

# Modeling batch kinetics of copper ions sorption using synthetic zeolite NaX

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## ABSTRACT

The sorptive removal of copper ions from aqueous solutions using zeolite NaX has been studied by a batch technique. The influences of solute concentration, temperature and particle size on the sorption process were examined. Several kinetic models were used to test the experimental rate data and to examine the controlling mechanism of the sorption process. Lagergren pseudo-first order, the pseudo-second-order (Ho) and Ritchie second-order models were analyzed using nonlinear regression technique while Weber–Morris model was analyzed using linear least squares method.

The obtained results indicated that synthetic zeolite NaX could be used as an efficient material for the sorption of copper ions.

A kinetic study has shown that the best fit is achieved when the Ritchie model was applied and that sorption did not involve film or intraparticle diffusion, i.e., they were not the rate controlling steps. The activation energy was found to be 12 kJ/mol in the present study.

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## 1. Introduction

The increasing levels of toxic metals that are discharged to the environment as industrial wastes represent a serious threat to human health, living resources and ecological systems [1].

The presence of copper in wastewater of several industries has contributed in no small way to water pollution. Although the copper is an essential element, acute doses cause metabolic disorders.

Treatment of wastewater containing copper could be achieved by chemical precipitation, ultrafiltration and sorption [2]. Copper sorption is an attractive option because of the basic simplicity of the application.

For sorption applications, zeolites were often reported to exhibit high sorption capacity for divalent sorbates. The 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 [3]. The Biškup et al. used zeolite A as an ion exchange material which also holds a great potential for the sorption of the copper, cadmium and nickel [4].

The overall sorption process may be controlled by film diffusion, intraparticle diffusion or sorption on the surface. In order to gain a better understanding of the sorption process, various kinetic models should be used to test the experimental data.

Zeolite NaX 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 six extra framework crystallographic sites i.e. cationic sites (SI, SI', SII, SII', SIII, SIII') limited by symmetry and charge conditions [5].

The goals of this work were to study the impact of concentration, temperature and particle size on removal of copper ions from aqueous solutions using zeolite NaX, and to examine the temperature and concentration effects on kinetic of copper sorption. Also, general predictive model was proposed to describe the relationship between initial concentration and sorption of the metal.

## 2. Materials and methods

### 2.1. Materials

Zeolite NaX (Sigma–Aldrich) with  $r_{Si/Al} = 1.23$  was crushed and sieved to obtain a particle diameter of: 0.1–0.125, 0.071–0.09, 0.04–0.063 mm. The ASAP 2000 (Micromeritics) was used to determine the BET specific surface area. The obtained results are: 573.956, 576.804 and 576.995 m<sup>2</sup>/g for 0.1–0.125, 0.071–0.09 and 0.04–0.063 mm, respectively.

Solutions containing copper ions were prepared by dissolving the appropriate amount of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (Kemika) in distilled water. The initial concentrations in the range from 3.881 to 11.593 mmol/L were checked by PerkinElmer Lambda 201 UV/Vis

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### Nomenclature

$c_0$	initial concentration of metal in solution (mmol/L)
$c_t$	concentration of metal in solution at time $t$ (mmol/L)
$k_1$	Lagergren rate constant (1/min)
$k_2$	rate constant of the pseudo-second-order kinetic model (g/mmol min).
$k_d$	intraparticle diffusion rate constant (mmol/g min <sup>0.5</sup> )
$m$	mass of the zeolite NaX (g)
$q_e$	amount of copper ions sorbed at equilibrium (equilibrium capacity) (mmol/g)
$q_t$	amount of copper ions sorbed after time $t$ (mmol/g)
$T$	temperature (K)
$t$	time (min)
$V$	volume of solution (L)
$\theta$	surface coverage at time $t$

spectrophotometer. Starting concentrations of the solutions were adjusted on the basis of preliminary experiments so that the concentrations in the solutions are suitable for measuring by UV/Vis spectrophotometer.

### 2.2. Batch experiments

The sorption of copper ions on zeolite NaX was studied in 0.35 L batch reactors. Each batch reactor was filled with 0.2 L of metal solution and 1 g of zeolite NaX. The mixture was agitated with a turbine impeller at 180 rpm. Different parameters were tested, Table 1, and the solutions were analyzed at the certain contact time.

