

A comparative study of ion exchange kinetics in zinc/lead—modified zeolite-clinoptilolite systems

M. Trgo*, J. Perić, N. Vukojević Medvidović

University of Split, Faculty of Chemical Technology, Teslina 10/V, 21000 Split, Croatia

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Abstract

The kinetics of zinc and lead ions removal by modified zeolite-clinoptilolite has been investigated. The rate of the ion exchange process for lead ions is faster than for zinc ions, as well as the time needed to reach the equilibrium. The ion exchange capacity of zeolite of lead ions is doubly higher than that of zinc ions. Diffusion models according to the Vermeulen's approximation, the parabolic diffusion model and the homogeneous diffusion model have been tested with the experimental data of ion exchange for zinc and lead. For both systems examined, the best fit of the models proposed with the experimental data was shown by the Vermeulen's approximation and the homogeneous diffusion model with $t \rightarrow t_{\infty}$. The diffusion coefficients are calculated from kinetic models of lead ions they are of the order of 10^{-6} cm²/min, constant for all examined initial concentrations and not dependent on time. The diffusion coefficients in the system of zinc ions is of the order of 10^{-8} cm²/min, also independent of initial concentrations, but decreasing with time from the beginning of ion exchange to the equilibrium.

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1. Introduction

High concentrations of heavy metals in the environment are mostly due to uncontrolled wastewater discharge. It is often the discharge of industrial wastewaters from plating, metal finishing and rinsing manufacturing processes. Some industries of organic compounds such as pesticides, pigments metal additives, petroleum refining and pulp industries produce large amounts of solid and liquid waste that contains different types and quantities of heavy metals. The stabilisation treatment of this waste always includes the operation of their removal and possible recycling in the process using ion exchangers. The natural zeolites have recently become recognized as an improved material for removal of heavy metals from wastewaters, contaminated surface and groundwaters using ion exchange process. The advantage of this process is the use of relatively low cost ion exchange materials, high removal efficiency and having no secondary pollution [1,2]. Among natural zeolites, clinoptilolite is the most abundant and commonly used as ion exchanger or sorbent for inorganic

or organic compounds. The specific structure of the clinoptilolite, consisting of a two-dimensional system of three types of channels (ten-member and eight-member rings) that are occupied by exchangeable Na, K, Ca and Mg ions, is responsible for its ion exchange and molecular sieve properties [3]. These exchangeable ions are located in the frame channels, coordinated with the defined number of water molecules that affect their mobility within the structure. It is well known that natural zeolite-clinoptilolite prefers uptake of ions with lower radius of hydrated ions such as lead and this ability is characterized as high selectivity of ion exchange. Clinoptilolite shows lower selectivity for zinc, copper and chromium that have higher hydrated radius as well as higher hydration energy [4]. The equilibrium and kinetics of ion exchange of these ions have recently been described in literature [5–14], and most of them are based on the fundamental kinetics described by Helfferich [15]. In these papers, authors discuss the applicability of kinetic models to systems of different natural zeolites in solutions containing different exchangeable cations. The established values of diffusion rates and diffusion coefficients vary relative to quality and particle size of the zeolitic material, type of exchangeable cations, and hydrodynamics of the system during the process.

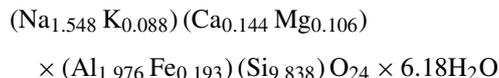
* Corresponding author. Tel.: +385 21 329 420; fax: +385 21 329 461.
E-mail address: mtrgo@ktf-split.hr (M. Trgo).

Diffusion coefficient is one of the main parameter for performance, design and optimization of water or wastewater purification plants. This study concentrates on examination of kinetics of lead and zinc uptake on modified clinoptilolite using empirical diffusion models, determination of their diffusion coefficients and establishing the mass balance of ions included in the ion exchange process.

2. Materials and methods

2.1. Experimental procedure

Experiments have been performed on samples of clinoptilolite tuff from the Vranjska Banja mineral deposit (Serbia and Montenegro). Characterisation by the qualitative X-ray analysis has indicated the major mineralogical component to be clinoptilolite (>80%), with quartz as main impurity, and a low content of clay minerals. A natural zeolitic sample has been milled and dry sieved, producing the fraction of 0.04–0.10 mm. The sample has been preconditioned with the 2 M NaCl solution at a solid/liquid ratio 5 g/100 ml in thermostated shaker (*Heidolph incubator shaker*) at 37 ± 2 °C. The suspension was decanted daily and fresh NaCl solution added. After 5 days, the suspensions were filtered, rinsed with 0.5 and 0.1 M NaCl solutions and five times with ethanol, and dried at 60 °C. From literature and our previous examinations is well known that chemical conditioning into homoionic form increase ion exchange capacity of the natural zeolite [16,17]. The samples, modified into the homoionic Na-form have been analysed [18], and the empirical formula has been calculated from the results of the chemical analysis



The theoretical exchange capacity (TEC) of homoionic Na-clinoptilolite equals 1.71 mequiv. g⁻¹ zeolite and has been calculated from the empirical formula according to the equation [19,20]

$$\text{TEC} = \frac{n(\text{Al}^{3+} + \text{Fe}^{3+}) - (n(\text{K}^+) + n/2(\text{Ca}^{2+} + \text{Mg}^{2+}))}{M(\text{zeolite})} \quad (1)$$

where n is the number of moles, M the molar weight of Na-clinoptilolite, mol/g.

