KINETICS OF COPPER ION-EXCHANGE ON ZEOLITE NaX

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INTRODUCTION

The presence of copper in wastewater of several industries has contributed in no small way to water pollution. Treatment of wastewater containing copper could be achieved by chemical precipitation, ultrafiltration, adsorption and ion exchange. Copper ion exchange is an attractive option because of the basic simplicity of the application.[1]

Zeolite 13X 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 and 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. [2]

The objective of this study is to examine the kinetic of copper ion exchange on zeolite 13X with the effect of temperature. Four kinetics models were used to test experimental rate data: Lagergren pseudo-first-order kinetic model, Ho pseudo-second-order kinetic model, Elovich model and Ritchie model.

EXPERIMENTAL

Zeolite 13X (NaX) (Sigma-Aldrich) with $r_{Si/Al} = 1.23$ was crushed and sieved to obtain a particle diameter of 0.1-0.125 mm. Solutions containing Cu^{2+} were prepared by dissolving the appropriate amount of $Cu(NO_3)_2{\cdot}3H_2O$ (Kemika) in distilled water. The initial concentrations of 11.593 mmol dm^{-3} were checked by UV/VIS spectrophotometer.

Kinetic studies of copper ions exchange on zeolite 13X were performed at different temperatures: 298, 308 and 318 K. The experiments took place in 0.35 dm^3 batch reactors. Each batch reactor was filled with 0.2 dm^3 of metal solution and 1 g of zeolite 13X. The mixture was agitated with a turbine impeller at constant agitation speed of 180 rpm. A fixed volume (0.0015 dm^3) was taken out from the system at certain contact time. The taken samples were filtrated; the concentration of the copper ions in the filtrate was determined by UV/Vis spectrophotometer.

The amount of copper retained in the zeolite phase, 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 [3]

$$q_t = \frac{(c_0 - c_t)\ V}{m} \qquad (1)$$

where c_0 is the initial concentration of metal in solution (mmol/dm^3), c_t is concentration of metal in solution at time t (mmol/dm^3), V is the volume of solution (dm^3), and m is the mass of the zeolite X (g).

RESULTS AND DISCUSSION

Fig. 1 shows the variation of the amounts of Cu^{2+} ions exchanged at the different time, for the fixed initial ion concentration of 11.593 mmol/dm^3 and at different ion exchange temperatures of 298, 308 and 318 K. The experimental data showed that the amount of the exchanged Cu^{2+} increases with the increase in temperature. This is expected since at higher temperature copper ions are moving faster and ions become smaller because solvation is reduced. This reduction effect allows ions to diffuse in the inner part of the pore system of the zeolite.[4,5]

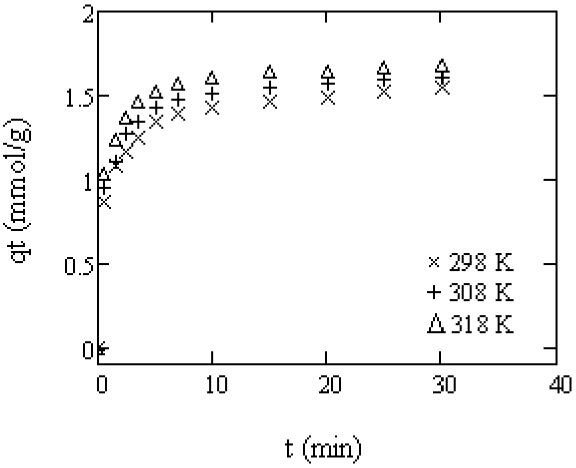

Figure 1. Effect of contact time on the amount of Cu^{2+} on zeolite NaX at different temperatures.

