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A COMPARATIVE STUDY OF THE REMOVAL OF LEAD, CADMIUM AND ZINC IONS FROM AQUEOUS SOLUTIONS BY NATURAL AND Fe(III)-MODIFIED ZEOLITE

Article Highlights

- Natural zeolite was modified by iron oxide for Pb²⁺, Zn²⁺ and Cd²⁺ adsorption
- Adsorption capacity of the modified zeolite is much higher than of natural zeolite.
- Main adsorption mechanisms are specific adsorption and ion exchange
- New functional groups due to surface modification enable higher specific adsorption
- Adsorption capacities of both zeolites increase with increasing temperature

Abstract

The main purpose of this research was to explain the differences in the adsorption mechanisms and adsorption capacities of natural and Fe(III)-modified zeolite for Pb²⁺, Zn²⁺ and Cd²⁺. The adsorbents were characterized with respect to their phase composition, morphology, specific surface area, cation exchange capacity and point of zero charge. Batch adsorption experiments were performed as a function of the initial ion concentration and temperature, at constant initial pH value of 5.5±0.1. The adsorption isotherms at 25, 40, 55 and 70 °C suggest that the sequence of adsorption efficiency of both zeolites is Pb²⁺ > Zn²⁺ > Cd²⁺. The adsorption capacities of both zeolites increased with increasing temperature. The equilibrium adsorption data were best described by the Langmuir adsorption isotherm. This study revealed that the adsorption capacity of the Fe(III)-modified zeolite is much higher than that of natural zeolite for all investigated ions owing to the higher: specific adsorption caused by the new functional groups formed on the zeolite surface, ion exchange due to the presence of easily exchangeable ions, and hydroxide precipitation caused by higher point of zero charge of the Fe(III)-modified zeolite compared to natural zeolite.

Keywords: Fe(III)-zeolite, adsorption, metal ions, mechanism.

The increasing levels of heavy metals in the environment are a serious problem for human health, living resources and ecological systems. Several methods have been employed to remove heavy metal ions from wastewater, which include precipitation, flotation, ion exchange, membrane-related processes, electrochemical techniques and biological processes. Currently, adsorption is believed to be a simple and effective technique for water and wastewater treat-

ment and the success of the technique largely depends on the development of efficient adsorbents. Among the different natural minerals, zeolites appear to be the most promising adsorbents in metal purification processes [1,2].

Natural zeolites are hydrated aluminosilicate minerals with a porous structure and valuable cation exchange, molecular sieve, catalytic and adsorption properties [3]. The zeolite structure consists of three relatively independent components: an aluminosilicate framework, exchangeable cations and zeolitic water. The aluminosilicate framework is the most stable component and defines the structure type. The water molecules can be present in the voids of large cavities and bonded between framework ions and exchangeable ions *via* aqueous bridges. The water

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can also serve as bridges between exchangeable cations [3]. A high content of exchangeable cations, *i.e.*, a high value of the cation exchange capacity (CEC), is a significant characteristic of zeolites, promoting their application as adsorbents for heavy metal ions. The CEC and the adsorption capacity for metal ions depend significantly on the origin of the zeolite [4–8].

In order to improve their adsorption capacity, modification of natural zeolites can be realized using several methods, such as acid or base treatment [1,5,9–12], ion exchange [6,9,13–18] and surfactant functionalizations [3,19]. Recently, zeolites were modified by oxides or hydroxides of metals, such as Al, Fe and Mn [20–29]. It was shown [26–32] that zeolite adsorption capacities for Cu^{2+} , Mn^{2+} , Zn^{2+} , Pb^{2+} , Cr(VI) and As increase significantly by loading the surface with iron oxide species.

The subject of this study was the adsorption of Pb^{2+} , Zn^{2+} and Cd^{2+} on natural zeolite and Fe(III)-modified zeolite. The main goal of this research was to explain the differences in adsorption mechanisms and adsorption capacities of these two adsorbents for Pb^{2+} , Zn^{2+} and Cd^{2+} . Adsorption experiments were also performed in order to investigate the influence of temperature on the adsorption.

EXPERIMENTAL

Materials

A natural zeolite (NZ) from the Slanci locality, Serbia, was used as the starting material in experiments.

Fe(III)-modified zeolite (ZFe) was synthesized according to the method applied for obtaining pure goethite [28]. A suspension was made by mixing 20.0 g of zeolite, 100 cm³ of freshly prepared 1 M FeCl_3 solution, and 180 cm³ of 5 M KOH solution in a 2 dm³ polyethylene flask. The KOH solution was added rapidly under stirring. The suspension was diluted with deionized water to 2 dm³ and held in a closed polyethylene flask at 70 °C for 60 h. Then, the obtained precipitate, brown-red in color, was centrifuged, washed to remove Cl⁻ ions and dried at 105 °C.

Characterization of the adsorbents

The phase composition of the NZ and ZFe samples was determined using an Ital Structures APD 2000 diffractometer equipped with a back monochromator operating at a tube voltage of 40 kV and a tube current of 30 mA using a copper cathode as the X-ray source ($\lambda = 0.15406$ nm), in the 2θ angle range from

10 to 50°. A step size of 0.02° and a time per step of 3 s were used.

The morphology of the particles of the natural and modified zeolite was observed by scanning electron microscopy (SEM) using a JEOL JSM 5800 instrument. The samples were sputter-coated with an Au-Pd mixture to ensure conductivity.

The TEM analysis of zeolite samples was performed on the JEOL T-100 instrument. The samples were prepared by grinding and subsequent dispersing of the powder in ethanol. A drop of the very dilute suspension was applied on carbon-coated grids.

The specific surface area of the samples was determined by the BET method. The samples were degassed under vacuum at 105 °C for 2 h. Nitrogen of 99.9% purity was adsorbed on the degassed sample surface at liquid nitrogen temperature (-196 °C).

The cation exchange capacities (CEC) of the samples were determined by the ammonium acetate method. The content of the exchangeable ions in solution after treatment of the zeolite with 1 M ammonium acetate solution was determined by atomic absorption spectroscopy (Perkin-Elmer).

