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Removal of lead from aqueous solutions by using the natural and Fe(III)-modified zeolite

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ABSTRACT

In the present study, the sorption of lead by the natural and Fe(III)-modified zeolite (clinoptilolite) is described. The characterization of the natural zeolite-rich rock and the Fe(III)-modified form was performed by chemical analysis, point of the zero charge (pH_{pzc}), X-ray powder diffraction, applying the Rietveld/RIR method for the quantitative phase analysis, and scanning electron microscopy. The effects of sorbents dose and the initial lead concentrations on its sorption by two sorbents were investigated. For both sorbents, it was determined that at lower initial concentrations of lead, ion exchange of inorganic cations in zeolites with lead, together with uptake of hydrogen dominated, while at higher initial lead concentrations beside these processes, chemisorption of lead occurred. Significantly higher sorption of lead was achieved with Fe(III)-modified zeolite. From sorption isotherms, maximum sorbed amounts of lead, under the applied experimental conditions, were 66 mg/g for the natural and 133 mg/g for Fe(III)-modified zeolite. The best fit of experimental data was achieved with the Freundlich model ($R^2 \geq 0.94$).

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1. Introduction

Natural zeolites are crystalline hydrated aluminosilicates of alkali and alkaline earth cations. Their crystal structure consists of an open-framework of tetrahedral TO_4 units (where T represents Si or Al sites) with regular channels or cages of size ranging between 3 and 20 Å, occupied by charge-balancing ions and H_2O molecules [1]. Clinoptilolite is the most common natural zeolite belonging to "heulandite group", with molar Si/Al >4 and its structure is characterized by large intersecting open channels of 10- and 8-member tetrahedral rings [2]. Due to their unique physico-chemical properties (e.g. high crystallinity, regular sub-nanometric cavities, highly selective ion-exchange capacity), zeolites are being used as heavy metals sorbents, as chemical sieves and as water softeners [3]. In addition, zeolites are widely distributed in nature, they are inexpensive and not toxic sorbents.

Most of the heavy metals are not biodegradable and tend to accumulate in organisms, causing numerous diseases and disorders. Lead, for example, has been found to be acute toxic to human

beings when present in high amounts (e.g. >15 µg/l in drinking water).

The efficiency of the natural clinoptilolite for heavy metals removal is well known. For example, Panayotova and Velikov [4] studied the kinetics of the uptake of Cd, Pb, Cu, Ni and Zn ions from single ion solutions and from their mixtures by Bulgarian zeolites-rich rock. They found that Pb was the most strongly immobilized by the zeolite and that its pre-treatment with NaCl led to increased rate of heavy metals immobilization, as well as to increased distributions coefficients. Cincotti et al. [5] examined Sardinian natural clinoptilolites for removal of heavy metals: Pb, Cd, Cu and Zn in as-received and sodium homoionic forms. They reported a selectivity scale: $Pb(II) > Cu(II) > Cd(II) - Zn(II)$. Also, Inglezakis et al. [6] studied ion exchange of Pb(II), Cu(II), Fe(III) and Cr(III) on natural clinoptilolite and found the following selectivity series: $Pb(II) > Cr(III) > Fe(III) > Cu(II)$.

Besides the natural zeolites, Fe-oxides are also active sorbents and play an important role in the reactions behavior of many ions. Several studies have been devoted to the synthesis protocols of mixed systems of iron oxides and clay minerals or zeolites (in particular clinoptilolite), proving that such systems are able to sorb high concentrations of inorganic species [7–9] and, in addition, for the case of Fe-zeolite systems, to improve the catalytic properties [10,11]. Concerning sorption of heavy metals by the iron oxides,

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Zhu et al. [12] studied the competitive sorption of Cu, Cr and Pb in binary and ternary systems on ferrihydrite, an Fe-oxide ubiquitously present in soils and sediments and two organomineral complexes, obtained by coprecipitating Fe with different amounts of oxalate and tartarate. They found that ferrihydrite sorbed larger amounts of Cu, Cr and Pb than the organomineral complexes when mmol/kg mass scale was considered, owing to the larger surface area of ferrihydrite, whereas an opposite trend was found when $\mu\text{mol}/\text{m}^2$ surface scale was considered. Recently, in many studies, zeolites were used as substrates for Fe modification, in order to improve the sorption selectivity for arsenate and arsenite [13,14]. Alkaline leaching could increase the uptake of Fe on zeolite. Significant increases of Fe(III) suggested that sorption of As was mainly due to accumulation of FeOOH and Fe(III) oxides during the Fe-loading process [14]. Doula [10,15] reported Fe-overexchanged clinoptilolite as an efficient material for removal of Cu and Mn from drinking water. She found that the loading of clinoptilolite surface with amorphous Fe-oxide species improve significantly metals sorption capacity. However, in the literature no data are reported for removal of lead by Fe(III)-modified zeolite.

The aim of the present study is the comparative analysis of the Pb sorption capacity of a volcanic clinoptilolite-rich rock and its Fe(III)-modified form. The influence of the sorbents dose and the initial Pb-concentrations on sorption of lead from aqueous solution by these sorbents was investigated.