In order to describe the changes in the exchange of metal ions with time various kinetic models have been used to test experimental data. These models are: Lagergren model, Ho model, Elovich model and Ritchie model, Table 1.[6]

Table 1. Kinetic models

Model	Equation	No.
Lagergren	$q_t = q_e(1-e^{-k_1 t})$	(2)
Ho	$q_t = \dfrac{t}{1/k_{2h}q_e^2 + t/q_e}$	(3)
Elovich	$q_t = \dfrac{1}{b}\ln(1+abt)$	(4)
Ritchie	$q_t = q_e\left\{1-\left[\dfrac{1}{1+k_{2r}t}\right]\right\}$	(5)

In these equations q_t is amount of copper ions exchanged after time t, q_e is amount of copper ions exchanged at equilibrium, t is time, k_1 is the Lagergren rate constant, k_{2h} is the Ho rate constant, a and b are constants in Elovich model, k2r is the Ritchie rate constant

The parameters, Table 2., of all kinetic models 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 coefficient (R^2) was also calculated and included in table 2.

Table 2. The calculated parameters of the Lagergren, Ho, Elovich and Ritchie models for Cu^{2+} ions exchanged onto zeolite 13X for various temperatures.

Model	Parameter	Temperature (K)		
		298 K	308 K	318 K
Lagergren	q_e (mmol/g)	1.406	1.483	1.561
	k_1 (1/min)	1.312	1.364	1.692
	R^2	0.944	0.927	0.947
Ho	q_e (mmol/g)	1.501	1.579	1.651
	k_{2h} (g/mmol min)	1.351	1.371	1.624
	R^2	0.977	0.972	0.976
Elovich	a	87.621	129.009	479.559
	b	6.136	6.066	6.638
	R^2	0.944	0.960	0.919
Ritchie	q_e (mmol/g)	1.501	1.586	1.651
	k_{2r} (g/mmol min)	2.028	2.109	2.680
	R^2	0.984	0.982	0.990

