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INFLUENCE OF ZEOLITE PARTICLE SIZE AND INITIAL LEAD CONCENTRATION ON SORPTION KINETIC STUDY BY BATCH EXPERIMENTS

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The effect of particle size and initial lead concentration on the kinetics of lead ions uptake onto natural zeolite has been examined by batch experiments. The uptake rate of lead ions increases with decreasing particle size and has no effect on the zeolite removal capacities. Also the removal capacities are not affected by initial lead concentrations. To identify the rate-determining step, experimental data have been tested by the Lagergren pseudo-first order, Ho pseudo-second order and Elovich reaction kinetic models, Vermeulen's, Parabolic and Homogeneous diffusion models. For different lead concentrations and particle sizes the kinetic constants obtained have been changed and have consequently been excluded as relevant for the description of kinetics. Vermeulen's and Homogeneous diffusion models have shown the best fitting with the experimental data, what confirms that intraparticle diffusion is rate-determining step of uptake process of lead ions onto natural zeolite.

Key words: zeolite, diffusion kinetic, lead, particle size.

Utjecaj veličine čestica zeolita i početne koncentracije otopine olovovih iona na kinetiku sorpcije šaržnim postupkom. Ispitan je utjecaj veličine čestica zeolita i početne koncentracije otopine olovovih iona na kinetiku vezanja iona olova na zeolitu šaržnim postupkom. Brzina vezanja olova na zeolitu raste sa smanjenjem veličine čestica i nema utjecaj na kapacitet zeolita. Na kapacitet, također, ne utječe ni početna koncentracija otopine olova. Kako bismo utvrdili najsporiji stupanj procesa vezanja, eksperimentalni rezultati su testirani prema sljedećim modelima: Lagergren pseudo-prvog reda, Ho pseudo-drugog reda, Elovich modelu, Vermeulen-ovom, Paraboličnom i Homogenom difuzijskom modelu. Izračunate kinetičke konstante se mijenjaju s početnom koncentracijom olova i veličinom čestica zeolita, zbog čega nisu relevantne u opisu kinetike procesa. Vermeulen-ov i Homogeni difuzijski model su pokazali najbolje slaganje s eksperimentalnim točkama što potvrđuje da je difuzija kroz česticu zeolita najsporiji stupanj procesa vezanja iona olova.

Ključne riječi: zeolit, kinetika difuzije, olovo, veličina čestica.

INTRODUCTION

The increase of human population and industrial development gives rise to the formation of different liquid and solid wastes which have to be treated prior to disposal. Industrial wastes are most dangerous due to their toxicity and persistency in the environment. The most common pollutants in

industrial discharges are heavy metals, with mines, metal plating facilities, landfills and tanneries as the most usual sources. The examination of their removal from solid and liquid wastes before disposal into the environment is a challenge for many researchers. For complete removal, the

suitable processes are those of advanced treatments, such as adsorption, ion exchange, membrane techniques, advanced oxidation methods etc. The use of natural zeolites as adsorbents and ion exchangers has become an important alternative method for the removal of heavy metals from wastewaters. Zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations possessing an infinite, open three-dimensional structure [1-3]. Their environmental purpose has been increasing in the last two decades, due to simple and low cost exploitation. The well-known chemical and thermal stability in the environment extends the scientific research of zeolites to practical applications. The uptake of heavy metal ions from aqueous solutions on natural zeolite is a complex process, due to the porous zeolite structure, mineralogical heterogeneity and various surface imperfections on the zeolite particle.

The rate of heavy metal ions uptake on zeolite particles is very important and the design of processes largely depends on the knowledge and understanding of sorption mechanism and kinetics. According to Helfferich [4], there are several possible

rate-controlling steps and their different mathematical representations are described in literature [3-5]:

- diffusion of ions in the solution phase surrounding the particle e.g. film diffusion,
- diffusion of ions through the porous zeolite structure,
- chemical reaction at exchangeable sites.

Many researchers assume that diffusion of ions through zeolite is the slowest process. Another, less popular approach assumes that zeolite is an open structure and that exchangeable cations in zeolite are instantaneously and simultaneously available for exchange so that the chemical reaction is slow compared to any diffusion process [6]. A number of kinetic models have been proposed for the description of kinetics of metal ions sorption onto natural zeolites, in order to identify the rate-determining step of the process. In this paper, a number of applicable reaction and diffusion kinetic models were used to examine the effect of zeolite particle size and initial lead concentration on its removal kinetics [2, 4, 6-16]. Table 1 lists the models used in this examination.