2. Experimental

2.1. Samples preparation

The natural zeolite-rich rock from Zlatokop deposit (Vranjska Banja, Serbia) used in this study was grinded and sieved with a final particle size <0.043 mm. The cation exchange capacity (CEC) of the natural sample was measured with $1 \text{ mol}/\text{dm}^3$ NH_4Cl . The certain amount (1 g) of sample was mixed with 100 ml of NH_4Cl solution for 2 h and then left in contact for 24 h. The suspension was then centrifuged at 10000 rpm for 10 min and in the supernatant the concentrations of inorganic cations (Ca, Mg, Na and K) were determined by using atomic absorption spectrophotometer "Analytic Jena Spekol 300" (AAS). The CEC of the natural sample was 146 meq/100 g.

The Fe(III)-modified zeolite was obtained combining the method for goethite preparation [16] and that for the preparation of Fe-coated zeolite [17]. Thus, 50 g of zeolite was mixed with 25 cm^3 of 10% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (p.a. Aldrich) solution and 700 cm^3 of $0.1 \text{ mol}/\text{dm}^3$ KOH (pH 10) was added in a 2 dm^3 container. The container was capped and the suspension was aged for 20 days at room temperature. During the aging period, dark red-brown color of suspension was transformed to a compact yellow-brown one. After the reaction period, the suspension was filtered and washed until Cl^- ions were no longer detected and dried at 60°C .

2.2. Samples characterization

The chemical composition of the natural and Fe(III)-modified zeolite was determined by the classical chemical analysis for aluminosilicates [18].

X-ray powder diffraction data of both samples were collected with an automated Panalytical X'Pert Pro modular diffractometer equipped with a X'Celerator detector. Operating conditions were: monochromatised Cu $K\alpha$ radiation, 40 kV, 40 mA, 2θ -range from 4 to 100° , step size of $2\theta = 0.017^\circ$, counting time of 240 s per step. The Rietveld/RIR method [19,20] was applied for the quantitative phase analysis with the GSAS computer package [21]. For the natural and Fe(III)-modified samples, the following crystalline phases

were detected: clinoptilolite, plagioclase (Ca-rich) and quartz. Silicon NIST 640c was used as internal standard to estimate the fraction of the amorphous phase. The starting structure models used for the Rietveld fit were obtained from the MSA Crystal Structure Database [22]. Further details pertaining the Rietveld full-profile fit protocol are given in Gatta et al. [23].

Scanning electron microprobe analysis of the natural and Fe(III)-modified sample was performed by using a "JEOL JSM-6610" type microprobe. Samples were embedded into a two component epoxy resin and successively polished for obtaining suitable surfaces for microanalyses, using a defocused beam in order to minimize cation migration under the electron beam.

The point of zero charge, pH_{pzc} , of Fe(III)-modified sample was determined using the method described by Milonjic et al. [24]. Potassium nitrate (p.a. Aldrich), in concentrations of 0.001 – $0.1 \text{ mol}/\text{dm}^3$ was used as a background electrolyte. The initial pH values (pH_i) of each solution were adjusted by small additions of $0.1 \text{ mol}/\text{dm}^3$ of HNO_3 or $0.1 \text{ mol}/\text{dm}^3$ of KOH. In each initial solution (50 cm^3), 100 mg of sample was added and the bottles were shaken for 24 h at room temperature, centrifuged at 10000 rpm for 10 min and the pH of each supernatant was measured (pH_f). The pH_{pzc} of Fe(III)-modified zeolite was determined as the pH value at the plateau of the curve $\text{pH}_f = f(\text{pH}_i)$ and compared with previously determined pH_{pzc} of the natural zeolite [25].

2.3. Lead sorption experiments

The influence of sorbents dose on sorption of lead at the constant initial Pb concentration – $1375 \text{ mg}/\text{dm}^3$ ($\text{Pb}(\text{NO}_3)_2$, p.a., Aldrich) was studied at pH 4.24, with the following protocol: in 50 cm^3 of Pb solution, 10, 25, 50, 75, 100, 250, 500 or 1000 mg of either the natural or Fe(III)-modified zeolite was added and the mixtures were shaken at room temperature for 24 h.

To study the effect of the initial lead concentrations, 1000 mg of both samples was mixed with 50 cm^3 of aqueous solutions, containing various initial concentrations of $\text{Pb}(\text{NO}_3)_2$ (350 – $7200 \text{ mg}/\text{dm}^3$) for a period of 24 h.

In all lead sorption experiments, after the reaction time, suspensions were centrifuged at 10,000 rpm for 10 min to separate the solution and solid. The initial and non-sorbed concentrations of Pb in supernatants were determined by AAS. The concentrations of Ca, Mg, Na, K and Fe in supernatants released from both zeolites were also determined by AAS.