The point of zero charge (pH_{pzc}) of the NZ and ZFe samples was determined by the batch equilibration technique [33]. KNO_3 solutions of different ionic strengths: 0.1, 0.01 and 0.001 mol dm⁻³ were used as the electrolyte solutions. The adopted procedure for determination of the point of zero charge, the same in all cases, was as follows: the initial pH values (pH_i) of electrolyte solutions (25 cm³ of each sample in a series) of the predetermined concentrations were adjusted by the addition of 0.1 mol dm⁻³ solutions of HNO_3 or KOH, in the pH range from 3.5 to 10. Then, 0.05 g of NZ or ZFe was added to each sample (at a ratio solid:liquid = 1:500). After 24 h of equilibration at room temperature under constant shaking, the suspensions were filtered and the pH of the filtrate was determined (pH_f). The value of the point of zero charge is the value of the plateau, *i.e.*, inflexion point, of the pH_f vs. pH_i plot [33–35]. To determine the effect of the solid/liquid ratio on the position of the point of zero charge, the whole procedure was repeated using 0.1 g of sample (at a ratio solid:liquid = 1:250).

Adsorption experiments

The batch equilibration method was used to investigate the specific adsorption of Pb^{2+} , Cd^{2+} and Zn^{2+} onto NZ and ZFe. The experiments were performed using solutions (concentration of 0.01 mol dm⁻³) of $\text{Pb}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$ in demineralized water at a sample to electrolyte solution ratio of 0.05 g:25 cm³. The specific adsorption was examined in

the pH range from ≈ 3 to ≈ 6 to avoid ion hydrolysis and hydroxide precipitation at higher pH values or dissolution of the zeolite at lower pH values.

Adsorption isotherms were determined using solutions of $\text{Pb}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$ in demineralized water with different initial Pb^{2+} , Cd^{2+} and Zn^{2+} concentrations in the range 20–800 mg dm^{-3} . The initial pH values of the solutions were adjusted to 5.5 ± 0.1 . An aliquot of 25 cm^3 of each solution with 0.05 g of sample was shaken for 24 h in a thermostated water bath at temperatures of 25, 40, 55 and 70 °C. After filtration, the pH values of the liquid phase were determined. The Pb^{2+} , Cd^{2+} and Zn^{2+} concentrations, as well as Ca^{2+} , Mg^{2+} , Na^+ and K^+ concentrations in the filtrate were determined by ICP OES (Spectro Genesis).

All the adsorption experiments were repeated twice; the reported value is the average of two measurements.

RESULTS AND DISCUSSION

Characterization of NZ and ZFe samples

The XRD patterns of the NZ and ZFe samples are given in Figure 1. The pattern of the NZ sample revealed clinoptilolite (C) as the dominant phase with lower contents of quartz (Q) and feldspar (F). It is clearly visible presence of all diffraction maximum on ZFe diffractogram that correspond to the peaks appeared on diffractogram of NZ sample, indicating no damage of clinoptilolite structure. Lower intensity of diffraction maximum, broadening of the peaks and expressed background intensity indicate lower crystallinity of ZFe sample due to applied modification. Absence of additional peaks belong to Fe(III)-oxide or

Fe(III)-oxohydroxide phases indicates that crystalline Fe(III)-phases have not been formed at zeolite surface.

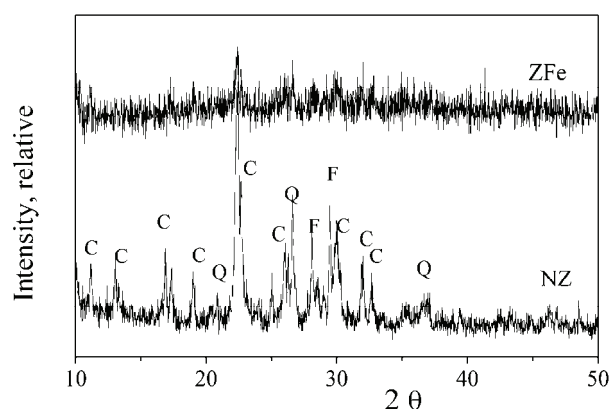
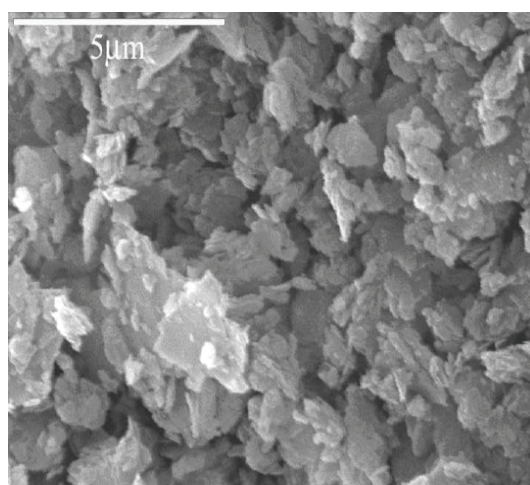


Figure 1. XRD Patterns of NZ and ZFe (C - clinoptilolite, F - feldspar, Q - quartz).

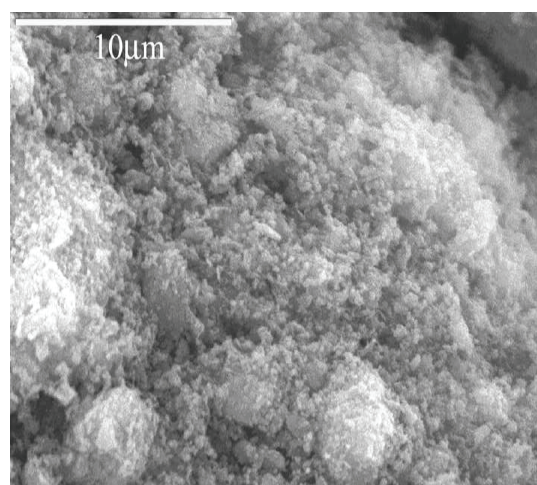
SEM and TEM micrographs of zeolite samples are given in Figures 2 and 3, respectively. Abundant deposits on the zeolite surface can be seen in the microphotograph of the ZFe sample, which confirms formation of Fe(III) phases at the zeolite surface.