Table 1. Kinetic models equations useable for batch mode of solid - liquid sorption systems
Tablica 1. Jednadžbe kinetičkih modela za opis sorpcije u sustavu kruto-tekuće "batch" metodom

Reaction kinetics based models		Diffusion kinetics based models	
Lagergren pseudo-first order	$q_t = q_e(1 - e^{-k_1 t})$	Vermeulen's model	$q_t = \left[1 - \exp\left(-\frac{Dt\pi^2}{r^2}\right) \right]^{1/2} \cdot q_e$
Ho pseudo-second order	$q_t = \frac{t}{1/k_2 q_e^2 + t/q_e}$	Parabolic diffusion model	$q_t = \left[\frac{4}{\pi^{1/2}} \left(-\frac{D}{r^2}\right)^{1/2} \frac{1}{t^{1/2}} - \frac{D}{r^2} \right] \cdot t \cdot q_e$
Elovich model	$q_t = \frac{1}{B} \ln(1 + ABt)$	Homogeneous diffusion model	$q_t = \left[1 - \frac{6}{\pi^2} \exp\left(-\frac{\pi^2 t D}{r^2}\right) \right] \cdot q_e$

For better comparison of models, the same symbols are used in all equations. They means as follows:

q_t - amount of lead ions sorbed at time t , mg/g

q_e - equilibrium amount of sorbed lead ions at, mg/g

t - time, min

k_1 - the Lagergren rate constant, 1/min

k_2 - the rate constant of the pseudo-second-order kinetic model, g/mg min

A - parameter of the Elovich model, mg/g min

B - parameter of the Elovich model, g/mg

D - the diffusion coefficient, m^2/min .

It is necessary to examine which of the proposed models successfully describe the aqueous solution of natural zeolite - lead ions system. Finding solutions to the kinetics of the process assumes testing of experimental results by equations proposed in Table 1. If the chemical reaction is the

rate-limiting step, the following conditions must be satisfied [5]:

- the rate constant should not change for any initial concentration,
- the rate constant should not change with the adsorbent particle size,
- the rate constant is independent of the agitation rate.

If any of these conditions is not met, the chemical reaction is not rate-controlling, even if the data successfully fitted the first or second pseudo kinetic model [5, 9].

Mass transfer in porous materials such as zeolites assumes diffusion of ions from the particle surface to sorption sites. One should consider the diffusion within pores and channels to be the slowest process. The following batch experiments and testing of experimental results by proposed models should provide guidelines about the kinetics of the lead sorption process on natural zeolites.

EXPERIMENTAL

Zeolite sample

The natural zeolite sample containing $\approx 80\%$ of clinoptilolite originated from the Vranjska Banja (Serbia) deposit. The sample was crushed and sieved to particle sizes of 0.6-0.8 mm, 0.1-0.5 mm and 0.04-0.1 mm, then rinsed in ultra pure water and dried at 60°C . Natural zeolite samples were pre-conditioned into the Na-form zeolite with a

NaCl solution of 2 mol/l, with stirring in an incubator shaker at a speed of 230-250 rpm for five days at 37°C . After equilibration, the solution was filtered and the solid phase rinsed up to a negative reaction to chloride. After drying at 60°C , the sample was stored in a desiccator.

Lead aqueous solution

Solutions of different initial lead concentrations (1177.10 - 3295.06 mgPb/l) were prepared by dissolving the appropriate amount of $\text{Pb}(\text{NO}_3)_2$ in ultrapure water, without adjusting the initial pH values. The

exact lead concentration was determined by complexometric titration in an acid medium, using the highly selective methylthymol blue indicator.

Batch kinetic study

The examination of sorption kinetics of lead ions was performed by means of the batch method. The mixtures of 1 g of zeolite sample and 100 ml of solutions of different initial concentrations were shaken at 240

rpm and at room temperature in closed vessels. For different contact times from beginning up to 1440 minutes, shaking was interrupted and the concentration of lead in supernatant was determined.

RESULTS AND DISCUSSION

The uptake of lead ions on natural zeolite occurs fast in the initial stage and then gradually increases until the equilibrium is reached (Figure 2). The fastest uptake is observed with the particle size of 0.04-0.1 mm, and equilibration is achieved in 20 minutes. With the particle size of 0.1-0.5 mm the equilibrium is reached in ≈ 120 minutes, and for the highest particle size of 0.6-0.8 mm, the equilibrium is reached in ≈ 500 minutes. The extended time needed for equilibration indicates the decrease of the

uptake rate with the increase of zeolite particle size. The equilibrium removal capacity slightly increases with the increase of initial Pb concentration (Figure 1). The exception is the lowest particle size, where the results for five out of six initial concentrations show almost the same removal capacities of zeolite. This confirms the strong effect of particle size on the uptake rate due to large outer specific surface of small particles, but it does not affect the removal capacity.

