

## **KINETIC OF SORPTION OF LEAD ON NATURAL AND IRON(III)-MODIFIED ZEOLITE**

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### **ABSTRACT**

The sorption of lead from water solutions on natural and iron(III)-modified zeolite was examined as a function of reaction time. Different kinetic models were performed to determine the rate parameters and rate controlling step. The best fit for both sorbents was obtained for pseudo-second order model, meaning that the rate controlling step is chemisorption. Initial rate constant for lead sorption on iron(III)-modified zeolite is twelve times higher than for natural one, confirming that sorption of lead on iron(III)-modified zeolite is much faster than on natural sample. At equilibrium, maximum lead sorption efficiency was 43 mg/g for the natural and 62 mg/g for iron(III)-modified zeolite.

**Keywords:** sorption kinetics, lead, natural zeolite, iron(III)-modified zeolite.

### **INTRODUCTION**

Wastewater contaminated with heavy metals is generated in many industrial activities, such as tanneries, metal plating facilities and mining operations. It is well known that heavy metals have harmful effects on human health in elemental forms as well as in combination with other materials. Regarding acute toxicity, Cd<sup>2+</sup> and Pb<sup>2+</sup>, together with Hg<sup>2+</sup>, form "the big three" of heavy metals with the greatest potential hazard to human and environment [1]. For lead it is known that it cause damage of kidney, liver, reproductive system, basic cellular processes and brain functions and according to the EU directive (98/83/EC) maximum lead concentration in drinking water is 0.01 mg/L. There are several methods to the treat heavy metals contaminated effluents such as ion exchange, chemical precipitation, oxidation, adsorption, reduction or osmosis. Adsorption and ion exchange are simple and effective processes for heavy metals removal, particularly when low-cost and eco-friendly natural materials (such as clay minerals) are employed [2].

Zeolites are crystalline hydrated aluminosilicates of alkali and alkaline earths built from three dimensional network of tetrahedral TO<sub>4</sub> units, where T is Si or Al. Due to substitution of Si<sup>4+</sup> with Al<sup>3+</sup>, framework of zeolite is negative charged, which is compensated by monovalent or divalent cations located together with water. Zeolites are effectively used as sorbent for heavy metal removal, owing to their advantageous ion exchange capacities, large specific surface area, high metal selectivity, low-cost and high reserves. Exchangeable cations in zeolite structure Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>, are not toxic, which makes the zeolites especially suitable for tertiary processes of wastewater treatment [3]. Among the zeolites, clinoptilolite is the most abundant natural zeolite and is widely used in the world. Recently, zeolites were used as substrates for iron modification, in order to improve the sorption selectivity and capacity for heavy metals, and results showed that such modified zeolite can be significantly better sorbent for same heavy metals (manganese, copper, zinc, lead) than natural one.

Predicting the rate of sorption for a given system is one of the most important factor in sorption system design. As reviewed previously [4] various kinetic models have been suggested in order to investigate the sorption mechanisms of various sorption-based systems. However, in the literature no data are reported for kinetics of removal of lead by iron(III)-modified zeolite, which is the subject of the presented work.

## EXPERIMENTAL

The starting material was the natural zeolite from the Zlatokop deposit, Vranjska Banja with the particle size <0.043 mm. The iron(III)-modified zeolite was synthesized combining the method for pure goethite preparation [5] and method for preparation of iron coated zeolite [6]. Details of the preparation of the iron(III)-modified zeolite are given elsewhere [7]. The effect of contact time on the lead sorption by the natural and iron(III)-modified zeolite was conducted at pH 4.24 by observing the sorption of lead by both sorbents from 0 to 48 h (2880 min) with the initial lead concentration of 1280 mg/L. In order to evaluate kinetic data, separate flasks were prepared for each time interval and only one flask was taken for desired time. In all experiments, after reaction, solution and each sorbent were separated through standard filter paper and concentrations of non sorbed lead and released exchangeable cations (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>) in supernatants were determined by atomic absorption spectrophotometry (AAS) using an “Analytic Jena Spekol 300“. Sorbed amount of lead was calculated from difference between starting concentration of lead and its concentration in the supernatant.

