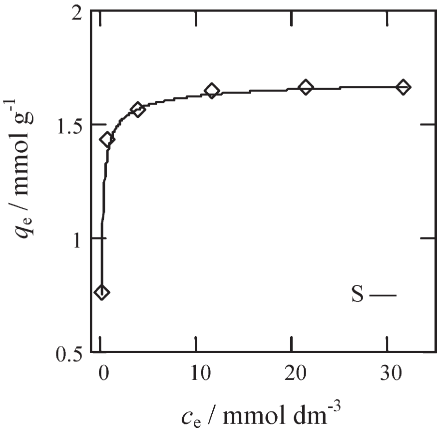

Fig. 4 – *Sips isotherm of copper ions sorbed on zeolite X at T = 298 K*

Sips isotherm is presented in Fig. 4.

Comparison of the isotherms

The most commonly used isotherm, Langmuir isotherm, does not show good agreement with the experimental data. 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. The same observation was made by El Kamash *et al.*[4] on synthetic zeolite A.

Heterogeneity may be explained by location of exchangeable cations in zeolite X. The exchangeable cations are mainly located on specific sites of the zeolite X framework (six extra framework crystallographic sites SI, SI', SII, SII', SIII. SIII'). These sites differ in position, number of coordinating oxygen atoms, and are energetically more or less favourable.[5,8,30]

All the isotherms show the same trend for values of R_L and β. These values decrease with increased temperature, and all these values are less than one, indicating favourable sorption and confirming heterogeneity of zeolite X. The decrease of β with increased temperature contributes the annotation that zeolite X is heterogeneous, even "more" heterogeneous with increased temperature (for examined process), because copper ions, as a result of reduced effective size, can accommodate sites that are free of copper ions at lower temperature.

Unfortunately, in our study, the determination of copper ions distribution in the zeolite X was not possible.

All the isotherms show the same trend for values $q_{\max}$. The values $q_{\max}$ increase with temperature. The explanation for this behaviour is the same as for the *Effect of temperature*.

According to values of r^2, RMSE and χ^2 Sips isotherm gives the most accurate values of maximum sorption capacity, 1.734 mmol g^{-1}, 1.762 mmol g^{-1} and 1.793 mmol g^{-1} for $T = 298$ K, 308 K and 318 K, respectively. In comparison, for $T = 298$ K, with the other sorbent: beer yeast – 0.009 mmol g^{-1};[31] clinoptilolite – 0.2 mmol g^{-1};[15] ($T = 296$ K) sugar beet pulp – 119.43 mg g^{-1};[32] zeolite X has higher sorption capacity almost as zeolite A – 2.25 mmol g^{-1}.[33]

Interesting property of zeolites, as sorbents for heavy metals, are in their harmful disposal as substitute additive to cement, this is an additional benefit in zeolite X use in environmental protection.[34]

Conclusions

The objectives of this study were to investigate the equilibrium data of copper ions removal from aqueous solutions using zeolite X in an agitated and temperature-controlled batch reactor. The experimental and calculated results led to the following main conclusions:

Sorption of copper ions on the zeolite X increases with temperature.

Langmuir, Freundlich, Dubinin-Radushkevich and Sips isotherms can be fitted to the experimental equilibrium data.

The isotherms that took surface heterogeneity into account (Freundlich, Dubinin-Radushkevich and Sips) explained the data better than the Langmuir isotherm.

Thermodynamic and Dubinin-Radushkevich parameters indicate that copper sorption on zeolite X was a spontaneous and endothermic process controlled by the ion-exchange mechanism.

These results show that zeolite X may be used for removal of copper ions.

List of symbols

d_p – particle diameter, mm

q_e – amount of copper sorbed per gram of zeolite, mmol g^{-1}

c_0 – initial concentration of metal in solutions, mmol dm^{-3}

c_e – equilibrium concentration of metal in solutions, mmol dm^{-3}

V – volume, dm^3

m – mass of zeolite X, g

K_d – distribution coefficient, $dm^3\ g^{-1}$

R – gas constant, J $mol^{-1}\ K^{-1}$

s – specific surface area, $m^2\ g^{-1}$

T – temperature, K

ΔG^0 – Gibbs free energy of change, J mol^{-1}

ΔH^0 – molar enthalpy change, J mol^{-1}

ΔS^0 – molar entropy change, J $mol^{-1}\ K^{-1}$

R^2 – determination coefficient

$q_{\max}$ – maximum sorption capacity, mmol g^{-1}

K – constant

β – constant

R_L – separation factor

r – mole ratio

r^2 – correlation coefficient

χ^2 – chi-square test

E – apparent free energy, kJ mol^{-1}

RMSE – residual root square error

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