The aqueous solutions of zinc and lead have been prepared by dissolving the appropriate amount of salts $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and PbNO_3 in doubly distilled water. Exact initial concentrations were determined complexometrically in acidic medium using highly selective indicators: 3,3-dimetilnaphthidine for zinc, and methylthymolblue for lead [21].

Lower concentrations of zinc and lead solutions were prepared by dilution of initial solutions.

Examination of ion exchange kinetics of zinc ions was performed by means of the batch method in Na-clinoptilolite/Zn aqueous solutions systems. The mixtures of 1 g of zeolitic sample and 100 ml of zinc ion solutions of different initial concentra-

tions were shaken at 240 rpm and a temperature of 23 ± 1 °C in vessels isolated from atmosphere. For each initial concentration, the ion exchange has been interrupted for different solid/liquid contact times (from 20 to 2280 min) and the suspension filtered. The concentration of zinc remaining in the filtrate was determined complexometrically.

The ion exchange of lead ions was also examined by the procedure described below, with same solid/liquid ratio of 1 g of zeolitic sample and 100 ml of lead ion solutions of different initial concentrations, at same hydrodynamic conditions. But the evaluated data show that the equilibrium is attained faster, for about 20–30 min, and we could not provide enough number of experimental points to the equilibrium. For this reason the performance of ion exchange should be changed, particularly the time needed for the separation of solid phase. Therefore, the examinations were carried out in one vessel volume of 3000 ml, by stirring a suspension of 20 g of sample with 2000 ml of lead solutions (solid/liquid ratio was also 1 g/100 ml) of different initial concentrations. The vessel was isolated from atmosphere and thermostated at 23 ± 1 °C. At different time intervals (from 1.5 to 60 min) small portions of 10 ml of the suspension were sampled, centrifuged and the remaining concentration of lead was determined complexometrically. During all experiments, for each initial concentration of the lead solution, the volume of suspension was reduced for a maximum of 10%.

pH values were measured in initial solutions of zinc and lead, as well as in solutions after ion exchange. Concentrations of exchangeable Na, K, Ca and Mg ions in solutions after ion exchange of zinc and lead were measured by liquid ion chromatography using the Metrohm IC 761 chromatograph type with a cationic Metrosep-250 column.

2.2. Kinetic diffusion models for heterogeneous systems

When the solid ion exchanger (zeolite), containing ions A, is immersed in a liquid phase, containing heavy metal ion Me, then a diffusion process is established where ions A diffuse out from and ions Me diffuse into the solid particle. The flux (J_A) of the exchangeable ion A from the zeolite to the solution, and flux (J_{Me}) of the heavy metal ion Me from the solution to the zeolite depends on the diffusion coefficient D and changes in concentrations of A and Me ions in the zeolite according to equations [15]

$$J_A = -D \text{grad } c_{Z(A)} \quad (2)$$

$$J_{Me} = D \text{grad } c_{Z(Me)} \quad (3)$$

where $c_{Z(A)}$ is the concentration of A (Na, K, Ca, Mg) on zeolite, mmol/g, $c_{Z(Me)}$ the concentration of Me on zeolite, mmol/g, D the diffusion coefficient, cm²/min.

With the assumptions of the constant shape of the particle (sphere particles) and the constant value of the diffusion coefficient, the change of Me concentration in the zeolite can be expressed by the second Fick's law [5,6,11,13,15,22]

$$\frac{\partial c_{Z(Me)}}{\partial t} = D \left(\frac{\partial^2 c_{Z(Me)}}{\partial r^2} + \frac{2}{r} \frac{\partial c_{Z(Me)}}{\partial r} \right) \quad (4)$$

where r is the medium radius of the zeolitic particle, cm, t the time, min.

