

## Kinetics and thermodynamics study of copper ions removal by natural clinoptilolite

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The process of removal of copper ions by means of clinoptilolite type natural zeolite has been studied as a function of the particle size and temperature. Results indicate that increase in temperature and decrease of particle size improves the removal of copper from aqueous solutions. The parabolic diffusion model is well described process in all examined range of time and it shows that the calculated diffusion coefficient increases with temperature. This increase is more visible at higher particle sizes what assume diffusion through zeolite particle as main mass transfer mechanism. The film diffusion model provides calculation of initial sorption rate ( $k'$ ) and dimensionless parameter proportional to the diffusion film thickness ( $x_f$ ), in relation of particle size and temperature. Diffusion from the surface of zeolite particles through the micro and macro pores is well described with homogenous diffusion model, where change of the calculated overall rate constant is observed at  $\approx 60$  min of the process. This indicates the change of mass transfer rate through porous zeolite particle.

The activation energy ( $E_a$ ), activation enthalpy ( $\Delta H$ ), activation entropy ( $\Delta S$ ) and free energy of activation ( $\Delta G$ ) have been calculated based on kinetic data. These thermodynamic parameters characterize process as diffusion dependent, weakly endothermic and nonspontaneous, where structural changes in structure of natural zeolite particle are not observed.

**Keywords:** Clinoptilolite, Copper, Diffusion, Kinetic models, Thermodynamic parameters

There has been an increasing interest in studying natural zeolites in the last three decades, particularly because of their role in reducing water pollution by metal ions. Natural zeolites are aluminosilicates that, due to isomorphous replacement of silicon by aluminium, behave as cation exchangers and are capable for removal of metal ions from water and wastewater. The low price of zeolite and the fact that exchangeable cations (sodium, potassium, calcium and magnesium) from zeolite are not toxic make zeolite an attractive alternative material for removal of undesirable toxic ions from wastewater. Heavy metals are not biodegradable and tend to accumulate as metalloorganic complexes in living organisms, which increase their concentration in biological cycles. One of the most dangerous ways of contamination is the continuous release of liquid effluents with relatively high concentrations, primarily of Cr, Pb, Ni, Zn, Cu and Cd ions. Many of these metals are essential for life in trace concentrations, but higher concentrations have various toxic effects. Copper ions are found in wastewater of many industrial processes, such as

electroplating, metal industry, production of pigments, paper, fibres, paints, photographic industry, and pesticide production. After wastewater treatment with natural zeolite, purified water may be reused in the production process or discharged into environment<sup>1-5</sup>.

Studies of the kinetics of ion exchange in systems natural zeolite-solutions of heavy metal ions are aimed at establishing the mechanisms of the process as well as theoretical prediction of the kinetic law of the exchange process. Ion exchange kinetics is governed by the processes in solution, at the solid-liquid interface and within the micro and macro pores of zeolitic particle. Each of these processes could be rate-limiting step in depending on particle size and concentration, temperature and mixing rate in solution<sup>6</sup>.

The overall mass transfer rate is governed by the slowest process, that is in conditions of higher mixing rate usually diffusion through the particle. However, it is not the only one that controls the speed and mechanism of the overall process. The entire course of exchange involves a number of consecutive mechanisms, each for a given time interval. The

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sequence and type of mechanism depends on the zeolite structure, particle diameter, non-uniformity of particle sizes, type and hydrated radius of the ion being exchanged, temperature, pH, and the time needed for equilibration<sup>7-10</sup>.

Our preliminary researches were pointed to good binding of metal ions to natural zeolites, however taking account of a number of factors: concentration and type of heavy metal ion, equilibrium time, grain size and chemical treatment of natural zeolite<sup>1,3,11,12</sup>. Many authors studied effect of temperature on kinetic of the heavy metal removal in order to improve practical application of these processes<sup>10,13-15</sup>. The purpose of this study is to determine the effect of particle size and temperature on removal efficiency of Cu ions onto natural zeolite from Croatian deposit Donje Jesenje.

## Materials and Methods

### Experimental procedure

All chemicals used in this study were analytical grade reagents of the highest quality available, including p.a. reagents and high purity ion-free water. The heavy metal solutions have been prepared by dissolving of salt  $\text{CuCl}_2$  in ion-free water. The exact concentrations of Cu ions were verified by atomic adsorption spectroscopy (Perkin Elmer Atomic Absorption Spectrometer, Model 3110). Atomic absorption standards for cation analyses were obtained from Merck.

