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Journal of Environmental Management 79 (2006) 298–304

Journal of Environmental Management

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Investigations of different kinetic models for zinc ions uptake by a natural zeolitic tuff

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Received 10 June 2004; revised 20 July 2005; accepted 21 July 2005

Abstract

The kinetics of uptake of zinc ions from aqueous solutions by natural zeolitic tuff has been investigated. Batch experiments at constant temperature and hydrodynamic conditions have been performed. A decrease in the initial zinc concentration in aqueous solutions prolongs the time needed for equilibrium. Various kinetic models including the film-diffusion model, the surface diffusion model and the heterogeneous diffusion model have been tested for the description of the experimental results of zinc concentration in the solution over time. Diffusion through the film and diffusion through the surface of the particle could be the rate limiting steps at the initial reaction time. However, the heterogeneous diffusion model seems to be the best model providing a satisfactory fitting of the experimental results from the beginning of the process to the point of equilibrium, particularly at lower initial zinc concentrations.

Keywords: Zinc uptake; Kinetic models; Clinoptilolite; Heterogeneous diffusion

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1. Introduction

Groundwater contamination with heavy metals represents a serious threat to human health and environmental resources. Heavy metals are not biodegradable and tend to accumulate as metalloorganic complexes in living organisms, which increase their concentrations in biological cycles. One of the most dangerous types 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. Zinc is also a trace element that is essential for human health. But oral contamination or exposure to an environment contaminated with a high concentration of zinc causes serious health problems such as stomach and skin irritations, respiratory disorders and disturbance of protein metabolism. The conventional methods of heavy metals removal, such as precipitation methods, usually do not meet the standard criteria for releasing heavy metal cations to the environment (Alvarez-Ayuso et al., 2003; Cerjan-Stefanović et al., 1996; Vaca Mier et al., 2001). These techniques produce a large amount of sludge, which is disposed of in landfills of solid waste and could cause contamination of the soil due to the leaching by rainwater. An alternative method for purification of contaminated waters and wastewaters with heavy metal cations is using low-cost sorbents such as natural zeolites. The porous three-dimensional structure of natural zeolites consisting of (Si, Al)O_4 tetrahedra is negatively charged. The negative charge in the zeolite framework is compensated by hydrated exchangeable cations such as Na, K, Ca, Mg, Ba, and Sr (Stolz et al., 2000). Zeolites have the ability to exchange most of their exchangeable cations as well as hydrate or dehydrate without major change of the structural framework. Besides their ion exchange capacity zeolites exhibit sorption behaviour that is based on the theory of acidic and basic sites in the framework structure. Sorption is the general term used to define the surface retention process without specifying the exact retention mechanism (Alvarez-Ayuso et al., 2003). Their structural properties give them a wide range of capabilities such as molecular sieves, e.g. uptaking of ammonium ions, radionuclides and heavy metal ions from wastewaters (Perić et al., 2004), adsorbents for odour and gas emissions control, as well as agricultural fertilizers. Furthermore, natural zeolites show high cation exchange capacity, good thermal and radiation resistance, and excellent compatibility with the environment.

The rate of heavy metals uptake in natural minerals (such as in clays and zeolites) is a critical parameter that could be used

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doi:10.1016/j.jenvman.2005.07.009

for determination of the rate of their contamination of the environment. This strongly depends on the hydrodynamics of the system, concentration of heavy metal ions, and porosity and heterogeneity of the soil. In the literature, the kinetic models that describe adsorption/ion exchange on porous particles with heterogeneous composition (such as zeolites) have been classified into three categories; staged equilibrium models, interference theory model, and rate equation models (Kithome et al., 1998; Robinson et al., 1994). In the literature, these models are applied to the experimental results of heavy metal ions removal, considering the possibilities of other resistances to the mass transfer process. The rate equation models consider diffusion as the mass transfer mechanism responsible for the overall rate of the processes in a zeolite–aqueous solution system. These models are the most applicable to the experimental results and will be discussed in this paper (Guibal et al., 1998; Jardine and Sparks, 1984; Liang and Tsai, 1995; Rengaraj and Moon, 2002).