A fixed volume (0.0015 L) was taken out from the system and the concentration of the copper ions in the filtrate was determined by UV/Vis spectrophotometer.

Preliminary investigations on the rate of uptake indicated that the processes are quite rapid and equilibrium is reached in about 30 min. Sampling intervals are a consequence of sorption rate; in the beginning sampling were done more often and how the sorption slows down so the frequency of sampling decreases.

In all experiments pH values were 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 was in the range from 4.99 to 6.68.

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:

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

where  $c_0$  is the initial concentration of metal in solution (mmol/L),  $c_t$  is concentration of metal in solution at time  $t$  (mmol/L),  $V$  is the volume of solution (L), and  $m$  is the mass of the zeolite NaX (g) [6].

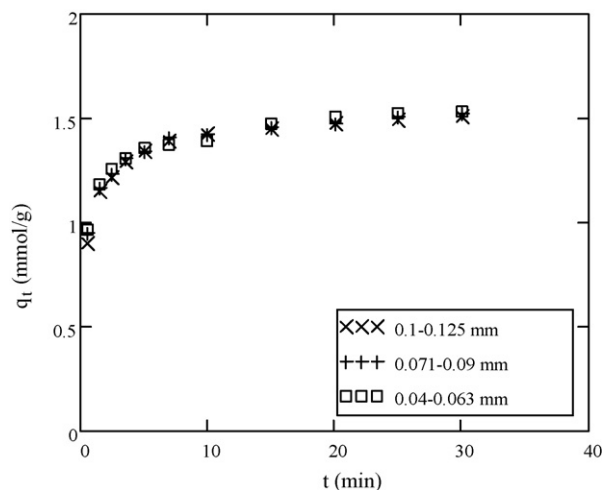
### 2.3. Kinetic studies

Experimental data obtained in batch experiments for various initial concentrations and temperatures were used in kinetics modeling.

**Table 1**

The various parameters tested on the sorption of copper ions on zeolite.

Parameter tested	Particle size (mm)	Concentration (mmol/L)	Temperature (K)
Particle size	0.1–0.125, 0.071–0.09, 0.04–0.063	11.593	298
Concentration	0.071–0.09	3.881, 5.661, 7.595, 9.559, 11.593	298
Temperature	0.071–0.09	11.593	298, 308, 318



**Fig. 1.** Effect of contact time on the amount of copper ions on zeolite NaX at different particle sizes.

Also, additional experiments were performed using three different initial concentrations of: 4.644, 10.746 and 18.996 mmol/L to verify data obtained by proposed generalized predictive model.

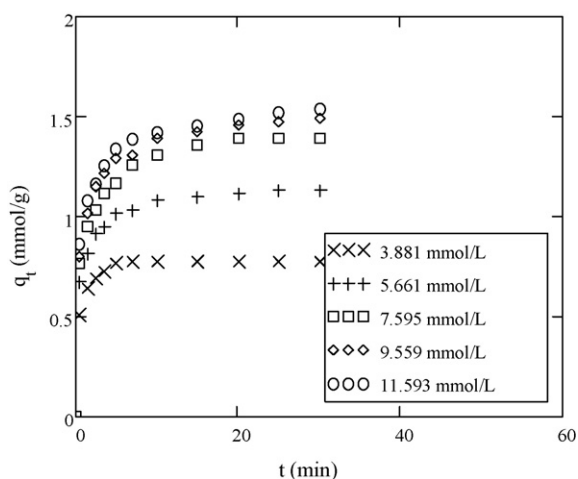
## 3. Results and discussion

### 3.1. Effect of particle size

Fig. 1 shows the amount of copper ions removed at the different time, for the fixed initial ion concentration of 11.593 mmol/L and temperature of 298 K at different zeolite particle size. It is clear from the figure that copper sorption is not dependent on the particle size. Should be mentioned that the total surface area of the zeolite takes into account external surface area as well as its internal area. When reducing the particle size only the total external surface area is increased. In porous material, the contribution of this area to the total surface area is very slight, for this reason, the total surface area increases very slightly as well. Expressed through the BET specific surface area the increase is from 573.956 to 576.955 m<sup>2</sup>/g when particle was reduced from 0.1–0.125 to 0.04–0.063 mm. Also, the sorption capacity does not depend on the particle size due to the location of cationic sites in the channels and cavities of zeolite particle [7].