The tested natural zeolite-clinoptilolite originates from the mine Donje Jesenje, Croatia, where it was ground and separated into three fractions of the following particle sizes: less than 0.5 mm, 0.5-2.0 mm, and 2.0-5.0 mm. Chemical composition of natural zeolite was determined by the standard chemical analysis of aluminosilicates and results in mass % are  $\text{SiO}_2$ -64.93;  $\text{Al}_2\text{O}_3$ -13.39;  $\text{Fe}_2\text{O}_3$ -2.07;  $\text{Na}_2\text{O}$ -2.40;  $\text{K}_2\text{O}$ -1.43;  $\text{CaO}$ -2.00;  $\text{MgO}$ -1.08; loss by ignition at  $1000^\circ\text{C}$ -9.63.

X-ray diffraction (XRD) analysis was performed by PHILIPS PW 1010 diffractometric system ( $\text{CuK}\alpha$  radiation,  $2\theta = 3-60^\circ$ ) on natural sample to confirm the mineral identity of the zeolites. The zeolite obtained from a deposit in Donje Jesenje was stated to be of 40-50% purity on clinoptilolite, while the impurities included illite, feldspar, quartz and muscovite<sup>1,11</sup>.

The porous characteristics of the sample were measured using the BET-method with Accelerated Surface Area and Porosimetry System (ASAP 2000).

The following parameters were determined<sup>1,11</sup>: BET surface area was  $12.055 \text{ m}^2\text{g}^{-1}$ , micropore area  $1.919 \text{ m}^2\text{g}^{-1}$ , micropore volume  $0.813 \text{ mm}^3\text{g}^{-1}$ , average pore diameter was  $118.525 \text{ \AA}$  and adsorption surface area of pores between  $17.0$  and  $3000.0 \text{ \AA}$  was  $0.036 \text{ cm}^3\text{g}^{-1}$ .

Investigation of ion exchange kinetics of Cu ions were performed by shaking of 1.0000 g of zeolitic sample of different particle sizes (<0.5 mm, 0.5-2.0 mm, and 2.0 – 5.0 mm) with 25.00 mL of Cu ion solution of initial mass concentration,  $\gamma_0=1000 \text{ mgL}^{-1}$ , during a time interval between 5 and 1440 min at different temperatures of 20, 30, 40 and  $50^\circ\text{C}$ . After shaking, the solid phase was separated from the solution by filtration, and the concentration of Cu was determined in the liquid phase using AAS.

### Kinetic diffusion models for heterogeneous systems

During the exchange process, increased concentration of outgoing and ingoing ions included in ion exchange process forms a film on the surface of the zeolitic particle that becomes resistance to the mass transfer. Diffusion through this film may be described using the diffusion model, which is expressed by equation<sup>16</sup>:

$$F = x_i + k' t^{1/2} \quad \dots (1)$$

where

$$F = q_t/q_\infty \quad \dots (2)$$

$F$  = fraction of ions bound at time  $t$ , dimensionless

$q_t$  = mass of ions bounded per gram of zeolite in time  $t$ ,  $\text{mg g}^{-1}$

$q_\infty$  = mass of ions bounded per gram of zeolite at equilibrium,  $\text{mg g}^{-1}$

$x_i$  = parameter that is proportional to the diffusion film thickness, dimensionless

$k'$  = initial sorption rate,  $\text{min}^{-1/2}$

$t$  = time, min.

Diffusion of ions from particle surface to macro and micro pores in literature is usually described using the second Fick's law. If the concentration of ingoing exchangeable ions is constant from the surface to the centre of the zeolitic particle and diffusion rate and radial diffusion coefficient are constant during ion exchange process, the homogeneous diffusion model can describe the intraparticle diffusion<sup>10,17-21</sup>.

$$F = 1 - \sum_{i=0}^{\infty} a_i \exp(-b_i t / \tau) \quad \dots (3)$$

where

$$\tau = r^2 / D \quad \dots (4)$$

$D$  = diffusion coefficient,  $\text{cm}^2\text{min}^{-1}$

$r$  = particle radius, cm

$i$  = number of experimental points.