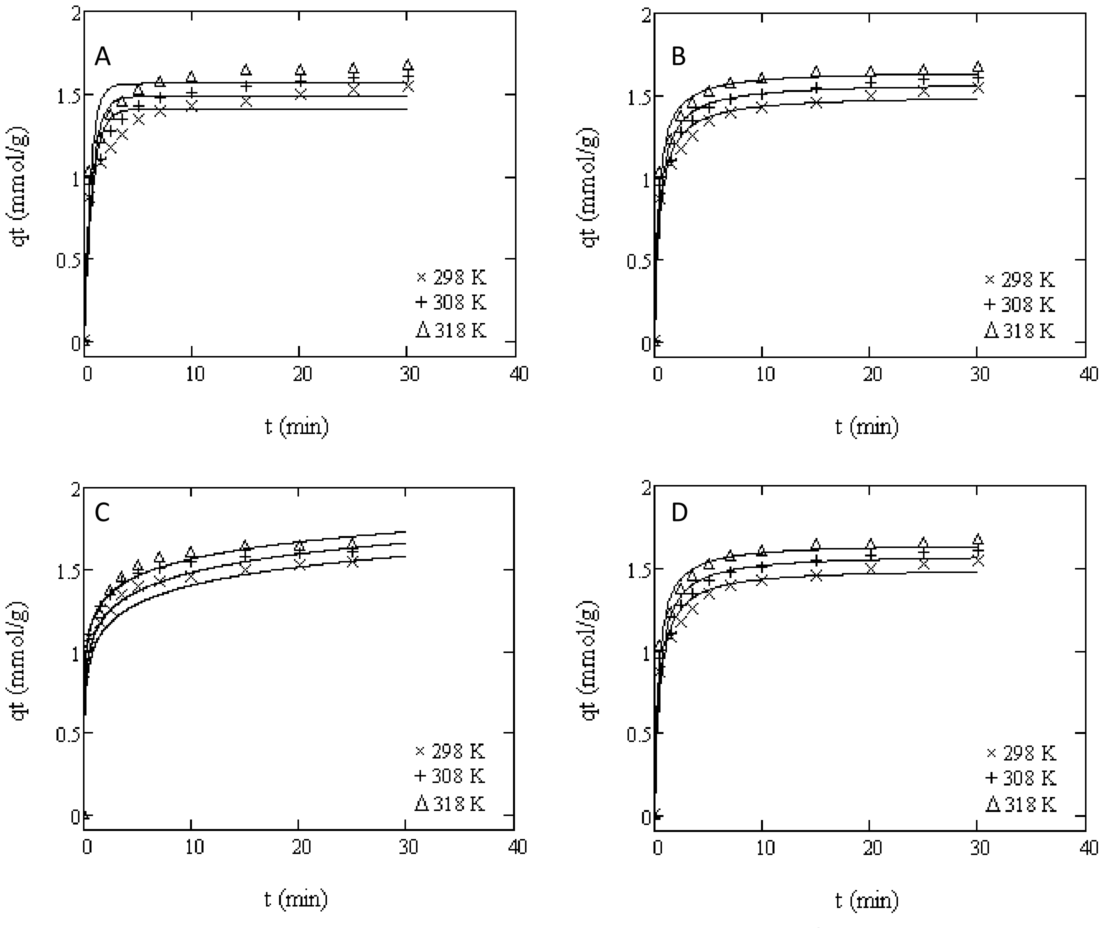

Figure 2. A) Lagergren B) Ho C) Elovich D) Ritchie plots for Cu^{2+} ions exchanged **onto** zeolite 13X for various temperatures.

From the table 1., it can be seen that the values of the rate constants and equilibrium capacity were increased with increase in temperature, for all models. These results indicated that, for the range of process variables investigated, the exchange kinetic parameters were dependent on temperature.

The correlation coefficients of the Ritchie model were higher than in all other models indicating that the Ritchie model best describes the exchange of Cu^{2+} on zeolite 13X. Other models were not as effective as the Ritchie model in describing the kinetic data, with the correlation coefficients obtained lower than those obtained from the Ritchie model.

Ritchie model is based on a general second-order reaction mechanism for heterogeneous sorption process. Therefore the rate of the ion exchange was suggested to be controlled by a second order mechanism.

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.[2,7]

CONCLUSION

The objectives of this study were to investigate the kinetics data of copper ions exchange from aqueous solutions using zeolite 13X in an agitated and temperature controlled batch reactor. The experimental and calculated results led to the following main conclusions:

Exchange of copper ions on the zeolite 13X increases with temperature.

Lagergren, Ho, Elovich and Ritchie models can be fitted to the experimental kinetics data. Kinetic plots and correlation coefficients confirm applicability of the Ritchie model on the exchange of Cu^{2+} on zeolite 13X.

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KINETIKE IZMJENA IONA BAKRA NA ZEOLITU NaX

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SAŽETAK

U ovom radu provedena su kinetička ispitivanja na sustavu bakar-zeolit NaX u neprotočnom kotlastom reaktoru uz miješanje.

Ispitivanja su vršena na način da se 0.2 dm^3 otopine bakrovog (II) nitrata, koncentracije 11.593 mmol dm^{-3} miješa sa 1 g zeolita NaX, različitih veličina čestica brzinom od 180 okr min^{-1} pri različitim temperaturama (298, 308 i 318 K). U određenim vremenskim intervalima uzimaju se uzorci volumena 0.0015 dm^3 koji se centrifugiraju i filtriraju, da bi se koncentracija bakrovih (II) iona u filtratu mogla odrediti UV/Vis spektrofotometrom.

Na temelju eksperimentalnih podataka, dobivenih pri različitim temperaturama, ustanovljeno je kako je temperatura bitan čimbenik koji utječe na ionsku izmjenu teškog metala na zeolitu. U većini slučajeva ionska izmjena raste sa povećanjem temperature. Vezanje bakra na zeolitu također je pospješeno porastom temperature. Kod najviše temperature (318 K) postiže se najuspješnija ionska izmjena bakra na zeolitu NaX.

Analiza kinetičkih podataka, dobivenih u eksperimentalnom dijelu rada, provedena je metodom nelinearne regresije za četiri različita kinetička modela: Lagergrenovu jednadžbu pseudo-prvog reda (LFO), Jednadžbu pseudo-drugog reda (PSO), Elovichev model (E) i Ritchiev model (R)

Na temelju dobivenih eksperimentalnih rezultata, njihovom usporedbom sa modelima, te usporedbom prikladnosti modela može se zaključiti kako je Ritchiev model najprikladniji.

Ključne riječi*:* zeolit X, ionska izmjena, kinetika