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ADSORPTION KINETICS OF Pb^{2+} ONTO NATURAL ZEOLITE

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ABSTRACT

The sorption of Pb^{2+} from aqueous solution onto natural zeolite has been studied using an agitated batch adsorber. The influence of agitation speed, initial lead concentration and particle size of the sorbent on the removal efficiency of lead from liquid phase has been studied. The parameters of Langmuir and Freundlich adsorption isotherms have been determined using the sorption data. The maximum sorption capacity of lead on natural zeolite is 32.97 mg g^{-1}. The batch sorption kinetics have been tested for pseudo-first order and pseudo-second order reaction. The rate constants of sorption for both kinetics models for all investigated parameters have been calculated. High values for the correlation coefficients were obtained for both models and for all investigated parameters. The pseudo-first order model fits the experimental data well for the initial period of the reaction step.

Keywords: lead sorption, natural zeolite, equilibrium, kinetics.

INTRODUCTION

Conventional treatment methods for heavy metal removal from wastewater based on precipitation, (e.g. oxidation/precipitation, concentration/precipitation and so on), are not always sufficient to meet the new regulatory challenges [1]. Motivation to move away from precipitation technologies in metal control processes derives from the fact that precipitation can only reduce dissolved metal concentrations to the solubility product level, which is often insufficient to meet the stringent discharge permit standards and consequently requires downstream polishing stages. Furthermore, usually low concentrations of heavy metals in wastewater makes the common removal methods either economically unfavourable (e.g. conventional ion exchange, classical liquid extraction) or technically complicated (e.g. precipitation, cementation, reverse osmosis) [2,3]. These problems make the arena ripe for new and innovative methods as adsorption, ion-exchange, membrane aided separations and bioconversion for treatment of metal contaminated wastewaters [3].

In the last few years, adsorption has been shown to be an alternative method for removing dissolved metal ions from liquid wastes [4]. The most generally used solid adsorbent is activated carbon which is a very efficient synthetic adsorbent in many different applications [5]. The metal may then be recovered by desorption from the activated carbon and the cost of such a process naturally limits its application to only the more valuable metals. In many cases, however, the heavy metals are not valuable enough to warrant the use of special selective adsorbents/exchangers from an economic point of view. This has encouraged research of using low-cost adsorbent materials to purify water contaminated with metals.

In order to minimise processing costs, several recent investigations have focused on the use of low-cost adsorbents, as for example: natural zeolite [6, 7], kaolinite [8], activated phosphate [9], coals [10, 11], agriculture waste [12].

Zeolites are low-cost naturally occurring hydrated aluminosilicate minerals, with wide geographic distribution and large size of deposits [13]. In the last decade there is increasing interest in use of natural zeolites as cation exchangers in treatment of heavy metal containing effluents. Beside their ion exchange capacity natural zeolites exhibit adsorption behaviour that is based on theory of acid and basic sites in the framework structure. The sorption on zeolite particles is a complex process because of their porous structure, presence of exchangeable ions, inner and outer changed surface, mineralogical heterogeneity, existence of crystal edges, broken bonds, and other imperfections on the surface [14]

Among natural zeolites, clinoptilolite is the most abundant and commonly used as ion exchanger or adsorbent for inorganic or organic compounds. The specific structure of the clinoptilolite, consisting of a three-dimensional system of two types of channels (ten-member and eight-member rings) occupied by exchangeable Na^+, K^+, Ca^{2+} and Mg^{2+}, is responsible for its ion exchange and molecular sieve properties [7,15]. These exchangeable ions are located in the frame channels, coordinated with the defined number of water molecules that affect their mobility within the structure. Several researchers have studied the removal performance and selectivity sequence of heavy metal ions by natural zeolites [16-19].

The study of sorption kinetics in wastewater treatment is important since it provides valuable insights into reaction pathways and mechanism of adsorption process. In addition, the kinetics describes the solute uptake rate and mass transfer resistance at the solid-solution interface.

In general, for the adsorption of a solute onto the porous surface of an adsorbent, the following steps are required:

1. External (interphase) mass transfer of the solute from the bulk fluid by convection, trough a thin film or boundary layer, to the outer, solid surface of the adsorbent;
2. Internal (intraphase) mass transfer of the solute by pore diffusion from the outer surface of the adsorbent to the inner surface of the internal porous structure;
3. Surface diffusion along the porous structure;
4. Adsorption of the solute onto the porous surface.