The different microstructures of ZFe and NZ can explain the great difference in the specific surface areas of these samples; the specific surface area of zeolite increased from 18 to 175 $\text{m}^2 \text{g}^{-1}$ on modification. The almost tenfold higher specific surface area of the modified zeolite indicated the formation of a porous layer of Fe(III) phases on the surface and in the zeolite structural channels.

The cation exchange capacity (CEC) and the percentage content of some exchangeable ions in the NZ and ZFe samples are given in Table 1, from which



(a)



(b)

Figure 2. SEM Micrographs of a) NZ and b) ZFe sample.

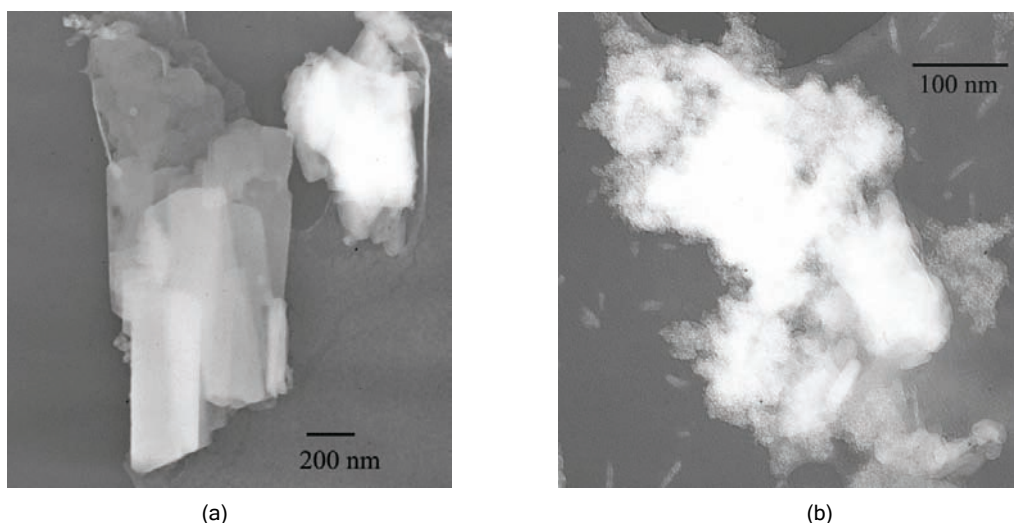


Figure 3. TEM Micrographs of a) NZ and b) ZFe sample.

it can be seen that the dominant exchangeable ions in NZ were Ca^{2+} and Mg^{2+} , while in ZFe, besides these ions, there was a significant amount of K^+ , introduced during the sample synthesis.

Table 1. Cation exchange capacity and percentage content of some exchangeable ions (% of CEC) in NZ and ZFe samples

Ion	CEC / mmol M^+ g^{-1}	
	NZ	ZFe
Ca^{2+}	68.0	45.4
Mg^{2+}	19.6	10.5
K^+	6.3	43.7
Na^+	5.1	0.4
Fe^{3+}	~ 0	~ 0

The results of determination of points of zero charge of NZ and ZFe samples are illustrated in Figure 4a.

Figure 4a shows that the position of the plateau on the pH_f vs. pH_i plot for both samples was independent of the ionic strength of the KNO_3 , indicating that the used electrolyte was indifferent, *i.e.*, that there was no specific sorption of K^+ and NO_3^- onto the NZ and ZFe surface. In the case of NZ sample, the plateau pH value, which remained constant even with change in solid:liquid ratio, was 7.5 ± 0.1 , which is actually the point of zero charge of the untreated zeolite. This value is in accordance with the results obtained by Alvarez-Azuso and coworkers [2]. In the case of the ZFe sample, the position of the plateau was to some extent dependent on the solid:liquid ratio. On increasing the ratio from $0.05 \text{ g}:25 \text{ cm}^3$ (1:500) to $0.10 \text{ g}:25 \text{ cm}^3$ (1:250), the plateau shifted

by ≈ 0.2 pH units, from 9.3 ± 0.1 to 9.5 ± 0.1 . This dependence of the plateau position, *i.e.*, the point of zero charge, on the solid:liquid ratio can be explained by incomplete rinsing of the ZFe sample after synthesis, resulting in small amounts of KOH being retained in the sample, which led to a shift in plateau pH towards higher values.

The higher point of zero charge value of the ZFe in relation to the NZ sample indicates increased alkalinity of the zeolite surface caused by modification, *i.e.*, the alkalinity of the groups formed by modification on the zeolite surface was greater than the alkalinity of the functional groups on the surface of untreated zeolite. It is important to note that both samples had a high buffer capacity, *i.e.*, over a wide initial pH range, the final pH value was equal to the value of the point of zero charge.

According to the value of pH_{pzc} of pure goethite ($\text{pH}_{\text{pzc}} 9.4 \pm 0.1$) [36], it can be assumed that a phase similar to goethite, but not crystalline, was formed on the whole zeolite surface. Recently synthesized Fe(III)-zeolite [29] has significantly lower pH_{pzc} (7.5 ± 0.1), which indicates lower coverage of zeolite surface by Fe(III)-phases.