If the concentration of Me ions is constant from the surface to the centre of the zeolitic particle and the volume of the solution is much higher than the volume of zeolite (batch method) the previous equation can be expressed as [6,9,12–14,22–25]

$$F = 1 - \frac{6}{\pi^2} \sum_{i=1}^{\infty} \frac{1}{i^2} \exp\left(-\frac{Dt\pi^2 i^2}{r^2}\right) \quad (5)$$

where

$$F = \frac{q_{Z(\text{Me})t}}{q_{Z(\text{Me})e}} \quad (6)$$

F is the fraction of Me bound at time t , $q_{Z(\text{Me})t}$ the mmol Me per gram of zeolite in time t , $q_{Z(\text{Me})e}$ the mmol Me per gram of zeolite at equilibrium, i the number of experimental points.

2.2.1. The diffusion model according to Vermeulen's approximation

Depending on the ratio of the initial concentration of Me in zeolite ($c_{0Z(\text{Me})}$) and in the solution ($c_{0S(\text{Me})}$), and of the volume of zeolite (V_Z) and the volume of the solution (V_S), the applicability of Vermeulen's approximation is limited. Namely, for the criterion of "infinite solution volume" that is given by the ratio ($c_{0Z(\text{Me})} V_Z \ll c_{0S(\text{Me})} V_S$), where the concentration of Me in the solution remains negligible throughout the process, and for the range $0 \leq F \leq 1$ in the solution of divalent exchangeable ions, Eq. (5) can be simplified [6,15,22]

$$F \left[1 - \exp\left(-\frac{Dt\pi^2}{r^2}\right) \right]^{1/2} \quad (7)$$

If Eq. (7) is linearized, it yields

$$\ln(1 - F^2) = -\frac{\pi^2 Dt}{r^2} \quad (8)$$

where plot of $\ln(1 - F^2)$ versus t provides a line from whose slope $-\pi^2 D/r^2$ the diffusion coefficient D can be calculated.

2.2.2. The parabolic diffusion model

This 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 Me on the particle surface is constant.

This model also assumes that the quantity of Me bound throughout the cylinder is uniform and can be expressed as [13,24,25]

$$F = \frac{4}{\pi^{1/2}} \left(\frac{Dt}{r^2}\right)^{1/2} - \frac{Dt}{r^2} - \frac{1}{3\pi^{1/2}} \left(\frac{Dt}{r^2}\right)^{3/2} \quad (9)$$

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

$$\frac{1}{t} F = \frac{4}{\pi^{1/2}} \left(\frac{D}{r^2}\right)^{1/2} \frac{1}{t^{1/2}} - \frac{D}{r^2} \quad (10)$$

2.2.3. The homogeneous diffusion model

This model has been also evaluated from the second Fick's law with the assumption that diffusion rate and radial diffusion coefficient is constant during ion exchange process, and expressed as [13,14,24]

$$F = 1 - \sum_{i=0}^{\infty} a_i \exp\left(-\frac{b_i t}{\tau}\right) \quad (11)$$

where a_i and b_i are parameters that depend on the shape of the zeolitic particle, and τ is the time needed for diffusion of the ion Me from the particle surface to the exchangeable site in the particle and equals

$$\tau = \frac{r^2}{D} \quad (12)$$

For sphere particles, Eq. (11) can be rewritten in a form that reduces at small values of time t to

$$t \rightarrow t_0 \quad F = \frac{6}{\pi^{1/2}} \frac{D^{1/2}}{r} t^{1/2} \quad (13)$$

and it reduces at large t to

$$t \rightarrow t_{\infty} \quad \ln(1 - F) = \ln\left(\frac{6}{\pi^2}\right) - \frac{\pi^2 D}{r^2} t \quad (14)$$

The diffusion coefficient may be calculated from the slope of the linear part of curves given by Eqs. (13) and (14).

3. Results and discussion

Based on the results for concentrations obtained from the examination of ion exchange kinetics, the amount of zinc and lead bound has been calculated for selected solid/liquid contact times (Figs. 1 and 2).

The ion exchange of zinc shown in Fig. 1 is rapid at initial times for all initial concentrations with prolonged slower uptake until equilibrium. At lower initial concentrations, the equilibrium is established at approximately 120 min, while at higher concentrations it is achieved within 480 min [16].

The ion exchange of lead is more rapid and the equilibrium is achieved within 20 min for all initial concentrations. The operating ion exchange capacity of zeolite has been calculated using

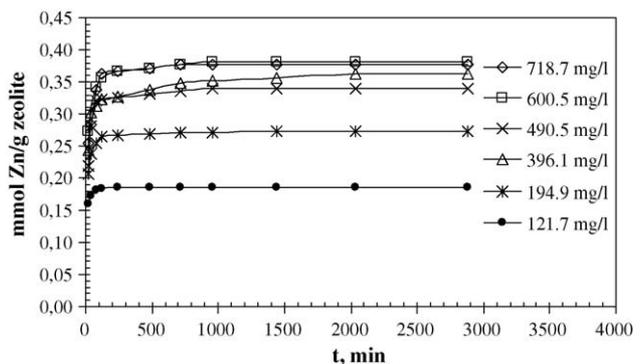


Fig. 1. The amount of zinc ions exchanged vs. time for different initial concentrations.