The aim of this paper is to evaluate the kinetic models that can be used to describe the rate of zinc ions uptake within heterogeneous and porous zeolitic particles.

2. Materials and methods

2.1. Reagents

Zinc ion solutions were prepared by dissolving the appropriate amount of $ZnSO_4 \times 7H_2O$ salt in double distilled water. The solutions with different initial concentrations of zinc (597.7, 420.6, 200.4, 128.6, and 68.3 mg/l) were prepared by dilution in double distilled water, and the exact concentration was determined by a complexometric method in acidic medium, using the highly selective indicator 3,3-dimetilnaphtidyne according to Complexometric Assay Methods with Triplex (Merck, 1982).

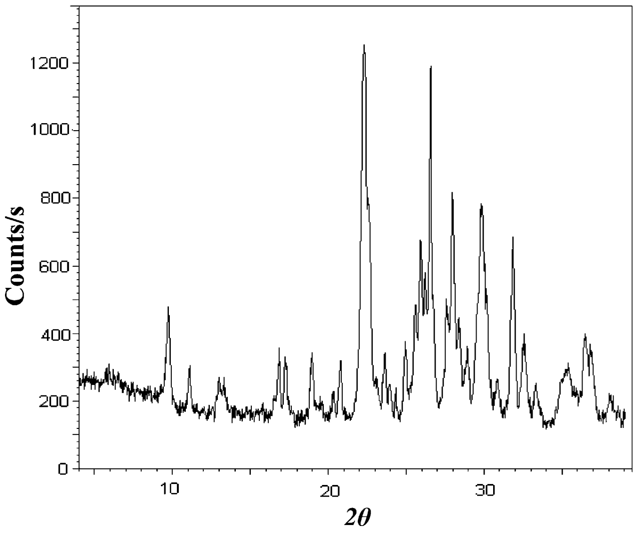

Fig. 1. XRD pattern of the used sample.

Table 1
Physico-chemical properties of the used sample

Surface of micropores	1.919 m^2/g
BET specific surface	12.055 m^2/g
Micropores volume	0.813 mm^3/g
Average diameter of pores	118.525×10^{-10} m
Adsorption specific surface of pores ($d = 17–3000 \times 10^{-10}$ m)	0.036 cm^2/g
Density	1812 g/l

2.2. Characterization and modification of zeolitic tuff sample

The zeolitic tuff was obtained from the sedimentary deposit Donje Jesenje-Croatia. The X-ray diffraction pattern (XRD) of the sample was obtained using a powder X-ray diffractometer type Siemens D 500/D501 (Cu K_α radiation, $2\theta = 2–60°$). The result of the diffraction analysis is shown in Fig. 1.

The major mineralogical phase was clinoptilolite (up to 50%); feldspar, calcite, and quartz were the main impurities with a low content of montmorillonite, ilite and halite. The chemical composition of the tested sample was as follows (wt%): SiO_2 55.80; Al_2O_3 13.32; CaO 5.57; K_2O 2.35; Na_2O 3.90; Fe_2O_3 1.30; MgO 0.70; loss of ignition 17.00. The physico-chemical properties of the natural sample are shown in Table 1 (Cerjan-Stefanović et al., 1996; Trgo and Perić, 2003).

The natural sample was milled and sieved to select the particle size fraction of 0.1–0.5 mm. This sample was modified to homoionic form by equilibration of 5 g of zeolite with 100 ml 2 mol/l NaCl solution in closed glass vessels for 3 days (Arcoya et al., 1996). The conditioning was performed in a thermostated shaker (Heidolph Incubator) at a temperature of 37 ± 1 °C. The suspension was filtered, washed and dried at room temperature for 1 day and then at 60 °C for 1 h. The prepared homoionic form was marked NaZ, and stored in a desiccator.