Adsorption of Pb^{2+} , Cd^{2+} and Zn^{2+} ions on NZ and ZFe

The removal of metal cations from water by an adsorbent can include: ion exchange, specific adsorption, metal hydroxide precipitation, dissolution-precipitation, *etc.* [1,2,4,5]. Ion exchange is the basic mechanism for removal of metal cations by zeolites owing to their high cation exchange capacities. However, metal hydroxide precipitation at higher pH values and the formation of complexes with surface

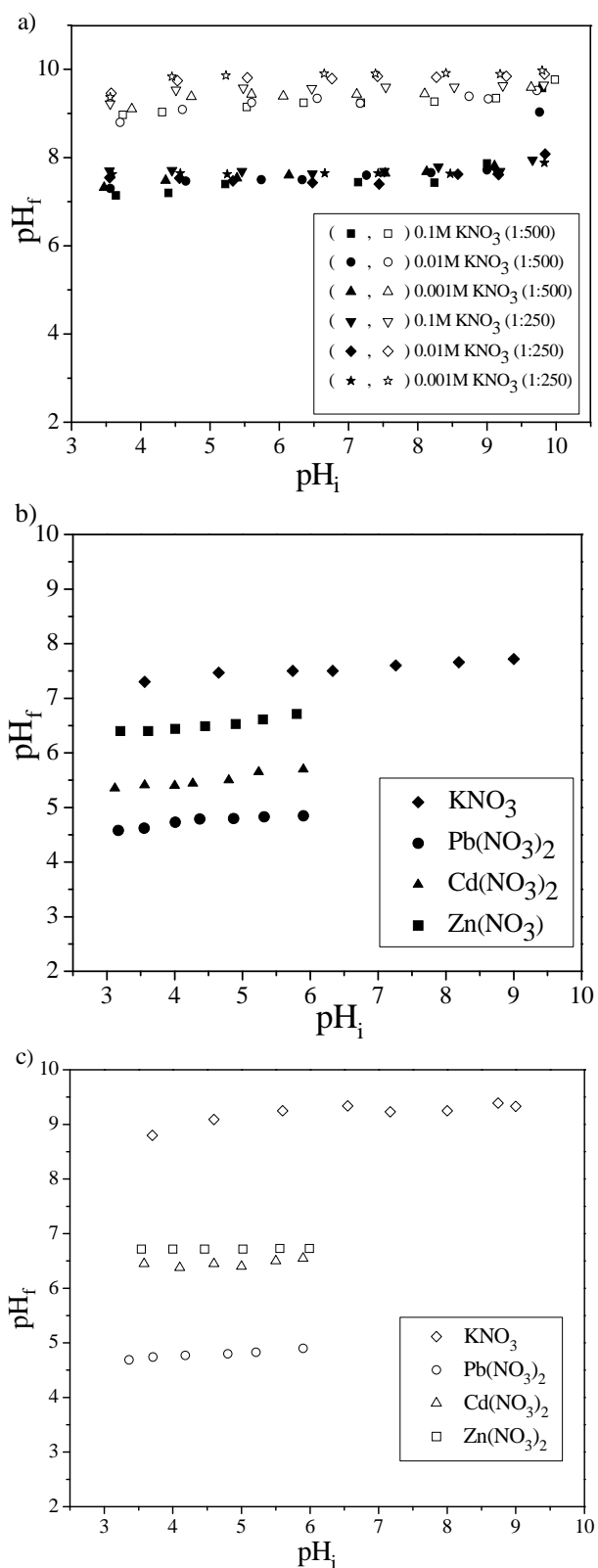


Figure 4. a) Determination of the pH_{pzc} of the NZ (black symbols) and ZFe (open symbols) samples in KNO_3 solutions of different concentrations and solid:liquid ration 1:250 and 1:500, b) pH_f vs. pH_i and c) pH_f vs. pH_i during the equilibration of 0.05 g NZ with 25 cm³ of 0.01 mol dm⁻³ solutions of $Pb(NO_3)_2$, $Cd(NO_3)_2$ and $Zn(NO_3)_2$.

functional groups (specific adsorption) followed by changes in pH can also contribute greatly to the total adsorbent capacity. Bearing in mind that many adsorption mechanisms, as well as the form of ions in water are pH dependent, the adsorption capacity of a given adsorbent is greatly affected by pH. When studying the adsorption capacity of an adsorbent as a function of pH, the initial pH is usually changed, but not sufficient attention has been paid to the changes in solution pHs during adsorption, which are the result of interactions of the adsorbent surface functional groups with water and ionic species present in the water. Therefore, in this study, attention was focused on specific adsorption and pH changes during adsorption in order to explain the adsorption mechanisms and differences between the adsorption capacities of the NZ and ZFe samples.

Specific adsorption of Pb^{2+} , Cd^{2+} and Zn^{2+} onto NZ and ZFe

The specific adsorption of lead, cadmium and zinc ions onto NZ and ZFe samples was studied based on the shifts in the points of zero charge. Generally, specific adsorption of cations shifts the point of zero charge towards lower, while the specific adsorption of anions towards higher pH values [34,35]. This fact was exploited to examine the affinity of NZ and ZFe for lead, cadmium and zinc ions because the shift in the point of zero charge caused by specific adsorption is proportional to the number of specifically adsorbed ions.

To determine whether specific adsorption of cations onto NZ and ZFe occurs, lead nitrate, cadmium nitrate and zinc nitrate solutions were used in the experiments. As already confirmed in the determination of the point of zero charge, there was no specific adsorption of NO_3^- onto the surface of the zeolites. Dependences of pH_f on pH_i during the equilibration of 0.05 g NZ, or ZFe, with solutions of investigated metal ions at a concentration of 0.01 mol dm⁻³ are shown in Figure 4b and c.

As can be seen in Figures 4b and c, there was a shift in the position of the point of zero charge in Pb^{2+} , Cd^{2+} and Zn^{2+} solutions towards lower pH values from that determined at a given solid:liquid ratio in the indifferent electrolyte (KNO_3) solution. The obtained results confirmed specific adsorption of the investigated ions onto NZ and ZFe. The shift in pH_{pzc} , for both samples, was the most pronounced in the case of Pb^{2+} , then Cd^{2+} , and the least pronounced in the case of Zn^{2+} . In addition, for all three investigated ions, the shift in the point of zero charge was more significant for the ZFe than NZ sample, confirming the

more pronounced specific adsorption onto the modified than onto the natural zeolite. The results indicated the presence of a large number of functional groups on the surface of the modified zeolite capable of forming complexes with the studied ions ($-M-O-Me$, where $M \equiv Fe, Al$ or Si and $Me \equiv Pb, Cd$ or Zn) or that the functional groups formed on the ZFe surface exhibited greater affinity for the studied ions. Obviously, the formed, amorphous iron oxide layer, with a high surface area, provides a large number of functional groups capable of participating in specific adsorption.

