



Characterization of lead sorption by the natural and Fe(III)-modified zeolite



Milan Kragović^a, Aleksandra Daković^{a,*}, Marija Marković^a, Jugoslav Krstić^b,
G. Diego Gatta^c, Nicola Rotiroli^c

^a Institute for Technology of Nuclear and Other Mineral Raw Materials, Franche d'Epere 86, 11000 Belgrade, Serbia

^b Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia

^c Dipartimento di Scienze della Terra, Università degli Studi di Milano, Via Botticelli 23, I-20133 Milano, Italy

ARTICLE INFO

Article history:

Received 25 April 2013

Received in revised form 28 June 2013

Accepted 6 July 2013

Available online 13 July 2013

Keywords:

Sorption

Desorption

Lead

Natural zeolite

Fe(III)-modified zeolite

ABSTRACT

The influence of contact time, temperature and particle size on lead sorption by the natural and Fe(III)-modified zeolites was investigated. Characterization of the natural and Fe(III)-modified zeolite before and after lead sorption was performed by determination of textural properties, by scanning electron microscopy and X-ray spectroscopy in energy-dispersive mode (SEM–EDS), transmission electron microscopy (TEM) and X-ray powder diffraction (XRPD) analysis. Lead sorption kinetics at 303–333 K, best represented by the pseudo-second order model and activation energy (13.5 and 8.5 kJ/mol for the natural and Fe(III)-modified zeolite respectively) confirmed an activated chemical sorption. Desorption experiments indicated that lead was irreversibly sorbed on both zeolites. XRPD, TEM and SEM results showed that modification of the natural zeolite with Fe(III) ions did not change its crystal structure and iron is mainly located at the zeolite surface, likely in form of amorphous iron oxy-hydroxides. Specific surface area significantly increases after modification of the natural zeolite with Fe(III) ions (from 30.2 for the natural to 52.5 m²/g for Fe(III)-modified zeolite). Characterization of both lead saturated sorbents suggested that besides ion exchange, lead is both chemisorbed and precipitated at their surfaces, and presence of amorphous iron in Fe(III)-modified zeolite favors sorption of lead.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Heavy metals are dangerous for living organisms because of their stability, toxicity and tendency to accumulate in the environment. With the rapid development of industries such as plating facilities, mining operations, fertilizers, tanneries, batteries, paper, and pesticides industries, heavy metals wastewaters are directly or indirectly discharged into the environment increasingly, especially in developing countries. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metals ions are known to be toxic and carcinogenic [1,2]. Toxic heavy metals of particular concern in treatment of industrial wastewaters include Zn, Cu, Ni, Hg, Cd, Pb and Cr.

Regarding acute toxicity, cadmium, lead along with mercury form “the big three” of heavy metals with the greatest potential hazard to human and environment [3]. Lead has been found to be acute toxic to human beings when present in high amounts (e.g. >15 µg

in drinking water) [4,5]. Also, it is well known that lead damages the kidney, liver and reproductive system, basic cellular processes and brain functions. Lead toxic symptoms are anemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination and renal damages. Therefore, the removal of excess lead ions from wastewater is essential. Treatment processes usually include chemical precipitation, adsorption, solvent extraction, ultrafiltration and ion exchange. Zeolites are inexpensive natural materials with a high and selective cation exchange capacity. Among natural zeolites, clinoptilolite is the most abundant and commonly used as ion exchanger or sorbent for inorganic ions. Exchangeable cations in zeolite structure, e.g. K, Na, Ca, and Mg are not toxic, making zeolites especially suitable for tertiary processes of wastewater treatment [6].

The efficiency of the natural zeolite for lead removal is well documented. Karatas [7] reported a sorption capacity of raw clinoptilolite for Pb²⁺ from aqueous solution of 16.8 mg/g, whereas Sprynsky et al. [8] determined the sorption capacity of clinoptilolite for Pb²⁺ in multi-component aqueous solution to be 27.8 mg/g. Although there are a large number of studies on the removal of Pb²⁺ ion from aqueous solutions using natural zeolites, any given zeolitic material requires specific experiments in this respect [9].

* Corresponding author. Tel.: +381 11 3691 722; fax: +381 11 3691 583.

E-mail addresses: a.dakovic@itnms.ac.rs, dakovic.a@yahoo.com (A. Daković).

Because it is well known that oxides of Fe and Mn are the potential carriers of heavy metals (e.g. lead) [10], in order to enhance the sorption capacity of the natural zeolites for heavy metal ions, some experiments have been devoted to modify their surface by these metal oxides [11]. Kragović et al. [12] reported a more efficient sorbent for Pb obtained through the modification of a natural zeolitic sample with Fe(III) ions under strongly basic conditions. They observed an increase of lead sorption by the natural and Fe(III)-modified zeolite with increasing of sorbent dose and the initial lead concentration. Maximum lead sorbed amount (SC_{max}), under applied experimental conditions, was 66 mg/g for the natural zeolite and 133 mg/g for Fe(III)-modified zeolite.

The aim of this paper is a further and extended investigation on the abilities of natural and Fe(III)-modified zeolite to remove lead from aqueous solutions. The influence of specific parameters, such as contact time, temperature and particle size on sorption of lead by both sorbents was studied. Furthermore, since desorption behavior of contaminants is at least as important as their sorption, estimation of the reversibility of sorption and possible mobility of metals in an aqueous solution is of great interest. Therefore, desorption of sorbed lead from the natural and Fe(III)-modified zeolite was also investigated. Characterization of the natural and Fe(III)-modified zeolite before and after sorption of lead was performed by determination of textural properties and by scanning electron microscopy and X-ray spectroscopy in energy-dispersive mode (SEM/EDS), transmission electron microscopy (TEM), and X-ray powder diffraction (XRPD) analysis.

2. Materials and methods

2.1. Samples preparation

The natural zeolite-rich rock sample used in this study comes from the Vranjska Banja (Serbia) deposit. The sample was crushed up and sieved to particle size <0.043 mm. Sample was rinsed with distilled water to remove possible impurities, dried at 60°C and stored in the desiccator. The Fe(III)-modified zeolite was obtained combining the method for pure goethite preparation [13] and that for the preparation of Fe-coated zeolite [14]. Briefly, 50 g of natural zeolite was mixed with 25 mL of 10% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (p.a. Aldrich) solution and 700 mL of 0.1 mol/L KOH (pH = 10) and added in a 2 L container. The container was capped and the suspension was aged for 20 days at room temperature. After the reaction period, suspension was filtered, rinsed with distilled water, dried at 60°C and stored in the desiccator [12].

2.2. Lead sorption experiments

The effect of temperature on the kinetics and sorption capacity for lead on natural and Fe(III)-modified zeolite was studied by adding 50 mL of 4000 $\text{mgPb}^{2+}/\text{L}$ solution (for kinetic) and 50 mL of 1000, 3000, 4500 or 6000 $\text{mgPb}^{2+}/\text{L}$ (for thermodynamic experiments) to 1.0000 g of both sorbents at 303, 313, 323 and 333 K and at time interval 0–2880 min (for kinetic) and in 1440 min (for thermodynamic study), respectively. In order to evaluate kinetic and thermodynamic data, separate flasks were prepared for each time interval and only one flask was taken for desired time. Initial pH (pH_i) in all experiments was 4.24.

In all experiments, after reaction, solution and each sorbent were separated through standard filter and concentrations of non sorbed lead in supernatant 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.

2.3. Sorption–desorption experiment

Sorption–desorption experiments were conducted using the protocol described by Hamidpour et al. [3]. For sorption experiments, in 100 mL containers, 1.0000 g of the natural or Fe(III)-modified zeolite was dispersed in 50 mL of 0.01 mol/L $\text{Ca}(\text{NO}_3)_2$ solutions, containing predetermined amounts of lead in the concentration range of 25–100% of Pb-maximum sorption capacity (SC_{max}) of each sorbent. The initial lead concentrations ranged from 350 to 1330 $\text{mgPb}^{2+}/\text{L}$ for the natural zeolite, and 690 to 2660 $\text{mgPb}^{2+}/\text{L}$ for Fe(III)-modified zeolite. The initial pH of the solutions was adjusted to 4.24 by adding negligible volumes of 0.1 mol/L of KOH or HNO_3 . After addition of lead, suspensions were shaken for 24 h. After reaction time, suspensions were centrifuged (10,000 rpm for 10 min) and one half of the supernatant volume (25 mL) was pipetted out of the container to determine lead concentration. The other half of supernatants, along with solids, was kept for desorption experiments.