$a_i$  and  $b_i$  are parameters that depend on the shape of the zeolitic particle, and  $\tau$  is the time needed for diffusion of the ingoing exchangeable ion from the particle surface to the exchangeable site in the particle. For sphere particles, Eq. (3) can be rewritten in a form that reduces at large  $t$  to:

$$t \rightarrow t_{\infty} \quad \ln(1 - F) = \ln\left(\frac{6}{\pi^2}\right) - \frac{\pi^2 D}{r^2} t \quad \dots (5)$$

The diffusion coefficient may be calculated from the slope of the linear part of curve given by Eq. (5).

The parabolic diffusion model is often used to indicate that diffusion controlled phenomena are rate-limiting. It was originally derived from the radial diffusion in a cylinder, where the concentration of metal ion on the particle surface is constant. This model also assumes that the quantity of ion bound throughout the cylinder is uniform and can be expressed as<sup>6,8,21</sup>:

$$F = \frac{4}{\pi^{1/2}} \left(\frac{Dt}{r^2}\right)^{1/2} - \frac{Dt}{r^2} - \frac{1}{3\pi^{1/2}} \left(\frac{Dt}{r^2}\right)^{3/2} \quad \dots (6)$$

For small values of time  $t$  the third term may be ignored, and from the slope of the linear relationship  $F/t$  versus  $1/t^{1/2}$ , the diffusion coefficient may be calculated by:

$$\frac{1}{t} F = \frac{4}{\pi^{1/2}} \left(\frac{D}{r^2}\right)^{1/2} \frac{1}{t^{1/2}} - \frac{D}{r^2} \quad \dots (7)$$

### Results and Discussion

Based on the experimental results, the amount of copper bound has been calculated for different particle sizes (Fig. 1) and different temperatures at selected solid-liquid contact times.

The ion exchange of copper shown in Fig. 1 is rapid at initial times for all particle sizes, with prolonged slower uptake up to equilibrium. At lower particle size, the equilibrium is established at approx. 500 min, while at higher particle sizes time needed for equilibration is slightly prolonged. This indicates diffusion as controlling mechanism particularly at higher particle sizes. From Fig. 1, it is clear that quantity of copper bound per mass of zeolite is higher for lower zeolite particles. This can be explained by higher specific surface available for sorption of exchangeable ions. Increasing of the temperature increases the quantity of copper bound for all particle sizes; while the sequence of particle sizes for each examined temperature remains constant, e.g.,  $F_{(<0.5 \text{ mm})} > F_{(0.5-2.0 \text{ mm})} > F_{(2.0-5.0 \text{ mm})}$ . Maximum sorption levels for copper ions obtained in present experiments

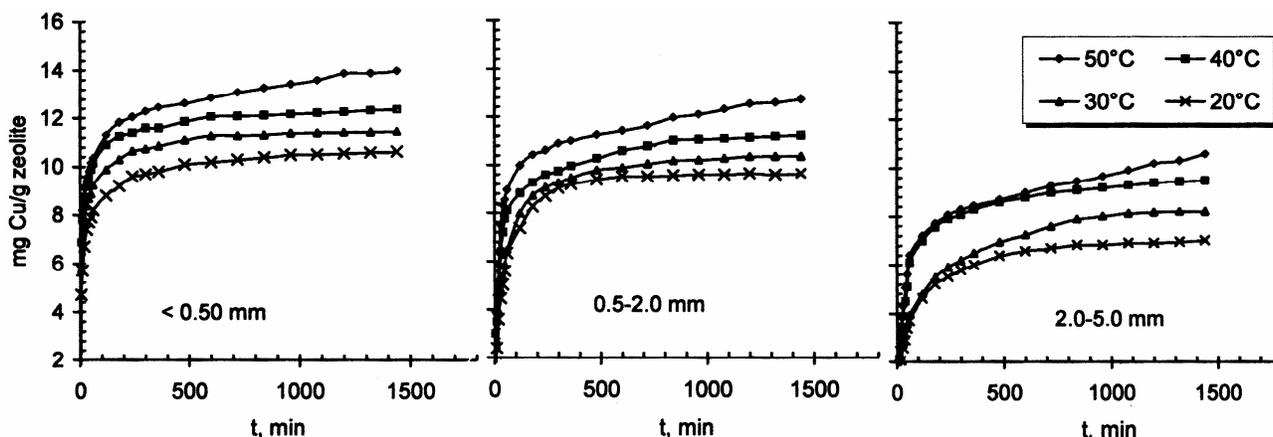


Fig. 1—The quantities of copper removed versus time in dependence on particle size

are shown in Table 1 and compared with removal of copper onto clinoptilolite from different deposits. The Bulgarian zeolite<sup>14</sup> shows nearest values, where Ukrainian zeolite<sup>9</sup> shows double higher values for copper removal compared to Croatian zeolite. Other low cost materials such as clays<sup>15</sup> and furnace slag<sup>22</sup> show capacities similar to Croatian zeolite.

