

## IMMOBILIZATION OF LEAD FROM AQUEOUS SOLUTIONS USING THE NATURAL AND Fe (III) MODIFIED ZEOLITE

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### ABSTRACT

The sorption of lead from water solutions onto natural and iron (III) modified zeolite was examined as a function of pH. Pseudo second order kinetic analyses were performed to determine the rate constant of sorption. Rate constants for lead sorption on zeolites are highest at pH = 4.24 and they are 0.381 and 0.201 min/pH for natural and iron (III) modified zeolite respectively. The results showed that there are no significant influence of pH on sorption of Pb<sup>2+</sup> ions on natural zeolite and iron (III) modified zeolite in pH range from 2.19 to 4.24, and the best pH value of the system to remove Pb(II) from aqueous solutions using zeolites is between 3.63 and 4.24.

Keywords: sorption, lead, zeolite, pH, pseudo second order kinetics

### INTRODUCTION

Wastewater contaminated with heavy metals generates many industrial activities, such as tanneries, metal plating, facilities and mining operations. Especially Pb(II), Cu(II), Fe(III) and Cr(III) are common metals found in industrial wastewaters. Heavy metals are not biodegradable and tend to accumulate in organisms, causing numerous diseases and disorders.

Lead has been found to be acute toxic to human beings when present in high amounts (e.g. > 15 µg/l in drinking water). Lead is known to damage the kidney, liver and reproductive system, basic cellular processes and brain functions. The toxic symptoms are anemia, insomnia, irritability, hallucination, renal damages, etc. [1].

The conventional methods for heavy metal removal from water and wastewater include oxidation, reduction, precipitation, and ion exchange/adsorption. Among all the methods ion exchange/adsorption on different materials (zeolite, bentonite, cellulose, peat, etc) is highly effective and economical. Zeolites have been widely used in heavy metal sorption experiments due to their unique physical and chemical properties (crystallinity, thermal stability, well-defined cage structure of molecular size, ion exchange, etc.) [2]. Moreover, they have large specific surface area (SSA), and contain high concentrations of exchangeable cations, which give them high cation exchange capacity (CEC). Also, zeolites are widely distributed in nature, inexpensive and not toxic sorbents [3]. According to their structure, zeolites are microporous crystalline hydrated aluminosilicates which can structurally be considered as inorganic polymers built from an infinitely extending three dimensional network of tetrahedral TO<sub>4</sub> units, where T is Si or Al. Each aluminium ion that is present in the zeolite framework yields a net negative charge, which is balanced by an extra framework cation, usually from group IA and IIA. The zeolite framework structure contains channels or interconnected voids of discrete size (in the range of 3-20 Å) occupied by the charge balancing ions and water molecules [4].

To establish better sorption of lead and other heavy metal ions, surface of zeolite is often modified with inorganic cations, e.g. iron (III) ions. Such iron modified zeolites can be several times better sorbents than natural zeolites. In the present work, immobilization of lead from aqueous solutions using the natural and iron (III) modified zeolite was investigated.

## EXPERIMENTAL

The starting material was the natural zeolitic tuff from the Zlatokop deposit, Vranjska Banja, Serbia. The mineralogical composition of the starting sample was primarily clinoptilolite (~80%) with small amounts of feldspar, quartz and pyrite as determined by qualitative X-ray powder diffraction analysis (XRPD). After crushing and grinding the zeolite was sieved to the particle size fraction below 0.043 mm.

The iron modified zeolite was synthesized combining the method for pure goethite preparation [5] and method for preparation of iron coated zeolite [6]. Thus, 50 g of zeolite was mixed with 25 ml of 10%  $\text{FeCl}_3 \times 6\text{H}_2\text{O}$  solution and 700 ml of 0.1 M KOH (pH = 10) in 2 l container. The container was capped and the suspension was aged for 20 days at room temperature. After the reaction period, the suspension was filtered and washed until  $\text{Cl}^-$  ions were no longer detected and dried. The content of  $\text{Fe}_2\text{O}_3$ , determined by the classical chemical analysis was found to be 2.30% for the natural and 3.97% for the iron (III) modified zeolite.

In this study, the effect of contact time on the final pH of solution during lead sorption by the natural and iron (III) modified zeolite was investigated. For that purpose, 1g of each sorbent was mixed with 50 ml of aqueous solution, containing the same initial concentration of  $\text{Pb}(\text{NO}_3)_2$  (1534 mg Pb/l) at 25°C. The pH of the initial lead solutions was adjusted to desirable values (2.19-4.24) by adding different volumes of 0.1M  $\text{HNO}_3$  or 0.1M KOH. The initial and non sorbed concentrations of lead in supernatants at equilibrium (plateau of curves pH versus contact time) were determined using titration by EDTA with methylene blue.