For chemisorption, which involves bond formation, the rate of the fourth kinetic step may be slow and even controlling; for the physical adsorption, however, step 4 is almost instantaneous because it depends only on the collision frequency and orientation of the molecules with the porous surface.

Numerous mathematical models with varying degrees of complexity have been developed for sorption in batch systems [4,5]. Most of these models, which may include surface reaction kinetics [6,16,20], as well as various steps of mass transfer resistance [21,22], have originated mainly from the research on metal adsorption to porous, spherical activated carbon. Use of these models to describe metal sorption by non-conventional adsorbents is somewhat cumbersome because most of these adsorbents, including the natural zeolite used in this study have an irregular shape.

Ho and McKay [23] reported a literature review of the sorption kinetics models that has been used to describe several sorbents used to treat polluted aqueous effluents. In their work, eleven systems previously reported as first order kinetics and one system previously reported as second order kinetics were tested and the highest correlation coefficients were obtained for pseudo-second order kinetic model.

The aim of this work is to study the influence of batch sorption specific parameters, such as initial metal concentration, agitation speed and adsorbent particle size, on the lead sorption kinetics and to evaluate the kinetic models for lead removal from aqueous solution by natural zeolite. The pseudo-first order and the pseudo-second order reaction model were used to describe the experimental kinetics data.

EXPERIMENTAL

Materials and methods

Chemicals

The Pb^{2+} single ion water solutions were prepared by dissolving respective amount metal nitric salts, $Pb(NO_3)_2$ (Merck-Germany), in distilled water. The initial total metal ion concentration used in the sorption equilibrium and kinetics experiments was in the range between 50 mg dm^{-3} and 500 mg dm^{-3}.

Sorbent

Natural zeolite was used as sorbent in the investigated systems. The natural zeolite was supplied by Nemetali-Vranjska Banja, Serbia. The mineralogical composition of the natural zeolite is 90 % clinoptilolite and the rest is mordenite and haylandrite. The chemical analysis of the zeolite shows that the oxides of silicon, aluminium, calcium and iron are the main constituents while other oxides are present in trace amounts [7]. Prior to an experiment, the natural zeolite was dried at 300°C for 48 hours in order to remove any traces of moisture or other contaminants. The properties of the sorbent used are listed in Table 1.

Equilibrium experiments

The equilibrium adsorption of Pb^{2+} on natural zeolite was determined at 25°C. Sorption equilibrium experiments were performed in batch mode. The pH of the solution was not adjusted. 100 ml of solution with selected metal ion concentration (50-500 mg dm^{-3}) and mass of natural zeolite (1 g) were placed in 250 ml Erlenmeyer flask and shaken predefined time period needed for reaching of equilibrium (4 days) in vertical rotary shaker (150 turns/min) at constant temperature.

Table 1. Physical properties of natural zeolite.

Property	Natural zeolite
Particle size, mm	1-2
Particle density, g cm^{-3}	1.425
Real density, g cm^{-3}	2.246
Bulk density, g cm^{-3}	0.70-0.75
BET area, m^2 g	17.83
Pore volume, cm^3 g	0.01597*
Micropore volume, cm^3 g	
CEC, meq g	2.19
Hardness (Moss scale)	3-3.5
Ballpan hardness	96-9 %

**pores smaller than 269.8 Å.*

After reaching the equilibrium the solid-liquid suspension was filtrated and the pH of the filtrate was measured. The filtrates were than acidified with HNO_3 to decrease the pH below 3, before Atomic Adsorption Spectrometry (AAS) measurements.

Batch contact-time experiments

The influence of agitation, initial metal concentration and sorbent particle size on the rate of uptake of Pb^{2+} was determined by carrying out contact time experiments using batch agitated reactor. The uptake experiments were conducted at 25°C, under constant pH values, with varying initial metal concentration in the range 50-500 mg dm^{-3} . The range of varying the agitation speed was between 150 - 190 rpm, and the range of average particle size was 700-1400 mm.