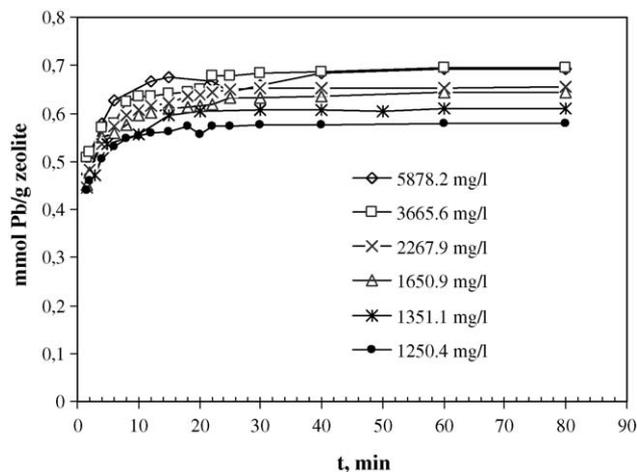


Fig. 2. The amount of lead ions exchanged vs. time for different initial concentrations.

the Langmuir empirical isotherm: for lead it is 0.62 mmol Pb/g zeolite and for zinc 0.32 mmol Zn/g zeolite. The doubly higher value of capacity for lead indicates higher selectivity of natural zeolite-clinoptilolite for lead than for zinc.

For both systems examined and for all initial concentrations of zinc and lead, the concentrations of exchangeable outgoing cations Na, K, Ca and Mg in suspensions increase at initial times of ion exchange, and remain constant until equilibrium. Fig. 3 and Table 1 shows concentrations of outgoing cations for similar initial molar concentrations of zinc $c_0 = 10.99$ mmol/l (600.5 mg/l) and lead $c_0 = 10.95$ mmol/l (2267.9 mg/l).

The concentration of Na ions in both systems (Zn solution–zeolite; Pb solution–zeolite) is significantly higher than the concentration of K, Ca and Mg ions due to the preconditioning of the zeolite-clinoptilolite to the Na form. For initial concentrations of ≈ 10 mmol/l, the quantity of Pb ions removed per gram of zeolite in equilibrium is doubly higher than for Zn ions (Figs. 1 and 2). The concentration of Na ions did not doubly increase in the suspension of lead compared to zinc (Table 1), that could be explained with lower exchangeability of zinc. Eq. (15) establishes the mass balance for outgoing exchangeable

Table 1

Increase in concentrations of exchangeable ions in suspensions during ion exchange of zinc or lead on natural zeolite

t (min)	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)
Zn ($c_0 = 10.99$ mmol/l, $\gamma_0 = 600.5$ mg/l)				
20	130.4	–	2.1	0.7
80	168.5	–	–	1.6
480	201.0	–	–	2.3
960	167.1	–	3.0	2.0
2040	165.2	–	3.6	2.7
2880	217.4	–	4.9	3.9
Pb ($c_0 = 10.95$ mmol/l, $\gamma_0 = 2267.9$ mg/l)				
2	211.6	0.92	1.8	0.40
10	254.8	2.38	0.7	0.42
20	269.3	2.58	1.8	0.36
40	280.3	3.38	2.6	0.40
60	281.4	3.86	1.3	0.42

Note: (–) concentration is below the detection limit.

cations (Na, K, Ca, Mg) and ingoing cations (Zn or Pb) as a difference in their concentrations at equilibrium (Δc in equiv./l). Calculation of mass balance at equilibrium for the same initial equivalent concentrations of Zn and Pb is provided by equation

$$\Delta c = c_e(\text{Na} + \text{K} + \text{Ca} + \text{Mg}) - c_e(\text{Zn or Pb}) \quad (15)$$

where $c_e(\text{Na} + \text{K} + \text{Ca} + \text{Mg})$ is the sum of concentrations of outgoing cations and $c_e(\text{Zn or Pb})$ is the concentration of Zn or Pb exchanged at equilibrium. From the experimental results in Table 1 and using Eq. (15), the difference in concentrations of outgoing and ingoing cations Δc has been calculated for the zeolite–zinc ions system (1.40×10^{-3} equiv./l) and for the zeolite–lead ions system (-0.62×10^{-3} equiv./l). The amount of zinc ions bound was lower, and amount of lead ions was higher than necessary for the stoichiometric ion exchange reaction. Namely, the hydration radius as well as the hydration energy of a divalent Zn ion (-2046 kJ/mol) is higher than that of Pb divalent ion (-1481 kJ/mol) with a higher atomic weight [1,4]. At pH values measured in the systems of zinc and lead, formation of monovalent ZnOH^+ and PbOH^+ ions is possible. These values for both systems examined are shown in Table 2.