The kinetic diffusion models described previously have been applied to the kinetic experimental results for copper that have been shown in Fig. 1. Testing of experimental results with diffusion model through the film given by Eq. (1), has shown fitting of experimental points up to 60 min of ion exchange. Same behaviour was observed for three examined particle sizes at all temperatures. The graph on Fig. 2 displays testing of film diffusion model for different particle sizes at all examined temperatures. From the linear part of the curves, the slope that corresponds to the initial sorption rate, and intercept that is a parameter proportional with the thickness of diffusion

film, have been determined for all temperatures and given in Table 2. Fitting of experimental points with model examined is shown as a coefficient of correlation ( $R^2$ ).

From Table 2, it can be seen that values of the parameter  $k'$  related to the initial sorption rate have same order of magnitude at all temperatures and particle sizes. This indicates that temperature has no effect on film diffusion probably due rapid mixing of suspension in the reaction vessel. The parameter  $x_i$  proportional to the thickness of diffusion film is higher for particle size <0.5 mm compared to higher particle sizes. There is no visible significant effect of

Table 1—Maximum sorption levels for different particle sizes of zeolite at examined temperatures

$d$ , mm	mg Cu/g zeolite			
	20°C	30°C	40°C	50°C
< 0.5	10.20	11.30	12.10	13.10
0.5-2.0	9.52	10.05	10.80	11.64
2.0-5.0	6.70	7.60	9.00	9.28

Table 2—The kinetic parameters and correlation coefficients for film diffusion model

$d$ , mm $T$ , °C	< 0.5			0.5-2.0			2.0-5.0		
	$k'$ , min <sup>-1/2</sup>	$x_i$	$R^2$	$k'$ , min <sup>-1/2</sup>	$x_i$	$R^2$	$k'$ , min <sup>-1/2</sup>	$x_i$	$R^2$
20	0.070	0.311	0.98	0.087	0.021	0.99	0.081	0.078	0.99
30	0.061	0.396	0.96	0.081	0.014	0.99	0.070	0.055	0.99
40	0.046	0.483	0.97	0.090	0.050	0.98	0.080	0.014	0.97
50	0.042	0.436	0.94	0.078	0.134	0.98	0.074	0.010	0.99