RESULTS AND DISCUSSION

SORPTION ISOTHERMS

The sorption equilibrium of Pb^{2+} on natural zeolite was determined at 25°C. (Fig 1). The experimental sorption equilibrium data were described by Langmuir and Freundlich equations:

Langmuir isotherm

$$q_e = \frac{Q_0 b c_e}{1 + b c_e} \tag{1}$$

where c_e (mg dm^{-3}) is the equilibrium concentration, q_e (mg g^{-1}) the amount adsorbed at equilibrium, and b (dm^3 mg^{-1}) the “affinity” parameter or the Langmuir constant, and Q_0 (mg g^{-1}) is the maximum sorption capacities.

Freundlich isotherm

$$q_e = K_F c_e^{(1/n)} \tag{2}$$

where, c_e and q_e have the same definitions presented for the Langmuir isotherm. K_F and n are the constants that can be related to the sorption capacity and the sorption intensity, respectively.

Table 2. Parameters in the equilibrium isotherms for the system Pb^{2+} - natural zeolite.

Langmuir isotherm			*Freundlich isotherm*		
b $dm^3\ g^{-1}$	Q^0 $mg\ g^{-1}$	R^2	K_F $mg\ g^{-1}$	n	R^2
1.004	*32.97*	*0.997*	*16.059*	*4.56*	*0.946*

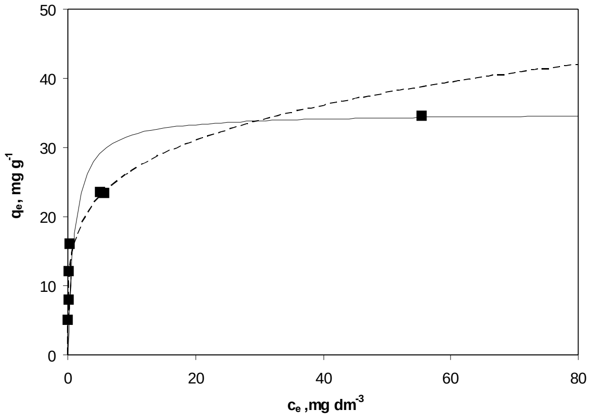

Fig. 1. Comparison of experimental and calculated data by Langmuir and Freundlich equilibrium isotherms for the system Pb^{2+} - natural zeolite. ■ - Experimental data ____ - Langmuir isotherm -------- - Freundlich isotherm

The experimental sorption equilibrium data of Pb^{2+} sorption on natural zeolite is correlated using the linear forms of the Langmuir and Freundlich isotherm, respectively:

$$\frac{c_e}{q_e} = \frac{1}{Q_0 b} + \frac{c_e}{Q_0} \qquad (3)$$

$$\log(q_e) = \log(K_F) + \frac{1}{n}\log(c_e) \qquad (4)$$

The Langmuir and Freundlich isotherm parameters for Pb^{2+} sorption on natural zeolite are presented in Table 2. Taking into consideration the values of the correlation coefficient as a criterion for goodness of fit for the investigated system, the Langmuir model shows better correlation between the theoretical and experimental data for the whole concentration range than Freundlich equation (Table 2).

SORPTION KINETICS

Effect of agitation speed

The effect of the agitation speed on the sorption was investigated by changing the agitation speed in the range of 150-190 rpm with constant particle diameter 1100 mm and initial concentration 250 mg dm^{-3}, sorbent dosage of 1 g, and temperature of 25°C (Fig. 2). The concentration of adsorbed Pb^{2+} on the natural zeolite was calculated according to the equation of material balance (Eq 5). The 190 rpm was the maximum rotation speed of the thermostated vertical rotary shaker used in this study.

$$q_t = \frac{V}{m}(c_0 - c_t) \qquad (5)$$

where: V - volume of the solution, dm^3,

m – mass of sorbent, g,

c_0 – initial concentracion, mg dm^{-3},

c_t –concentracion at time t, mg dm^{-3}.

The rate of lead removal was not significantly influenced by the degree of agitation. This results show that the mass transfer through the external film is not affecting the sorption rate, and therefore is not rate controlling step of whole sorption process. McKay at al. [24] found that the variation of the external mass transfer coefficient with the agitation have been more significant when very low agitation speeds were used (rpm<50).