3. Results and discussion

3.1. Characterization of the natural and Fe(III)-modified zeolite

The chemical composition of the natural and Fe(III)-modified zeolite is given in Table 1. The natural zeolite contains a significant amount of Ca, if compared to Na, K and Mg. A significant amount of Fe is also detected in the natural sample. Although the treatment of the natural zeolite with Fe(III) ions was done under strongly basic conditions, no significant change was observed in Si or Al content in the Fe(III)-modified sample [26]. The Na content in the Fe(III)-modified sample is lower (*i.e.* $\text{Na}_2\text{O} = 0.80\%$) than that in the natural one (*i.e.* $\text{Na}_2\text{O} = 1.27\%$), whereas the K content, due to the modification procedure, increased from $\text{K}_2\text{O} = 1.17\%$ for the natural zeolite to 4.36% in the Fe(III)-modified sample. After the treatment, the bulk content of Fe_2O_3 increased from 2.30% (natural zeolite) to 3.97% (Fe(III)-modified zeolite). Depending on the protocol used for the modification of zeolites, Fe(III)-ions could lie in the zeolitic channels (*i.e.* in extra-framework sites) or forming oxo- or hydroxo complexes on the zeolitic surface. Thus, in Fe(III)-modified zeolites, as well as in other metal exchanged zeolites, the active sites are

Table 1
Average chemical composition of natural and Fe(III)-modified zeolite.

	Content (wt%)							
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	I.L. ^a
Natural zeolite	66.57	13.13	2.30	3.85	0.56	1.17	1.27	11.05
Fe(III)-modified zeolite	63.44	12.71	3.97	3.85	1.06	4.36	0.80	9.43

^a Ignition loss, $T_{\max} = 900\text{ }^{\circ}\text{C}$, referred to the whole rock-sample.

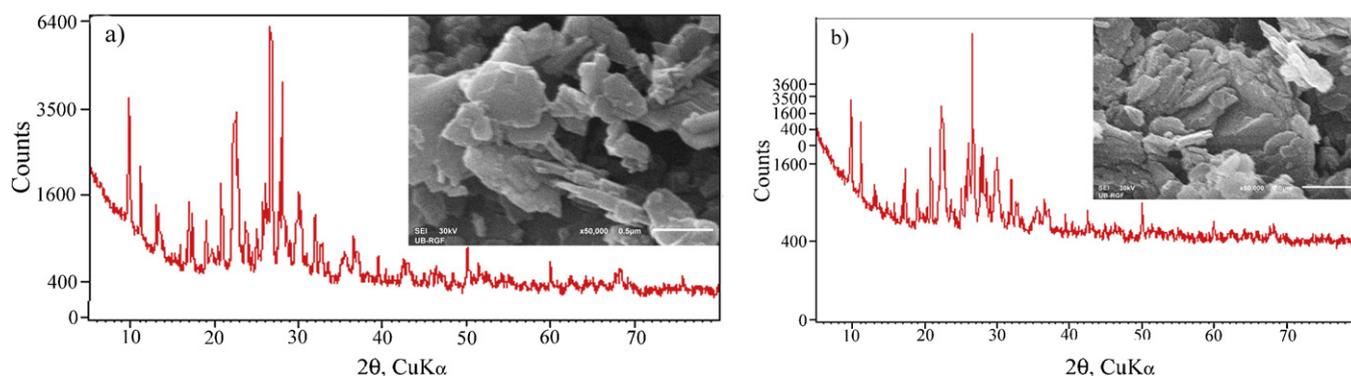


Fig. 1. Part of the XRPD patterns (up to $2\theta_{\max} = 80^{\circ}$) and SEM micrographs for: (a) the natural and (b) Fe(III)-modified sample. XRPD collected without the internal standard.

principally located in the structure channels, but also on the external surface of the crystallites. The metallic sites likely consist of isolated cations and/or metallic complexes as $(\text{Fe}-\text{O}-\text{Fe})^{4+}$ oxocations or $(\text{FeO})^{+}$ cations. Additionally, the active species may also be binuclear $[\text{HO}-\text{Fe}-\text{O}-\text{Fe}-\text{OH}]^{2+}$ clusters [10,27].

XRPD patterns of the natural and Fe(III)-modified sample are shown in Fig. 1a and b. The refined amount of the crystalline phases (wt%) by Rietveld/RIR method are: clinoptilolite 69 (1%), plagioclase 18 (1%), and quartz 12 (1%) for the natural sample and clinoptilolite 75 (1%), plagioclase 12 (1%), and quartz 13 (1%) for the Fe(III)-modified sample. The estimated fraction of the amorphous phase was below the detection limit (*i.e.* <3 wt%). No Fe-rich crystalline phase was detected in the modified sample. It appears, therefore, that there is no drastic change of the crystal-chemistry of the sample after the Fe(III)-treatment.

The full-width-at-half-maximum of the diffraction peaks of clinoptilolite show a slight, but significant, increase in the Fe(III)-modified sample ($\leq 10\%$). A general slight decrease of the diffraction peaks intensity is observed for all the crystalline phases, but it is more pronounced for clinoptilolite. The quality of the data, collected with a conventional diffractometer, along with the polycrystalline nature of the samples, did not allow to obtain a high-quality structure refinement of clinoptilolite aimed to prove the change in the extra-framework population between the natural and modified sample, respectively.