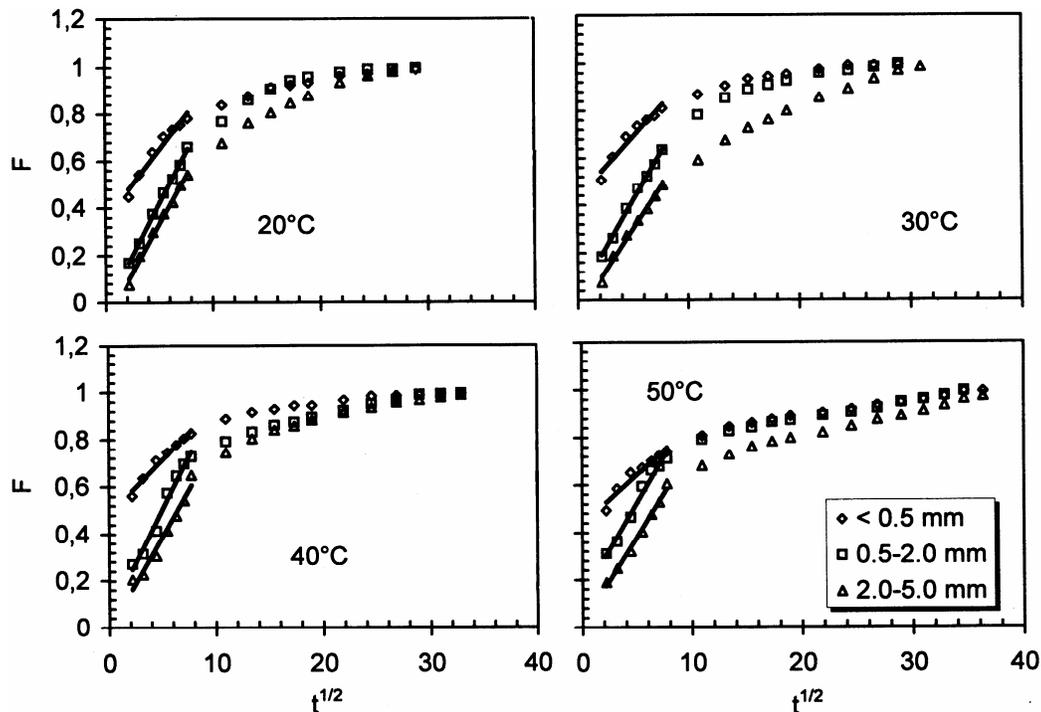


Fig. 2—Application of film diffusion model on experimental results

temperature on the thickness of diffusion film ( $x_i$ ) for particle sizes <0.5 mm and 0.5-2.0 mm, while for particle size 2.0-5.0 mm it slightly decreases with temperature. At higher particle diameter, diffusion path of ions through particle is longer and which reduces their accumulation on the surface. For that reason equilibrium is prolonged for temperature of 50°C, particularly for 2.0-5.0 mm particle size.

The graphs in Fig. 3 show fitting of experimental results with the homogeneous diffusion model for the initial condition  $t \rightarrow t_\infty$  and for temperatures of 20, 30, 40 and 50°C. From Fig. 3, it is clear that homogeneous diffusion model for the initial condition  $t \rightarrow t_\infty$ , gives curves with an inflection point that separate curves into two areas. At these areas the plots approach linearity, so linearization of the curves for all particle sizes at all examined temperatures was performed at two time intervals; first at 0-60 min and second from 60 min until equilibrium. These types of curves indicate the change of mass transfer mechanism during time and they are observed by some researchers in systems where ion exchange occurs inside porous solid structure<sup>10,17,21</sup>. Equation (5) was applied to each time interval and diffusion coefficients have been calculated from the slope of the lines<sup>21</sup>. Fitting of experimental results with

proposed model is shown as a correlation coefficient  $R^2$ , and with all calculated parameters presented in Table 3.

Calculated diffusion coefficients for all particle sizes and all temperatures have same order of magnitude ( $10^{-6} \text{ cm}^2 \text{ min}^{-1}$ ), with high values of correlation coefficients. Diffusion in the first time interval corresponds to the diffusion of exchangeable ions through the surface layers of the particles, and in the second time interval corresponds to the diffusion through micro and macro pores to the exchangeable site. In the first time interval (0-60 min) diffusion coefficients are higher than in the second time interval (60 min- $t_e$ ) due to longer diffusion path through particle. Increasing temperature doesn't show significant effect on the diffusion coefficient values in time interval 0-60 min for all particle sizes. But diffusion through microporous structure of the particle (interval from 60 min- $t_e$ ) is getting slightly slower by increasing the temperature for all particle sizes. This effect is just opposite to the results that have found in related studies<sup>10,14,17</sup>. This can be explained by steric effects between the exchangeable ions and pores inside structure. Namely, copper ions are hydrated and their mobility is limited inside pores with number of water molecules, e.g., hydrated ionic