## RESULTS AND DISCUSSION

The iron (III) modified zeolite was synthesized under strongly basic conditions, thus to investigate does the presence of iron (III) oxyhydroxides at the zeolitic surface has influence on lead sorption, pH values of solution in the 290 min period of the lead sorption process were measured. To compare the obtained results, similar experiment was performed with the natural zeolite. The obtained results are presented at Figures 1a and b.

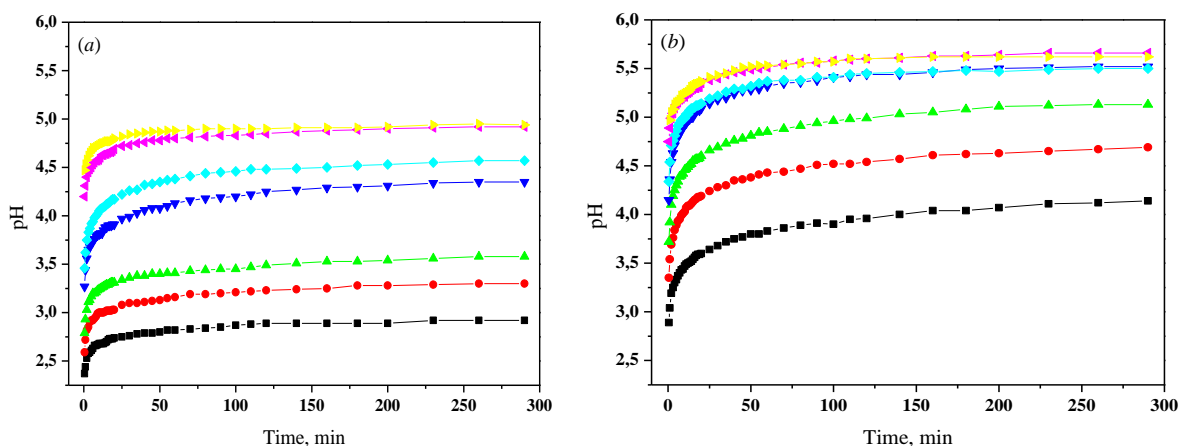


Figure 1. Diagram of pH of solution against time for lead sorption onto (a) natural zeolite and (b) iron (III) modified zeolite for different initial pH of solutions. Initial pH values: 2.19 (-■-), 2.35 (-●-), 2.50 (-▲-), 2.80 (-▼-), 2.98 (-◆-), 3.63 (-◄-), and 4.24 (-►-).

From Figure 1a, it can be seen that during lead sorption by the natural zeolite, the pH values changed from the initial pH value of the lead solution, showing a rapid increase during first 30 min of reaction period for lower initial pH values, and during first 60 min for the higher initial pH values. For lead sorption by iron (III) modified zeolite, for all initial pH values a rapid increase of pH during first 50 min was observed and followed by constant

value. Also in system with modified zeolite is observed higher increase and higher equilibrium pH value.

It is well known that pH of solution has strong influence on sorption of lead from aqueous solutions. Depending on the pH values of solution, following forms of lead may be present:  $\text{Pb}^{2+}$ ,  $\text{Pb}(\text{OH})^+$ ,  $\text{Pb}(\text{OH})_2$ , or  $\text{Pb}(\text{OH})_3^-$ . The distribution of various hydrolyzed lead species as a function of pH at a total lead concentration of 1534 mg/l is presented at Figure 2a. As can be seen from Figure 2a, at  $\text{pH} < 4.5$ , the predominant lead specie is  $\text{Pb}^{2+}$ , the main species at pH range 5.5-11 are  $\text{Pb}(\text{OH})^+$  and  $\text{Pb}(\text{OH})_2$ , and in range of  $\text{pH} > 11$  main specie of lead is  $\text{Pb}(\text{OH})_3^-$ .