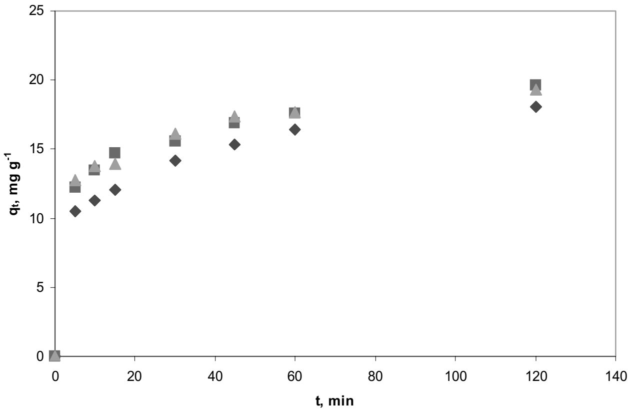

Fig. 2. Effect of agitation speed for the system Pb^{2+} - natural zeolite (c_o=250 mg dm^{-3}, d_p = 1100 mm, m=1 g, T=25°C). ♦ - 150 rpm, ■ 175 rpm, ▲ - 190 rpm.

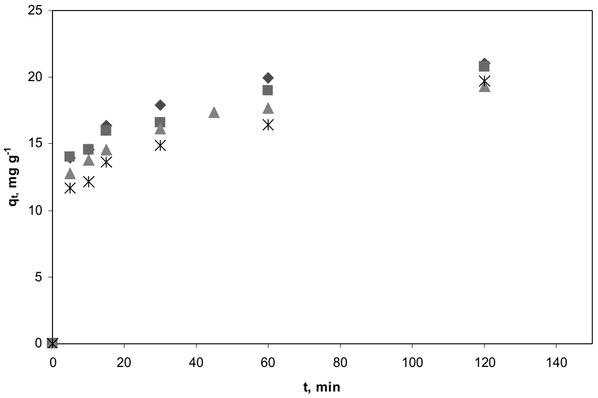

Fig. 3. Effect of particle size for the system Pb^{2+} - natural zeolite (190 rpm, c_o=250 mg dm^{-3}, m=1 g, T=25°C). ♦ d_p=700 µm; ■ d_p=900 µm; ▲ d_p=1100 µm; * d_p=1400 µm

The agitation speed of 190 rpm was selected in the studies of the influence of the particle size and initial lead concentration on the sorption kinetics.

Effects of particle size

The effect of the range of average particle size on the sorption was investigated by changing the particle size in the range of 700-1400 mm, with constant agitation speed of 190 rpm and initial concentration 250 mg dm^{-3}, sorbent dosage of 1 g and temperature 25°C.

The influence of particle size on the lead sorption kinetics is presented on Fig. 3. Sorption of Pb^{2+} on natural zeolite is slightly increased by decreasing average particle size from 1400 to 700 mm. Nevertheless, similar results have been obtained for particle size 700 and 900 mm. The relatively higher sorption with smaller sorbent particle may be result to the fact that smaller particles yield large surface area. The results of this study also anticipate the internal (particle) mass transfer as a rate controlling step of lead sorption kinetics.

Effects of initial concentration

The initial Pb^{2+} concentration of an effluent is important since a given mass of sorbent can only adsorb a fixed amount of heavy metal. Therefore, the more concentrated an effluent, the smaller is the volume of effluent that a fixed mass of zeolite can purify.

The effect of initial Pb^{2+} concentration on the sorption was investigated by changing the initial Pb^{2+} concentration in the range of 50–500 mg dm^{-3} with constant agitation speed 190 rpm and particle size d_p=1100 mm, sorbent dosage 1 g, and temperature 25°C. The effect of initial concentration is shown on Fig. 4.