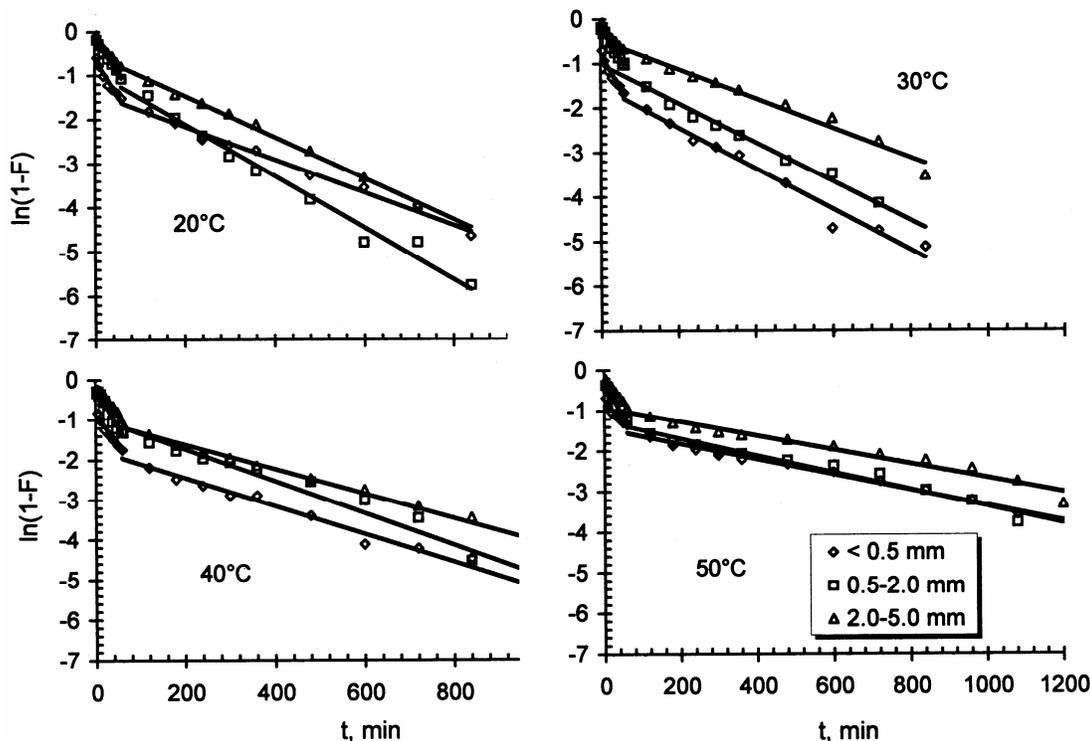


Fig. 3—Application of homogeneous diffusion model ( $t \rightarrow t_\infty$ ) on experimental results

radius. Although increase in temperature increases diffusion of ions, but it is limited inside micropores. Sorption or ion exchange of ion inside pore disables diffusion of other ions through same pore channel. For that reasons overall effect seems temperature independent. Similar behaviour is observed at exchange of zinc ions onto natural zeolite because of similar hydrated ion radius, while higher diffusion coefficient is calculated for exchange of lead ion due to its smaller hydrated ion radius<sup>21</sup>.

Application of parabolic diffusion model on experimental results using Eq. (7) observed linearity in all examined range of particle sizes and temperatures. The diffusion coefficients are calculated from the slope of lines shown in Fig. 4, and are given in Table 4.

Diffusion coefficients shown in Table 4 are in agreement with values previously calculated by homogenous diffusion model. These are also in agreement with values calculated for ion exchange of other heavy metals onto natural zeolites<sup>7,10,17,21,23</sup>. Diffusion rate increases with increase of particle size due to long diffusion path and slightly increases with temperature that is in agreement with Fig. 1. Since parabolic diffusion model covers all examined points, it is used for calculation of thermodynamic parameters of the process. The thermodynamic parameters for intraparticle diffusion help us

understand the mechanism and interactions during this part of ion exchange process<sup>17,24,25</sup>. These are calculated using Eyring equation that describes dependence of diffusion rates with temperatures.

$$\ln(k/T) = \ln(k_b/h) + (\Delta S/R) - (\Delta H/RT) \quad \dots (8)$$

where

$k = D/r^2$ ,  $k$  = diffusion rate ( $s^{-1}$ ),  $k_b$  = Boltzmann's constant,  $h$  = Plank's constant,  $R$  = gas constant,  $\Delta H$  = change of enthalpy of activation,  $\Delta S$  = change of entropy of activation and  $T$  = thermodynamic temperature (K).

The entropy of activation  $\Delta S$  and enthalpy of activation  $\Delta H$  have been calculated from the intercept and the slope of linear dependences given by Eq. (8) and presented in Fig. 5. The energy of activation  $E_a$  has been calculated using Arrhenius equation:

$$\ln(k) = \ln A - (E_a/RT) \quad \dots (9)$$

where  $A$  is Arrhenius constant.

The free energies of activation  $\Delta G$  equal to  $\Delta H - T\Delta S$  have also been calculated and are given in Table 5.

