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## REMOVAL OF LEAD IONS FROM SIMULATED AND REAL POLLUTANT SOLUTIONS BY USING THE NATURAL AND Fe(III)-MODIFIED ZEOLITE

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### ABSTRACT

The efficiency of the natural and Fe(III)-modified zeolite for Pb<sup>2+</sup> removal at different initial pH (2.5, 4.2 and 5.0) was investigated. For initial pH 2.5, for all concentrations and both adsorbents ion exchange of inorganic cations in zeolites with lead ions, together with uptake of hydrogen occurred. For initial pH 5.0 it was determined that at lower initial concentrations of lead ion, ion exchange occurred, while at higher initial concentrations beside these processes, chemisorption of lead ions occurred on both adsorbents. Preliminary experiments on waste water obtained after flotation process in facility of lead and zinc mine showed that waste water treatment with both adsorbents reduced the content of all investigated heavy metal cations. However, better removal was achieved with the Fe(III)-modified zeolite.

Keywords: Natural zeolite, Fe(III)-modified zeolite, influence of pH, lead ions; waste water

### INTRODUCTION

The contamination of water by lead through the discharge of industrial waste water is a worldwide environmental problem. In water solutions, depending on the pH, lead may be present in different forms: Pb<sup>2+</sup>, Pb(OH)<sup>+</sup>, Pb(OH)<sub>2</sub>, or Pb(OH)<sub>3</sub><sup>-</sup>. Industrial waste water usually have acidic pH where lead exists predominantly in Pb<sup>2+</sup> form, with highest bioavailability and toxicity for human, animals and plants. Consequently, removal of Pb<sup>2+</sup> ions from waste water has become an important issue today. Adsorption and ion exchange are processes which are very useful for heavy metals ions (including Pb<sup>2+</sup>) removal because they are simple, effective and economical, particularly when low-cost natural materials (such as zeolite) are employed [1]. The efficiency of the natural zeolite (clinoptilolite) for removal of lead ions is well documented [2]. However, in order to enhance the adsorption capacity for heavy metals, modification of the natural zeolites is usually performed [3]. In our previous paper [4], we reported a more efficient adsorbent for Pb<sup>2+</sup> ions obtained through the modification of natural zeolite (clinoptilolite) with Fe(III) ions under strongly basic conditions (maximum adsorbed amount for the natural zeolite was 66 mgPb<sup>2+</sup>/g and 133 mgPb<sup>2+</sup>/g for the Fe(III)-modified zeolite). Also, it was showed that removal of lead ions by both adsorbents takes place over complex mechanism including ion exchange and chemisorption [4]. In another paper [5] complete characterization of both adsorbents was performed and lead ions adsorption kinetics, thermodynamics and adsorption-desorption were described. Obtained kinetic results showed that pseudo-second order model best represented adsorption kinetics and activation energy of 13.5 and 8.5 kJ/mol for the natural and Fe(III)-modified zeolite, respectively. Desorption experiments indicated that lead ions were irreversibly adsorbed, while thermodynamic investigations indicated that adsorption process is spontaneous in nature, for both zeolites [5].

The aim of this paper is further investigations on the abilities of Fe(III)-modified zeolite to remove lead ions from aqueous solutions. Since initial pH may have an influence on removal of lead ions, in this research efficiency of the Fe(III)-modified zeolite for Pb<sup>2+</sup> removal at different initial pH was tested. Also, using Fe(III)-modified zeolite as a potential purifier of mining waste waters contaminated with lead ions was investigated. For that purpose, preliminary experiments of removal of heavy metals from waste water obtained after flotation

process in lead and zinc mine facility were performed. The objective was to investigate potential use of Fe(III)-modified zeolite as a material in production of overflow collector filters on tailings. To compare efficiency, same experiments were done with the starting (natural) zeolite.