SEM micrographs of the natural and Fe(III)-modified zeolite crystals are also given in Fig. 1a and b which show a tabular morphology of the crystals of clinoptilolite. Form and size of the crystallites are preserved despite the strongly basic conditions of the Fe(III)-enrichment protocol.

It is well known that pH has a primary role in cation sorption because it influences chemical speciation of the metal in solution and also on the ionization of chemically active sites on the sorbent surface. The pH at which sorbent surface charge takes a zero value is defined as the point of zero charge (pH_{pzc}). The knowledge of pH_{pzc} allows one to hypothesize on the ionization of functional groups at sorbent surface and their interactions with metal species in solution; at solution pHs higher than pH_{pzc} , sorbent surface is negatively charged and could interact with metal species, while at pHs lower than pH_{pzc} , solid surface is positively charged and could interact

with negative species [28]. In order to consider if Fe-species at the surface of Fe(III)-modified zeolite changed sorbent surface charge, the evolution of pH_{pzc} of the Fe(III)-modified zeolite as a function of pH and ionic strength of electrolytes was studied (Fig. 2), and discussed together with previously determined pH_{pzc} of the natural zeolite [25].

As can be seen from Fig. 2, the curves $\text{pH}_f = f(\text{pH}_i)$ show the same shape for Fe(III)-modified zeolite as for the natural sample. The plateaus obtained at $\text{pH } 7.5 \pm 0.1$ corresponds to the pH_{pzc} of Fe(III)-modified zeolite, while pH_{pzc} was 6.8 ± 0.1 for the natural zeolite [25]. It was mentioned above that Fe(III)-modified zeolite was synthesized combining the method for pure goethite preparation and for the preparation of Fe-coated zeolite. In the method for goethite preparation, during the heating stage, the voluminous red-brown suspension of ferrihydrite is converted to a compact yellow brown precipitate of goethite [16]. We noticed the similar change of color of suspension of Fe(III)-modified zeolite during

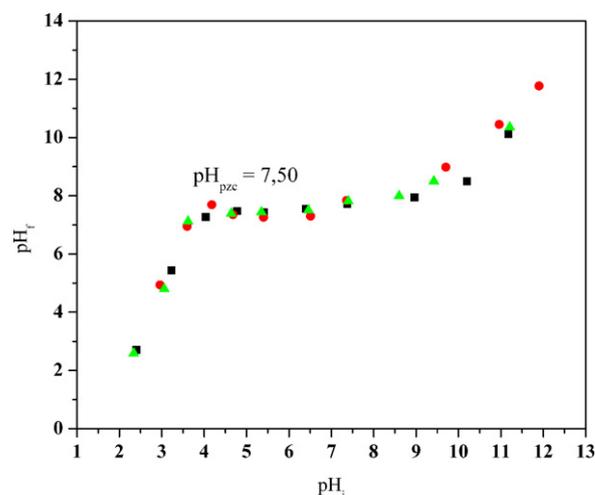


Fig. 2. pH_f as a function of pH_i for Fe(III)-modified zeolite, for different ions strengths: (■) $[\text{KNO}_3] = 0.1 \text{ mol/dm}^3$; (●) $[\text{KNO}_3] = 0.01 \text{ mol/dm}^3$ and (▲) $[\text{KNO}_3] = 0.001 \text{ mol/dm}^3$.

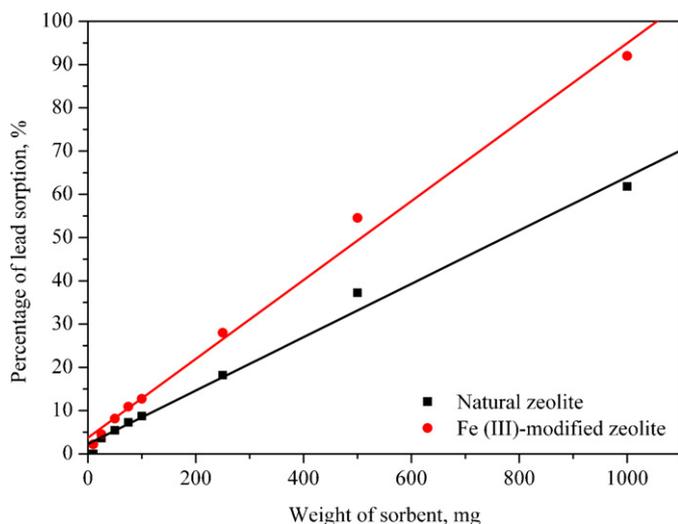


Fig. 3. Effect of sorbent dose on sorption of Pb on the natural and Fe(III)-modified zeolite.

the aging period, assuming that goethite was formed at the surface of the natural zeolite. However, the comparison of pH_{pzc} of the pure goethite ($\text{pH}_{\text{pzc}} 9.4 \pm 0.1$) [29], pH_{pzc} of the natural zeolite, along with that of the pH_{pzc} of Fe(III)-modified zeolite, indicates Fe-oxide/clinoptilolite mixed system forms, with Fe-complexes at the surface of the natural zeolite.