2.3. Batch kinetic studies

The removal of zinc ions was studied by carrying out batch tests. The mixtures of 1 g NaZ sample and 100 ml of prepared zinc solutions of different initial concentrations were shaken at ≈240 rpm in a thermostated shaker at a temperature of 23 ± 1 °C in the closed glass vessels. Shaking was interrupted at different solid/liquid contact times (from 10 min to 30 h) depending on the initial Zn concentration. Following filtration of the suspensions, the concentration of zinc ions in the filtrate was determined complexometrically using the highly selective indicator 3,3-dimetylnaphtidine according to Complexometric Assay Methods with Triplex (Merck, 1982). Lower zinc concentrations (under ≈10 mg/l) were measured with a UV/vis spectrophotometer (Perkin Elmer Lambda 201) using the standard zincon method (Standard Methods for the Examination of Water and Wastewater, 1995). The pH value in suspensions was measured before and after the experiment by a pH-meter type WTW 431.

The zeolitic sample was equilibrated with the highest concentration of zinc, which was marked NaZZn, and was analysed by the scanning electron microscopy–energy disperse system (SEM-EDS) using the apparatus Zeiss DSM 962. Elemental analysis of Si, Al, O, Na and Zn was performed on the surface of the chosen zeolitic particle, by the line marked on the SEM image.

3. Results of kinetic studies and discussion

The chemical analysis of zeolitic samples has shown that the deposit contained sodium, potassium, calcium and magnesium exchangeable ions. In the modified sample K^{+}, Ca^{2+} and Mg^{2+} ions were mainly exchanged with Na^{+} ions, depending on their position in the clinoptilolite structure (Arcoya et al., 1996). During the ion exchange process, exchangeable cations of zeolite are replaced by zinc ions, resulting in a decrease in zinc concentration vs time until equilibrium is attained as shown in Fig. 2 (Trgo and Perić, 2003).

As seen in Fig. 2, a rapid initial uptake is followed by slower sorption. Decreasing the initial concentration of zinc in the suspension prolongs the time needed for equilibrium. This could be explained by taking into consideration the different resistances to the motion of exchangeable ions through the solution and through the porous particle. Namely, the motion of zinc ions from the solution to the exchangeable site as well as the motion of exchangeable cations to the solution are affected by a number of principal resistances. They include: (i) diffusion of ions from the solution to the film surrounding the zeolitic particle; (ii) diffusion through the film to the particle surface; (iii) diffusion from the surface to the intraparticle sites, and (iv) binding of ions that could involve several mechanisms, e.g. physico-chemical sorption, ion exchange, complexation or precipitation (Guibal et al., 1998). Diffusion through the solution (i) is not considered if suspensions are shaken to avoid a concentration gradient. Furthermore, intraparticle diffusion (iii) could involve the simultaneous sorption in surface layers, macroporous and microporous diffusion. These diffusion processes are conceptually shown in Fig. 3 (Robinson et al., 1994).

The kinetic model of diffusion through the film surrounding a zeolitic particle is relatively poorly applied to experimental results in the literature, although it could affect the overall mass transfer rate of the process at early contact times (from 0 to 30 min). This is particularly possible at the interface of the aqueous solution and a mineralogical heterogeneous solid such as the natural zeolitic tuff used. Namely, the dissolution of some mineralogical components increases the thickness of the film formed on the solid/liquid interface, which affects the rate and mechanism of the mass transfer process (Trgo and Perić, 2003). The rate laws for the film-diffusion controlled exchange have been derived using the following assumptions: (a) diffusion across the film is fast in comparison with concentration changes at film boundaries; (b) the film is treated as a planar layer and its thickness is much smaller than the particle radius. Using these conditions the following equation has been derived (Helferich, 1962):

$$\alpha_t = 1 - \exp(-3Dct/r\delta c_z) \tag{1}$$

where

α_t	fraction of zinc ions bounded at time t, dimensionless
D	diffusion coefficient, cm^2/min
c	concentration of zinc in the solution, mg/l
c_z	concentration of exchangeable ions on the zeolite, mg/l
t	time, min
r	particle radius, cm
δ	thickness of the film, cm

