

Sorption of cadmium ions from saline waters onto Fe(III)-zeolite

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Abstract

The sorption of Cd²⁺ from natural seawater, artificial seawater, distilled water and NaCl solution of the same ionic strength as the seawater onto zeolite modified by iron(III) oxide (Fe(III)-zeolite) was investigated. The sorption was found to be time, concentration and pH dependent. The sorption capacity at the initial pH 7 decreased in the following order: distilled water > NaCl solution > artificial seawater > natural seawater. The isotherm study showed that Langmuir isotherm model could be adequately applied for the sorption in distilled water, indicating the homogeneous monolayer coverage at Fe(III)-zeolite surface, while the Freundlich isotherm model showed a better fit than the Langmuir model of the sorption data in saline waters, indicating multilayer heterogeneous coverage at the sorbent surface. The values of Freundlich parameter *n* suggested that the sorption was a favorable process and bonds between Cd²⁺ and Fe(III)-zeolite surface were stronger in NaCl solution than in natural and artificial seawater. Kinetics analysis showed that the mechanism of Cd²⁺ sorption from natural seawater differed from the sorption mechanism out of distilled water, NaCl solution and artificial seawater. The intra-particle diffusion kinetic model indicated that both boundary layer diffusion and intra-particle diffusion influenced the rate of sorption.

Keywords: sorption, cadmium ions, Fe(III)-zeolite, seawater, modeling.

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Cadmium is one of the most toxic heavy metals. It tends to accumulate in the body and it has varying degrees of toxicity. Cadmium causes serious diseases such as renal damage, anemia, hypertension, cancer, and kidney failure [1,2]. According to the World Health Organization (WHO) the maximum concentration of cadmium in drinking water should be 0.003 mg/L [3].

The common sources of cadmium in natural waters are soil and air pollution due to the several industrial applications such as cadmium plating and production of Cd-Ni batteries, copper alloys, paints, plastics, phosphates, fertilizers, and pigments [3,4].

There are various technologies for the removal of cadmium and other heavy metals from water systems: chemical precipitation, ion exchange, sorption, membrane processing, electrochemical treatment, etc. [5,6]. Among these procedures, the sorption is considered as one of the most attractive and powerful technique for heavy metals removal from solutions at low concentrations. By proper selection of the sorbent, the sorption can be a simple, environmental friendly and low cost operation of high efficiency [7,8]. A variety of sorbents, including clay minerals, zeolites, agricultural waste bio-

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mass, biopolymers, metal oxides, different industrial by-products, microorganisms, and activated carbon have been used for cadmium removal [8].

Zeolites have been extensively used as sorbents for heavy metals because they have great affinity for divalent metal ions [9]. The sorption capacity and selectivity of zeolite to heavy metal ions can be further improved by various modifications. It was shown that zeolites modified by oxides or hydroxides of trivalent iron had significantly higher affinity for Zn²⁺, Cu²⁺, Mn²⁺, Pb²⁺ and Cd²⁺, compared to the unmodified zeolite [10–14]. Iron(III) could be present in zeolite in different forms [15]: a) in framework positions (isomorphously substituted), b) in cationic positions in the zeolite channels, c) as binuclear or oligonuclear iron complexes in the extra-framework positions, d) as iron oxide FeO_x nanoparticles and e) as large iron oxide particles (Fe₂O₃) located on the surface of the zeolite crystals. Much higher capacity of the iron(III)-modified zeolite for Pb²⁺, Cd²⁺ and Zn²⁺ in comparison to parent zeolite was explained [14] by: higher specific sorption resulting from the new functional groups on the surface; ion exchange due to the presence of easily exchangeable ions; the hydroxide precipitation caused by the higher point of zero charge.

The purpose of this work was to investigate the sorption of cadmium ions from natural seawater and various aqueous solutions on zeolite, modified by

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iron(III) oxide. Cadmium ion solutions of different concentrations in natural and artificial seawater were used for the experiments. For comparison, the sorption of cadmium from solutions prepared with distilled water was studied, as well as using NaCl solution of the same ionic strength as the seawater. The influence of the initial pH (pH_i) on the sorption from different water systems was evaluated. The sorption capacities of the sorbent at pH_i 7 were determined based on sorption isotherms, and experimental results were analyzed using theoretical models of sorption isotherms. The results of sorption kinetics of cadmium from different water systems were processed using the kinetic models.

EXPERIMENTAL

Materials

Sorbent

Zeolite modified by iron(III) oxide (Fe(III)-zeolite) was synthesized according to previously published method [10–14]. A natural zeolite from the Slanci locality, Serbia, was used as a starting material. The natural zeolite contained clinoptilolite, as a dominant phase, with lower contents of quartz and feldspar. The modified zeolite was prepared by adding, under stirring, of 180 cm³ of 5 M KOH solution to a suspension of 20.0 g of the natural zeolite and 100 cm³ of a freshly prepared 1 M FeCl₃ solution. The suspension was diluted by distilled water up to 2 dm³ and held in a closed polyethylene flask at 70 °C for 60 h. Then, the reaction vessel was removed from the oven, and the red precipitate was centrifuged and washed until the negative reaction of Cl⁻ ions occurred and it was finally dried.

XRD analysis showed lower crystallinity of Fe(III)-zeolite in comparison to the parent zeolite. In addition, it was shown that Fe(III)-zeolite contained amorphous iron(III) oxides. The modification caused the specific surface area increasing from 18 to 175 m²/g and the point of zero charge increasing from 7.5±0.1 to 9.3±0.1 [14].