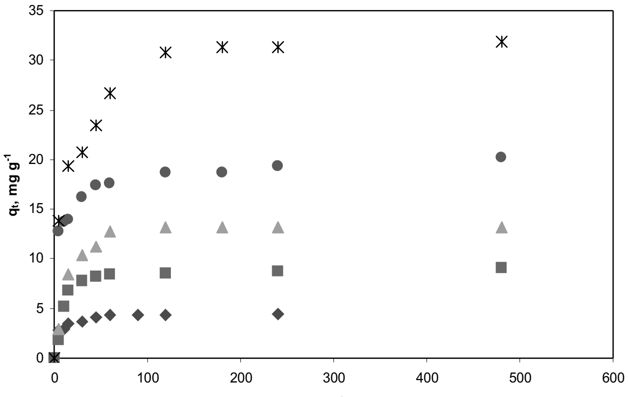

Fig. 4. Effect of initial concentration for the system Pb^{2+} - natural zeolite (190 rpm, d_p =1100 mm, m=1 g, T=25°C). ♦ c_o = 50 mg dm^{-3} ■ c_o = 100 mg dm^{-3} ▲ c_o = 150 mg dm^{-3} ● c_o = 250 mg dm^{-3} * c_o = 500 mg dm^{-3}.

From Fig. 4 is evident that with lower initial concentration of Pb^{2+} the amount of Pb^{2+} attained on the solid phase is smaller than the amount attained when higher initial concentration is used. The sorption of lead at different concentration is increased instantly at initial stage (approximately 60 min) and then keeps increasing gradually until the equilibrium is reached. After 240 min 90 % of the adsorbed equilibrium concentration was reached.

Sorption kinetics modelling

In order to develop a fast and effective sorption kinetics model, investigations are deliberately made with kinetic viewpoint. The kinetic studies involve effect of some major parameters, initial concentration in the aqueous solution, agitation speed and particle size on the uptake of Pb^{2+} on the natural zeolite. The models of sorption kinetics correlate the solute uptake, so these models are important in water treatment process design. In this study two kinetics models were used to describe kinetics of sorption of Pb^{2+} onto natural zeolite: pseudo-first order model (M1) and pseudo- second order model (M2) [25]. The used models take into consideration that the rate of chemisorption is slow and controlling step.

Pseudo-first order model

The sorption of lead from liquid phase to solid may be considered as a pseudo-first order reaction, with an equilibrium state being established between two phases. A simple pseudo-first order reaction model was used to correlate the rate of reaction (Eq. 6)

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{6}$$

Integrating and applying boundary conditions: at t=0, q_t=0 and at t=t, q_t=q_t Eq. (6) may be rearranged to following linear correlation, Eq. (7):

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{1.303}t \tag{7}$$

In order to obtain the rate constants (k_1), the straight line plots of log(q_e-q_t) versus t for different experimental parameters have been analyzed. Fig. 5 is shown as an example for these plots, for the experimental data obtained in the study of the influence of initial lead concentration of the sorption kinetics. The pseudo-first order reaction model gives good prediction of the experimental kinetics data until 60 min. Above this time the experimental data do not follow the linearity of the model equation (Eq. 7). Linear fits were also observed for the lead sorption kinetics data obtained at different agitation speed and particle size, in the time range between 0 to 60 min and 0 to 120 min, respectively. The calculated rate constant k_1 for all performed sorption kinetics experiment are summarized in Table 3.

In order to represent the whole range of lead sorption onto natural zeolite, multiple pseudo-first order kinetics was applied. Basically a multiple pseudo-first order process means that a plot of log(q_e-q_t) versus time can be divided into two or three linear sections, each linear section representing a pseudo-first order reaction mechanism. In our case we divided the plot of log(q_e-q_t) versus time into two linear sections (Fig. 5a and Fig. 5b). In the case of two kinetic steps, the first step of sorption was more rapid than the second one. This might be because in the fist step, the lead is adsorbed on the surface where there are no such sorbates and consequently the sorbate-sorbent interaction is negligible, leading to the formation of a monolayer. As this monolayer approaches saturation, a process of rearrangement may start with a further increase in the sorbate, which constitutes the second step.

Pseudo-second order model

A pseudo-second order model [25] is used to describe the kinetics of lead sorption. Differential equation for this reaction model is (Eq.8)

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{8}$$

Integrating Eq.8 for the boundary conditions: at t=0, q_t=0 to t=t, q_t=q_t and rearranging to obtain the linear correlation, (Eq.9):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{9}$$

In order to obtain the rate constants, k_2 and q_e the linear plots of t/q_t versus t for different experimental parameters have been analyzed. The experimental

Table 3. Pseudo-first order and pseudo-second order reaction rate constants at different experimental conditions.