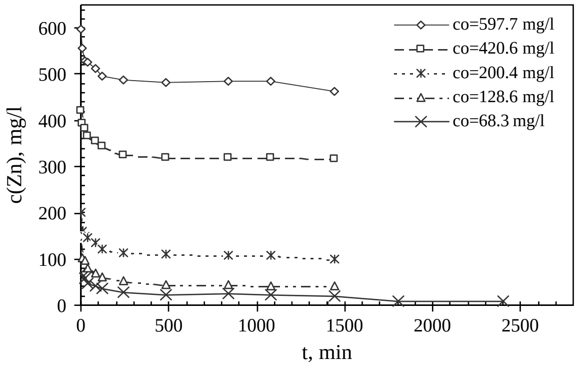

Fig. 2. Decreasing of zinc concentration vs time for different initial concentrations.

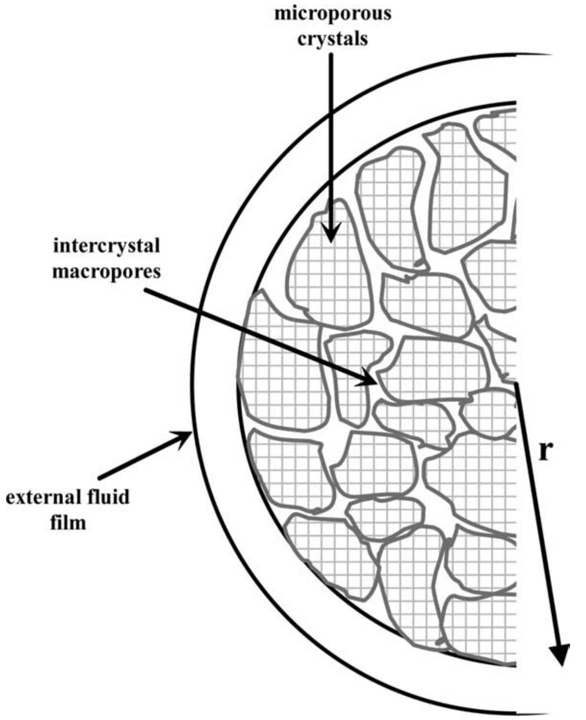

Fig. 3. The three principal resistances to mass transfer on the aqueous solution/zeolitic particle interface (Robinson et al., 1994).

The value α_t is calculated from the experimental results

$$\alpha_t = \frac{c_0 - c_t}{c_0 - c_\infty} \tag{2}$$

c_0 initial concentration of zinc in the solution, mg/l
c_t concentration of zinc in the solution at time t, mg/l
c_∞ equilibrium concentration of zinc in the solution, mg/l.

Other authors also give analogous relations based on first-order kinetic equations (Aharoni and Sparks, 1991; Aharoni et al., 1991; Guibal et al., 1998; Jardine and Sparks, 1984; Rengaraj and Moon, 2002; Sparks, 1998).

A plot of the fraction of zinc bound to the zeolite against time may be used to estimate the relative film-diffusion rate at several values of the initial Zn concentration (Fig. 4). The dimensionless time parameter $Dct/r\delta c_z$ corresponds to the relative rate of the diffusion. The relative film-diffusion rate according to relation (1) is the slope of the linear part of curves expressed by Eq. (3). It is proportional to the diffusion coefficient in the film and to the concentration of zinc in the solution, and inversely proportional to the particle radius, the film thickness, and exchangeable ions concentration in the zeolite

$$\ln(1 - \alpha_t) = -\frac{3Dc}{r\delta c_z} t. \tag{3}$$

The plots of fractions of zinc bound vs time give the curves with clear linear parts at initial solution/zeolite contact times (10–80 min) as shown in Fig. 4. The equations derived from the linear regression analysis of the above plots as well as the corresponding correlation coefficients R^2 values are given in Table 2.