Immediately after removal of 25 mL of each supernatant, the rest of supernatants together with solids was quantitatively transferred into new containers and mixed with the same volume (25 mL) of Pb^{2+} -free 0.01 mol/L $\text{Ca}(\text{NO}_3)_2$ solution (with the same pH as in sorption experiments) for 24 h. After desorption cycle, suspensions were centrifuged, 25 mL of the supernatants were kept for lead analyses, while solids with another 25 mL of the supernatants were treated again with the same volume (25 mL) of metal free background electrolyte. Desorption cycles were repeated four successive times for each sample. Desorption isotherms were prepared by plotting the amounts of lead remained in the solid phase after each desorption cycle versus the corresponding equilibrium lead concentrations in solution.

2.4. Characterization of lead saturated natural and Fe(III)-modified zeolite

2.4.1. Scanning electron microscopy and elemental analysis

The surface morphology and the chemical composition of samples were investigated using a “JEOL JSM-6610” scanning electron microscope (SEM) equipped with X-ray energy dispersive detector (EDS). Observations aimed to describe the morphology of the crystals were performed with samples coated with gold. For the experiments aimed to perform chemical micro-analysis in energy dispersive mode, the samples were sputtered with carbon. EDS elemental analyses were performed on a significantly high number of points, in order to detect a potential heterogeneous distribution of the elements on the surfaces.

2.4.2. XRPD analysis

X-ray powder diffraction data were collected using a Philips X’Pert Pro diffractometer equipped with a multi-channel X’celerator detector and Ni-filtered $\text{CuK}\alpha$ radiation. Each pattern was collected with angular range $2\theta = 5\text{--}70^{\circ}$, steps of $2\theta = 0.016^{\circ}$, and a counting time of 450 s/step. Samples were grinded in an agate mortar, with a final grain size of 1–5 μm . The Rietveld/RIR method [15,16] was applied for the quantitative phase analysis with the GSAS computer package [17]. Silicon NIST 640c was used as internal standard to estimate the fraction of the amorphous phase. The whole diffraction patterns were fitted using the pseudo-Voigt profile function proposed by Thomson et al. [18] and the background curve was refined with a Chebyshev polynomial. For both the natural and Fe(III)-modified samples, the following crystalline phases were detected: clinoptilolite, plagioclase (Ca-rich), quartz and a very minor amount of mordenite. The starting

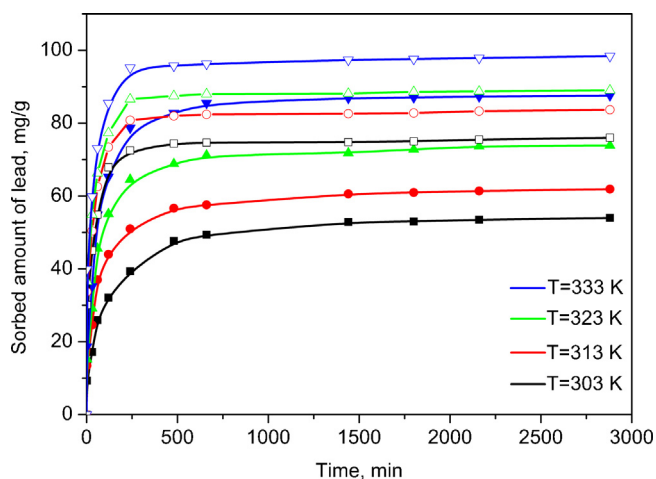


Fig. 1. Effect of contact time on sorption of lead by the natural (filled symbols) and Fe(III)-modified zeolite (empty symbols).

structure models used for the Rietveld fit were obtained from the MSA Crystal Structure Database [19].

2.4.3. Transmission electron microscopy

Samples for transmission electron microscopy were prepared by gentle grinding in an agate mortar, suspension in isopropyl alcohol and deposition on a holey carbon coated grid. TEM observations have been carried out on a field emission gun FEI Tecnai F20 super twin electron microscope equipped with Gatan Slow Scan CCD 794 and operated at 200 kV at the DST-MI. The microscope is equipped with an EDS detector, for qualitative and semi-quantitative chemical analysis.

2.4.4. Textural properties

Adsorption–desorption isotherms of all samples were obtained by nitrogen adsorption at 77 K using a Sorptomatic 1990 Thermo Finnigan device. Prior to adsorption, the samples were degassed first for 1 h at room temperature under vacuum and then for 16 h at 383 K at the same residual pressure. The resulting isotherms were analyzed by Software ADP Version 5.13 Thermo Electron. Values of the total pore volume (V_{tot}) and the specific surface area (S_{BET}) of the samples were determined by applying Gurevitsch's rule at a relative pressure $p/p_0 = 0.98$ (p and p_0 represent the equilibrium and saturation pressures of nitrogen at the temperature of adsorption) and according to the Brunauer, Emmet, Teller (BET) method from the linear part of the nitrogen adsorption isotherms, respectively [20]. The Dubinin–Radushkevich (DR) equation was applied to the nitrogen adsorption isotherms to obtain the micropore volume (V_{mic-DR}) [21]. Mesopore volume (V_{meso}) was determined by the Dollimore and Heal (DH) method [22].

3. Results and discussion

3.1. Lead sorption by the natural and Fe(III)-modified zeolite

3.1.1. Effect of contact time

The effect of contact time on lead retention onto natural and Fe(III)-modified zeolite was studied at different temperatures and is shown at Fig. 1. The contact time varied in the range 0–2880 min and the initial metal concentration was 4000 mgPb²⁺/L. The pH_i of suspensions were adjusted to 4.24 and the final pHs (pH_f) were from 4.80 at 303 K to 4.96 at 333 K for the natural zeolite, and from 4.96 at 303 K to 5.25 at 333 K for Fe(III)-modified zeolite.

Table 1
Kinetics data for sorption of lead by the natural and Fe(III)-modified zeolite.

Temperature (K)	Parameters	Natural zeolite	Fe(III)-modified zeolite
303	$q_{e,exper}$ (mg/g)	54.00	76.00
	q_e (mg/g)	55.34	76.33
	k_2 (g/(mg min))	2.77×10^{-4}	7.56×10^{-4}
	h (g/(mg min))	0.85	4.88
	R^2	0.999	0.999
313	$q_{e,exper}$ (mg/g)	61.90	83.70
	q_e (mg/g)	62.81	84.03
	k_2 (g/(mg min))	3.89×10^{-4}	8.78×10^{-4}
	h (g/(mg min))	1.53	6.20
	R^2	0.999	0.999
323	$q_{e,exper}$ (mg/g)	73.89	89.04
	q_e (mg/g)	74.79	89.44
	k_2 (g/(mg min))	4.07×10^{-4}	9.40×10^{-4}
	h (g/(mg min))	2.28	7.52
	R^2	0.999	0.999
333	$q_{e,exper}$ (mg/g)	87.60	98.40
	q_e (mg/g)	88.34	98.72
	k_2 (g/(mg min))	4.63×10^{-4}	10.38×10^{-4}
	h (g/(mg min))	3.61	10.12
	R^2	0.999	0.999

As presented in Fig. 1, 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 Fe(III)-modified zeolite. It is clear from Fig. 1 that Fe(III)-modified zeolite is a quicker and efficient sorbent of lead than the natural zeolite.

Lead sorption data (Fig. 1) were fitted according to the pseudo-second order kinetics 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 [23]. Pseudo-second order kinetic model is expressed as [24]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (1)$$

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)). Integration of Eq. (1) leads to Eq. (2):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

From the pseudo-second order model it is possible to define the initial sorption rate, h (mg/(g min)), as $t \rightarrow 0$:

$$h = k_2 q_e^2 \quad (3)$$

Then Eq. (3) becomes:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (4)$$

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 (curves not shown) and were collected in Table 1.