	Pseudo-first order		Pseudo-second order		
	k_1	R^2	k_2	$q_e(cal)$	R^2
c_o, mg dm^{-3}					
50	0.0398	0.9882	0.0478	4.53	0.9998
100	0.0315	0.9251	0.0125	9.19	0.9991
150	0.0352	0.9619	0.0073	13.77	0.9993
250	0.0166	0.9680	0.0062	20.32	0.9993
500	0.0154	0.9611	0.0025	32.77	0.9993
rpm					
150	0.0136	0.9956	0.0067	18.94	0.9964
175	0.0083	0.9905	0.0077	20.24	0.9960
190	0.0117	0.9611	0.0090	19.92	0.9979
d_p					
700	0.0223	0.9854	0.0101	21.74	0.9999
900	0.0147	0.9926	0.0067	22.22	0.9997
1100	0.0161	0.9688	0.0071	20.41	0.9998
1400	0.0106	0.9899	0.0043	21.83	0.9991

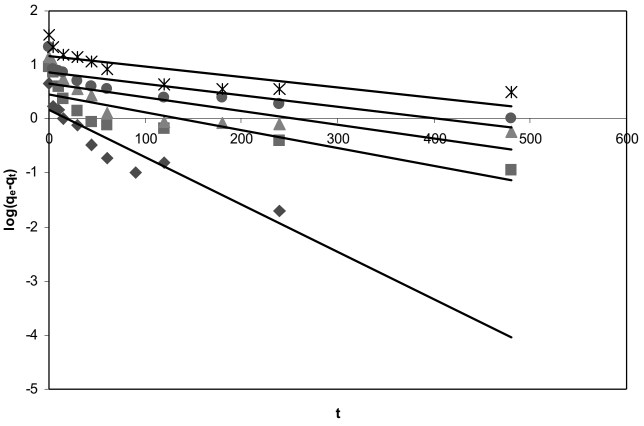

Fig. 5. Pseudo-first order reaction kinetics plots for the system Pb^{2+} - natural zeolite (190 rpm, d_p =1100 mm, m=1 g, T=25°C). ♦ c_o = 50 mg dm^{-3} ■ c_o = 100 mg dm^{-3} ▲ c_o = 150 mg dm^{-3} ● c_o = 250 mg dm^{-3} * c_o = 500 mg dm^{-3}.

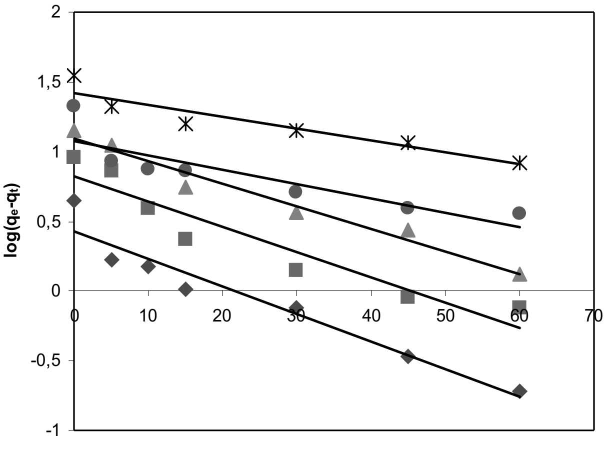

Fig. 5a. Pseudo-first order reaction kinetics plots for the system Pb^{2+} - natural zeolite (first period), (190 rpm, d_p =1100 mm, m=1 g, T=25°C).♦ c_o = 50 mg dm^{-3} ■ c_o = 100 mg dm^{-3} ▲ c_o = 150 mg dm^{-3} ● c_o = 250 mg dm^{-3} * c_o = 500 mg dm^{-3}.