### 3.2. Effect of initial concentration and contact time

The effect of the initial concentration was studied at five different initial concentrations and constant temperature and particle size of 298 K and 0.071–0.09 mm, respectively. The results of this study are shown in Fig. 2. It is clear that the copper sorption capacity increased with increasing of initial ion concentration. This is the result of increase in the driving force, which is concentration of the solution [8]. Also, the time for achieving equilibrium was higher for the higher initial concentrations. As mentioned in Section 1 in zeolite NaX there are six different cationic sites. Taking into account the position of individual cationic sites for different times to establish equilibrium the following explanation can be



**Fig. 2.** Effect of contact time on the amount of copper ions on zeolite NaX at different initial concentrations.

offered: copper sorption on more accessible cationic sites should be fast and at the experimental research for which lower initial concentrations were used the reaction was fast. The longer reaction time should be required for “entry” of hydrated copper ions into less accessible cationic sites which is why the increase in concentration, and the number of copper ions, increases the time for achieving equilibrium.

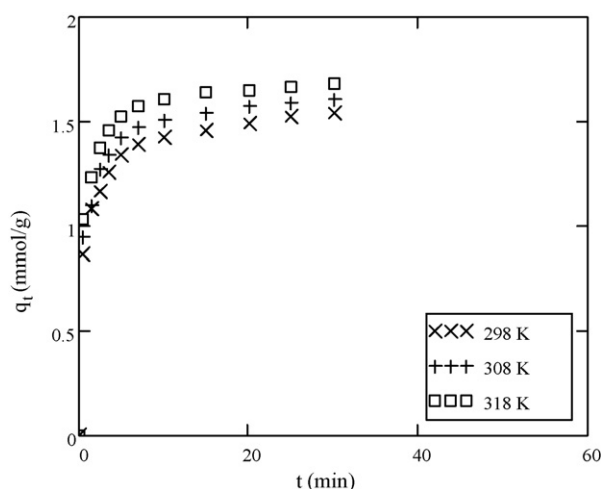
The shape of the curves in Fig. 2 shows that amount of copper ion sorbed sharply increases with the time in the initial stage and then gradually increases until the equilibrium is reached. The reason of the variation in the extent of sorption could be the fact that initially all sites on the surface of the zeolite NaX were vacant and the copper concentration gradient high. As the time elapses the extent of copper sorption decreases significantly because the number of vacant sites as well as concentration gradient decreases [9].

### 3.3. Effect of temperature

Fig. 3 shows the variation of the amounts of copper ions exchanged at the different time, for the fixed initial ion concentration of 11.593 mmol/L and particle size of 0.071–0.09 mm at different sorption temperatures of 298, 308 and 318 K. The experimental data showed that the amount of the sorbed copper ions 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 [10,11].

### 3.4. Kinetic models

In order to describe the changes in the sorption of metal ions with time various kinetic models have been used to test experimental data. These models can be divided into two main types: diffusion based models and reaction based models [12].



**Fig. 3.** Effect of contact time on the amount of copper ions on zeolite NaX at different temperatures.

#### 3.4.1. Diffusion based model

Generally, a process is diffusion controlled if its rate is dependent upon the rate at which components diffuse through the film or particle. The possibility of film or intraparticle diffusion was explored by using the Weber–Morris model [13]:

$$q_t = I + k_d t^{1/2} \quad (2)$$

where  $k_d$  is the intraparticle diffusion rate constant ( $\text{mmol/g min}^{0.5}$ ),  $t$  is time (min) and  $I$  is the intercept of the vertical axis. This intercept could be employed to examine the effect of diffusion mechanisms of the solute i.e. film and intraparticle diffusion.

If the Weber–Morris plot of  $q_t$  vs.  $t^{0.5}$  gives a straight line through the origin,  $I = 0$ , intraparticle diffusion is considered as the rate limiting step, while, at  $I > 0$  both film and intraparticle diffusion are considered as rate limiting steps.