From Fig. 2, it can be seen for Fe(III)-modified zeolite, the increase of pH_f with the increase of pH_i up to 4.0 ± 0.1 where the plateau began. In the pH_i range from 4.0 ± 0.1 to 8.0 ± 0.1 for Fe(III)-modified zeolite, and in the range from 4.0 ± 0.1 to 9.8 ± 0.1 for the natural zeolite [25], pH_f values were independent on the initial ones. The changes of the solution pH in these ranges caused the protonation or deprotonation of active surface sites. This means that in these ranges, both sorbents exhibit amphoteric properties and act as a buffer. The plateaus of the curves correspond to the pH range where the buffering effect of the sorbents surfaces take place, i.e. where for all pH_i in this range pH_f is almost the same and corresponds to pH_{pzc} . The plateaus ended at pH 8.0 ± 0.1 for Fe(III)-modified and at pH 9.8 ± 0.1 for the natural zeolite, and further increase of the pH_i led to an increase the pH_f values. It is observed that much narrower pH range at the plateau was obtained in the case of the Fe(III)-modified zeolite, pointing up a noticeably higher negative surface charge of this sorbent.

Since lead sorption by the natural and Fe(III)-modified zeolite was studied at $\text{pH}_i \leq 4.2 \pm 0.1$ (see below), the results obtained for the point of zero charge indicated that the surfaces of these sorbents are positive at almost all investigated pH values. As for the natural zeolite, the value of pH_{pzc} for Fe(III)-modified zeolite (Fig. 2) is the same for all the electrolyte concentrations, suggesting that the pH_{pzc} of this material is also independent on the ionic strength of KNO_3 and that the specific adsorption of K^+ or NO_3^- did not occur on the surface of these sorbents.

3.2. Sorption of lead by the natural and Fe(III)-modified zeolite

The amount of lead sorbed by the natural and Fe(III)-modified zeolite with the sorbent dose (mg), at constant initial lead concentration is shown in Fig. 3. As shown in Fig. 3, sorption of lead by the natural and Fe(III)-modified zeolite increased with increasing sorbents dose, suggesting a higher number of active sites in both sorbents onto which lead is sorbed.

The pH_i of each solution was adjusted to 4.2 ± 0.1 and the pH_f was 4.4 ± 0.1 for 10 mg of the natural zeolite, and for the same

amount of Fe(III)-modified zeolite was 5.0 ± 0.1 . For the highest sorbents dose (1000 mg), pH_f was 5.2 ± 0.1 for the natural and 5.8 ± 0.1 for Fe(III)-modified zeolite, respectively.

One of the main mechanisms involved in heavy metals sorption is ion exchange which is defined as stoichiometric replacement of one equivalent of an ion in solid phase by equivalent of another ion in liquid phase. Ion exchange reaction is also referred as out sphere complexation and does not involve formation of bonds between metal ions and zeolitic surface. Another mechanism involved in heavy metals uptake is adsorption. This mechanism is often referred to as chemisorption or inner sphere complexation [30]. Fractions of amounts of heavy metal sorbed to the zeolitic surface and exchanged with zeolite cations depend mainly on the type of heavy metal cation. Mozgawa and Bayda [31] studied sorption of Pb(II), Cd(II), Cr(III) and Ni(III) by clinoptilolite and reported that for chromium and lead, chemisorption predominates, whereas in the case of nickel and cadmium, the participation of ion exchange and chemisorption seems to be equal. In another study, Mozgawa et al. [32] reported for lead and cadmium sorption on zeolite that both cations were sorbed with comparable ion-exchange and chemisorption processes proportions. They also found that the amount of lead sorbed in clinoptilolite was comparable with cadmium sorption via ion-exchange. However, the total amount of lead sorbed on zeolite was significantly higher than cadmium due to the domination of lead chemisorption process over cadmium. In order to consider these two processes, the relationship between cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) released from zeolitic structure and lead ions removed from aqueous solution at different sorbents doses are presented in Fig. 4a and b.