The quantity of specifically adsorbed ions on the surface of solids [35,37,38] is strongly dependent on electric charge, hydrated ion radii, hydration energy, metal electronegativity, *etc.* The electric charge of Pb^{2+} , Cd^{2+} , Zn^{2+} is the same, but there are differences in the other parameters. The hydrated cation radii increase in the following sequence: $r(Pb^{2+}) = 0.401$ nm $<$ $r(Cd^{2+}) = 0.426$ nm $<$ $r(Zn^{2+}) = 0.430$ nm, as well as the hydration energy $E_h(Pb^{2+}) = -1481$ kJ mol $^{-1}$ $<$ $E_h(Cd^{2+}) = -1807$ kJ mol $^{-1}$ $<$ $E_h(Zn^{2+}) = -2046$ kJ mol $^{-1}$, while the metal electronegativity decreases as follows: 1.9 (Pb) $>$ 1.7 (Cd^{2+}) $>$ 1.6 (Zn^{2+}) [2,35,39]. Decreases in hydrated cation radii and hydration energy, and increases in metal electronegativity lead to a growing tendency of the ion for specific adsorption [35,37,38]. The specific adsorption was, therefore, the highest with Pb^{2+} , then Cd^{2+} , and the lowest with Zn^{2+} .

Adsorption isotherms of Pb^{2+} , Cd^{2+} and Zn^{2+} onto NZ and ZFe at 25 °C

The amounts of adsorbed lead, cadmium and zinc ions as a function of their equilibrium concentrations in solutions (adsorption isotherms) onto NZ and ZFe at 25 °C are shown in Figure 5a. It can be seen that the adsorption capacities of the modified zeolite for all three investigated ions were significantly higher than those of the untreated zeolite.

The adsorption isotherms of Pb^{2+} onto NZ and ZFe samples show a rapid increase in adsorption at lower concentrations, followed by a moderate increase to a plateau, which corresponds to the maximum adsorption, *i.e.*, the adsorption capacity. The adsorption capacity of NZ for Pb^{2+} was ≈ 0.30 mmol g $^{-1}$, while that of the ZFe sample was more than three times higher, ≈ 1.0 mmol g $^{-1}$. Based on the adsorption isotherms of Cd^{2+} onto NZ and ZFe, it is obvious that the adsorption capacity of the untreated zeolite of ≈ 0.05 mmol g $^{-1}$ for Cd^{2+} was considerably lower in relation to that for Pb^{2+} . However, the adsorption capacity of the modified zeolite for Cd^{2+} adsorption

was considerably higher (over 10 times) than that for the unmodified zeolite, attaining a value of ≈ 0.60 mmol g $^{-1}$. The adsorption capacity of the NZ sample for Zn^{2+} ions was ≈ 0.23 mmol g $^{-1}$. This value is lower than that for Pb^{2+} but higher than that for Cd^{2+} . As in the case of Pb^{2+} and Cd^{2+} , the adsorption capacity of ZFe for Zn^{2+} was considerably higher than that of NZ and amounted to 0.74 mmol g $^{-1}$.

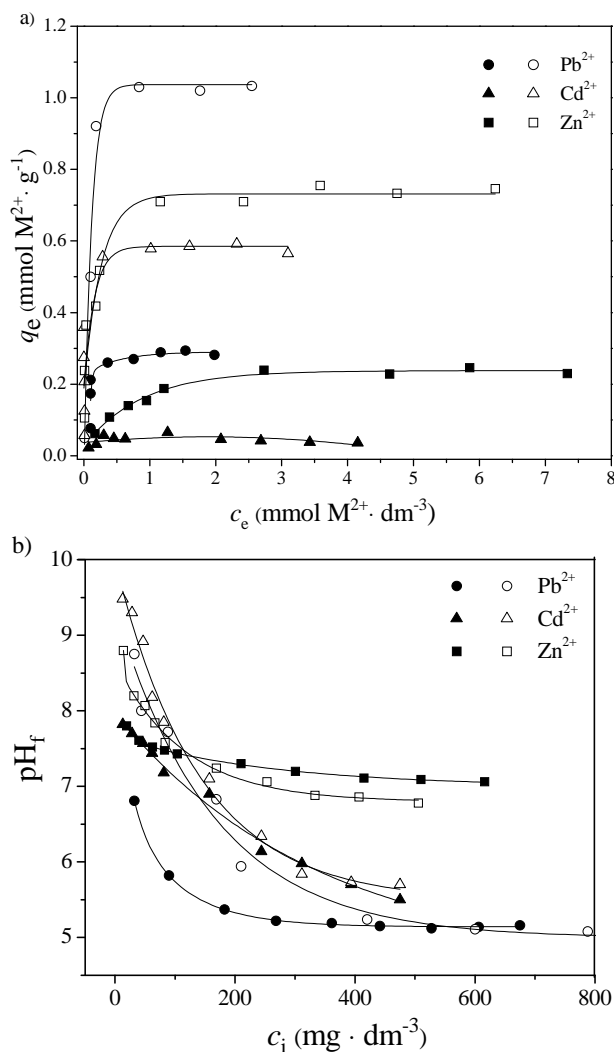


Figure 5. a) Adsorption isotherms for Pb^{2+} , Cd^{2+} and Zn^{2+} onto NZ (black symbols) and ZFe (open symbols) at 25 °C; b) dependence of final pH values after equilibration of NZ (black symbols) and ZFe (open symbols) with ion solutions at pH_i 5.5 and 25 °C, on initial concentrations of Pb^{2+} , Cd^{2+} and Zn^{2+} .