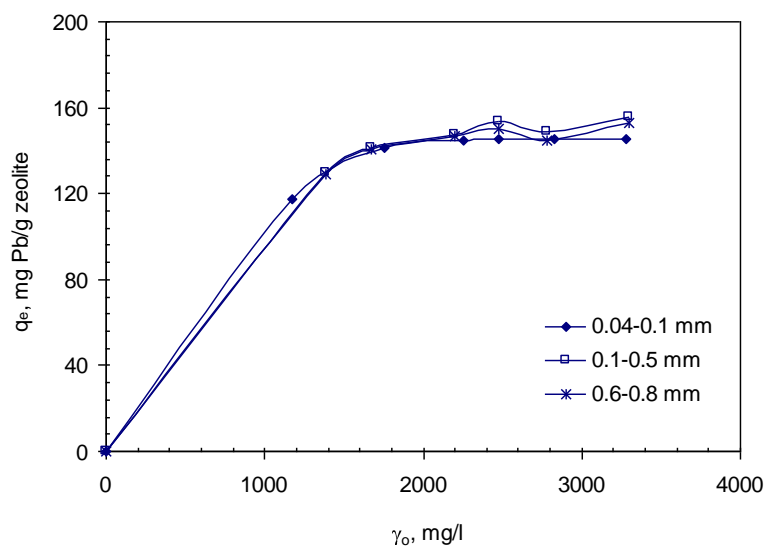


Figure 1. Removal capacities of zeolite for different particle sizes

Slika 1. Kapaciteti uklanjaња zeolita za različite veličine čestica

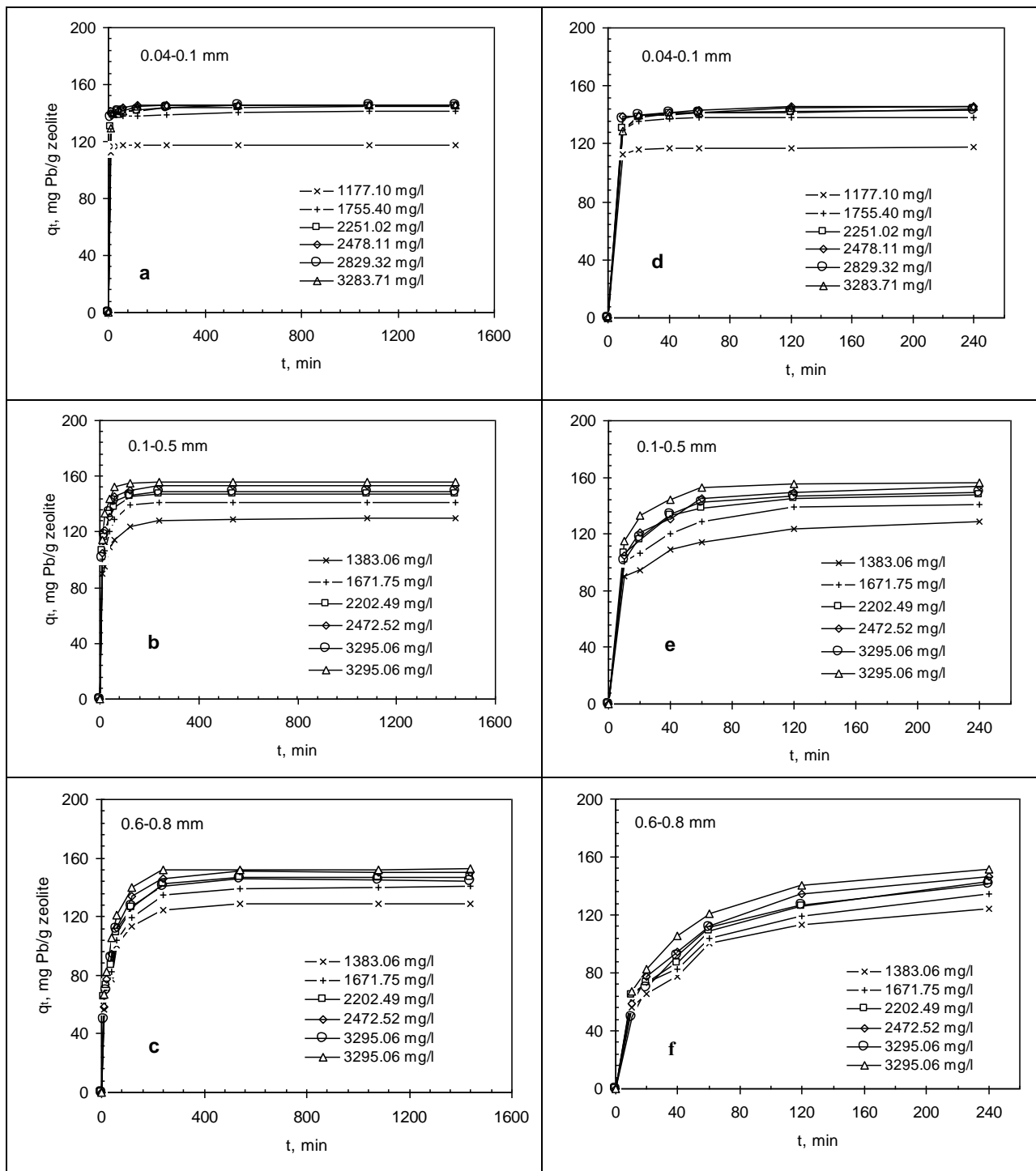


Figure 2. Influence of zeolite particle size and initial concentrations on removal kinetic of lead ions. Note: a, b, c - all examined time; d, e, f - up to 240 minutes