The regression lines were obtained by the least squares method and shown in Table 2 along with determination coefficient,  $r^2$ . As can be seen from the values of  $r^2$  the Weber–Morris model does not fit well to the experimental data indicating that the overall sorption process is not controlled by diffusion.

#### 3.4.2. Reaction based models

The parameters of all reaction based model 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 also calculated and included into the tables.

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

The Lagergren pseudo-first-order model is expressed as [14]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

**Table 2**

The regression lines and intraparticle diffusion rate constants of the Weber–Morris model for copper ions sorbed on zeolite NaX for various concentrations.

Model	Parameter	Concentration (mmol/L)				
		3.881	5.661	7.595	9.559	11.593
Weber–Morris	Regression line	$0.324t^{1/2}$	$0.382t^{1/2}$	$0.4t^{1/2}$	$0.436t^{1/2}$	$0.461t^{1/2}$
	$k_d$ ( $\text{mmol/g min}^{0.5}$ )	0.324	0.382	0.400	0.436	0.461
	$r^2$	0.485	0.360	0.270	0.272	0.220

**Table 3**

The calculated parameters of the Lagergren, Ho and Ritchie models for copper ions sorbed on zeolite NaX for various concentrations.

Model	Parameter	Concentration (mmol/L)				
		3.881	5.661	7.595	9.559	11.593
Lagergren pseudo-first order	$q_e$ experimental (mmol/g)	0.779	1.132	1.390	1.491	1.559
	$q_e$ (mmol/g)	0.579	1.052	1.243	1.363	1.443
	$k_1$ (1/min)	1.956	1.509	1.337	1.271	1.229
	$R^2$	0.977	0.934	0.918	0.922	0.943
Ho pseudo-second order	$q_e$ (mmol/g)	0.791	1.119	1.329	1.456	1.539
	$k_{2h}$ (g/mmol min)	4.308	2.080	1.526	1.356	1.271
	$R^2$	0.997	0.982	0.978	0.984	0.990
Ritchie second-order model	$q_e$ (mmol/g)	0.791	1.119	1.329	1.456	1.539
	$k_{2r}$ (g/mmol min)	3.408	2.327	2.029	1.974	1.956
	$R^2$	0.999	0.986	0.989	0.984	0.990

**Table 4**

The calculated parameters of the Lagergren, Ho and Ritchie models for copper ions sorbed on zeolite NaX for various temperatures.

Model	Parameter	Temperature (K)		
		298	308	318
Lagergren pseudo-first order	$q_e$ experimental (mmol/g)	1.543	1.610	1.687
	$q_e$ (mmol/g)	1.443	1.483	1.561
	$k_1$ (1/min)	1.229	1.364	1.692
	$R^2$	0.943	0.927	0.947
Ho pseudo-second order	$q_e$ (mmol/g)	1.539	1.586	1.651
	$k_{2h}$ (g/mmol min)	1.271	1.371	1.624
	$R^2$	0.990	0.972	0.976
Ritchie second-order model	$q_e$ (mmol/g)	1.539	1.586	1.651
	$k_{2r}$ (g/mmol min)	1.956	2.109	2.680
	$R^2$	0.990	0.982	0.990

where  $q_t$  is amount of copper ions sorbed after time  $t$  (mmol/g),  $q_e$  is amount of copper ions sorbed at equilibrium (equilibrium capacity) (mmol/g),  $t$  is time (min),  $k_1$  is the Lagergren rate constant (1/min).

By integrating, Eq. (3), for the boundary conditions  $q_t = 0$  at  $t = 0$  and  $q_t = q_e$  at  $t = t$ , gives:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (4)$$

The rate constants,  $k_1$ , were found to be in the range of 1.956–1.229 1/min for the initial copper concentration values of 3.881–11.593 mmol/L (Table 3) that is 1.229–1.692 1/min for the temperature values of 298–318 K (Table 4). The data presented in these tables also demonstrate that order of rate constant decreased with initial concentration and increased with temperature. Equilibrium sorption capacity,  $q_e$ , increased with both initial concentration and temperature. But, as can be seen from these tables and Fig. 4, although the correlation coefficients of the plots have values higher than 0.9, the  $q_e$  (calculated) values are not in agreement with  $q_e$

(experimental) for all studied sorption processes. So, it could suggest that the sorption of copper ions onto zeolite NaX is not a first-order reaction.