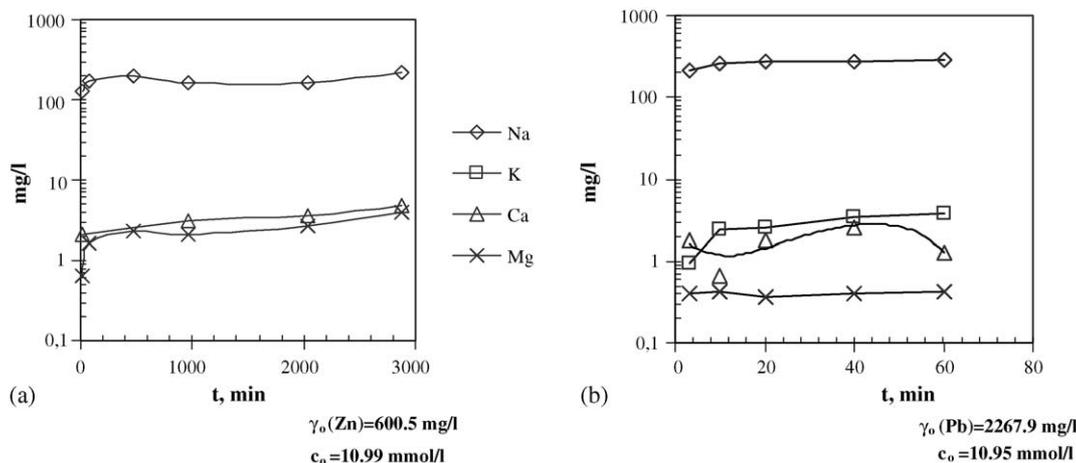


Fig. 3. Increase in concentration of exchangeable Na, K, Ca and Mg ions during ion exchange of (a) zinc and (b) lead on natural zeolite.

Table 2
Changes of pH values in solutions of lead and zinc for different initial concentrations

γ_0 (Zn) mg/l	t (min)										
	0	20	40	80	120	240	480	720	960	1440	
194.8	5.56	6.15	6.10	6.08	6.20	6.16	6.45	6.42	6.35	6.20	
396.1	5.36	4.71	5.24	5.91	5.91	4.90	4.73	4.73	4.93	5.49	
490.5	5.42	5.31	5.23	5.45	5.02	5.31	5.50	5.43	5.46	5.22	
600.5	5.33	4.61	5.05	5.22	5.11	5.01	4.73	4.52	4.73	5.50	
718.7	5.26	5.30	5.26	5.17	5.29	5.17	5.49	5.28	4.98	5.07	

γ_0 (Pb) mg/l	t (min)										
	0	2	4	8	10	15	20	30	40	60	
1250.4	5.08	4.73	4.81	4.83	4.81	4.75	4.73	4.89	4.91	4.79	
1650.9	4.96	4.67	4.68	5.05	4.68	4.68	4.78	4.66	4.72	4.72	
2267.9	4.84	4.64	4.55	4.58	4.63	4.56	4.52	4.52	4.60	4.58	
3665.6	4.65	4.70	4.72	4.68	4.62	4.64	4.69	4.66	4.68	4.72	
5878.2	4.61	4.29	4.24	4.35	4.37	4.35	4.30	4.41	4.36	4.37	

The pH values in solutions of zinc are somewhat higher (up to ≈ 1.5 pH unit) than in solutions of lead, and change slightly over the time for all initial concentrations. In initial solutions of lead, pH slightly decreases with the increase of the initial concentration, and also slightly decreases during ion exchange. The positive exchangeable ions $\text{Zn}(\text{OH})^+$ can be adsorbed inside the zeolitic particle channels, and result in their lower mobility, so ion exchange may be completely disabled. That explains its lower exchange capacity. Ion exchange of $\text{Pb}(\text{OH})^+$, due its lower hydration radius, may result as higher quantity of lead ion bounded as was observed by mass balance ($\Delta c = -0.62 \times 10^{-3}$ equiv./l). The observed non-stoichiometry of the process indicates that intraparticle adsorption may be taking place together with ion exchange. Therefore, the diffusion through a zeolitic particle, as the main resistance to the mass transfer of the exchangeable ion to the exchangeable site in the framework zeolitic structure, might be significantly slower [25,26].

Diffusion in the solution and diffusion through the film on the zeolitic particle have no impact on the overall process rate due to the high rate of mixing in the suspensions [27]. Therefore, diffusion models, used in examination of ion exchange kinetics, refer to diffusion through macro and micro pores of zeolitic particles, as the main resistance to the mass transfer of exchangeable ions.