## RESULTS AND DISCUSSION

The effect of contact time on lead retention onto natural and iron(III)-modified zeolite is shown at Fig. 1a.

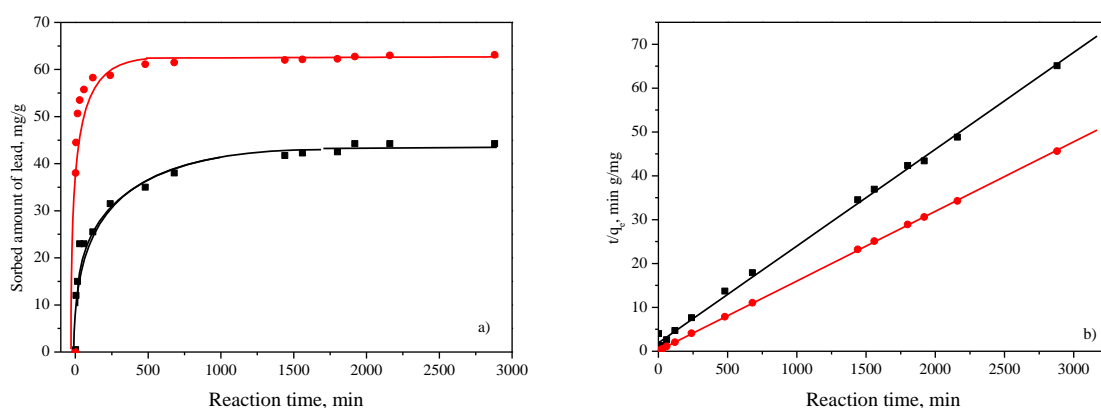


Figure 1. Effect of contact time on sorption of lead on natural (-■-) and iron(III)-modified zeolite (-●-) - left; Pseudo-second order model fitted for sorption of lead on natural (-■-) and iron(III)-modified zeolite (-●-) - right.

As presented in Fig. 1 (left), the removal of lead by sorption on both zeolites showed steady increase for the first 230 min, followed by an appreciable stabilization trend attaining a maximum value at about 900 min for the natural zeolite and about 300 min for iron(III)-modified zeolite. At equilibrium, maximum lead sorption efficiency was 43 mg/g for the natural and 62 mg/g for iron(III)-modified zeolite. It is clear from Fig. 1a that iron(III)-modified zeolite is a faster and efficient sorbent of lead than the natural zeolite.

Lead sorption data (left: Fig. 1) were fitted according to the pseudo-second order kinetics (Eq.1) because it was shown to be more likely to predict the behavior over the whole range of sorption being based on the assumption that the rate-determining step may be a chemical sorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate [8]. Pseudo-second order kinetic model is expressed as:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t \quad (1)$$

where  $q_t$  and  $q_e$  are sorbed amount at time  $t$  and equilibrium (mg/g) and  $k_2$  is the rate constant of pseudo-second order sorption of lead (g/(mg min)). From the pseudo-second order model it is possible to define the initial sorption rate,  $h$  (mg/(g min)), as  $t \rightarrow 0$ , as  $h = k_2 q_e^2$ .

The values of  $q_e$  and  $k_2$  were calculated from the slope and intercept of the straight line obtained by plotting  $t/q_t$  against  $t$  (right: Fig. 1) and were collected in Table 1.

**Table 3.** Kinetics data for sorption of lead by the natural and iron(III)-modified zeolite

Kinetic model	Parameters	Natural zeolite	Iron(III)-modified zeolite
		$q_{e, \text{ exper}}$ (mg/g)	44.25
	$q_e$ (mg/g)	45.45	62.89
Pseudo-second order	$k_2$ (g (mg min))	$2.53 \cdot 10^{-4}$	$15.90 \cdot 10^{-4}$
	$h$ (mg g <sup>-1</sup> min <sup>-1</sup> )	0.52	6.26
	$R^2$	0.9999	0.9999

As can be seen from Table 1, the excellent correlation coefficients ( $r^2 = 0.9999$ ), as well as the good agreement of calculated and experimental  $q_e$  for the natural and iron(III)-modified zeolite, indicated the validity of the pseudo-second order model for lead sorption by these sorbents. The pseudo-second order kinetics supports that the chemical sorption could be the rate-determining step controlling lead sorption process, and is in agreement with the results reported by other researchers [9]. Predicted initial lead sorption rate,  $h$ , for iron(III)-modified zeolite was twelve times higher than for the natural zeolite. The much faster lead uptake (higher initial rate) by iron(III)-modified zeolite may be evidence that this modification increase the number of active surface sites that are more available for sorption of lead. The experimental data were also fitted using pseudo-first order and intra-particle diffusion models (data not shown), but the correlation coefficients for both models were much lower than those obtained according to the pseudo-second order model.