Slika 2. Utjecaj veličine čestica zeolita i početne koncentracije na kinetiku uklanjanja iona olova. Napomena: a, b, c - cijeli ispitani vremenski interval; d, e, f - interval do 240 minuta

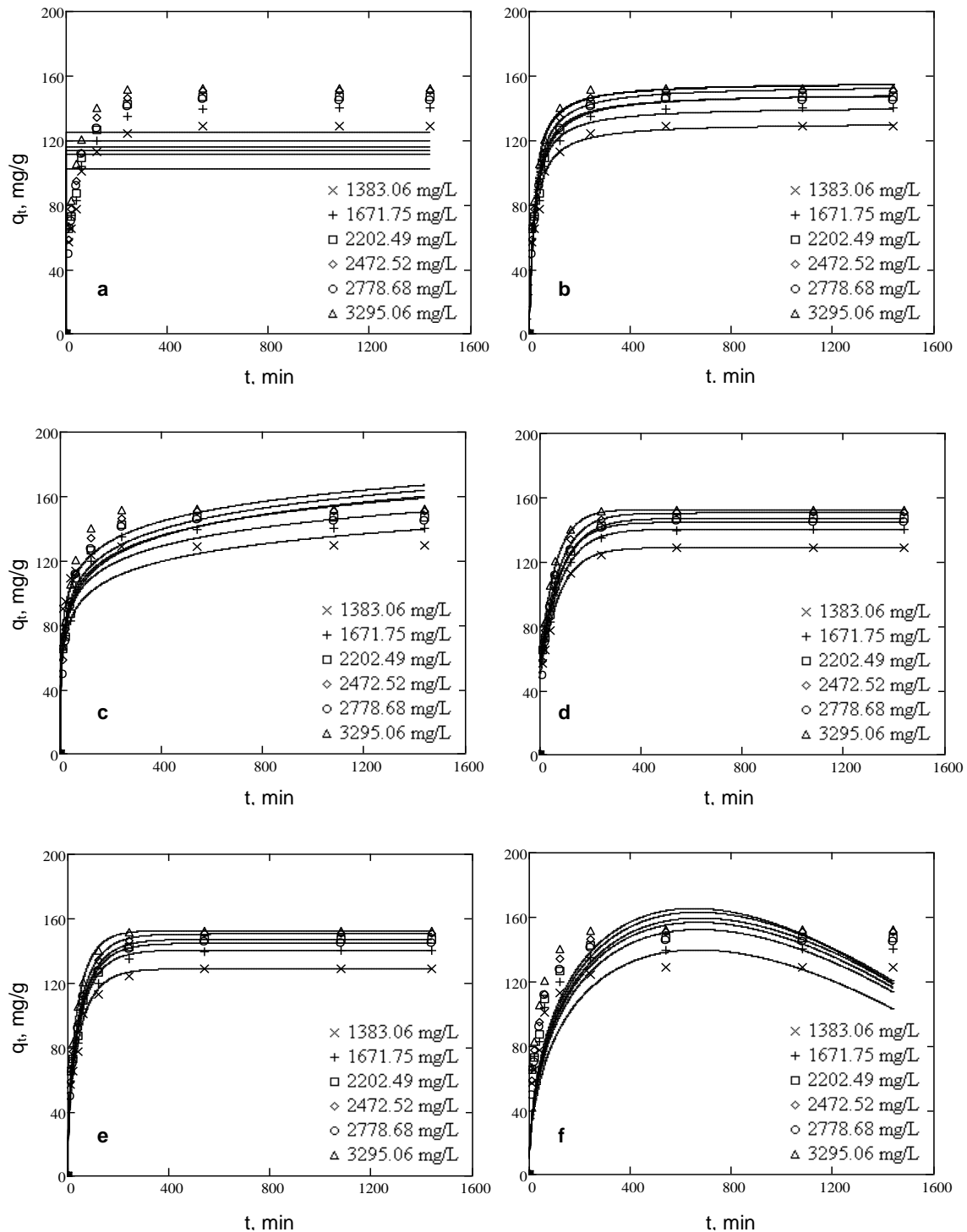


Figure 3. Fitting of experimental data (points) for different lead concentrations and modelled curves for particle size 0.6 - 0.8 mm. a - Lagergren pseudo-first order; b - Ho pseudo-second order; c - Elovich model; d - Homogeneous diffusion model; e - Vermeulen's model; f - Parabolic diffusion model