## EXPERIMENTAL

In experiments, natural zeolite-clinoptilolite (NZ) from the Zlatokop deposit, Serbia with particle size below 43  $\mu\text{m}$  and its Fe(III)-modified form (FeZ) [4] were used. Influence of initial pH on  $\text{Pb}^{2+}$  ions adsorption was investigated at three different initial pH values ( $\text{pH}_i$ ): 2.5, 4.2 and 5.0, by shaking 1g of each adsorbent with 50  $\text{cm}^3$  of aqueous solution containing various initial concentrations of lead (350 – 6500  $\text{mg Pb}^{2+}/\text{dm}^3$ ) at 25°C for 24 h. After 24 h, suspensions were centrifuged, and the initial and non-adsorbed concentrations of  $\text{Pb}^{2+}$ , as well as concentration of exchanged inorganic cations ( $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$ ) in the supernatants were determined on atomic absorption spectrophotometer “Analytic Jena Spekol 300”.

For investigations of potential application of FeZ as material for overflow collector filters on tailings, waste water sample have been taken from the outlet pipe of the flotation facility of mining Trepča, in Leposavić, Serbia, in accordance with standard procedure (SRPS ISO 5667-10:2007, Water quality. Taking of sample. Part 10: Guidance on waste waters sampling). Collected sample was kept in the capped container and left for 2 days at room temperature in order to separate liquid from solid phase. After 2 days, liquid phase was decanted and filtered through qualitative filter paper in order to remove large particles and impurities. Adsorption experiments were carried out by shaking 1g of NZ or FeZ with 50  $\text{cm}^3$  of waste water at 25 °C for 24 h. Then, suspensions were centrifuged and the initial and non-adsorbed concentrations of heavy metals in the supernatants were determined by using inductively coupled plasma mass spectrometry.

## RESULTS AND DISCUSSION

Results on removal of  $\text{Pb}^{2+}$  ions by NZ and FeZ at different  $\text{pH}_i$  values are presented at Fig. 1.

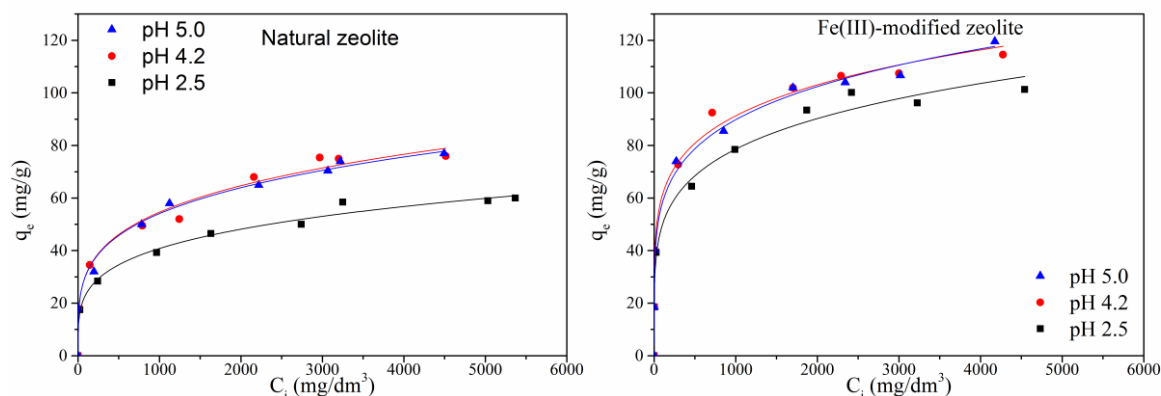


Figure 1. Lead ions adsorption isotherms for the NZ and FeZ at different initial pHs.

As can be seen, for both, NZ and FeZ, in investigated pH range (2.5-5.0), removal of lead ions increased with increasing its initial concentration in solution. It was observed that, for all the initial pHs, significantly higher adsorption was achieved with the FeZ. The maximum adsorbed amount of lead ions were 61, 79 and 77  $\text{mg/g}$  for NZ and 106, 117 and 118  $\text{mg/g}$  for FeZ at  $\text{pH}_i$  2.5, 4.2 and 5.0, respectively. Results were fitted to the Langmuir and Freundlich adsorption model and the best fit of the data was obtained using the Freundlich model ( $R^2 > 0.98$ ). These results showed that, for both adsorbents, initial pH doesn't have an influence on shape of the adsorption isotherms but, has slight influence on  $\text{Pb}^{2+}$  adsorption capacities, and the highest adsorption was achieved at  $\text{pH}_i \geq 4.2$ . During experiments final pHs were also measured.