The positive values of  $\Delta H$  confirm weakly endothermic character of diffusion, suggesting that energy should be consumed for transfer of copper

Table 3—The kinetic parameters for homogeneous diffusion model ( $t \rightarrow t_\infty$ )

$T, ^\circ\text{C}$	$d, \text{mm}$ Time interval	<0.5		0.5-2.0		2.0-5.0	
		$D \times 10^6$ $\text{cm}^2 \text{min}^{-1}$	$R^2$	$D \times 10^6$ $\text{cm}^2 \text{min}^{-1}$	$R^2$	$D \times 10^6$ $\text{cm}^2 \text{min}^{-1}$	$R^2$
20	0-60 min	1.01	0.94	6.14	0.98	37.58	0.98
	60 min- $t_e$	0.24	0.99	2.34	0.98	14.60	0.99
30	0-60 min	1.01	0.94	5.59	0.99	30.75	0.98
	60 min- $t_e$	0.29	0.98	2.06	0.95	10.25	0.98
40	0-60 min	1.01	0.97	7.61	0.98	44.73	0.98
	60 min- $t_e$	0.22	0.98	1.59	0.98	9.63	0.99
50	0-60 min	0.069	0.92	6.62	0.97	39.14	0.99
	60 min- $t_e$	0.12	0.98	0.83	0.97	5.28	0.97

$t_e$  = equilibrium time

Table 4—The kinetic parameters and correlation coefficients for parabolic diffusion model

$d, \text{mm}$ $T, ^\circ\text{C}$	<0.5			0.5-2.0			2.0-5.0		
	slope	$D \times 10^6$ $\text{cm}^2/\text{min}$	$R^2$	slope	$D \times 10^6$ $\text{cm}^2/\text{min}$	$R^2$	slope	$D \times 10^6$ $\text{cm}^2/\text{min}$	$R^2$
20	0.209	1.34	0.98	0.083	5.33	0.99	0.070	28.78	0.99
30	0.235	1.69	0.97	0.090	6.20	0.99	0.065	25.24	0.99
40	0.251	1.93	0.96	0.124	11.77	0.99	0.091	49.97	0.98
50	0.219	1.48	0.96	0.141	15.13	0.98	0.088	46.65	0.99

Table 5—Thermodynamic parameters for intra-particle diffusion

<i>d</i> , mm	$\Delta H$ kJmol <sup>-1</sup>	$E_a$ kJmol <sup>-1</sup>	$\Delta S$ Jmol <sup>-1</sup> K <sup>-1</sup>	$\Delta G^*$ , kJmol <sup>-1</sup>				$R^2$
				298 K	303 K	313 K	333 K	
< 0.5	11.48	13,99	-203	71.97	72.99	75.02	79.08	0.98
0.5-2.0	25.27	29,59	-199	84.57	85.57	87.56	91.54	0.99
2.0-5.0	25.44	31,21	-200	85.04	86.04	88.04	92.04	0.99