The pseudo-second-order kinetic model of Ho is based on the adsorption capacity of the solid phase.

The Ho pseudo-second-order kinetic model is usually presented as [15,16]:

$$\frac{dq_t}{dt} = k_{2h}(q_e - q_t)^2 \quad (5)$$

where  $k_{2h}$  is the rate constant of the pseudo-second-order kinetic model (g/mmol min).

After integration, with the boundary conditions  $q_t = 0$  at  $t = 0$  and  $q_t = q_e$  at  $t = t$ , Eq. (5) becomes:

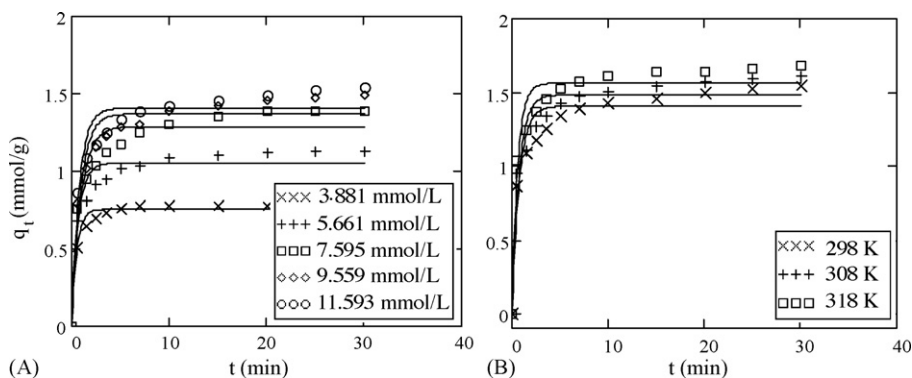
$$q_t = \frac{t}{1/k_{2h}q_e^2 + t/q_e} \quad (6)$$

The same trend, as for Lagergren pseudo-first order, in correlation between rate constant and initial concentration (temperature), as well as between equilibrium sorption capacity and initial concentration (temperature) was observed (Tables 3 and 4), but the values were higher (only the constants calculated for 318 K did not follow this trend).

The correlation coefficients  $R^2$ , for this model have higher values than for pseudo-first (>0.972), and its calculated equilibrium sorption capacity ( $q_e$ ) are more consistent with the experimental data (Fig. 5). These results indicated that the pseudo-second-order sorption mechanism is predominant i.e. that copper ion occupied two cationic sites. The literature review has shown the same observation [6,9,13,15,16].

As Ritchie has a different idea on the pseudo-second-order kinetics the Ritchie model is also applied on experimental data [17].

The Ritchie mode was developed originally to describe the kinetics of gas–solid phase adsorption, but its use was extended

**Fig. 4.** Lagergren plots for copper ions sorption on zeolite NaX for (A) various initial concentrations and (B) various temperatures.

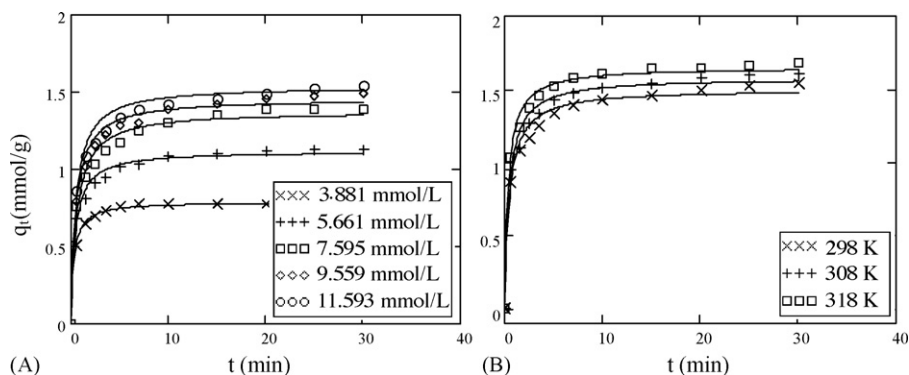


Fig. 5. Ho plots for copper ions sorption on zeolite NaX for (A) various initial concentrations and (B) various temperatures.

to liquid-solid sorption [18–20]. The basic assumptions of Ritchie second-order model are: one sorbate is sorbed onto two reaction sites, rate of sorption depends solely on the fraction of the sites which are unoccupied at time  $t$  [18,20].