Increasing of pH of all suspensions was observed, and maximum final pH was 6.3, meaning that lead was mainly in cationic-Pb<sup>2+</sup> form [6].

In order to study the adsorption mechanism, the amounts of cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup>) released from zeolitic structure and Pb<sup>2+</sup> ions removed from the solution at pH<sub>i</sub> 2.5 and 5.0 are presented in Fig. 2.

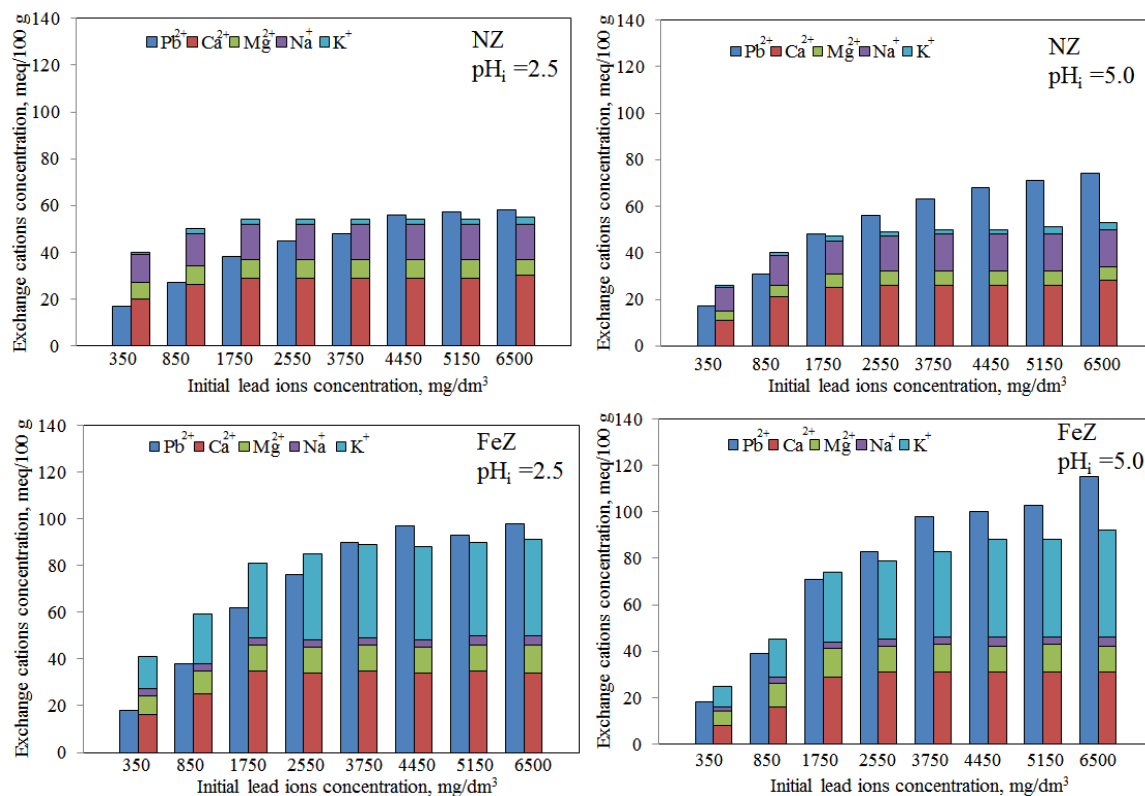


Figure 2. The relations between released and adsorbed amounts of cations for NZ and FeZ at different pH<sub>i</sub>.