As can be seen from Table 1, for all temperatures, the excellent correlation coefficients ($R^2 = 0.999$), as well as the good agreement of calculated and experimental q_e for the natural and Fe(III)-modified zeolite, indicated the validity of the pseudo-second order model for lead sorption by these sorbents.

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.

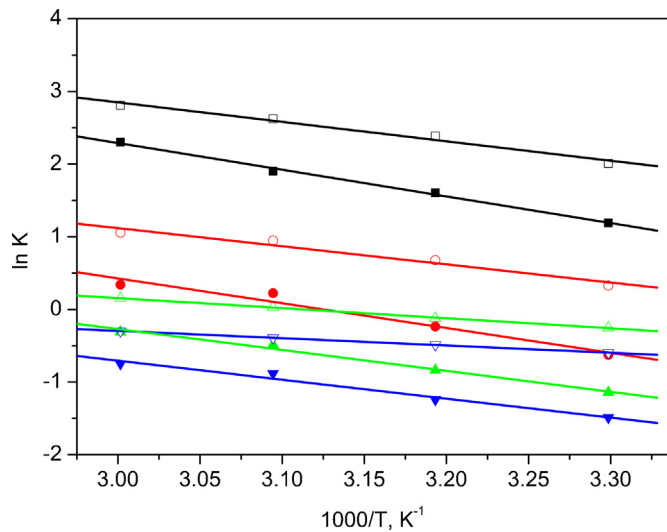


Fig. 2. The plot of $\ln K$ vs. $1/T$ for the natural (filled symbols) and Fe(III)-modified zeolite (empty symbols) for different temperatures: 303 K (black line), 313 K (red line), 323 K (green line) and 333 K (blue line).

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 [24]. The rate constant k_2 and q_e increased with increasing the temperature for the natural zeolite and Fe(III)-modified zeolite which indicate that the high temperature favors lead sorption. Predicted initial lead sorption rate, h , for Fe(III)-modified zeolite was four times higher than for the natural zeolite. The much faster lead uptake (higher initial rate) by Fe(III)-modified zeolite

may be an additional evidence that this modification increase the number of active surface sites available for sorption of lead.

The activation energies for metal ion sorption on natural and Fe(III)-modified zeolite were calculated according to the Arrhenius equation [25]:

$$k_2 = k_0 \exp \left[\frac{-E_a}{RT} \right] \quad (5)$$

where k_0 (g/(mg min)) is the temperature independent factor, E_a (kJ/mol) is the activation energy of the reaction of sorption, R is the gas constant (8.314 J/(K mol)) and T is the sorption absolute temperature in K. The magnitude of activation energy may give an idea about the type of sorption. There are two main types of sorption: physical and chemical. Usually, the activation energy for physical sorption is no more than 4.2 kJ/mol, since the forces involved in this process are weak. Chemical sorption is specific, involves forces much stronger than in physical sorption and may be activated or non-activated. Activated chemical sorption means that the rate varies with temperature according to a finite activation energy (8.4–83.7 kJ/mol) in the Arrhenius equation, while for non-activated chemical sorption, the activation energy is near zero [26]. The energies of activation determined from slopes of $\ln k_2$ versus $1/T$ for both sorbents (figure not shown) were found to be 13.46 for the natural and 8.53 kJ/mol for Fe(III)-modified zeolite confirming activated chemical sorption. The positive values of energy activation suggest that rise in temperature favors sorption and this process is an endothermic in nature.

3.1.2. Thermodynamic study

The data collected for lead sorption on the natural and Fe(III)-modified zeolite, at four different initial concentrations (1000, 3000, 4500 and 6000 mgPb²⁺/L) and at 303, 313, 323 and 333 K were used for estimation of some thermodynamic parameters. The pH_i of each solution was adjusted to 4.24 and the final pH_f (pH_f), for

Table 2
Thermodynamic parameters for lead sorption on natural and Fe(III)-modified zeolite.

	C_0 (mg/L)	T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/(K mol))	R^2
Natural zeolite	1000	303	-3.00	30.53	110.64	0.998
		313	-4.18			
		323	-5.11			
		333	-6.38			
	3000	303	1.58	28.39	88.72	0.981
		313	0.61			
		323	-0.60			
		333	-0.94			
	4500	303	2.88	23.96	69.64	0.994
		313	2.18			
		323	1.30			
		333	0.86			
6000	303	3.75	21.72	59.29	0.989	
	313	3.23				
	323	2.37				
	333	2.07				
Fe(III)-modified zeolite	1000	303	-5.06	22.25	90.47	0.991
		313	-6.21			
		323	-7.05			
		333	-7.78			
	3000	303	-0.83	20.75	54.95	0.982
		313	-1.76			
		323	-2.54			
		333	-2.93			
	4500	303	0.64	11.52	35.87	0.999
		313	0.32			
		323	-0.08			
		333	-0.43			
6000	303	1.50	5.96	8.35	0.999	
	313	1.27				
	323	1.05				
	333	0.82				

the initial concentration of 1000 mgPb²⁺/L were from 5.21 at 303 K to 6.47 at 333 K for the natural zeolite, and from 5.96 at 303 K to 6.38 at 333 K for Fe(III)-modified zeolite. At the highest initial concentration, pH_f was from 4.73 at 303 K to 4.80 at 333 K for the natural zeolite, and from 4.81 at 303 K to 5.09 at 333 K for Fe(III)-modified zeolite.

The standard free energy of sorption (ΔG°), standard enthalpy (ΔH°) and entropy (ΔS°) were calculated from following equations:

$$\Delta G^\circ = -RT \ln K \quad (6)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7)$$

where R is the gas constant (8.314 J/(K mol)) and K is the equilibrium constant at the temperature T . The constant K was calculated as the ratio of the equilibrium lead sorbed amount and equilibrium concentration in solution. The values of ΔH° and ΔS° were calculated from the slope and the intercept of linear regression of $\ln K$ vs. $1/T$ (Fig. 2). The obtained parameters are presented in Table 2.

From Table 2, it is observed that for the lower initial lead concentrations, ΔG° was negative at all temperatures, for both the natural and Fe(III)-modified zeolite, indicating that sorption process is spontaneous in nature. With increasing the initial lead concentration, ΔG° was positive suggesting that at these lead concentrations sorption process becomes non-spontaneous. For Fe(III)-modified zeolite, ΔG° is lower than for the natural one, and more negative in the wider concentration range, suggesting the higher number of active sites available for spontaneous sorption of lead. Also, ΔG° becomes more negative with increasing temperature, suggesting that sorption is more favorable at high temperature. Changing in enthalpy (ΔH°) values was positive showing that the sorption of lead at both the natural and Fe(III)-modified zeolite is endothermic in nature. It is observed that for the highest initial lead concentration, ΔH° is much lower for the Fe(III)-modified zeolite (5.96 kJ/mol) than for the natural one (21.7 kJ/mol), confirming more favorable sorption by Fe(III)-modified zeolite. The positive values of entropy ΔS° suggests an increase in randomness at the solid–solution interface by the fixation of lead ions onto both sorbents. Namely, based on pH measurements, even at higher initial concentrations, lead is present in solution predominantly in the cationic forms [27], thus lead ions are surrounded by a firmly bound hydration layer where water molecules are more highly ordered. When lead ions enter the hydration surface of sorbent, the ordered water molecules disturbed, that causes increase of entropy of water molecules. Sorption of lead also involves release of cations from sorbents, which influence increase in the entropy. Furthermore, the observed decrease in entropy with increasing the initial concentration of lead indicates that chemisorption cause decrease in randomness at the solid–solution interface. This effect is much pronounced for Fe(III)-modified zeolite.

Based on the amount of released cations during lead sorption by the natural and Fe(III)-modified zeolite, sorption include ion exchange at lower initial concentrations of lead, while at higher initial concentrations, chemical sorption of lead at surface was much pronounced than ion exchange [9]. In the lead initial concentration range when ion exchange was dominant, the amounts of released cations were higher than amount of sorbed lead, while when chemisorption mainly occurred the opposite trend was observed. Thus, since the amounts of released cations from both zeolites are similar in whole initial lead concentration range, the observed decrease in entropy with increasing the initial concentration of lead indicates that chemisorption cause decrease in randomness at the solid–solution interface. This effect is much pronounced for Fe(III)-modified zeolite.