The Ritchie rate equation is expressed as [18]:

$$\frac{d\theta}{dt} = k_r(1 - \theta)^n \quad (7)$$

where  $\theta = q_t/q_e$ ,  $k_r$  is the rate constant of the Ritchie model.

After integration, for the boundary conditions  $\theta = \theta_0$  at  $t = t_0$  and  $\theta = \theta$  at  $t = t$ , Eq. (7) becomes:

$$q_t = q_e \left\{ 1 - \left[ \frac{1}{\beta_n + k_r(n-1)(t-t_0)} \right]^{1/(n-1)} \right\} \quad (8)$$

where  $\beta_n = 1 - \theta_0$ .

If  $t_0 = 0$ ,  $\theta_0 = 0$  and  $n = 2$  equation becomes:

$$q_t = q_e \left\{ 1 - \left[ \frac{1}{1 + k_{2r}t} \right] \right\} \quad (9)$$

where  $k_{2r}$  is the rate constant of the Ritchie-second-order kinetic model (g/mmol min).

The correlation coefficients  $R^2$  for this model have the highest values ( $>0.982$ ) and its calculated equilibrium sorption capacities ( $q_e$ ) are, not only consistent with the experimental data but have the same values as those calculated by Ho second-order model. As, also, can be seen from Tables 3 and 4 rate constant decreases with the concentration and increases with the temperature indicating that in a system with lower initial concentration equilibrium is established faster as well as at the higher temperatures. Ritchie second-order model is based on a general second-order reaction mechanism for sorption on heterogeneous solid phase [19]. These results have again suggested that the copper ions sorption is controlled by second-order mechanism. Assessment of validity of Ritchie model is shown in Fig. 6.

Heterogeneity of the zeolite particle may be explained by location of exchangeable cations in zeolite X. The exchangeable cations are mainly located on specific cationic sites, of the zeolite X framework. These cationic sites differ in position, number of coordinating oxygen atoms, and are energetically more or less favorable [5,21].

The energy of activation,  $E_a$ , was determined from the linear form of Arrhenius equation (least squares method) and was found to be 12 kJ/mol.

$$\ln(k_{2r}) = \ln(k_0) - \frac{E_a}{RT} \quad (10)$$

The positive value of activation energy suggests that rise in temperature favors the sorption and that sorption process is an endothermic process.

#### 3.4.3. Predicting the sorption kinetics

Further, thanks to the existence of trend, in order to predict the sorption of copper ions on zeolite NaX for the any initial concentration and at any time of contact the relationships between  $q_e$  (mmol/g) and  $c_0$  (mmol/L) as well as  $k_{2r}$  (g/mmol min) and  $c_0$  (mmol/L) were found.

Equilibrium capacity increased with an increase in initial concentration as shown in Fig. 7 and gave a relationship in form:

$$q_e = \frac{-12.218}{c_0^2 + 0.129} + 1.57 \quad (11)$$

While the relationship between rate constant and initial concentration is shown in Fig. 8 and expressed by following equation:

$$k_{2r} = \frac{25.332}{c_0} + 1.666 \quad (12)$$

Substituting the values of  $q_e$  and  $k_{2r}$  from the equations above in the Ritchie-second-order kinetic model (Eq. (9)) the relationship

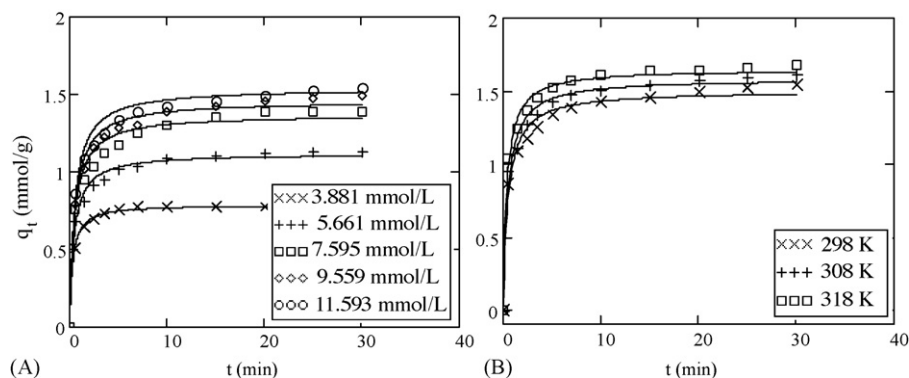


Fig. 6. Ritchie plots for copper ions sorption on zeolite NaX for (A) various initial concentrations and (B) various temperatures.