The quantification of diffusion properties in the Zn ions solution–zeolite and Pb ions solution–zeolite systems is possible by calculation of diffusion coefficients using empirical kinetic models.

3.1. Application of kinetic models on experimental data

The kinetic diffusion models described below have been applied to the kinetic experimental results for zinc and lead that have been previous shown in Figs. 1 and 2.

Testing of experimental results for zinc ions has shown lower fitting with the parabolic diffusion model and the homogeneous diffusion model at the initial condition $t \rightarrow t_0$. That indicates

that diffusion is not only mechanism that describes mass transfer from the particle surface to the exchangeable site. The best fit was obtained with the model according to the Vermeulen's approximation and the homogeneous diffusion model for the initial condition $t \rightarrow t_\infty$. Application of these models to the Zn solution–natural zeolite system is shown in Figs. 4 and 5.

For the diffusion model according to the Vermeulen's approximation plotted in Fig. 4, curves are shown with inflection points that separate each curve into two areas. At these areas, the plots approach linearity, so that linearization of the curves for all initial concentrations was performed at two time intervals of the ion exchange; first at 0–120 min and second from 80 min until equilibrium. Eq. (8) was applied to each time interval and diffusion coefficients have been calculated from the slope of the lines.

Application of the homogeneous diffusion model (for the initial condition $t \rightarrow t_\infty$ to experimental results, plotted in Fig. 5, yields the same shape of curves as the Vermeulen's approxi-

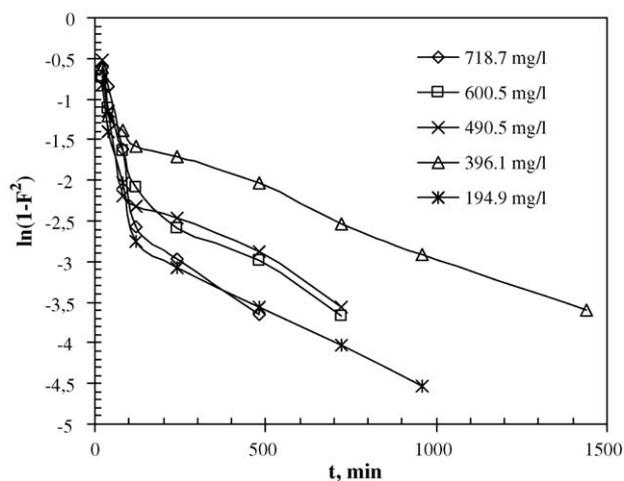


Fig. 4. Application of the Vermeulen's approximation to experimental results of zinc ions exchange on natural zeolite.

Table 3

Diffusion and determination coefficients calculated from the Vermeulen’s approximation and the homogeneous diffusion model for the zinc ions solution–natural zeolite system

γ_0 (Zn) mg/l	Vermeulen’s approximation				Homogeneous diffusion model, $t \rightarrow t_\infty$			
	0–120 min		80 min, up to equilibrium		0–120 min		80 min, up to equilibrium	
	$D \times 10^8$ cm ² /min	R^2	$D \times 10^8$ cm ² /min	R^2	$D \times 10^8$ cm ² /min	R^2	$D \times 10^8$ cm ² /min	R^2
194.8	2.30	0.990	0.26	0.999	2.58	0.967	0.26	0.998
396.1	3.73	1.000	0.20	0.995	4.30	1.000	0.21	0.994
490.5	3.42	0.998	0.25	0.979	3.74	0.994	0.26	0.980
600.5	1.85	0.988	0.31	0.980	2.81	1.000	0.36	0.944
718.7	2.15	0.986	0.37	0.999	2.67	0.993	0.37	0.999

mation. Therefore, the curves were also linearized at two time intervals and diffusion coefficients were calculated by Eq. (14).

Fitting of experimental points with both models examined is shown as a coefficient of determination (R^2) (Table 3).

High values of calculated R^2 show an agreement of experimental points with the models proposed. The order of magnitude of the calculated diffusion coefficients do not change with different initial concentrations, which indicate independence of diffusion through the zeolitic particle on the initial concentration of zinc ions in solution. Two linearization areas for both diffusion models and for all initial concentrations may be explained by a change of the diffusion rate from the surface to the centre of the particle or to the exchangeable site. In the first area, this could be attributed to diffusion through macro pores, and in the second area to diffusion through the crystal lattice.

Figs. 6–8 show testing of experimental results for ion exchange of lead ions on natural zeolite, for the previous kinetic models.

The models applied to experimental results for lead ions given linear dependencies for all examined initial concentrations, from the beginning of ion exchange until equilibrium. Using empirical Eqs. (8), (10) and (14), the diffusion coefficients and coefficients of determination have been calculated for a particular kinetic model. Table 4 displays the calculated data.