Table 3

Refined parameters for Freundlich equation fit to the lead sorption data.

	Natural zeolite	Fe(III)-modified zeolite
k_{sorb} (L/mg)	14.36	28.81
n_{sorb}	0.203	0.183
R^2	0.977	0.982

3.1.3. Effect of the particle size

Sorption isotherms were previously determined for the natural and Fe(III)-modified zeolites for two different particle sizes: <0.043 mm and 0.6–0.8 mm [12,28]. For both fraction of the natural and Fe(III)-modified zeolite, sorption of lead increased with increasing the initial concentration of lead. The results of sorption were fitted to the Langmuir and Freundlich sorption model and the best fit was obtained using the Freundlich model. Under the applied experimental conditions, for the particle sizes of <0.043 mm, the maximum sorbed amount (SC_{max}) of lead was 66 mg/g for the natural and 133 mg/g for Fe(III)-modified zeolite. For the particle size 0.6–0.8 mm, SC_{max} was 62 and 102 mg/g for the natural and Fe(III)-modified zeolite, respectively. These results showed that sorption of lead by the natural zeolite slightly decrease with increasing particle size, while for Fe(III)-modified zeolite, this phenomenon is much more pronounced as the result of decreasing of surface area of sorbent. Still, much higher sorption of lead was observed for Fe(III)-modified zeolite, for both particle sizes. It was already mentioned that sorption of lead by Fe(III)-modified zeolite include ion exchange and chemisorption and most probably iron deposited at the surface creates active sites responsible for enhanced lead sorption. Thus, because sorption is a surface phenomenon, the smaller sorbent size offered comparatively larger available surface area for iron during modification and hence higher number of active sites for lead removal at equilibrium [29]. The highest initial lead concentration point on the sorption isotherms was used for preparation of lead saturated sorbents for the characterization experiments (Section 3.3).

3.2. Sorption–desorption of lead

The sorption–desorption isotherms were calculated using the Freundlich equations [3].

$$q_e = k_{sorb} C_e^{n_{sorb}} \quad (8)$$

$$q_e = k_{desorb} C_e^{n_{desorb}} \quad (9)$$

where q_e , C_e , k_{sorb} (k_{desorb}), n_{sorb} (n_{desorb}) are the quantity of lead in solid phase (mg/g), equilibrium liquid phase concentration (mg/L), the Freundlich bounding constant (L/mg) for sorption (desorption) and sorption (desorption) coefficient, respectively.

Lead sorption–desorption isotherms fitted by the Freundlich model for the natural and Fe(III)-modified zeolite are presented in Fig. 3, and characteristic parameters of the isotherms are given at Table 3 for sorption and Table 4 for desorption of lead from both sorbents.

As can be seen from Tables 3 and 4 the correlation coefficients for sorption and desorption of lead are greater than 0.900 confirming Freundlich model very well described lead sorption–desorption process on both sorbents. Using of the Freundlich model for describing sorption process for heavy metals on different sorbents is well known. For example, Hamidpour et al. [3] used Freundlich equation for investigation of desorption of lead and cadmium from natural zeolite and bentonite.

The desorption isotherms of lead on both sorbents deviates significantly from the corresponding sorption isotherms, and sorption–desorption hysteresis occur, meaning that

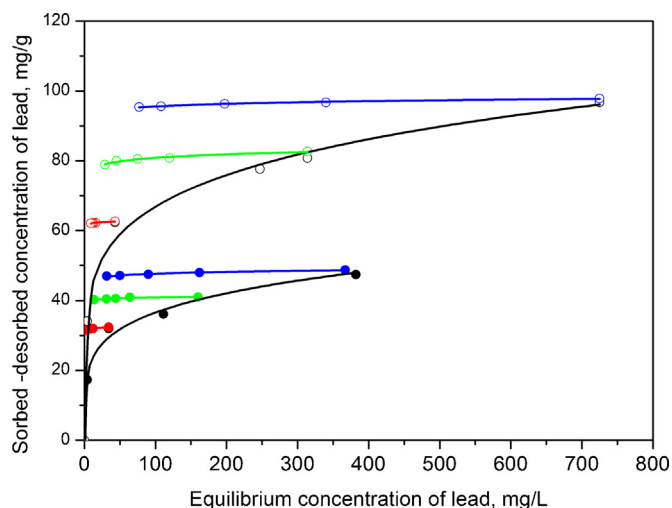


Fig. 3. Lead sorption (black line) - desorption isotherms at three metal ion concentrations: 50% (red line), 75% (green line), and 100% (blue line) of SC_{max} , for the natural (filled symbols) and Fe(III)-modified zeolite (open symbols).

Table 4

Refined parameters for Freundlich equation fit to the lead desorption data.

Initial lead load (% of SC_{max})	Parameter	Natural zeolite	Fe(III)-modified zeolite
50	k_{desorb} (L/mg)	31.05	61.28
	n_{desorb}	0.009	0.006
	R^2	0.990	0.992
75	k_{desorb} (L/mg)	39.29	74.47
	n_{desorb}	0.012	0.010
	R^2	0.911	0.964
100	k_{desorb} (L/mg)	44.37	90.64
	n_{desorb}	0.016	0.013
	R^2	0.972	0.987

sorption-desorption of lead from both sorbents were not reversible (Fig. 3). At the initial lead concentrations of 50%, 75% and 100% of SC_{max} , the quantity of lead desorbed, after four cycles were: 0.95%, 1.99% and 2.95% for the natural zeolite and 0.41%, 1.22% and 2.02% for Fe(III)-modified zeolite. These results are very comparable with results obtained by Hamidpour et al. [3]. They found that 1%, 3% and 5% of lead was released from zeolite for initial concentration of lead of 50%, 75% and 100% of SC_{max} and release of such a relatively low proportion of sorbed lead was attributed to the strong bonding to the high affinity sites in zeolite. The Freundlich constant k (a quantity parameter representing the amount of lead retained on the solid phase) for each sorbent obtained from the desorption isotherms was significantly higher than that calculated from sorption isotherms (Tables 3 and 4), and also, this constant for Fe(III)-modified zeolite was almost twice

higher than for the natural zeolite, confirming positive hysteresis and indicating approximately slightly higher desorption of sorbed lead from the natural than from Fe(III)-modified zeolite.

3.3. Characterization of the natural and Fe(III)-modified zeolite after sorption of lead

3.3.1. Scanning electron microscopy and elemental analysis

SEM images of the natural and Fe(III)-modified zeolites before and after sorption of lead are shown in Figs. 4 and 5.

Field observation and microscopic study of the sample revealed that the natural zeolite occurs mainly as well-formed fine sized crystals. Many of the zeolite crystals show a tabular morphology, as expected for a (monoclinic) clinoptilolite (Fig. 4a). As we previously reported [12], after modification with Fe(III) ions, form and size are preserved despite the strongly basic conditions used for modification (Fig. 4b).

SEM coupled with EDS provides a semi quantitative elemental analysis of the crystals surface. In the EDS spectra of the natural zeolite, Si, Al, O, Mg, Ca, K, Na, Ti and Fe were detected. Iron is certainly due to (non-zeolitic) Fe-bearing minerals in the volcanic rocks [30], while Ca, Na, K and Mg are mainly the extra framework cations that compensate the net negative charge of the zeolite (clinoptilolite-heulandite) network [31]. After modification of the natural zeolite with Fe(III) ions, iron and potassium content increased ($Fe_2O_3 = 2.03\%$ for the natural and $Fe_2O_3 = 5.70\%$ for Fe(III)-modified zeolite; $K_2O = 1.41\%$ for the natural and $K_2O = 5.81\%$ for Fe(III)-modified zeolite), while content of sodium and calcium decreased ($Na_2O = 1.27\%$ for the natural and $Na_2O = 0.49\%$ for Fe(III)-modified zeolite; $CaO = 3.26\%$ for the natural and $CaO = 2.18\%$ for Fe(III)-modified zeolite).