For same initial pH almost same trends were obtained for both adsorbents (Fig.2), suggesting that, there is no difference in reaction mechanism between NZ and FeZ. For lower initial concentrations, for pH<sub>i</sub> 2.5 as well as 5.0, the amount of lead ions adsorbed by the NZ or FeZ was lower than total amount of cations released from both adsorbents. That means that ion exchange was the main mechanism included in removal of Pb<sup>2+</sup> ions. Higher total amount of cations released from both adsorbents, together with increasing of pH of the suspensions during this process, suggests that ion exchange also involves uptake of competitive hydrogen ions from solution onto both adsorbents. However, for higher initial concentrations, change of pH<sub>i</sub> from 2.5 to 5.0 changed reaction mechanism but, in the same way for both adsorbents. Our previous study [4] showed that surface of NZ as well as FeZ has positive charge for pH<sub>i</sub> < 4.0. Because of positive charge of lead ions in solution, repulsive forces between same charged lead ions and surface of adsorbents occurred at pH<sub>i</sub> = 2.5. As a consequence, binding of lead ions on the adsorbents active centers by chemical bonds (chemisorption) was difficult and only small part of them was chemisorbed. That means that, ion exchange (more energetically favorable than chemisorption) was the main mechanism involved in removal of lead ions by both adsorbents. Because of that, almost same amount of removed lead ions and total amount of exchanged cations from both adsorbents was obtained (Fig.2). However, for pH<sub>i</sub> = 5.0 adsorbents surface charge takes a zero value [4], meaning that surface charge does not have an influence on removal of lead ions from solution. Thus, due to the absence of repulsive forces, beside ion exchange, larger amount of lead ions can bind specifically by chemical bonds on surface of NZ

as well as FeZ. As a consequence, lower total amounts of released cations from both adsorbents than amounts of removed lead ions were obtained (Fig.2).

Second part of our research was testing of NZ and FeZ as potential purifiers of mining waste waters. For that purpose, preliminary experiments on removal of heavy metals from waste water from flotation tail from facility of lead and zinc mine were performed, and obtained results are shown in Table 1. As can be seen, the content of lead, iron, cadmium, cobalt and nickel, except silver, copper and zinc in waste water was very high and dangerous for human health (e.g. the content of lead was 33 times higher than maximum allowed concentration in drinking water – 0.01 mg/dm<sup>3</sup>).

Table 1. Results of the preliminary investigations using FeZ and NZ as cleaner of mining waste waters

Investigated element	wastewater	After treatment with NZ	After treatment with FeZ
<b>Pb, mg/dm<sup>3</sup></b>	<b>0.333</b>	<b>0.009</b>	<b>&lt;detection limit</b>
<b>Fe, mg/dm<sup>3</sup></b>	<b>20.60</b>	<b>8.89</b>	<b>0.047</b>
Zn, mg/dm <sup>3</sup>	2.51	2.50	0.619
Cu, mg/dm <sup>3</sup>	0.191	0.117	0.025
<b>Cd, mg/dm<sup>3</sup></b>	<b>0.005</b>	<b>0.004</b>	<b>0.0011</b>
Co, mg/dm <sup>3</sup>	0.045	0.026	0.019
Ni, mg/dm <sup>3</sup>	0.182	0.147	0.137
Ag, mg/dm <sup>3</sup>	0.010	0.009	0.001

After treatment of waste water with NZ and FeZ, the content of all heavy metal cations was reduced. However, much better heavy metal removal was achieved with FeZ. After treatment with FeZ, concentrations of lead, iron and cadmium ions in waste water were below detection limit, 0.047 and 0.0011 mg/dm<sup>3</sup>, respectively, which is lower than upper permitted limit for drinking water. Previously we showed that maximum adsorption capacity for lead ions of FeZ is 133 mg/g [3]. That means, for concentration of lead ions in waste water of 0.333 mg/dm<sup>3</sup>, 1 g of FeZ could purify about 400 dm<sup>3</sup> of contaminated waste water. From that point, FeZ could be used as material for production of overflow collector filters for tailings. However, these are just preliminary results, and for practical applications, additional investigations on waste water in real conditions must be done, and that will be the aim of our further research.

## CONCLUSION

The results presented in this study showed that, for both adsorbents, initial pH doesn't have an influence on the adsorption isotherms shape but, has slight influence on lead ions adsorption capacities and changed adsorption mechanism. The highest adsorption achieved at pH<sub>i</sub> ≥ 4.2. Experiments on removal of heavy metals from waste water from flotation tail showed that Fe(III)-modified zeolite could be a material suitable for potential practical application.

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