The experimental points show low fitting with the homogeneous diffusion model at the initial condition $t \rightarrow t_0$. The best

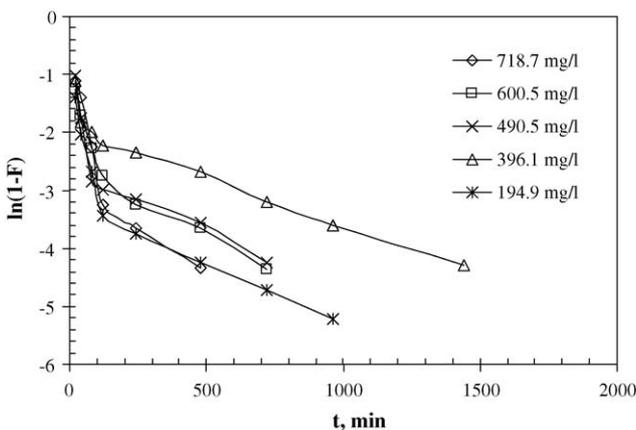


Fig. 5. Application of the homogeneous diffusion model, $t \rightarrow t_\infty$ to experimental results of zinc ions exchange on natural zeolite.

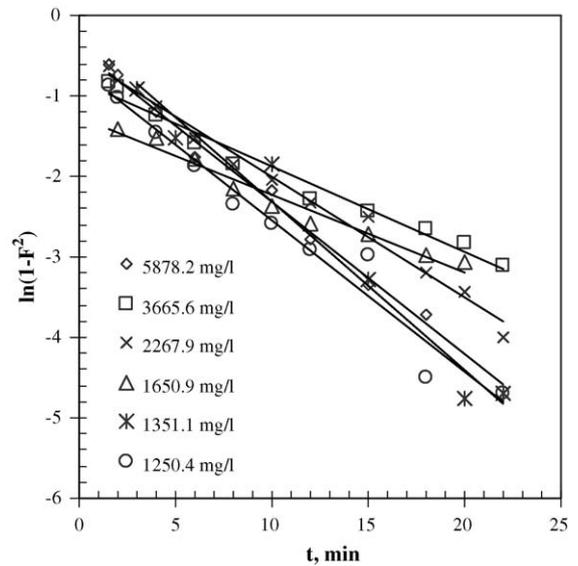


Fig. 6. Application of the Vermeulen’s approximation to experimental results of lead ions exchange on natural zeolite.

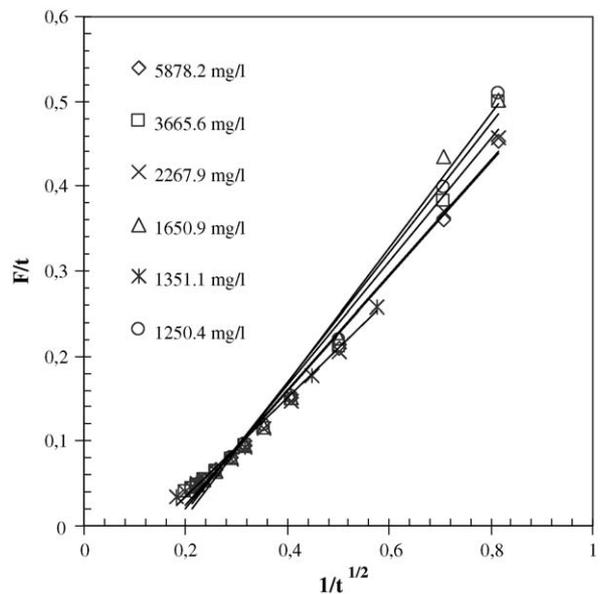


Fig. 7. Application of the parabolic diffusion model to experimental results of lead ions exchange on natural zeolite.

Table 4
Diffusion and determination coefficients calculated from the Parabolic diffusion model, the Vermeulen's approximation and the homogeneous diffusion model for the lead ions solution–natural zeolite system

γ_0 (Pb) mg/l	Parabolic diffusion model		Vermeulen's approximation		Homogeneous diffusion model, $t \rightarrow t_\infty$	
	D ($\times 10^6$ cm ² /min)	R^2	D ($\times 10^6$ cm ² /min)	R^2	D ($\times 10^6$ cm ² /min)	R^2
1250.4	5.55	0.989	0.93	0.966	0.87	0.927
1351.1	3.23	0.994	1.04	0.968	1.00	0.953
1650.9	6.02	0.988	0.48	0.966	0.50	0.964
2267.9	4.37	0.991	0.75	0.987	0.78	0.986
3665.6	5.09	0.985	0.53	0.974	0.55	0.945
5878.2	4.38	0.995	0.94	0.989	1.16	0.958

fitting was shown by the Vermeulen's approximation and the parabolic diffusion model with highest values of R^2 . But the values of diffusion coefficients calculated from these models show slight disagreement (Table 4). The homogeneous diffusion model for the initial condition $t \rightarrow t_\infty$ shows satisfactory fitting with experimental results, with the best agreement with the values of diffusion coefficients calculated by the Vermeulen's approximation. The constancy of diffusion coefficients for all examined initial concentrations indicates a constant diffusion rate from the surface to the exchangeable site in the zeolitic particle. The constant diffusion rate through the zeolitic particle also shows independence of the initial concentration of lead ions in solution.