In Fe(III)-modified zeolite, the amount of iron exceeds cation exchange capacity of the natural zeolite, which together with EDS results confirm that, in addition to the ion exchange between the exchangeable cations from the zeolite network and the Fe from the solution, most of the iron is deposited on the surface of the zeolite crystals and may be in the form of Fe-oxides [32].

For lead saturated samples, the content of lead determined by EDS was 6.30% for the natural and 14.22% for Fe(III)-modified zeolite and it was close to the maximum capacities of both samples obtained from sorption experiments. For this initial concentration of lead used for preparation saturated samples, it was postulated that sorption of lead include ion exchange together with chemisorption of lead on the surface [12]. Sorption complexes of Pb(II) with various adsorbents including alumina, clay minerals (such as montmorillonite), manganese(III,IV) oxyhydroxide as well as Pb(II) mononuclear bidentate inner sphere sorption complexes (with hematite and goethite over a wide range of conditions), were reported in the literature [33]. Thus, similar results of EDS analysis and maximum sorption capacity suggested that for both zeolites besides ion exchanged lead, it is also retained on

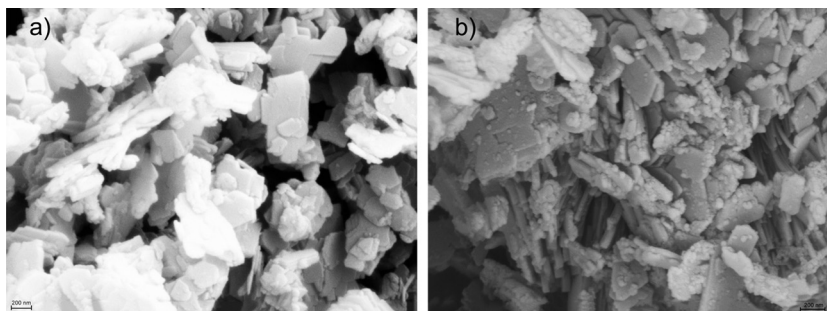


Fig. 4. SEM micrographs of the: (a) natural and (b) Fe(III)-modified zeolite.

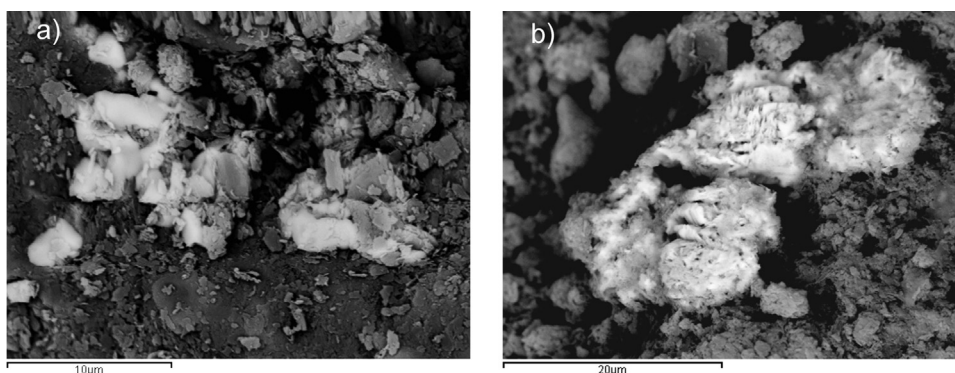


Fig. 5. SEM micrographs of lead saturated: (a) natural and (b) Fe(III)-modified zeolite.

hydroxyl surface sites particularly at $\equiv\text{FeOH}$ sites associated with Fe-oxyhydroxide mineral phases, and/or $>\text{SOH}$, which represents both zeolite mineral edges and Al-oxyhydroxide functional groups [34]. Besides these processes, the mixed effect of sorption with coprecipitation or even coagulation of lead at the mineral surface may occur [35]. The SEM micrographs of both lead saturated zeolites (fraction 0.6–0.8 mm) presented at Fig. 5, show rare randomly distributed agglomerates with significant amount of lead (60.16 wt% – the natural zeolite and 71.50 wt% – Fe(III)-modified zeolite).

Lu et al. [36] reported that coprecipitation of Pb^{2+} with ferric oxyhydroxides occurred at $\text{pH} \sim 4$, and it was more efficient than sorption of lead from aqueous solutions at similar sorbate/sorbent ratios and pH. Their desorption experiments showed that more Pb^{2+} was released from loaded sorbents collected from sorption experiments than from Pb to Fe coprecipitates. They hypothesized that Pb^{2+} was first sorbed on the nanometer-sized metastable Fe-oxyhydroxide polymers and, as these nano-particles assembled into larger particles, some Pb^{2+} was trapped in the Fe-oxyhydroxide structure and re-arranged. Low desorption of lead described in the previous section, similar content of lead in both samples obtained from EDS and from sorption experiments, as well as the presence of random agglomerates of lead at the mineral surfaces, confirmed complex lead sorption mechanism including ion exchange, surface complexation and co-precipitation. The much higher sorption of lead by Fe(III)-modified zeolite than by the natural one, suggested that these lead sorption processes are more pronounced when iron is present at the zeolitic surface.

3.3.2. XRPD analyses

XRPD patterns of the lead-saturated natural and Fe(III)-modified samples are shown in Fig. 6.

The refined amount of the crystalline phases (wt%) by Rietveld/RIR method are: clinoptilolite 66(1)%, mordenite 3(1)%, plagioclase 18(1)%, and quartz 12(1)% for the natural sample and clinoptilolite 73(1)%, mordenite 3(1)%, plagioclase 14(1)%, and quartz 10(1)% for the Fe(III)-modified sample. The estimated fraction of the amorphous phase was below the detection limit (i.e. <3 wt%). The two diffraction patterns show that there is no drastic change of the crystal-chemistry of the sample after the Fe(III)-treatment. As the Fe(III)-modified zeolite was prepared according to the protocol for pure goethite, we expected to find evidence, in the diffraction pattern, of iron hydroxides and/or iron oxides. Nevertheless, no Fe-rich crystalline phase was detected. However, a careful inspection of the profiles showed that: (a) the full-width-at-half-maximum of the diffraction peaks of clinoptilolite experienced increased (~ 8 – 10%) in the Fe(III)-modified sample, (b) a general slight decrease of the of the diffraction peaks intensity is observed

for all the crystalline phases, though more pronounced for clinoptilolite.

Additionally, crystal Fe–Pb-bearing oxides/hydroxides were also not observed in XRPD pattern of both lead saturated natural and Fe(III)-modified zeolite. The polyphase nature of the samples, coupled with the quality of the data collected with a conventional diffractometer, hindered high-quality structure refinements of clinoptilolite in order to prove a variation of the extra-framework population between the natural and Fe(III)-modified sample, respectively.

3.3.3. Transmission electron microscopy

A TEM investigation of the lead-saturated Fe(III)-modified zeolite showed a high fraction of idiomorphic crystals of clinoptilolite (Fig. 7), along with and plagioclase and quartz, and a secondary fraction of nano-aggregates which have been found to be amorphous (Fig. 8). The EDS analyses showed that: (1) The amount of Fe and Pb in idiomorphic crystals of clinoptilolite is negligible (i.e. below the EDS detection limit), and so Fe and Pb are not concentrated in zeolite structure (i.e. as extra-framework population); (2) Fe and Pb appear to be mainly concentrated into the amorphous fraction. These experimental findings can explain the absence of Fe–Pb-bearing oxides/hydroxides (e.g. goethite, limonite, etc.) in the X-ray diffraction patterns of the lead-saturated natural and Fe(III)-modified samples.

A further experimental finding concerns the presence of spherical nano-clusters on the crystal faces, as shown in Fig. 9. The dispersion of the clusters does not allow us to have a representative chemical composition of the clusters, but the image contrast suggests that the clusters have a different composition with respect to the host crystals of zeolite. In other words, clusters could be made by Fe or Pb oxides, but we cannot prove that. The TEM high-resolution images suggest that the spherical nano-clusters are amorphous (Fig. 9).

3.3.4. Textural properties

In Fig. 10, the nitrogen adsorption–desorption isotherms of natural zeolite, Fe(III)-modified zeolite and pure goethite¹ are shown.