The dependences of the final pH values after equilibration of the NZ and ZFe samples with solutions of the metal ions (pH_i 5.5) on the initial Pb^{2+} , Cd^{2+} and Zn^{2+} concentrations in solution are presented in Figure 5b. For NZ and ZFe samples equilibrated with an inert electrolyte (KNO_3) solution, the final pH values were independent of the ion concen-

tration (Figure 4a), and at an initial pH value of 5.5, they were 7.5 (NZ sample) and 9.3 (ZFe sample), which correspond to the point of zero charge values of the given samples. However, after equilibration of NZ and ZFe with solutions of Pb^{2+} , Cd^{2+} and Zn^{2+} , the final pH values decreased with increasing initial ion concentration, *i.e.*, with increasing amount of adsorbed ions. The change in final pH values with the change in the ion concentrations is a further proof of specific adsorption of the ions. The greatest change in the final pH in relation to pH_{pzc} for both samples was observed in the case of Pb^{2+} , then Cd^{2+} , and the smallest in the case of Zn^{2+} , which is in agreement with the shift in the point of zero charge, *i.e.*, the adsorbents affinity for specific adsorption decreased in the sequence: $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$. The changes in final pH values in relation to pH_{pzc} were greater for ZFe than for NZ sample, indicating removal of greater amount of ions from the solution by specific adsorption onto the ZFe sample than onto the NZ sample, which is one of the reasons that the adsorption capacity of ZFe was higher than that of the NZ sample.

In addition, other reasons exist for the higher adsorption capacity of ZFe in relation to that of NZ. The higher point of zero charge of ZFe compared to NZ causes higher final pH values at lower ion concentrations (when the amount of specifically adsorbed ions is small), which facilitates precipitation of metal hydroxides. At higher ion concentrations, the specific adsorption is more pronounced, so that the pH values are lower and the contribution of hydroxide precipitation to the total adsorption capacity is negligible. As already stated, the specific adsorption of Zn^{2+} was the least pronounced, and therefore the decrease in pH was the lowest, *i.e.*, the final pH was the highest (Figure 5b). Bearing in mind that $\text{Zn}(\text{OH})_2$ is the least soluble of the metal hydroxides, the contribution of hydroxide precipitation to the total adsorption capacity was the greatest in the case of Zn^{2+} . This could be one of the reasons for higher adsorption capacity of both zeolite samples for Zn^{2+} than for Cd^{2+} , for which specific adsorption was more pronounced.

The adsorption capacity of NZ was the highest for Pb^{2+} ($\approx 0.30 \text{ mmol g}^{-1}$), but even in this case, it was lower than the cation exchange capacity ($1.38 \text{ mmol M}^+ \text{ g}^{-1} = 0.69 \text{ mmol M}^{2+} \text{ g}^{-1}$). On the contrary, the adsorption capacity of ZFe for Pb^{2+} was higher (1.0 mmol g^{-1}) than the CEC ($1.20 \text{ mmol M}^+ \text{ g}^{-1} = 0.60 \text{ mmol M}^{2+} \text{ g}^{-1}$). In the NZ sample, most of the exchangeable ions were Ca^{2+} and Mg^{2+} , while K^+ were dominant in ZFe (Table 1). During equilibration of the zeolite samples with Pb^{2+} , Cd^{2+} and Zn^{2+} solutions, low charge ions participate in ion exchange much easier;

hence the ion exchange will be more pronounced when the exchangeable ion is K^+ than when the exchangeable ions are Ca^{2+} and Mg^{2+} . It was shown (data not presented) that ion exchange as a mechanism of removal of Pb^{2+} , Cd^{2+} and Zn^{2+} from solutions is more effective in the case of ZFe than in the case of NZ sample, contributing to the increase in the adsorption capacity of ZFe. Similar results were obtained for the adsorption of Zn^{2+} [26] and Pb^{2+} [29] ions on natural and Fe(III)-modified zeolite. After equilibration with ZFe, iron was not detected in the solutions, which confirms that neither iron oxide layer dissolution nor ion exchange of the studied ions with possibly present exchangeable iron ions occurred. Among the investigated ions, the ion exchange of Pb^{2+} was the highest, because the hydrated ion radii and the hydration energy of Pb^{2+} are the smallest [7,35,39]. On the contrary, the least exchangeable were Zn^{2+} , because these hydrated ions are the largest and the hydration energy is the highest, and therefore it is difficult to remove the hydrated layer to enable the ions to enter the zeolite channels.

Bearing in mind the discussed adsorption mechanisms, it can be said that ZFe and NZ exhibited the highest affinity for Pb^{2+} , because of the highest ion exchange and specific adsorption and approximately to the same degree as other ions of hydroxide precipitation. The higher adsorption capacity for Zn^{2+} than for Cd^{2+} , despite their lower specific adsorption and ion exchange, is probably the result of higher hydroxide precipitation due to the higher pH value arising from their lower specific adsorption.

Effect of temperature on the adsorption of Pb^{2+} , Cd^{2+} and Zn^{2+}

The adsorption isotherms of Pb^{2+} , Cd^{2+} and Zn^{2+} onto NZ and ZFe at different temperatures are shown in Figure 6.

The adsorption capacity of both samples for all three investigated ions increased with increasing temperature, but differently. In the case of the NZ sample, the temperature affects strongly its adsorption capacity, especially for Cd^{2+} ($\approx 0.05 \text{ mmol g}^{-1}$ at $25 \text{ }^\circ\text{C}$; $\approx 0.20 \text{ mmol g}^{-1}$ at $70 \text{ }^\circ\text{C}$), then Pb^{2+} ($\approx 0.30 \text{ mmol g}^{-1}$ at $25 \text{ }^\circ\text{C}$; $\approx 0.62 \text{ mmol g}^{-1}$ at $70 \text{ }^\circ\text{C}$) and finally for Zn^{2+} ($\approx 0.23 \text{ mmol g}^{-1}$ at $25 \text{ }^\circ\text{C}$; $\approx 0.40 \text{ mmol g}^{-1}$ at $70 \text{ }^\circ\text{C}$). The effect of temperature on the ion adsorption onto ZFe was smaller, especially for Pb^{2+} .