As can be seen from Fig. 4a and b, the amount of sorbed lead, at the lowest sorbent dose (10 mg), was 1.2 meq/100 g for the natural and 1.5 meq/100 g for Fe(III)-modified zeolite. The amounts of cations released from the natural zeolite were: $\text{Ca}^{2+} = 0.2$ meq/100 g, $\text{Mg}^{2+} = 0.2$ meq/100 g, $\text{Na}^+ = 0.3$ meq/100 g and $\text{K}^+ = 1.0$ meq/100 g. The amounts of cations released from Fe(III)-modified zeolite were: $\text{Ca}^{2+} = 0.2$ meq/100 g, $\text{Mg}^{2+} = 0.3$ meq/100 g, $\text{Na}^+ = 0.1$ meq/100 g and $\text{K}^+ = 1.7$ meq/100 g. When each sorbent dose increased to 1000 mg, the amounts of sorbed lead were 41.0 and 61.0 meq/100 g for the natural and Fe(III)-modified zeolite, respectively. The amounts of cations released from the natural zeolite were: $\text{Ca}^{2+} = 10.0$ meq/100 g, $\text{Mg}^{2+} = 8.2$ meq/100 g, $\text{Na}^+ = 14.5$ meq/100 g and $\text{K}^+ = 1.4$ meq/100 g, while the amounts of cations released from Fe(III)-modified zeolite were: $\text{Ca}^{2+} = 12.5$ meq/100 g, $\text{Mg}^{2+} = 17.8$ meq/100 g, $\text{Na}^+ = 2.1$ meq/100 g and $\text{K}^+ = 25.2$ meq/100 g. We observed a direct correlation between the amount of lead sorbed in the natural and Fe(III)-modified zeolite and those of calcium, magnesium and sodium released. A different behavior is observed for potassium, because of its known strong bond to clinoptilolite framework. For the natural zeolite, comparing the amounts of lead sorbed with the amounts of cations released, it can be seen that at lower sorbent dose, the amount of cations released is almost equal to the amount of lead sorbed, suggesting ion exchange mechanism. For Fe(III)-modified zeolite, at lower sorbent dose, the amount of sorbed lead is slightly higher than amount of cations released, suggesting that ion exchange may also involve the uptake of hydrogen. Namely, it is well known that the increase of the pH value during lead sorption by zeolite may be due to the simultaneous uptake of hydrogen ions [33]. Thus, H^+ ions should then be considered as competitive ones in the ion exchange processes. For Fe(III)-modified zeolite, based on the increase of pH_f during lead sorption, it appears that this material sorbs larger amounts of hydrogen ions, a further evidence that Fe(III)-modified zeolite possesses a noticeably higher negative surface charge [10,15]. Additionally, during lead sorption, Fe(III) ions released from Fe(III)-modified zeolite were not detected in the supernatants, suggesting that Fe(III) ions are not in soluble

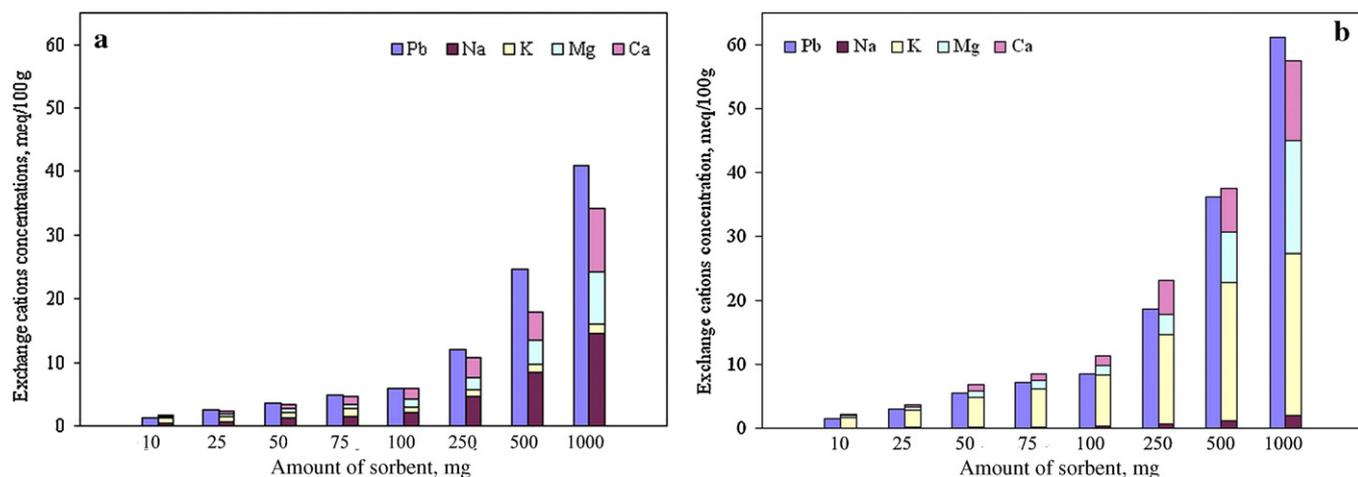


Fig. 4. The amounts of lead sorbed and amounts of cations (Na, K, Ca, Mg) released as a function of sorbents dose: (a) the natural and (b) Fe(III)-modified zeolite.

phase and are not involved in ion exchange with lead ions. Based on measurement of the point of zero charge of both the natural and Fe(III)-modified zeolite, surfaces of both sorbents are positive to pH 4 and lead ions exist in solution at investigated pH values predominantly as Pb^{2+} cation. Increasing each sorbent dose (1000 mg), the amount of cations released from both zeolites was lower than the amount of lead sorbed, suggesting that with increasing the number of active sites in both sorbents, chemisorption occurred along with ion exchange processes. Higher amount of lead sorbed by Fe(III)-modified zeolite suggests higher number of active sites onto this cation is sorbed. We have also observed that the amount of aluminium released from the natural and Fe(III)-modified zeolite was negligible, showing that dissolution of both zeolites did not occur.

Lead sorption isotherms of the natural and Fe(III)-modified zeolite were determined and the results are presented at Fig. 5 [34].