The obtained isotherms, although similar, according to IUPAC nomenclature can be defined as two separate classes. Isotherm of pure goethite¹, due to existence of barely noticeable but visible plateau at high relative pressure, narrow hysteresis loop and almost vertical and nearly parallel hysteresis branches, with the desorption part end at relative pressure close to 0.85, can be classified as Type IV with hysteresis loop of type H1. This type of hysteresis is associated with porous materials which

¹ Pure goethite was synthesized under the same procedure as Fe(III)-modified zeolite.

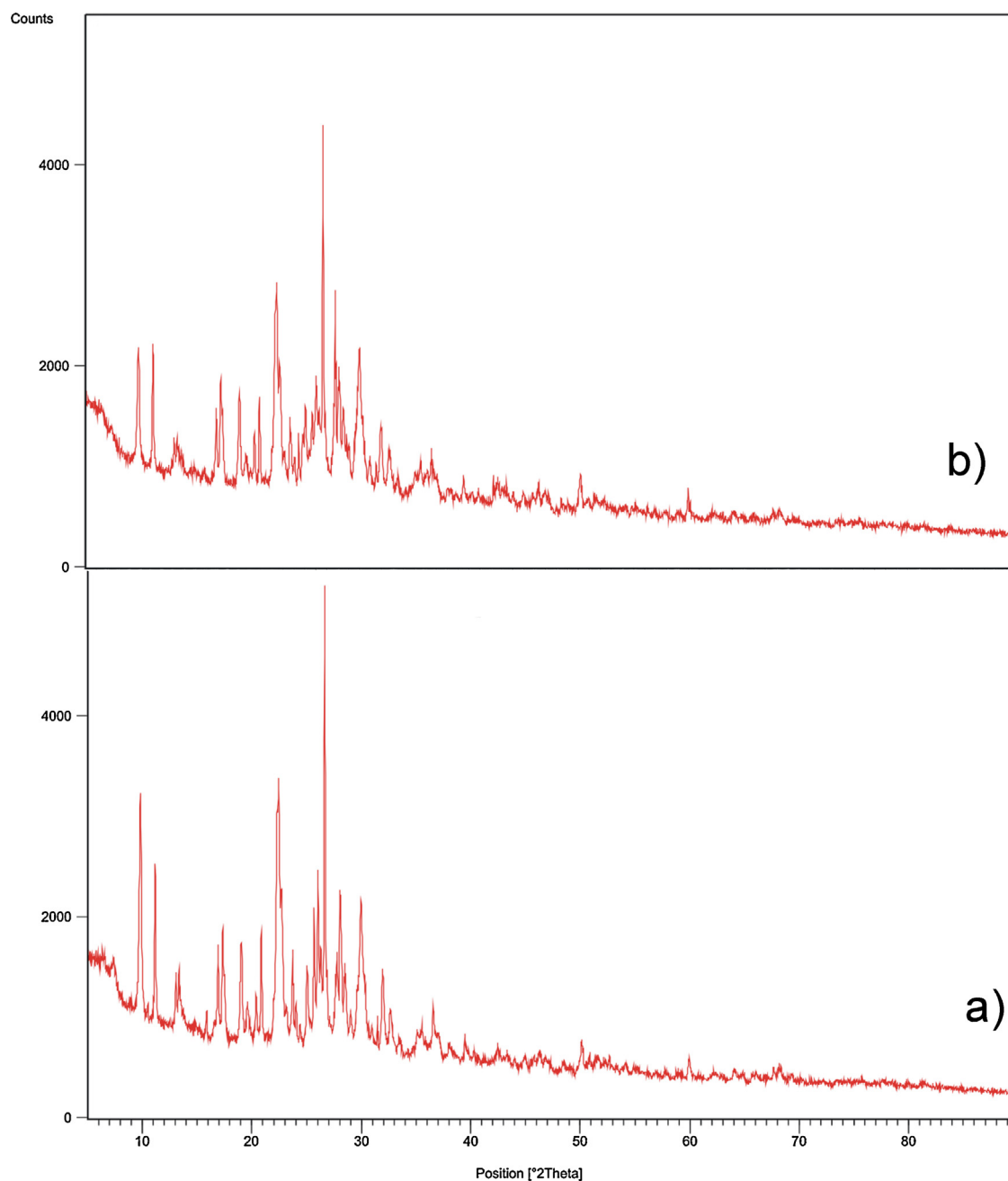


Fig. 6. X-ray powder diffraction pattern of the lead saturated: (a) natural zeolite and (b) Fe(III)-modified zeolite.

consist of agglomerates or compacts of approximately uniform spheres in fairly regular array and hence these materials have a narrow pore size distribution. Overall, it appears that synthesized pure goethite behaves like a mesoporous material. The pore size distribution (results not presented) estimated from desorption branches of isotherm shows the maximum at 44.7 nm, confirming mesoporosity of synthesized goethite.

For the natural and Fe(III)-modified zeolite, the obtained isotherms do not have a plateau at high relative pressure and for both sorbents hysteresis loops end at $p/p_0 \approx 0.42$. The position of hysteresis loop ending for both samples is typical for measurements with nitrogen at 77 K and is not the consequence of the pore system network of sorbents. Isotherms can be classified as Type II, typical for non porous materials. Additionally, hysteresis loop of H3 type can be recognized and is characteristic for the aggregates of plate-like particles.

The isotherms of natural and Fe(III)-modified zeolite after lead sorption (results not shown) are very similar to isotherms of corresponding materials before lead sorption, although some reduction of total amount of adsorbed nitrogen and slightly widening of hysteresis loop can be recognized. The type of isotherms (type II) and hysteresis loops (type H3) stay unchanged.

The results of calculated textural parameters of the natural and Fe(III)-modified zeolite before and after sorption of lead, as well as for pure goethite¹, are presented in Table 5.

Results showed that specific surface area significantly increases after modification of the natural zeolite with Fe(III) ions, from 30.20 m²/g for the natural zeolite to 52.50 m²/g for Fe(III)-modified zeolite. From the chemical analysis, the modification of the natural zeolite with Fe(III) ions under basic condition, increased the iron content for only 1.1% (from Fe₂O₃ = 2.30% for the natural to Fe₂O₃ = 3.97% for Fe(III)-modified zeolite) [12]. So, addition of

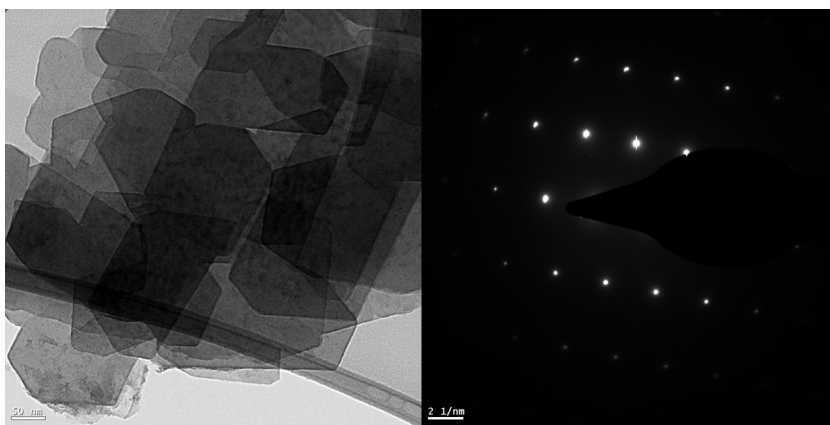


Fig. 7. Idiomorphic single-crystals of clinoptilolite (left) and a diffraction pattern of one individual (right). The EDS chemical analysis of the idiomorphic crystals shows Fe and Pb content below the detection limit.