The increase in adsorption capacity with temperature may be attributed to either an increase in the number of active surface sites available for adsorption on the adsorbent or a decrease in the thickness of the

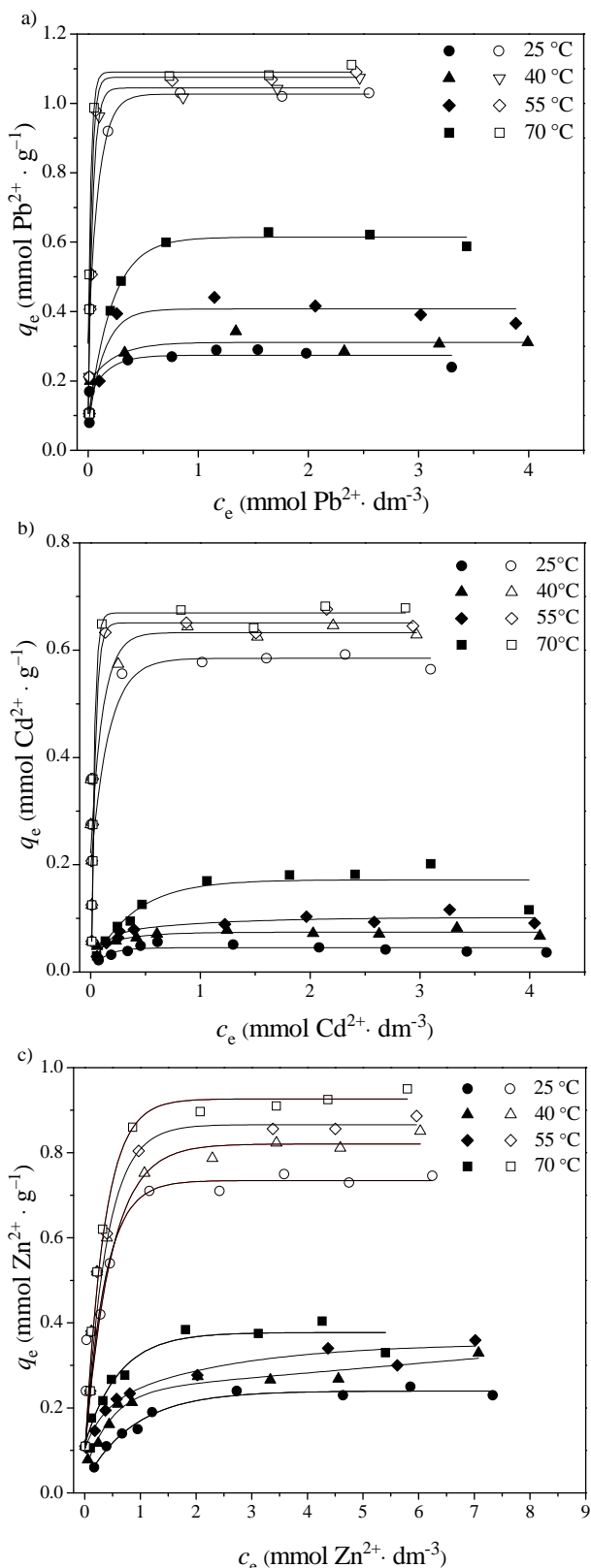


Figure 6. Adsorption isotherms of Pb^{2+} (a), Cd^{2+} (b) and Zn^{2+} (c) onto NZ (black symbols) and ZFe (open symbols) at different temperatures.

boundary layer surrounding the adsorbent with temperature [40], resulting in a decrease in the mass transfer resistance of adsorbate in the boundary layer. The increase in adsorption capacity of the zeolites with increasing temperature implies that the adsorption of Pb^{2+} , Cd^{2+} and Zn^{2+} onto the zeolites was endothermic. The explanation of the endothermicity of adsorption is the well-known fact that ions, such as Pb^{2+} , Cd^{2+} and Zn^{2+} , are well hydrated. In order to be adsorbed, these ions have to some extent been denuded of their hydration sheath [1,4]. The removal of water from ions is essentially an endothermic process, and it appears that the endothermicity of the dehydration process exceeds that of the enthalpy of adsorption by a considerable extent. With increasing temperature, more hydrate water could be shelved and ion adsorption increased. The total thermal effect of adsorption depends not only on the nature of ions, but also on the nature of the adsorbent used. Obviously, the enthalpy of adsorption of a Pb^{2+} onto ZFe sample is approximately the same as the enthalpy of dehydration of a hydrated Pb^{2+} ; therefore, the influence of temperature on the adsorption of this ion on ZFe was negligible. The same is valid for a Cd^{2+} , but the somewhat greater influence of temperature on the adsorption of a Zn^{2+} indicates either a lower enthalpy of adsorption or a higher enthalpy of dehydration. As has already been stated, the energy of hydration, *i.e.*, dehydration of Zn^{2+} is the highest of the studied ions. The different nature of NZ from that of ZFe is the cause of the different temperature influences on their adsorption capacities for Pb^{2+} , Cd^{2+} and Zn^{2+} .

Equilibrium data modeling

The obtained experimental results were analyzed using the linear forms of the Langmuir, Freundlich, and Dubinin-Radushkevich (DR) models with the quality of the fit assessed using the correlation coefficient, R^2 . Correlation coefficient values were highest for the Langmuir model, for all investigated ions at all investigated temperatures, on both adsorbents (Table 2). In addition, there is a good agreement between the maximum adsorption capacity values obtained from the plateau of the dependence $q_e = f(c_e)$ and the values obtained applying the Langmuir equation. The adsorption capacities for both adsorbents are in the order: $Pb^{2+} > Zn^{2+} > Cd^{2+}$ and $70 > 55 > 40 > 25$ °C.