As shown in Fig. 5, for both the natural and Fe(III)-modified zeolite, sorption of lead increased with increasing the initial lead concentration. The natural zeolite has a satisfactory sorption capacity and it is capable of sorbing lead from aqueous solution. However, a significantly higher lead sorption is observed with the Fe(III)-modified zeolite. Under our experimental conditions, the maximum amount of sorbed lead was 66 mg/g for the natural sample and 133 mg/g for the Fe(III)-modified one. During these

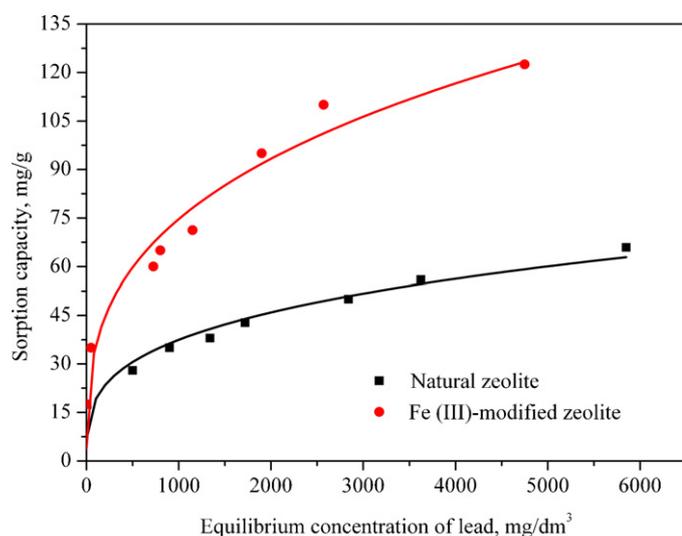


Fig. 5. Lead sorption isotherms for the natural and Fe(III)-modified zeolite.

experiments, the pH of the initial lead solutions was not adjusted, it was only measured. Thus, the pH_i was in the range from 4.4 ± 0.1 for the lowest initial lead concentration to 2.9 ± 0.1 for the highest initial lead concentration.

For any given initial lead concentration, the concentrations of cations released from the natural and Fe(III)-modified zeolite are shown in Fig. 6a and b.

As can be seen from Fig. 6a and b, for both sorbents the relation between released and sorbed equivalents of positive charges was not stoichiometric, for all the initial lead concentrations. As in the previous experiment, it was noticed that for all the initial lead concentrations, during lead sorption by Fe(III)-modified zeolite, no Fe(III) ions were detected in supernatants. At lower initial lead concentrations (e.g. 1163 mg/dm^3), the amount of Pb sorbed by the natural and Fe(III)-modified zeolite was similar (27 meq/100 g for the natural and 29 meq/100 g for Fe(III)-modified zeolite). At this initial lead concentration, the amounts of cations released from the natural zeolite were 44 meq/100 g for the natural and 62 meq/100 g for Fe(III)-modified zeolite. During the experiment, pH_i 3.8 ± 0.1 increased to pH_f 5.2 ± 0.1 for the natural and pH_f 5.7 ± 0.1 for Fe(III)-modified zeolite. The increase of pH_f and higher amounts of cations released from either the natural or Fe(III)-modified zeolite than the amount of lead sorbed by both sorbents confirmed that the ion exchange involves also sorption of hydrogen ions from solution onto both sorbents. When the initial lead concentration was higher (e.g. 7200 mg/dm^3), the amounts of released cations from both the natural and Fe(III)-modified zeolite were lower than the sorbed amounts of lead by the two sorbents. Thus, at the highest initial concentration, the amounts of lead sorbed by the natural and Fe(III)-modified zeolite were 64 meq/100 g and 128 meq/100 g, respectively. The amounts of cations released from the natural zeolite were 52 meq/100 g and 93 meq/100 g for Fe(III)-modified zeolite. The pH of suspension increased from pH_i 2.9 ± 0.1 to pH_f 4.4 ± 0.1 for the natural and pH_f 4.6 ± 0.1 for Fe(III)-modified zeolite. The lower amounts of cations released from both zeolites than the amount of sorbed lead and increase of pH_f indicated that ion exchange and simultaneous uptake of hydrogen, along with chemisorption of lead, occurred.

Fig. 5 shows that the sorption process of lead by both the natural and Fe(III)-modified zeolite follows non linear sorption isotherms. Fitting our data to the Langmuir and Freundlich sorption model, the best fit was obtained using the Freundlich model. The correlation coefficient for the Freundlich isotherm was $R^2 = 0.94$ for the natural and $R^2 = 0.95$ for the Fe(III)-modified sample. Sprynsky et al. [35] studied the mechanism of heavy metal (Pb, Cu, Ni and Cd) sorption on clinoptilolite, modeling the sorption process from aqueous