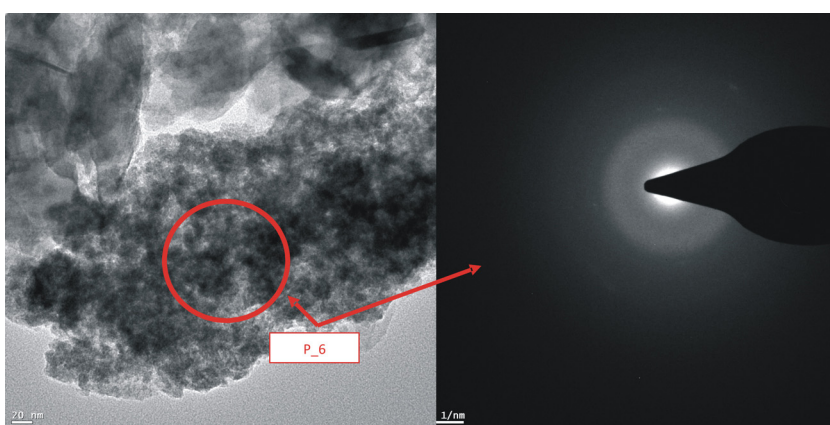


Fig. 8. Amorphous aggregate (left) and its diffraction pattern (right). The EDS chemical analysis at P.6 yields: Fe = 15.2(3)% and Pb = 7.5(8)% (given as atomic %).

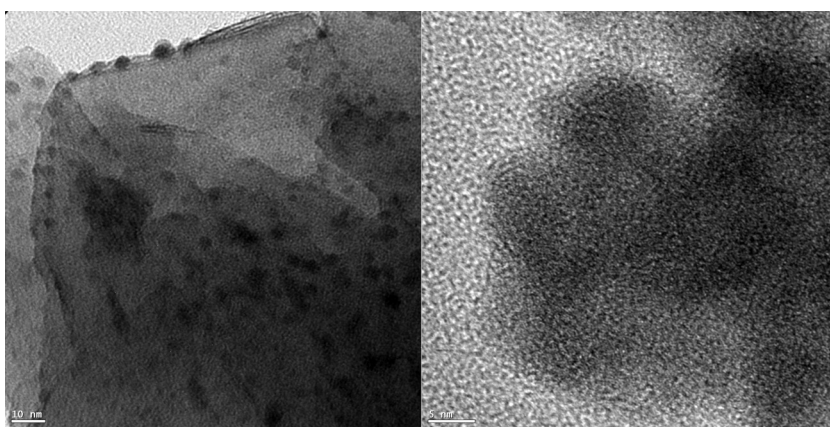


Fig. 9. High-resolution images of sub-spherical nano-clusters which appear to be amorphous (left) and lying on the surface of the crystals of clinoptilolite (right).

Table 5
Textural parameters of the natural and Fe(III)-modified zeolite before and after lead sorption and of pure goethite.^a

Sample	S_{BET} (m^2/g)	V_{tot} (cm^3/g)	V_{meso} (cm^3/g)	V_{mic} (cm^3/g)
Natural zeolite	30.20	0.135	0.078	0.012
Natural zeolite + lead	29.70	0.082	0.042	0.011
Fe(III)-modified zeolite	52.50	0.151	0.092	0.019
Fe(III)-modified zeolite + lead	46.50	0.131	0.058	0.017
Goethite ^a	55.50	0.528	0.489	0.020

^a Pure goethite was synthesized under the same procedure as Fe(III)-modified zeolite.

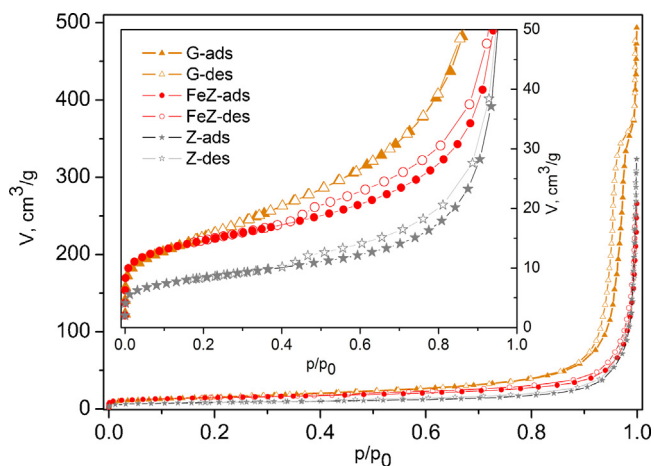


Fig. 10. Nitrogen isotherms of natural zeolite (Z), Fe(III)-modified zeolite (FeZ) and pure goethite (Pure goethite was synthesized under the same procedure as Fe(III)-modified zeolite) (G); filled symbols adsorption, empty symbols desorption points.

such small amount of iron elevated S_{BET} close to the value of pure goethite¹ (55.50 m²/g). Increase of the specific surface area observed by Jiménez-Cedillo et al. [32] for zeolites treated with both iron and manganese, indicated that metallic species are not only exchangeable by the cations from the zeolite network but are also deposited on the surface of the zeolitic materials. Doula [11] also reported for Fe-modified clinoptilolite that only a small amount of Fe could be exchanged with the cations of extra-framework population of the zeolite structure. She indicated that, as a result of the presence of iron in the zeolite structure channels, the textural properties of this material changed notably. Compared to the natural zeolite, the increase of the specific surface area of Fe(III)-modified zeolites through the increase of micropores volume (especially on ultra-micropores with diameter less than 1 nm) may be an additional evidence of ion exchange, because micropore volume previously inaccessible to the molecule of nitrogen becomes accessible after exchange of larger cations (K⁺, Na⁺, Ca²⁺, Mg²⁺) with considerable smaller one Fe³⁺ [37]. On the other hand, the increase in mesopore volume can be correlated with the formation of a new phase at the zeolitic surface which is itself mesoporous. Thus, the Fe(III)-modified zeolite shows both increase of micro- and mesopores volume, confirming formation of new Fe-bearing phases on zeolite beside to the mechanism of ion exchange.

After lead sorption, specific surface area of the natural and Fe(III)-modified zeolite, compared to the corresponding source materials, slightly decreased. In fact, all textural parameters decrease, especially mesopore volume. The decrease of V_{tot} and V_{meso} may further suggest that lead is considerably deposited on the surface of both sorbents, confirming that (for this initial concentration) besides ion exchange, chemisorption of lead occurred.

Finally, since it is well known that amorphous Fe-oxides have larger sorption capacities for metal contaminants than crystalline oxides such as goethite [33], to support observations that amorphous iron at the zeolitic surface increased lead sorption, we did preliminary lead sorption experiment (initial lead concentration ~ 1300 mg/L, amount of solid phase 1.0000 g/50 mL and pH=4.24) with pure goethite.¹ The result was compared with lead sorption, under the same conditions, by the natural and Fe(III)-modified zeolite. We observed that lead sorption increased in the following order: goethite¹ (17.5%) < the natural zeolite (61.5%) < Fe(III)-modified zeolite (91.6%). Thus, results on lead sorption by the natural and Fe(III)-modified zeolite, along with characterization of materials before and after sorption of lead reported in this study, confirmed that amorphous

Fe-oxy/hydroxides at the surface of Fe(III)-modified zeolite are responsible for enhanced sorption of lead.

4. Conclusion

Results reported in this paper showed that significantly higher sorption of lead was achieved with modification of the natural zeolite with Fe(III) ions under basic conditions. Sorption experiments as well as characterization of both the natural and Fe(III)-modified zeolite before and after sorption of lead confirmed complex lead sorption mechanism including ion exchange as well as chemisorption and precipitation of lead at the zeolitic surface. Characterization of Fe(III)-modified zeolite after sorption of lead confirmed enhanced lead sorption is due to presence of amorphous phase at the surface of modified zeolite. High lead sorption and high stability of lead saturated modified zeolite make Fe(III)-modified zeolite as promising material for water purification.

Acknowledgements

These investigations were conducted under the Projects 172018 and 34013 funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia. G. Diego Gatta and Nicola Rotiroti thank the Italian Ministry of Education, MIUR-Project: "ImPACT-RBFR12CLQD". The authors acknowledge the agreement for international cooperation among the Università degli Studi di Milano and the Institute for Technology of Nuclear and Other Mineral Raw Materials in Belgrade. The company "Nemetali" from Vranjska Banja, Serbia kindly provided the natural zeolitic sample.