The values of R^2, ranging from 0.961 to 0.996 show a good fitting of experimental results to the model proposed, at initial reaction times. The slope of these lines is proportional to the relative rate, and slowly increases with a decrease in the initial concentration.

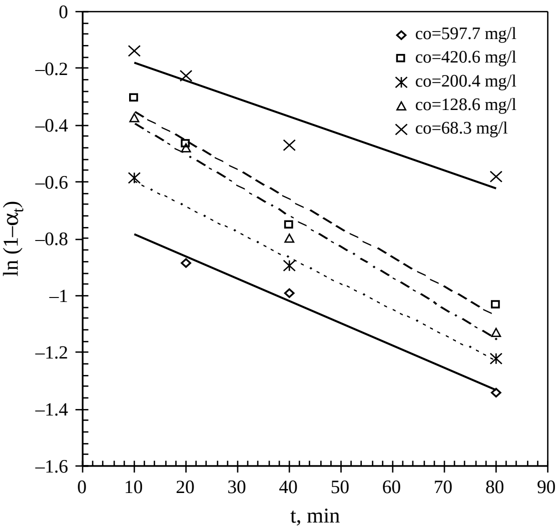

Fig. 4. The linear dependences of fraction of zinc bounded vs time for the film diffusion model.

Table 2
Regression equations and correlation coefficients for film-diffusion model

c_0 (mg/l)	Film-diffusion equation	R^2
597.7	$y = -0.008x - 0.708$	0.988
420.6	$y = -0.010x - 0.255$	0.961
200.4	$y = -0.009x - 0.511$	0.996
128.6	$y = -0.011x - 0.288$	0.979
68.3	$y = -0.011x - 0.017$	0.993

y = corresponds to the fraction of zinc bounded; x = time.

The diffusion through the film is followed by the sorption on external sites of the particle. These sites have different degrees of accessibility (internal, external), different sorbent types due to the mineralogical heterogeneity, and different sorption mechanisms (Sparks, 1998). Depending on the pH value in the solution and the radius of the hydrated ingoing exchangeable cation, the intensity of occupation of these sites could vary, and significantly affect the surface sorption rate or possibly inhibit further intraparticle diffusion. Namely, at higher initial concentrations fast sorption takes place on sites with different energies due to the mineralogical heterogeneity and surface imperfections observed on the SEM image of the chosen particle (Fig. 5). The EDS analysis was performed across the marked line in the SEM image. The content of major elementary constituents Si, O and Al, and exchangeable Na, shows the uniform chemical composition originating from the same mineralogical component—clinoptilolite. The homogeneous distribution of Zn by the examined line could be attributed to the surface sorption.

The diffusion through the particle surface can be expressed by the relation (Guibal et al., 1998; Jardine and Sparks, 1984; Kithome et al., 1998)

$$\alpha_t = a + \left(\frac{D}{r^2}\right)^{1/2} t^{1/2} \tag{4}$$

where a is the dimensionless constant.

Testing of the experimental kinetic results against this model yields curves with a linear part at solution/zeolite contact times from 20 to 120 min as shown in Fig. 6.

The slope of the linear part of the curves $(D/r^2)^{1/2}$ is proportional to the initial rate of sorption, and the intercept a is proportional to the thickness of the boundary sorption layer. The equations derived from the linear regression analysis of these plots and the corresponding correlation coefficients R^2 are presented in Table 3.