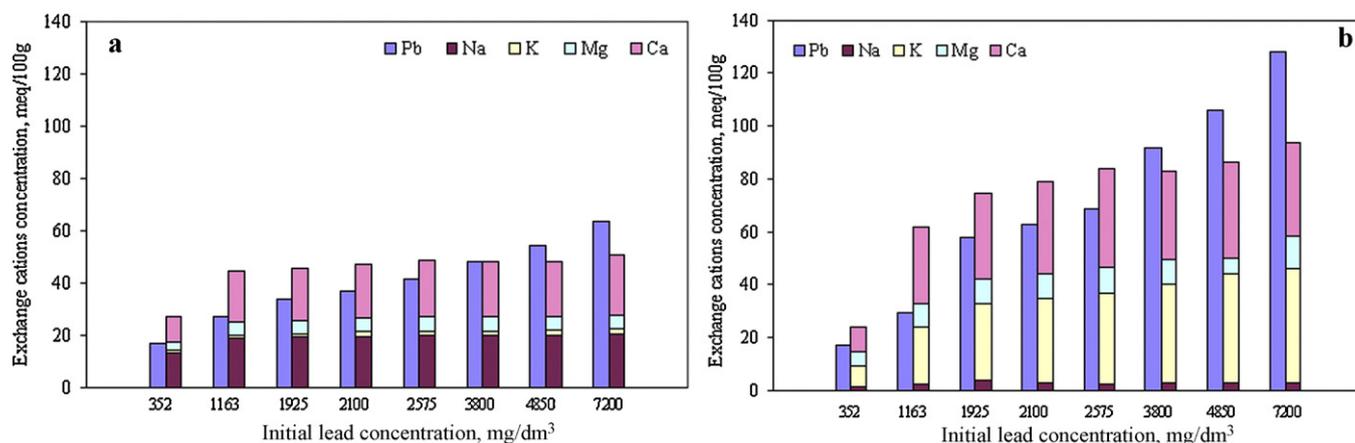


Fig. 6. The amounts of lead sorbed and amounts of cations released as a function of the initial lead concentrations for: (a) the natural and (b) Fe(III)-modified zeolite.

solutions by the Freundlich and the Langmuir protocols. They found that Langmuir model was more appropriate for modeling the equilibrium sorption of clinoptilolite at high metal concentrations, whereas the Freundlich model was found to be better for low initial metal concentrations. Ponyzovsky and Tsadilas [36] studied sorption of lead by Alfisol soil and a natural clinoptilolite, at pH 3–5 and reported that clinoptilolite sorbed more Pb than soil and the sorbed amount and the pH of the solution were independent variables. Hysteresis between sorption and desorption isotherms indicated that Pb-retention by both Alfisol soil and clinoptilolite reflects an ion exchange process with strong (soil) or very strong (zeolite) specific bonding of Pb. Three times higher sorption of Cu^{2+} by Fe-clinoptilolite system (37.5 mg/g) than that obtained by natural clinoptilolite (13.6 mg/g) were reported by Doula and Dimirkou [37], who suggested that the high sorption capacity of the Fe-clinoptilolite system is owed to Fe-clusters located on the crystals surface, to the high surface negative charge, and to its high specific surface area. We can extend the same considerations to the higher sorption of Pb observed for the Fe(III)-modified zeolite observed in this study. Additionally, all lead sorption experiments were done at pHs where the surfaces of both zeolites were positive, the obtained results suggested that their surface charge do not play a role in sorption process. However, in order to define the actual mechanisms which govern the lead sorption by Fe(III)-modified zeolite, detailed physicochemical characterization will be performed and together with lead desorption experiments will be the subject of a future study.

4. Conclusion

The results presented in this study show that a more efficient sorbent for Pb removal from aqueous solution was obtained through the modification of a natural zeolitic sample from the Zlatokop deposit, Vranjska Banja, Serbia (clinoptilolite 69 (1) wt%, plagioclase 18 (1) %, quartz 12 (1) %, and amorphous phase <3%) with Fe(III) ions under strongly basic conditions. No significant change in the general crystal chemistry of the Fe(III)-modified sample was observed (clinoptilolite 75 (1) wt%, plagioclase 12 (1) %, quartz 13 (1) %, and amorphous phase <3%), if compared to the natural one. The diffraction pattern of the Fe(III)-modified sample shows no evidence of new Fe-rich crystalline phase (detection limit ~ 1 wt%). The increase in Fe of the Fe(III)-modified zeolite compared to the natural one (*i.e.* $\text{Fe}_2\text{O}_3 = 2.30$ wt% in the natural clinoptilolite and 3.97 wt% in Fe(III)-modified one) suggest the Fe(III) ions lie in the zeolitic channels (as extra-framework sites) or forming oxo- or hydroxo complexes on the zeolite crystals surface.

Lead sorption by the natural and Fe(III)-modified zeolite increased with increasing of each sorbent dose. The sorption isotherms showed that the Pb sorption by the natural and Fe(III)-modified sample follow non linear trends. Maximum sorbed amount of Pb, under our experimental conditions, was 66 mg/g for the natural zeolite and 133 mg/g for Fe(III)-modified zeolite. The best fits of the experimental data were obtained to the Freundlich isotherm model. The significantly higher sorption of lead by Fe(III)-modified zeolite, along with the fact that natural zeolite is inexpensive and can be easily modified with Fe(III) ions under alkaline conditions, make this material suitable for potential practical application.

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