Slika 3. Slaganje eksperimentalnih podataka (točke) i modelnih krivulja za različite početne koncentracije olova i veličinu čestica zeolita 0.6 - 0.8 mm. a - Lagergren pseudo-prvog reda; b - Ho pseudo-drugog reda; c - Elovich model; d - Homogeni difuzijski model; e - Vermeulenov model; f - Parabolični difuzijski model

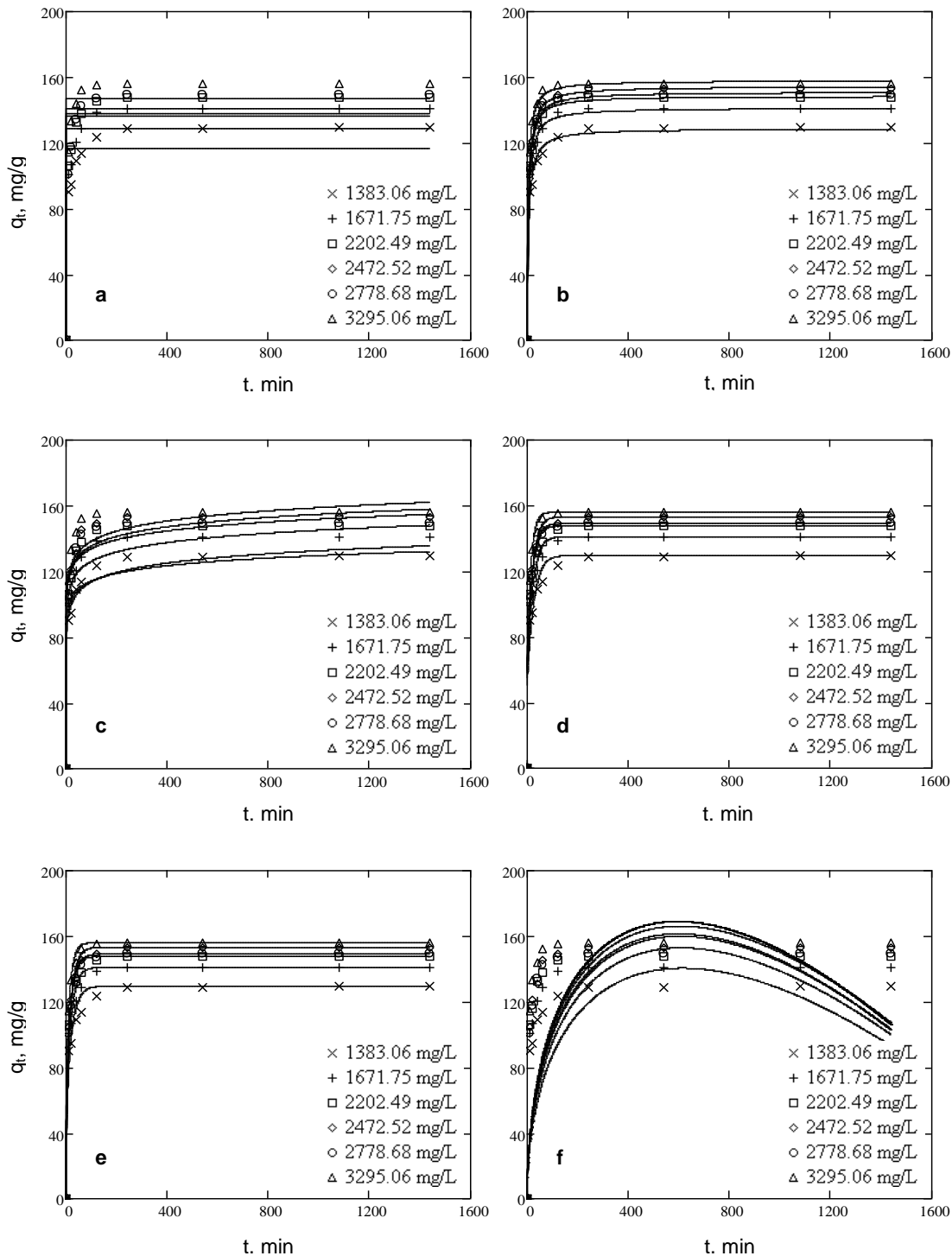


Figure 4. Fitting of experimental data (points) for different lead concentrations and modelled curves for particle size 0.1 - 0.5 mm. a - Lagergren pseudo-first order; b - Ho pseudo-second order; c - Elovich model; d - Homogeneous diffusion model; e - Vermeulen's model; f - Parabolic diffusion model

Slika 4. Slaganje eksperimentalnih podataka (točke) i modelnih krivulja za različite početne koncentracije olova i veličinu čestica zeolita 0.1 - 0.5 mm. a - Lagergren pseudo-prvog reda; b - Ho pseudo-drugog reda; c - Elovich model; d - Homogeni difuzijski model; e - Vermeulenov model; f - Parabolični difuzijski model