Diffusion coefficients calculated in this paper were compared with those calculated by other authors who have examined ion exchange of heavy metals on natural zeolites [2,6,8,10,28,29]. Diffusion coefficients for the exchange of zinc ions were not found in literature, but for lead ions we have found the values for diffusion coefficients, calculated using the Vermeulen's approximation, with same order of magnitude. That means that our results agree satisfactorily with the results of relevant authors [2,6,28,29].

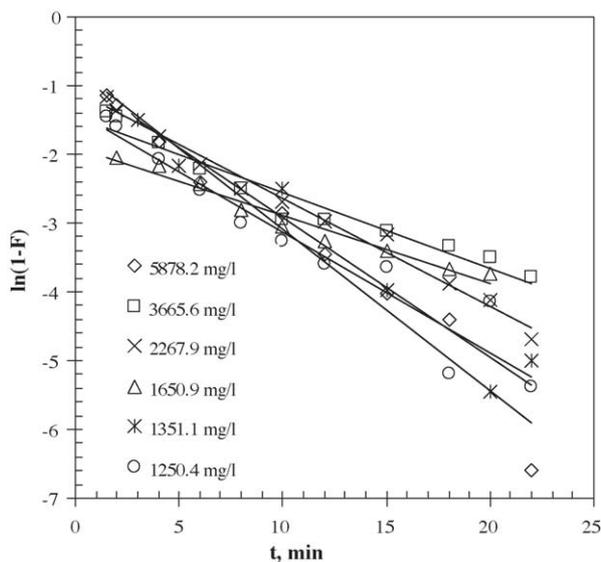


Fig. 8. Application of the homogeneous diffusion model, $t \rightarrow t_\infty$ to experimental results of lead ions exchange on natural zeolite.

4. Conclusions

The comparative study of ion exchange of zinc and lead ions on natural zeolite-clinoptilolite has shown their different equilibrium and kinetic behaviour. The doubly higher operating exchange capacity for lead ions than for zinc ions has confirmed a higher selectivity of natural zeolite-clinoptilolite for lead. This could be explained by lower hydration enthalpy for Pb^{2+} than for Zn^{2+} ions. A mass balance of ions included in ion exchange process observed non-stoichiometry between relation of ingoing and outgoing ions during ion exchange, particularly in the system of zinc ions. This is possible due the adsorption in the zeolitic particle that effect on mobility of ionic species included in ion exchange. Our previous investigation has shown that the intraparticle diffusion is a rate-limiting step for ion exchange of zinc on natural zeolite-clinoptilolite [27]. Therefore, similar kinetic models that describe diffusion inside the zeolitic particle have been examined in this paper: the model using the Vermeulen's approximation, the parabolic diffusion model and the homogeneous diffusion model that operates under two assumptions $t \rightarrow t_0$ and $t \rightarrow t_\infty$. The Vermeulen's approximation and the homogeneous diffusion model with $t \rightarrow t_\infty$ describe ion exchange in both systems (zinc ions–zeolite and lead ions–zeolite) well, with satisfied agreement of calculated diffusion coefficients and high R^2 values. But ion exchange of lead is about 100 times faster than that of zinc. This is confirmed by calculation of diffusion coefficients for zinc (order of 10^{-8} cm²/min) and lead (order of 10^{-6} cm²/min) for each tested model and initial concentrations. Moreover, diffusion does not depend on the initial concentration of zinc and lead in the suspensions. Diffusion coefficients for lead ions show the same order of magnitude as the data found in literature [2,6,28,29], while the comparable data for diffusion of zinc ions have not been found. The diffusion rate in the system of lead is constant and not time-dependent, while in the system of zinc it changes during the ion exchange process. This change is confirmed by calculations of diffusion coefficients for two time intervals from the beginning of exchange until equilibrium. The decrease of diffusion coefficients in the time interval from 80 min until equilibrium may be due to possible adsorption on intraparticle surfaces. That can affect the ion exchange in the network of channels and cages within the crystal structure and lead to variations in diffusion coefficients as we have observed in this study.

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