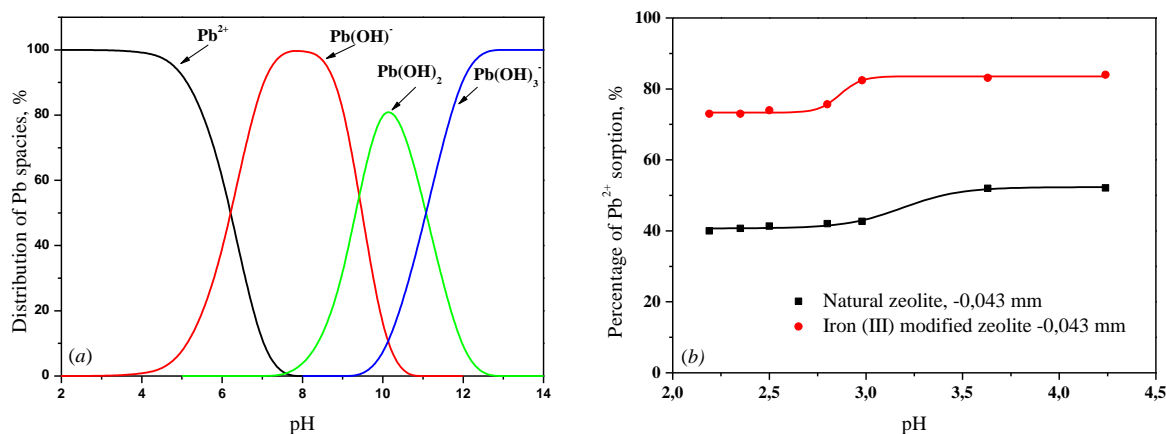


Figure 2. (a) Distribution of Pb (II) species as a function of pH based on the equilibrium constants at ionic strength of 0.01 mol/l, and from the hydrolysis constants  $\log k_1 = 6.48$ ,  $\log k_2 = 11.16$ , and  $\log k_3 = 14.16$  [7]. (b) Percentage of lead sorption on natural zeolite (-■-) and iron (III) modified zeolite (-●-) as a function of pH.

As can be seen from Figure 2a, the predominant lead specie in investigated pH range is  $\text{Pb}^{2+}$ . From Figure 2a and from results presented at Figure 1b, it is obvious that even iron (III) oxihydroxides are most probably present at the zeolitic surface and increased the pH during sorption process; the precipitation of lead is not occurred. The amounts of bound  $\text{Pb}^{2+}$  ions by natural and iron (III) modified zeolites at equilibrium, as a function of solution pH are presented on Figure 2b. The results are given in terms of percentage of sorption. The sorption in pH range from 2.19 to 2.98 for natural zeolite and from 2.19 to 2.80 for iron (III) modified zeolite does not increase significantly with increasing pH of solutions. In a narrow initial pH range, from 2.98 to 3.63 for natural zeolite and from 2.80 to 2.98 for iron (III) modified zeolite, sorption of  $\text{Pb}^{2+}$  slightly increased with increasing pH of solutions. In the initial pH range from 3.63 to 4.24 for natural zeolite and from 2.98 to 4.24 for iron (III) modified zeolite sorption of lead reached a maximum (53 % for natural zeolite and 84 % for iron (III) modified zeolite). From these results it can be concluded that initial pH of lead solution has not significant influence on sorption of its sorption by natural zeolite and iron (III) modified zeolite in that pH range, and the best pH value of the system to remove Pb(II) from aqueous solutions using zeolites is between 3.63 and 4.24.

Changing of pH of solution during reaction period also can be used for determination of kinetic parameters of lead sorption reaction on zeolites. The sorption studies, carried out as a function of pH of solution versus contact time (Figures 1a and b) for natural and iron (III) modified zeolite indicated fast sorption of lead by both zeolites which suggested that removal of lead from solution to zeolites was mainly dominated by chemical sorption rather than physical sorption, and ion exchange may contribute to the sorption of lead on natural and iron (III) modified zeolites.

To analyze the sorption rate of lead on both sorbents, a pseudo second order rate equation was used to simulate the kinetic sorption.

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

where,  $q_t$  is pH at time  $t$ ,  $k$  is rate constant (min/pH) and  $q_e$  is equilibrium pH. The straight line plot of  $t/q_t$  versus  $t$  (plot are not shown), indicates that kinetic sorption of lead on both zeolite samples is well described by the pseudo second order rate equation. The parameters of equation 1 are given in Table 1.

Table 1: Pseudo second order model parameters for various pH values.

Natural zeolite				Iron(III)-modified zeolite		
pH <sub>0</sub>	$q_e$	$k$ (min/pH)	$r^2$	$q_e$	$k$ (time/pH)	$r^2$
2.19	2.94	0.275	0.999	4.11	0.091	0.999
2.35	3.30	0.199	0.999	4.67	0.102	0.999
2.50	3.57	0.184	0.999	5.13	0.093	0.999
2.80	4.35	0.118	0.998	5.52	0.117	0.999
2.98	4.56	0.134	0.999	5.52	0.156	0.999
3.63	4.92	0.218	0.998	5.68	0.163	0.999
4.24	4.95	<b>0.381</b>	0.998	5.65	<b>0.201</b>	0.999

## CONCLUSION

The natural and iron (III) modified zeolites are found to be suitable materials for the removal of lead from water solutions in pH range from 2.19 to 4.29. In that pH range, lead is only at Pb<sup>2+</sup> form. It was determined that the percent of bound lead increased with increasing in initial pH in pH range from 2.98 to 3.63 for natural zeolite and from 2.80 to 2.98 for iron (III) modified zeolite. The kinetic of lead sorption on both samples followed pseudo second order model. Rate constants for lead sorption on both zeolites are highest for pH equal to 4.24.

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