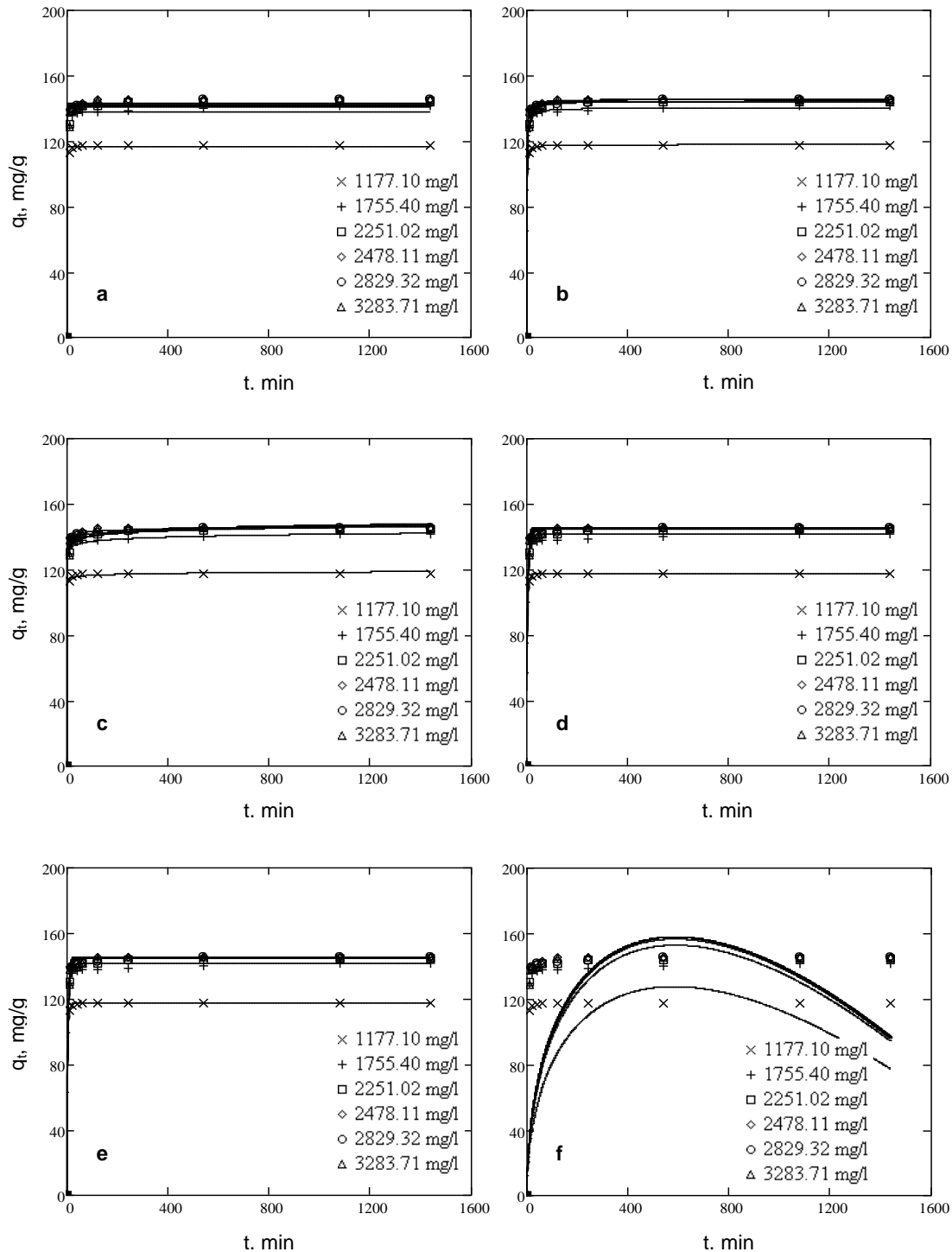


Figure 5. Fitting of experimental data (points) for different lead concentrations and modelled curves for particle size 0.04 - 0.1 mm. a - Lagergren pseudo-first order; b - Ho pseudo-second order; c - Elovich model; d - Homogeneous diffusion model; e - Vermeulen's model; f - Parabolic diffusion model

Slika 5. Slaganje eksperimentalnih podataka (točke) i modelnih krivulja za različite početne koncentracije olova i veličinu čestica zeolita 0.04 - 0.1 mm. a - Lagergren pseudo-prvog reda; b - Ho pseudo-drugog reda; c - Elovich model; d - Homogeni difuzijski model; e - Vermeulenov model; f - Parabolični difuzijski model

Prolonged equilibration for medium and higher particle sizes is due to the porous structure of zeolite particles with the first stage of rapid sorption on the outer surface followed by the diffusion of ions through structural channels to the sorption places. Rapid equilibration for the lowest particle size indicates that the reaction kinetics controls the rate of the overall process. On the other side, diffusion is the rate-limiting step for medium and highest particle sizes. Compared to natural sorbents, where higher sorption capacities are observed for lower particle sizes [13, 17, 18], our experiments confirmed similar removal capacities for the three examined zeolite particle sizes. Obviously, these systems have different effects on the uptake kinetics and a different mechanism of metal ion binding on the sorbents.