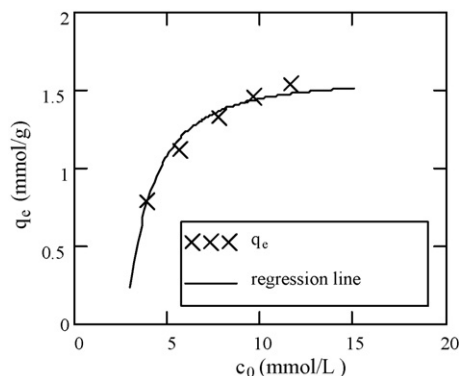


Fig. 7. Equilibrium capacity vs. initial concentration.

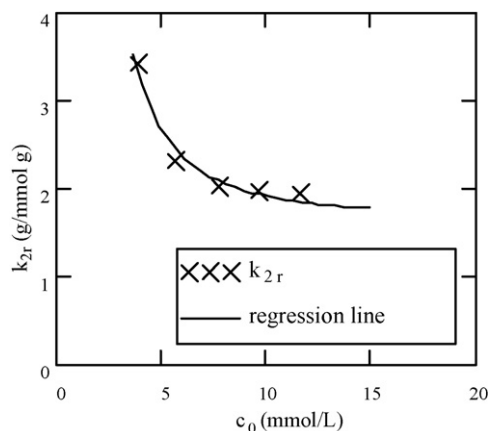


Fig. 8. Ritchie second-order rate constant vs. initial concentration.

between  $q_t$ ,  $c_0$  and  $t$  can be represented as:

$$q_t = \left( \frac{-12.218}{c_0^2 + 0.129} + 1.57 \right) \left[ 1 - \frac{1}{1 + ((25.332/c_0^2) + 1.666)t} \right] \quad (13)$$

This generalized predictive model was tested with three different concentrations. As can be seen from Fig. 9 the experimental data show a good agreement with the data obtained by a generalized predictive model. Obtained values of  $R^2$  were 0.989, 0.993, 0.980 for 4.644, 10.746, 18.996 mmol/L, respectively. So Eq. (13) can be used to calculate the amount of the copper ions sorbed, on tem-

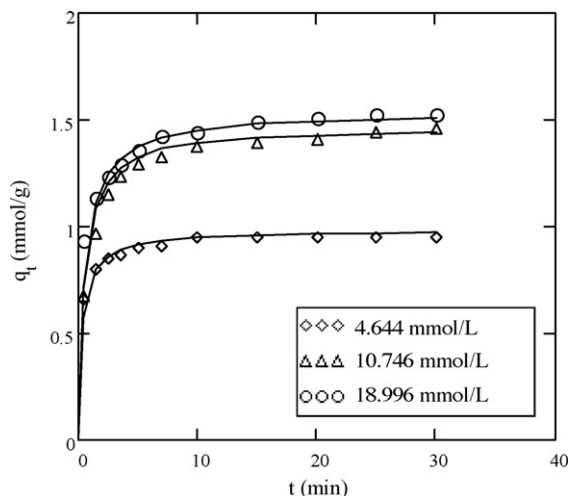


Fig. 9. Assessment of the validity of the generalized predictive model (Eq. (13)).

perature of 298 K, for different initial concentrations at any reaction time [22].

#### 4. Conclusion

Synthetic zeolite NaX was tested for the removal of copper ions from aqueous solutions. Obtained experimental and calculated results led to the following main conclusions.

Sorption of copper ions on the zeolite NaX is affected by temperature and initial concentration while the impact of zeolite particle size is negligible.

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 experimental kinetics data was analyzed using diffusion and reaction based kinetic models. The correlation coefficients of the Ritchie model were higher than in all other models indicating that the Ritchie model best describes the exchange of copper ions on zeolite NaX.

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