From sorption isotherms, we previously reported [7] that at lower initial concentrations of lead (up to 3800 mg/L), sorption of lead by the natural and iron(III)-modified zeolite occurred through ion exchange, while at higher initial lead concentrations (greater than 3800 mg/L) chemisorption dominated. In the concentration range where ion exchange dominates, the amounts of released cations were higher than amounts of sorbed lead, assuming that during sorption of lead by both sorbents slight sorption of hydrogen occurred and these processes are more pronounced for the natural zeolite.

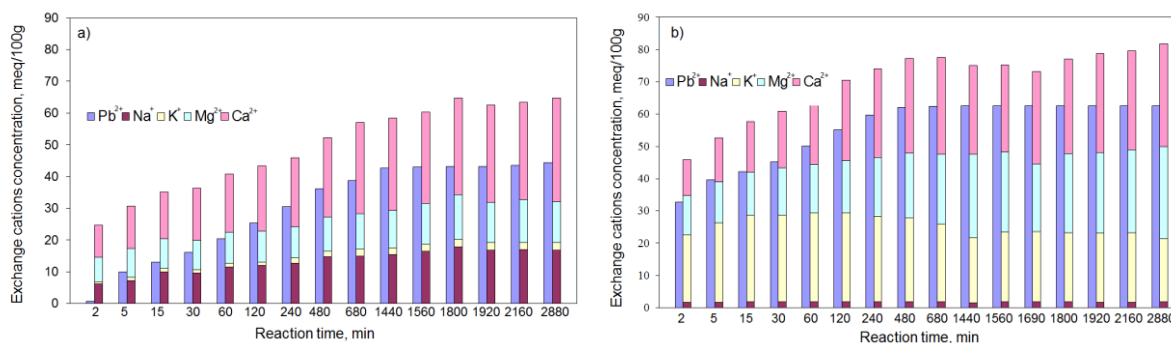


Figure 2. The amounts of lead sorbed and amounts of cations released as a function of the reaction time for the a) natural and b) iron(III)-modified zeolite.

The initial concentration of lead used for kinetics experiment was in the initial part of the isotherms, thus we followed amounts of released exchangeable cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) from both sorbents during lead sorption kinetic experiments, and these results are presented at Fig. 2.

Similar to the isotherm study, kinetics experiment showed that for both sorbents, the amounts of released cations were higher than the amounts of sorbed lead. Also, during kinetic experiments pH of the suspensions was continuously measured. The final pH at equilibrium was 4.8 for the natural and 5.4 for the iron(III)-modified zeolite. Thus, the higher amounts of released cations than amounts of sorbed lead together with increase of pH of suspension indicated that simultaneous sorption of lead and hydrogen occurred. Additionally, from Fig. 2a and b, the release of calcium, magnesium, sodium and potassium from the natural and iron(III)-modified zeolite was much faster than lead sorption. That may be additional evidence revealing an ionic exchange mechanism [10]. The higher rate of releasing exchangeable cations than sorbing of lead, supported that chemisorption could be the rate-determining step controlling lead sorption process obtained from pseudo-second order model.

## CONCLUSION

The results reported in this paper showed that efficient sorbent for lead was prepared by treatment of the natural zeolite with iron(III) ions. Kinetics experiment showed that sorption of lead by iron(III)-modified zeolite was much faster than its sorption by the natural zeolite. Kinetics of lead sorption on both samples followed pseudo-second order model. The previous determined high lead sorption capacity of the iron(III)-modified zeolite, fast sorption kinetics, together with simple modification procedure, make this material suitable for potential application in wastewater treatment technologies.

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