The testing of experimental results by models listed in Table 1 would show which model successfully describes the uptake of lead ions on zeolites. The parameters of all models presented in Table 1 were calculated by fitting the experimental data with the proposed models using nonlinear regression analysis. The algorithm for nonlinear regression analysis was developed in Mathcad 14. According to parameters calculated in Tables 2-4, modelled curves were plotted for each model and compared to the experimental points in Figures 3-5. In order to describe the goodness-of-fit of the experimental data to the proposed models, the chi squares (χ^2) were calculated and also shown in Tables 2-4:

$$\chi^2_i = \sum_{i=1}^n \frac{(q_{i,exp} - q_{i,cal.})^2}{q_{i,cal.}} \quad (1)$$

where:

q_{cal} - calculated value

q_{exp} - experimental value.

Figures 3-5 and Tables 2-4 clearly show that the Parabolic diffusion model does not fit the experimental data, has high χ^2 values and cannot be considered appropriate

for the description of kinetics. The Lagergren pseudo-first model does not fit experimental points and has also shown high χ^2 values for medium and higher particle sizes, while the data for the lowest particle size fit the model. The Ho pseudo-second order and Elovich model fit all experimental data and become better with the decrease of particle sizes. Better fitting of tested reaction kinetic models for the lowest particle sizes confirms that the reaction occurs on the large external surface and that diffusion is not dominant. The fitting of these models does not mean that the reaction kinetics is the rate-controlling process. Namely, the condition should also be met that kinetic constants are the same for all initial concentrations and particle sizes [5].

From Tables 2-4 it is clear that constants vary for different initial concentrations, and it is even more evident for different particle sizes. These facts make the fitting of reaction kinetic models to the experimental data quite questionable. On the other side, the Vermeulen's model provides similar values of diffusion coefficients for a specific particle size independently of the initial concentration, with satisfactory values of χ^2 . The coefficients are in agreement with values calculated by the Homogeneous diffusion model. If the diffusion coefficients calculated by the Vermeulen's model using nonlinear regression are compared with the results of linear regression for other sets of initial lead concentrations which have been published in a previous paper [16], the values are very close. This confirms that the diffusion of ions from the particle surface to the sorption places is responsible for the overall mass transfer rate. The calculated diffusion coefficients in Tables 2-4 decrease with particle size which agrees with descriptions found in literature [17, 18]. Mass transfer in porous materials such as zeolites is generally controlled by the transport of ions within pores and channels.

Table 2. Parameters of the tested models for zeolite particle size 0.6 - 0.8 mm
Tablica 2. Parametri testiranih modela za veličinu čestica zeolita 0.6 - 0.8 mm

Model	Parameter	$\gamma_o(\text{Pb})$ mg/l					
		1383.06	1671.75	2202.49	2472.52	2778.68	3295.06
	$q_{e \text{ exp}}$ mg/g	128.82	140.46	147.07	150.41	144.63	152.65
Lagergren pseudo-first order	q_e mg/g	102.61	111.11	116.01	119.41	113.94	124.91
	k_1 1/min	67.65	74.47	70.77	40.48	51.99	68.25
	χ^2	66.429	67.573	78.139	83.944	91.583	70.447
Ho pseudo- second order	q_e mg/g	131.13	141.05	149.44	154.30	149.75	156.24
	$k_2 \times 10^4$ g/mg min	4.00	3.84	3.32	3.20	3.01	3.91
	χ^2	4.506	7.526	6.693	1.981	0.680	1.767
Elovich model	A mg/g min	82.627	96.852	79.732	77.335	54.862	166.927
	B g/mg	0.064	0.060	0.055	0.053	0.052	0.0057
	χ^2	7.267	5.353	7.118	9.384	12.364	10.037
Homogeneous diffusion model	$D \times 10^{10}$ m ² /min	6.50	5.94	5.92	6.45	6.33	8.08
	χ^2	1.288	0.593	0.886	2.273	5.983	0.865
Vermeulen's model	$D \times 10^{10}$ m ² /min	7.06	6.74	6.55	6.89	6.61	8.49
	χ^2	2.866	6.299	4.216	0.660	0.291	0.785
Parabolic diffusion model	$D \times 10^{10}$ m ² /min	5.98	5.92	5.92	5.98	5.95	6.13
	χ^2	69.381	78.356	72.333	71.006	59.094	103.286

Table 3. Parameters of the tested models for zeolite particle size 0.1 - 0.5 mm
Tablica 3. Parametri testiranih modela za veličinu čestica zeolita 0.1 - 0.5 mm