References

- [1] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: a review, *Journal of Environmental Management* 92 (2011) 407–418.
- [2] W. Yang, P. Ding, L. Zhou, J. Yu, X. Chen, F. Jiao, Preparation of diamine modified mesoporous silica on multi-walled carbon nanotubes for the adsorption of heavy metals in aqueous solution, *Applied Surface Science* (2013), <http://dx.doi.org/10.1016/j.apsusc.2013.05.028>.
- [3] M. Hamidpour, M. Kalbasib, M. Afyunib, H. Shariatmadarib, P.E. Holmc, H.C.B. Hansenc, Sorption hysteresis of Cd(II) and Pb(II) on natural zeolite and bentonite, *Journal of Hazardous Materials* 181 (2010) 686–691.
- [4] V.J. Inglezakis, M.A. Stylianou, D. Gkantzou, M.D. Loizidou, Removal of Pb(II) from aqueous solutions by using clinoptilolite and bentonite as adsorbents, *Desalination* 210 (2007) 248–256.
- [5] M.J. Baniamerian, S.E. Moradi, A. Noori, H. Salahi, The effect of surface modification on heavy metal ion removal from water by carbon nanoporous adsorbent, *Applied Surface Science* 256 (2009) 1347–1354.
- [6] M. Trgo, J. Perić, N. Vukojević-Medvidović, A comparative study of ion exchange kinetics in zinc/lead-modified zeolite–clinoptilolite systems, *Journal of Hazardous Materials* 136 (2006) 938–945.
- [7] M. Karatas, Removal of Pb(II) from water by natural zeolitic tuff: kinetics and thermodynamics, *Journal of Hazardous Materials* 199/200 (2012) 383–389.
- [8] M. Sprynskyy, B. Buszewski, A.P. Terzyk, J. Namieśnik, Study of the selection mechanism of heavy metal (Pb²⁺, Cu²⁺, Ni²⁺, and Cd²⁺) adsorption on clinoptilolite, *Journal of Colloid and Interface Science* 304 (2006) 21–28.
- [9] A. Günay, E. Arslankaya, I. Tosun, Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics, *Journal of Hazardous Materials* 146 (2007) 362–371.
- [10] S. Mustafa, S. Khan, M. Iqbal Zaman, S. Yar Husain, The role of Pb²⁺ ions doping in the mechanism of chromate adsorption by goethite, *Applied Surface Science* 255 (2009) 8722–8729.
- [11] M.K. Doula, Removal of Mn²⁺ ions from drinking water by using clinoptilolite and a clinoptilolite–Fe oxide system, *Water Research* 40 (2006) 3167–3176.
- [12] M. Kragović, A. Daković, Ž. Sekulić, M. Trgo, M. Ugrina, J. Perić, G.D. Gatta, Removal of lead from aqueous solutions by using the natural and Fe(III)-modified zeolite, *Applied Surface Science* 258 (2012) 3667–3673.
- [13] G. Mustafa, B. Singh, R. Kookana, Cadmium adsorption and desorption behavior on goethite at low equilibrium concentrations: effects of pH and index cations, *Chemosphere* 57 (2004) 1325–1333.
- [14] C. Jeon, K. Baek, J. Park, Y. Oh, S. Lee, Adsorption characteristics of As(V) on iron-coated zeolite, *Journal of Hazardous Materials* 163 (2009) 804–808.
- [15] H.M. Rietveld, A profile refinement method for nuclear and magnetic structures, *Journal of Applied Crystallography* 2 (1969) 65–71.
- [16] A.F. Gualtieri, Accuracy of XRPD QPA using the combined Rietveld–RIR method, *Journal of Applied Crystallography* 33 (2000) 267–278.

- [17] A.C. Larson, R.B. Von Dreele, General Structure Analysis System (GSAS), National Laboratory Report LAUR, Los Alamos, 2004, pp. 86–748.
- [18] P. Thompson, D.E. Cox, J.B. Hastings, Rietveld refinement of Debye–Scherrer synchrotron X-ray data from Al_2O_3 , *Journal of Applied Crystallography* 20 (1987) 79–83.
- [19] <http://www.minsocam.org/MSA/Crystal.Database.html>
- [20] S.J. Gregg, K.S.W. Sing, Adsorption, Surface Area and Porosity, Academic Press, London, 1982, pp. 35–120.
- [21] M.M. Dubinin, Physical adsorption of gases and vapors in microspores, in: D.A. Cadenhead (Ed.), *Progress in Surface and Membrane Science*, vol. 9, Academic Press, New York, 1975, pp. 1–70.
- [22] D. Dollimore, G.R. Heal, An improved method for the calculation of pore size distribution from adsorption data, *Journal of Applied Chemistry* 14 (1964) 109–114.
- [23] E.S. Dragan, M.V. Dinu, D. Timpu, Preparation and characterization of novel composites based on chitosan and clinoptilolite with enhanced adsorption properties for Cu^{2+} , *Bioresource Technology* 101 (2010) 812–817.
- [24] Y.S. Ho, G. McKay, Pseudo second order model for sorption process, *Process in Biochemistry* 34 (1999) 451–465.
- [25] W. Zou, R. Han, Z. Chen, Z. Jinghua, J. Shi, Kinetic study of adsorption of Cu(II) and Pb(II) from aqueous solutions using manganese oxide coated zeolite in batch mode, *Colloids and Surfaces A* 279 (2006) 238–246.
- [26] Z. Aksu, Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of lead(II) ions onto *Chlorella vulgaris*, *Process in Biochemistry* 38 (2002) 89–99.
- [27] D. Xu, X.L. Tan, C.L. Chen, X.K. Wang, Adsorption of Pb(II) from aqueous solution to MX-80 bentonite: effect of pH, ionic strength, foreign ions and temperature, *Applied Clay Science* 41 (2008) 37–46.
- [28] M. Kragović, S. Miličević, A. Daković, J. Perić, M. Trgo, N. Vukojević-Medvidović, M. Ugrina, Ž. Sekulić, I. Nuić, Removal of copper and lead by clinoptilolite and clinoptilolite–iron system, in: O.E. Pertov, Y.K. Tzvetanova (Eds.), 8th International Conference on the Occurrence, Properties and Utilization of Natural Zeolites, Sofia, Bulgaria, 2010, pp. 149–150 (Book of Abstracts).
- [29] N. Bektaş, S. Kara, Removal of lead from aqueous solutions by natural clinoptilolite: equilibrium and kinetic studies, *Separation and Purification Technology* 39 (2004) 189–200.
- [30] A.D. Vujaković, M. Djuričić, M.R. Tomašević-Čanović, Thermal study of surfactant and anion adsorption on clinoptilolite, *Journal of Thermal Analysis and Calorimetry* 63 (2001) 161–172.
- [31] M.K. Doula, A. Dimirkou, Use of an iron-overexchanged clinoptilolite for the removal of Cu^{2+} ions from heavily contaminated drinking water samples, *Journal of Hazardous Materials* 151 (2008) 738–745.
- [32] M.J. Jiménez-Cedillo, M.T. Olguín, Ch. Fall, A. Colín, Adsorption capacity of iron- or iron-manganese-modified zeolite-rich tuffs for As(III) and As(V) water pollutants, *Applied Clay Science* 54 (2011) 206–216.
- [33] P. Trivedi, J.A. Dyer, D.L. Sparks, Lead sorption onto ferrihydrite: 1. A macroscopic and spectroscopic assessment, *Environmental Science and Technology* 37 (2003) 908–914.
- [34] S. Serrano, P.A. O'Day, D. Vlassopoulos, M.T. Garcia-Gonzalez, F. Garrido, A surface complexation and ion exchange model of Pb and Cd competitive sorption on natural soils, *Geochimica et Cosmochimica Acta* 73 (2009) 543–558.
- [35] S.-M. Lee, C. Laidawngliana, D. Tiwari, Iron oxide nano-particles-immobilized-sand material in the treatment of Cu(II) , Cd(II) and Pb(II) contaminated waste waters, *Chemical Engineering Journal* 195/196 (2012) 103–111.
- [36] P. Lu, N.T. Nuhfer, S. Kelly, Q. Li, H. Konishi, E. Elswick, C. Zhu, Lead coprecipitation with iron oxyhydroxide nano-particles, *Geochimica et Cosmochimica Acta* 75 (2011) 4547–4561.
- [37] Y. Marcus, Thermodynamics of solvation of ions: part 5. Gibbs free energy of hydration at 298.15 K, *Journal of the Chemical Society, Faraday Transactions* 87 (1991) 2995–2999.