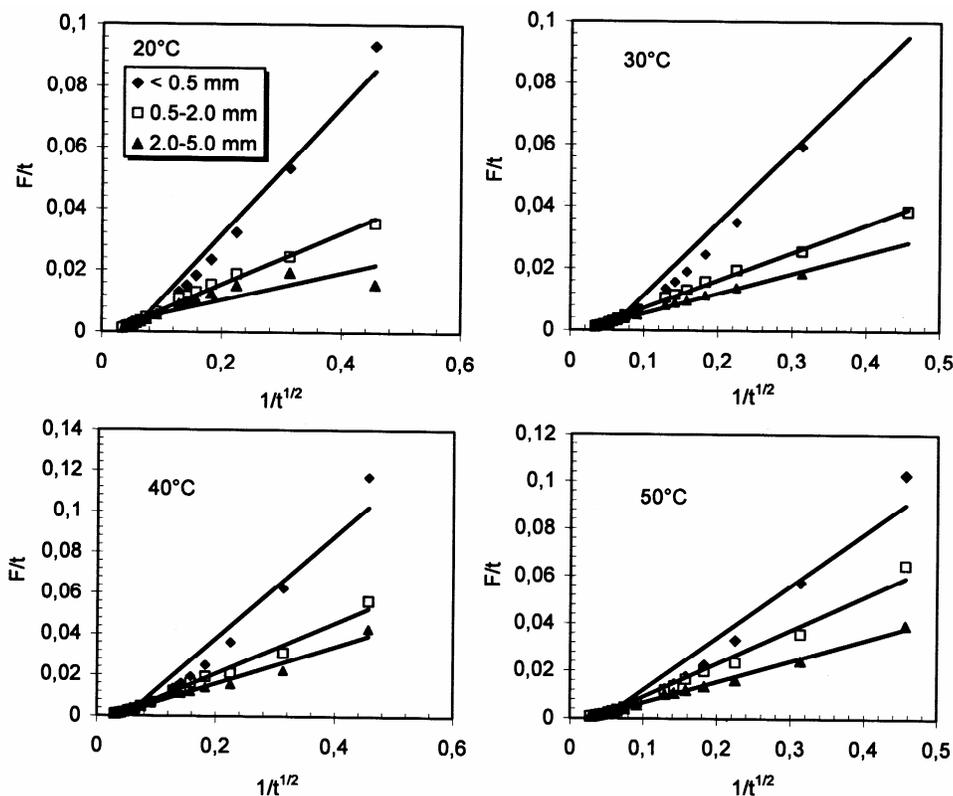


Fig. 4—Application of parabolic diffusion model on experimental results

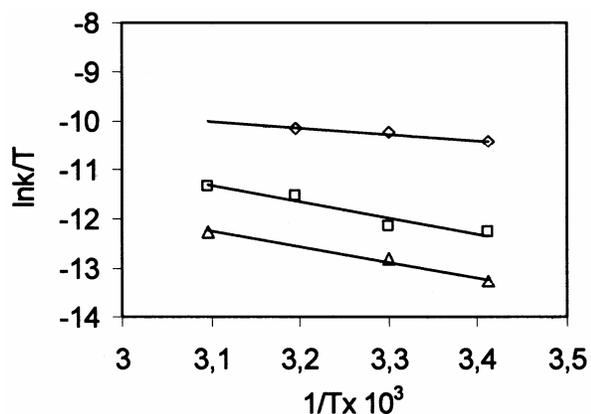


Fig. 5—Plot  $\ln k/T$  against  $1/T$  for intra-particle diffusion of copper ions

ions into the zeolite particle<sup>10,14</sup>. The activation energy is low and in range observed for ion exchange reaction and physisorption process<sup>10,17,26,27</sup>. Change of entropy depends of hydration radius of outgoing and ingoing ions included in an ion exchange process. The negative values of  $\Delta S$  indicate decreasing of entropy and disorder in the system during the process and ion exchanged copper ions has no significant change in the internal structure of zeolitic particle. It also indicates that hydrated copper ions don't release water molecules before they could enter into macro and micro pores<sup>28</sup>. The positive values obtained for  $\Delta G$  indicate non-spontaneous nature of diffusion of copper ions with clinoptilolite, while it becomes less favourable at higher temperature.

## Conclusions

Cation exchange features of the Croatian natural zeolite obtained from the deposit Donje Jesenje confirmed good properties for removal of copper ions from aqueous solutions. The removal efficiency increases with decreasing the particle size of the sample and with increasing the temperature. Testing of the experimental results with diffusion model through film, homogeneous diffusion model and parabolic diffusion model, give the kinetic parameters that describe particular diffusion process in dependence on temperature and particle size.

The film diffusion model fits experimental kinetic curves at first 60 min of the process, where increasing temperature has no significant effect on the diffusion rate. The homogeneous diffusion model ( $t \rightarrow t_{\infty}$ ) satisfactory describes intraparticle diffusion rate that decreases within the time. Initially (0-60 min), diffusion take place in the surface layer of the particle, occurs simultaneously with diffusion through the film, it is independent on temperature, but diffusion coefficients significantly increase for higher particle sizes. Intraparticle diffusion through surface layers of the solid particle is continued by diffusion through the porous structure to the exchangeable site. In this time interval (60 min- $t_c$ ), diffusion rate slightly decreases with temperature. Although the diffusion coefficients decrease with temperature, the time needed for equilibration is higher at increased temperatures that contribute to higher quantity of copper ions bounded as well as to higher ion exchange capacity. The parabolic diffusion model shows linearity at overall examined time for all experiments. For that reason calculated diffusion rates based on this model are used for calculation of thermodynamic parameters of the process. Based on previous experimental results the mass transfer kinetics of the ion exchange should be described by different diffusion kinetic models. Each diffusion model is responsible for mass transfer of the exchangeable ions at a defined time interval.

The calculated thermodynamic parameters  $E_a$ ,  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  characterize process as diffusion dependent, weakly endothermic and non-spontaneous,

where structural changes in structure of natural zeolite particle are not observed.

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