The validity of the Langmuir isotherm, according to Stumm and Morgan [41], is regulated by the following rules: 1) the equilibrium is obtained when there is a formation of a monolayer on the adsorbent; 2) all the adsorption sites are equivalent and the surface is

Table 2. Adsorption parameters (Langmuir constant, K_L / mmol^{-1} , and maximum adsorption capacity, q_m / mmol g^{-1}) and correlation coefficients (R^2) according to the Langmuir model for the adsorption of Pb^{2+} , Cd^{2+} and Zn^{2+} onto NZ and ZFe at 25, 40, 55 and 70 °C

Ion	Adsorbent	T= 25 °C			T= 40 °C			T= 55 °C			T= 70 °C		
		K_L	q_m	R^2	K_L	q_m	R^2	K_L	q_m	R^2	K_L	q_m	R^2
Pb^{2+}	NZ	7.77	0.287	0.998	6.23	0.305	0.996	3.01	0.377	0.995	0.366	0.600	0.998
	ZFe	51.7	1.03	0.997	55.4	1.05	0.995	181.2	1.09	0.998	552.5	1.11	0.999
Cd^{2+}	NZ	0.044	0.036	0.983	0.03	0.060	0.999	0.010	0.100	0.664	0.060	0.305	0.874
	ZFe	73.7	0.589	0.999	158.7	0.640	0.999	326.4	0.653	0.999	84.5	0.676	0.999
Zn^{2+}	NZ	0.136	0.25	0.994	0.25	0.749	0.99	0.420	0.354	0.982	1.48	0.369	0.978
	ZFe	9.27	0.75	0.999	18.4	0.844	0.998	46.1	0.876	0.999	19.9	0.935	0.994

uniform; 3) the capacity of an adsorbate to be adsorbed on a specific site is independent of the occupation of the other near sites. However, this isotherm is only accurate when the ionic force, the pH and the ligands concentrations of the media are constant. It also assumes that there is only one type of adsorption site, which is not always the case [41–43]. Although the application of the Langmuir model is limited by conditions, which were not fulfilled in our adsorption experiments, the experimental results were best fitted with this equation, *i.e.*, the Langmuir isotherm can be used for mathematical modeling of the equilibrium data. There are many examples in the literature that Langmuir model fits equilibrium data of metal ions adsorption onto zeolites better than other theoretical models [1,2,4,5,9,15,16]. Considering the assumptions of the Langmuir model, it can be supposed that adsorption sites on the surface of NZ and ZFe are equivalent and Pb^{2+} , Zn^{2+} and Cd^{2+} form monolayer at the surface of the adsorbents.

CONCLUSIONS

The changes that occurred by loading the surface of natural zeolite with Fe(III) species were observed by XRD, SEM and TEM, and differences based on the specific surface area, point of zero charge and the cation exchange capacity were determined.

Metal ion adsorption onto both natural and Fe(III)-modified zeolite at an initial pH of 5.5 and at 25, 40, 55, 70 °C increased in the following order: $\text{Cd}^{2+} < \text{Zn}^{2+} < \text{Pb}^{2+}$. The adsorption capacity of the modified zeolite was much higher than that of natural zeolite for all the investigated ions, owing to higher specific adsorption resulting from the new functional groups on the surface, ion exchange due to the presence of easily exchangeable ions, and hydroxide precipitation caused by the higher point of zero charge of the Fe(III)-modified zeolite compared to natural zeolite.

The equilibrium data obtained at all investigated temperatures for both samples were best described by the Langmuir adsorption isotherm. The quantity of adsorbed Pb^{2+} , Cd^{2+} , and Zn^{2+} onto both zeolites increased with increasing temperature, indicating the endothermic nature of the adsorption. A more pronounced increase in adsorption capacity with increasing temperature was observed for the natural than for the Fe(III)-modified zeolite.

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NAUČNI RAD

UPOREDNA ANALIZA UKLANJANJA JONA OLOVA, KADMIJUMA I CINKA IZ VODENIH RASTVORA ADSORPCIJOM NA PRIRODNOM I Fe(III)-MODIFIKOVANOM ZEOLITU

U ovom radu je ispitivana adsorpcija Pb^{2+} , Zr^{2+} i Cd^{2+} iz vodenih rastvora na prirodnom i Fe(III)-modifikovanom zeolitu u cilju objašnjenja uticaja modifikacije prirodnog zeolita hidratiranim gvožđe(III)-oksidom na mehanizam adsorpcije i adsorpcioni kapacitet. Karakterizacija adsorbenata je obuhvatila određivanje faznog sastava, morfologije, specifične površine, kapaciteta izmene katjona i tačke nultog naelektrisanja. Adsorpcioni eksperimenti su izvođeni u šaržnim uslovima, pri konstantnoj pH vrednosti od $5,5 \pm 0,1$, pri različitim početnim koncentracijama jona i na različitim temperaturama. Adsorpcione izoterme određene na 25, 40, 55 i 70 °C pokazuju da je afinitet oba adsorbenta u svim slučajevima najveći za Pb^{2+} , zatim za Zr^{2+} i najmanji za Cd^{2+} . Adsorpcioni kapaciteti oba adsorbenta za sva tri jona rastu sa povišenjem temperature. Rezultati adsorpcije se najbolje opisuju Lengmirovom adsorpcionom izotermom. Rezultati ispitivanja su pokazali da je adsorpcioni kapacitet Fe(III)-zeolita za Pb^{2+} , Zr^{2+} i Cd^{2+} znatno veći od kapaciteta prirodnog zeolita zahvaljujući: većoj specifičnoj adsorpciji zbog formiranja novih funkcionalnih grupa na površini zeolita, većoj jonskoj izmeni zbog prisustva jona koji se lakše izmenjuju i većoj precipitaciji hidroksida usled više tačke nultog naelektrisanja Fe(III)-zeolita.

Ključne reči: Fe(III)-zeolit, adsorpcija, joni metala, mehanizam.