For the examined time interval this model describes the surface sorption well, with R^2 values ranging from 0.974 to 0.993. The slope of equations calculated in Table 3 shows that the initial rate of uptake and corresponding diffusion coefficients do not depend on the initial concentrations of zinc in the solution. The intercept is proportional to the thickness of the boundary sorption layer that decreases with the increase of the initial concentration.

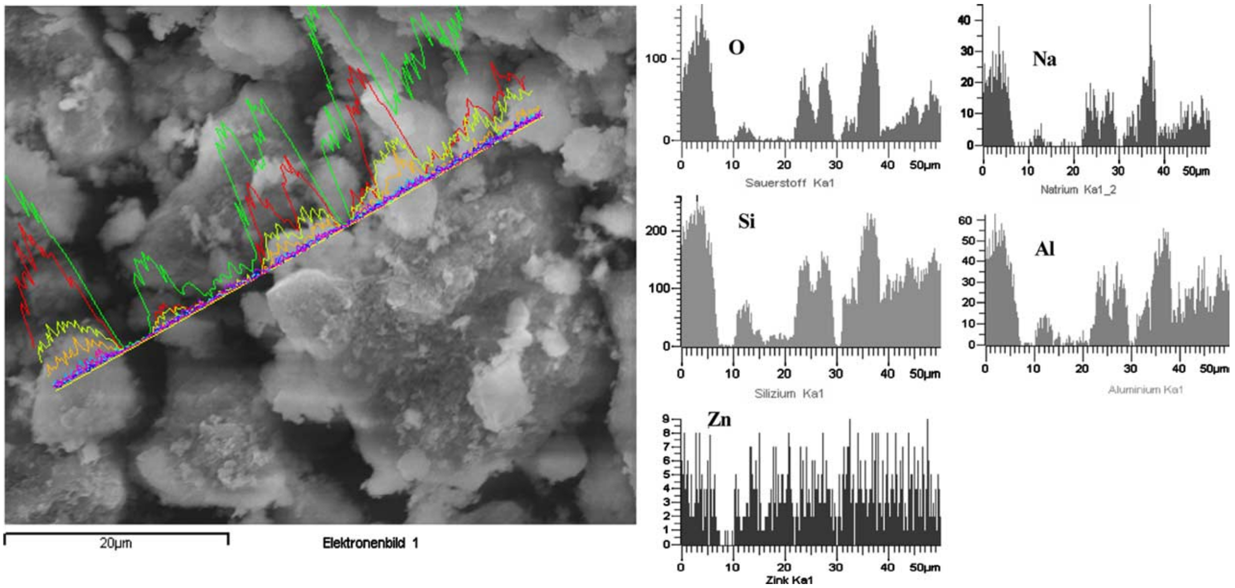

Fig. 5. SEM image of the NaZZn sample with the EDS analysis by the line on the image.

The finding that the rate of zinc ions uptake is rapidly decreased from 20 min to the equilibrium (Fig. 2) indicates that possible intraparticle diffusion becomes the rate-controlling step. Due to the porous structure of the zeolite, consisting of a network of cages and channels, diffusion of the ions through the particle could be slower compared to the surface diffusion. Also the exchange of ions of different hydrated radiuses could affect the mobility within the structure that leads to variations of the intraparticle diffusion rate. Therefore, at neutral pH in the solution, ranging from 6.83 to 7.32, with Zn^{2+}, the formation of zinc-hydroxy species, particularly $ZnOH^{+}$ is possible (Benefield and Judkins, 1982; Farrah and Pickering, 1976). This specie could be exchanged as a monovalent cation and/or adsorbed on internal particle surfaces and also affect the mobility of other species within structure (Trgo and Perić, 2003). The internal adsorption of $ZnOH^{+}$ could inhibit the ion exchange as the main process. The above effects induce variations in the diffusion rate vs time that could be discussed as heterogeneous diffusion. The heterogeneous diffusion model assumes variations of the diffusion rate through zeolitic particles and is the most representative in the literature (Aharoni and Sparks, 1991; Aharoni et al., 1991; Kithome et al., 1995). It can be expressed by Eq. (5)