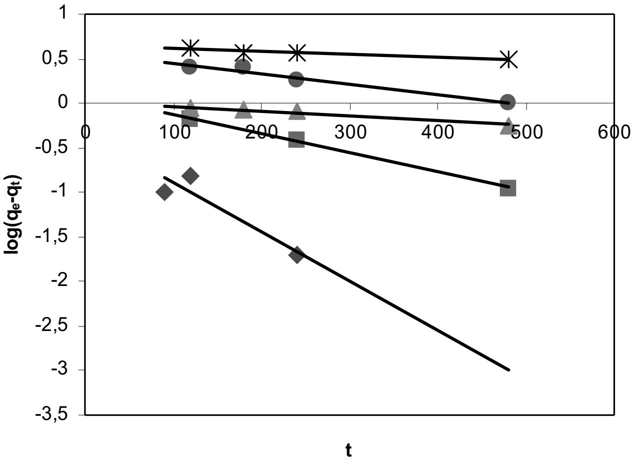

Fig. 5b. Pseudo-first order reaction kinetics plots for the system Pb^{2+} - natural zeolite (second period), (190 rpm, d_p =1100 mm, m=1 g, T=25°C).♦ c_o = 50 mg dm^{-3} ■ c_o = 100 mg dm^{-3} ▲ c_o = 150 mg dm^{-3} ● c_o = 250 mg dm^{-3} * c_o = 500 mg dm^{-3}.

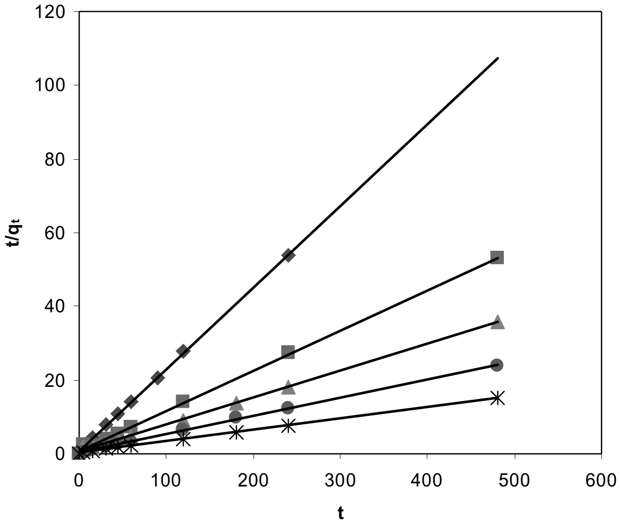

Fig. 6. Pseudo-second order reaction kinetics plots for the system Pb^{2+} - natural zeolite, (190 rpm, d_p =1100 mm, m=1 g, T=25°C).♦ c_o = 50 mg dm^{-3} ■ c_o = 100 mg dm^{-3} ▲ c_o = 150 mg dm^{-3} ● c_o = 250 mg dm^{-3} * c_o = 500 mg dm^{-3}.

kinetics data obtained for different lead initial concentrations for the whole time range are presented in a t/q_t versus t plot in Fig. 6. Linear fits (t/q_t versus t) were also obtained for all experimental data obtained at different agitation speed and particle size, during whole time range. The calculated values of the rate constant k_2 and equilibrium adsorbed concentration q_e for all experimental studies were calculated and summarized in Table 3.

In Table 3 are also given the correlation coefficients of two models and for all investigated sorption kinetics influencing parameters. The values of correlation coefficients for the linear plots of t/q_t versus t from pseudo-second order rate law extremely high (>0,996).

CONCLUSIONS

Certain general conclusions may be deduced from the experimental and theoretical analysis of sorption kinetics of lead onto natural zeolite:

The equilibrium studies have shown that the Langmuir equilibrium model indicates better correlation between the theoretical and experimental data, for the whole lead concentration range, than the Freundlich model.

For the kinetic study in this paper, two models i.e., the pseudo-first order model and the pseudo-second order model were used in prediction of the experimental data.

For the studied system, chemical reaction seems significant in the rate controlling step and the pseudo-second order chemical reaction kinetics provides the best correlation of the experimental data. Whereas the pseudo-first order model proposed fits the experimental data well for an initial period of the reaction step only.

For modelling of the kinetics of lead removal by natural zeolite, the pseudo-second order reaction model can be used, although does not coincide with the real nature of the sorption process (ion exchange and adsorption). However, from the mathematical point of view the use of this simple model would bring less calculation and computation effort during the design of the fixed bed sorption unit, commonly used in the sorption wastewater treatment processes. It should be pointed out that the real sorption rate-determining step (ion exchange) taking into consideration the mass transfer resistance would be analysed more deeply in future.

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