Model	Parameter	$\gamma_o(\text{Pb})$ mg/l					
		1383.06	1671.75	2202.49	2472.52	2778.68	3295.06
	$q_{e \text{ exp}}$ mg/g	129.67	141.08	147.59	153.30	148.99	155.93
Lagergren pseudo-first order	q_e mg/g	116.45	128.84	136.43	140.55	137.55	147.02
	k_1 1/min	101.56	104.23	46.00	35.93	98.04	135.68
	χ^2	16.637	15.988	14.193	17.718	17.307	11.298
	q_e mg/g	128.84	141.42	148.60	154.49	151.14	157.99
Ho pseudo- secondorder	$k_2 \times 10^3$ g/mg min	1.39	1.41	1.49	1.27	1.30	1.72
	χ^2	1.392	1.249	0.453	0.467	0.201	0.160
Elovich model	A mg/g min	8.77×10^4	4.03×10^5	2.5×10^6	5.57×10^5	9.80×10^5	1.66×10^8
	B g/mg	0.122	0.122	0.129	0.113	0.120	0.149
	χ^2	2.279	3.066	3.368	4.196	5.187	3.903
Homogeneous diffusion model	$D \times 10^{10}$ m ² /min	3.66	4.29	5.13	4.57	4.89	6.69
	χ^2	3.227	2.926	1.935	1.876	0.459	0.539
Vermeulen's model	$D \times 10^{10}$ m ² /min	3.88	4.39	5.05	4.54	4.75	6.33
	χ^2	4.295	3.64	1.935	1.972	0.702	0.575
Parabolic diffusion model	$D \times 10^{10}$ m ² /min	1.19	1.20	1.21	1.21	1.22	1.23
	χ^2	254.123	305.073	346.821	334.245	334.816	334.816

Table 4. Parameters of the tested models for zeolite particle size 0.04 - 0.1 mm
Tablica 4. Parametri testiranih modela za veličinu čestica zeolita 0.04 - 0.1 mm

Model	Parameter	$\gamma_o(\text{Pb})$ mg/l					
		1177.10	1755.40	2251.02	2478.11	2829.32	3283.71
Lagergren pseudo-first order	$q_{e \text{ exp}}$ mg/g	117.72	141.47	144.57	145.59	145.61	145.61
	q_e mg/g	116.74	137.80	141.07	143.53	142.508	141.83
	k_1 1/min	158.33	320.47	317.40	414.07	394.51	304.02
	χ^2	0.189	0.768	1.205	0.416	0.479	1.684
Ho pseudo-second-order	q_e mg/g	117.89	140.30	144.34	145.27	144.42	145.69
	$k_2 \times 10^3$ g/mg min	19.00	8.79	6.62	13.00	12.00	5.53
	χ^2	0.834	0.065	0.036	0.087	0.081	0.080
Elovich model	A mg/g min	1.64×10^{60}	2.18×10^{30}	7.43×10^{25}	1.63×10^{43}	1.88×10^{36}	6.08×10^{21}
	B g/mg	1.1231	0.538	0.451	0.725	0.617	0.382
	χ^2	0.081	0.151	0.352	0.086	0.023	0.496
Homogeneous diffusion model	$D \times 10^{10}$ m^2/min	1.29	0.936	0.854	1.25	1.11	0.797
	χ^2	0.025	0.487	0.315	0.373	0.525	0.437
Vermeulen's model	$D \times 10^{10}$ m^2/min	1.20	0.861	0.785	1.16	1.03	0.732
	χ^2	0.024	0.474	0.301	0.366	0.515	0.421
Parabolic diffusion model	$D \times 10^{12}$ m^2/min	6.84	6.77	6.79	6.82	6.78	6.79
	χ^2	507.425	559.756	556.522	606.422	545.462	591.468

CONCLUSION

The examination of removal of lead ions onto natural zeolites of different particle sizes has shown that the uptake rate increases with decreasing particle sizes and has no effect on the removal capacity. The initial lead concentration has a very slight effect on the removal capacity for all particle sizes. The testing of experimental results according to reaction and diffusion kinetic models has shown the best fit of reaction kinetic models for the lowest particle sizes, where the reaction occurs on the external surface. Fitting of these models does not mean that the reaction kinetics is the rate-controlling process because the relevant constants calculated from the modelled curves do not show constancy for all examined concentrations and particle sizes.

The best fit with the experimental results is achieved with curves calculated by the Vermeulen's model and the calculated diffusion coefficients have close values for a specific particle size. Very similar values have been calculated by the Homogeneous diffusion model and the data agree with coefficients calculated for the same systems in a previous paper. It may be concluded that diffusion through the solid particle controls the uptake rate of lead ions onto natural zeolite. The same removal capacities for all the examined range of particle sizes indicate that higher zeolite particle sizes should be used in practical application. This would decrease expenses for milling and separation of the solid from the liquid phase after removal of heavy metals from wastewater.

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