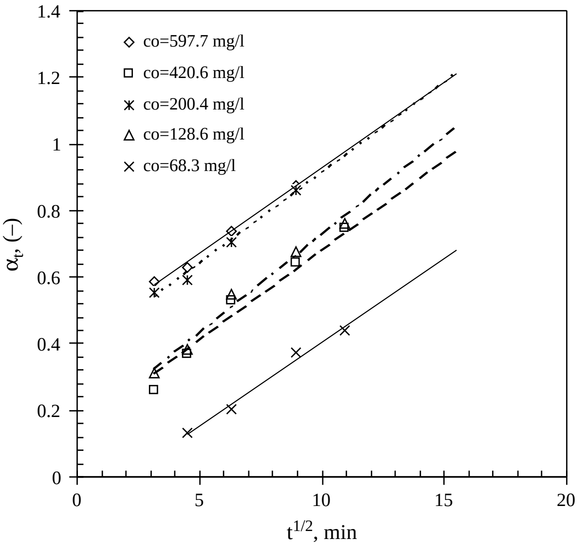

Fig. 6. The linear dependences of fraction of zinc ions bounded vs $t^{1/2}$ for the surface diffusion model.

$$\frac{\mathrm{d}(\alpha_t)}{\mathrm{d}\ln t} = \frac{1}{\rho}\left[1-\left(\frac{4t}{\pi\tau_{\mathrm{m}}}\right)^{1/2} - \frac{8}{\pi^2}\exp\left(-\frac{\pi^2 t}{4\tau_{\mathrm{i}}}\right)\right] \tag{5}$$

where

ρ = $\ln(\tau_{\mathrm{m}}/\tau_{\mathrm{i}})$, dimensionless
τ = s^2/D, min
s maximum length of the diffusion path, m
τ_{m} maximum value of τ, min
τ_i minimum value of τ, min

Table 3
Regression equations and corresponding parameters for surface diffusion model

c_0 (mg/l)	Surface diffusion equation	R^2	D (cm^2/min)
597.7	$y=0.051x-0.413$	0.993	2.34×10^{-6}
420.6	$y=0.054x-0.140$	0.977	3.92×10^{-6}
200.4	$y=0.055x-0.366$	0.987	2.72×10^{-6}
128.6	$y=0.059x-0.138$	0.981	3.13×10^{-6}
68.3	$y=0.050x-0.100$	0.983	2.25×10^{-6}

y = correspond to the fraction of zinc bounded; x = time.

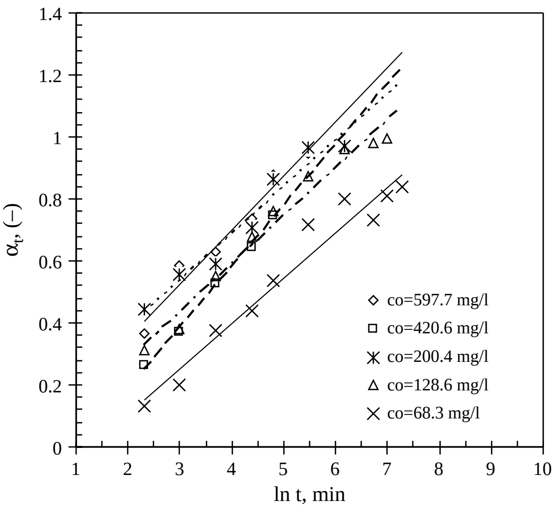

Fig. 7. The linear dependences of fraction of zinc ions bounded vs ln *t* for the heterogeneous diffusion model.

For values of $\tau_i \ll \tau_m$, negative terms of Eq. (5) are negligible, and it reduces to:

$$\frac{d(\alpha_t)}{d\ln t} = \frac{1}{\rho}, \tag{6}$$

$$\alpha_t = \frac{1}{\rho}\ln t + C, \tag{7}$$

C is the integration constant.

The plots of the fraction of zinc bound at time *t* vs ln *t* show a linear dependence at the time interval from 10 min to the equilibrium (Fig. 7).

By applying the linear regression analysis to the experimental results the linear equations and corresponding squared correlation coefficients have been calculated, and are given in Table 4.

The values of R^2 were satisfactory for all initial concentrations (ranging from 0.953 to 0.991), and this indicates that the heterogeneous diffusion model can provide a good description of the sorption 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. They are schematically shown in Fig. 8.

Table 4
Regression equations and corresponding parameters for heterogeneous diffusion model

c_0 (mg/l)	Heterogeneous diffusion equation	R^2
597.7	$y = 0.175x - 0.001$	0.964
420.6	$y = 0.196x - 0.199$	0.996
200.4	$y = 0.150x - 0.091$	0.953
128.6	$y = 0.155x - 0.028$	0.972
68.3	$y = 0.147x - 0.189$	0.955

y = correspond to the fraction of zinc bounded; x = time.

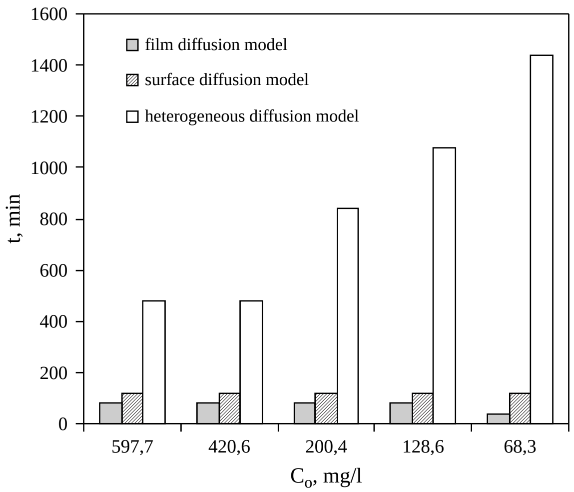

Fig. 8. Validity of particular diffusion model at different reaction time intervals in dependence on initial zinc concentration.

The diffusion through the film is significant at the initial time of the ion exchange/sorption process. The mass transfer is continued by diffusion through the surface of the particle, while the heterogeneous diffusion model is rate limiting from the beginning to the equilibrium of the process. This indicates changes in the radial diffusion rate and diffusion coefficient from the surface to the sorption/exchangeable site in the structure during that time.

4. Conclusions

The mobility of hydrated exchangeable ions from the solution to the exchangeable site inside the particle depends on the initial concentration, specific zeolitic framework structure and mineralogical heterogeneity of the sample used. The time interval needed for the equilibrium of zinc uptake increased with a decrease in the initial concentration in the solution. The mass transfer kinetics in the Zn-containing-solution/natural zeolitic tuff system cannot be described by a simplified kinetic model. The film-diffusion model provides a good description of the process at initial contact times, where the diffusion rate through the film and the thickness of the boundary sorption layer in the zeolitic particle slowly decrease with an increase in the initial zinc concentration. The increased initial zinc concentration increases the quantity of outgoing exchangeable ions (Na^+, K^+, Ca^{2+}, Mg^{2+}) on the solid–liquid interface that could produce a resistance to diffusion through the film and the particle surface. The heterogeneous diffusion model satisfactorily describes the diffusion within the particle to the exchangeable site, indicating the changes in the diffusion rate and diffusion coefficients over time. These factors have an impact on the time needed for equilibrium attainment, as well as on the effective cation exchange capacity of the zeolitic sample. However, the examination of kinetics in suspensions of zeolite and zinc ion solutions has important practical aspects for design of continuous systems for wastewater purification.

Acknowledgements

We are grateful to the Croatian Ministry of Science and Technology, which has been financing the project a part of which is presented in this paper.

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