Water samples

The four types of water were used:

1. Distilled water.

2. Natural seawater obtained of the coast of Greece and passed through 2 µm filter. The pH value of natural seawater was about 8. The analysis of seawater was done by a Metrohm ion chromatography instrument, 861 Advanced Compact IC MSM II. The concentrations of the main ions in the natural seawater are presented in Table 1.

3. Artificial seawater, prepared by dissolving 28.6 g NaCl, 0.65 g KCl, 5.26 g MgCl₂·6H₂O, 4.77 g MgSO₄·7H₂O, 1.16 g CaSO₄ and 0.05 g NaBr in 1 dm³ of

distilled water in order to obtain the composition similar to the composition of the natural seawater.

4. NaCl solution, prepared by dissolving 40.2 g NaCl in 1 dm³ of distilled water in order to obtain the solution of the same ionic strength as the seawater.

Table 1. Composition of the natural seawater used in the experiments

Ion	mg/dm ³	mmol/dm ³
Cl ⁻	19990	564.13
Na ⁺	11244	488.9
K ⁺	342	8.74
Mg ²⁺	1099	45.22
Ca ²⁺	343	8.56
SO ₄ ²⁻	2679	27.91
Br ⁻	49.4	0.62

Sorbate solution preparation

The stock solutions of cadmium, containing 100 mg Cd²⁺/dm³, were prepared by dissolving 0.1372 g of Cd(NO₃)₂·4H₂O in 500 cm³ of each type of water. The solutions of different cadmium concentration ranging from 5 to 75 mg/dm³, were prepared from stock solutions, by dilution.

The pH of the solutions for the sorption experiments was adjusted by 0.1 M KOH or 0.1 M HNO₃ solution.

Sorption experiments

The sorption experiments were performed by batch technique at room temperature (25±1 °C). The general method used for this study is described as follows: 20 cm³ of different cadmium solutions were placed in 50 cm³ reagent bottle, the pH value was adjusted and then the constant amount of Fe(III)-zeolite (0.02 g) was added to each bottle, followed by shaking for a given period of time.

The effect of initial pH value (pH_i) on Cd²⁺ sorption onto Fe(III)-zeolite was investigated with Cd²⁺ solution of 50 mg/dm³ concentration, by varying pH_i from 4.0 to 8.0. The suspensions were shaken for 24 h.

The sorption isotherms for Cd²⁺ sorption out of different types of water onto Fe(III)-zeolite at pH_i 7.0±0.1 were determined by establishing the equilibration of Cd²⁺ solution of different concentration and Fe(III)-zeolite for 24 h.

The kinetics analysis of the sorption was done by using Cd²⁺ solutions of 100 mg/dm³, at pH_i 7.0±0.1.

After all the experiments, the sorbent was separated from the solution using filter paper. The final solution pH (pH_f) was measured using a pH meter (InoLab WTW series pH 720). The initial concentrations of Cd²⁺, as well as the concentrations after the sorption, were

determined using the atomic absorption spectrometer (AAS) (Perkin Elmer 730).

The equilibrium sorption capacity, q_e , was calculated using the equation:

$$q_e = \frac{c_i - c_e}{m} V \text{ (mg Cd}^{2+}/\text{g Fe(III)-zeolite)} \quad (1)$$

while the quantity of Cd²⁺ sorbed after the period of time t (q_t) was calculated according to equation:

$$q_t = \frac{c_i - c_t}{m} V \text{ (mg Cd}^{2+}/\text{g Fe(III)-zeolite}) \quad (2)$$

where V is the volume of the solution; c_i is the initial Cd²⁺ concentration, c_e is the equilibrium (residual) Cd²⁺ concentration; m is the weight of sorbent and c_t is the concentration of Cd²⁺ after period of time t .

Models of isotherms

The Langmuir [16] and Freundlich [17] isotherms were applied to the experimental data to study the sorption capacity and to describe the solid–liquid sorption process:

$$\text{Langmuir model: } q_e = \frac{q_m k_L c_e}{1 + k_L c_e} \quad (3)$$

$$\text{Freundlich model: } q_e = k_F c_e^{1/n} \quad (4)$$

where q_e is the amount of solute sorbed per unit mass of the sorbent at equilibrium (mg/g); c_e is the equilibrium concentration of the solute in the bulk solution (mg/dm³); q_m is the maximum sorption capacity (monolayer capacity, mg/g); k_L is the Langmuir constant related to the free energy of sorption (dm³/mg); k_F is a constant which is an indicator of the sorption capacity ((mg/g)(mg/dm³)ⁿ); and n is an sorption intensity parameter.

Sorption kinetics

The pseudo-first order equation [18] and the pseudo-second order equation [19,20] were applied to sorption kinetic data to describe the mechanism of sorption:

Pseudo-first order equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (5)$$

Pseudo-second order equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where q_e and q_t are sorption capacity at equilibrium and at time t , respectively (mg/g); k_1 is the rate constant of pseudo first order model (1/min); and k_2 is the

rate constant of the pseudo second order model (g/(mg·min)).

In order to assess the nature of the diffusion process in Cd²⁺ sorption onto Fe(III)-zeolite, the intra-particle diffusion model, proposed by Weber and Morris [21] was used:

$$q_t = k_{td} t^{0.5} + C \quad (7)$$

where k_{td} (mg/(g·min^{0.5})) is the intra-particle diffusion rate constant, and C (mg/g) is a constant that gives information about thickness of the boundary layer. This model considered the intra-particle diffusion as the rate controlling step when the value of C is close to zero.

RESULTS AND DISCUSSION

Effect of the initial pH

The influence of initial pH value on the sorption capacity of Fe(III)-zeolite for Cd²⁺ in different types of water is presented in Fig. 1. The final pH values are indicated in this figure.

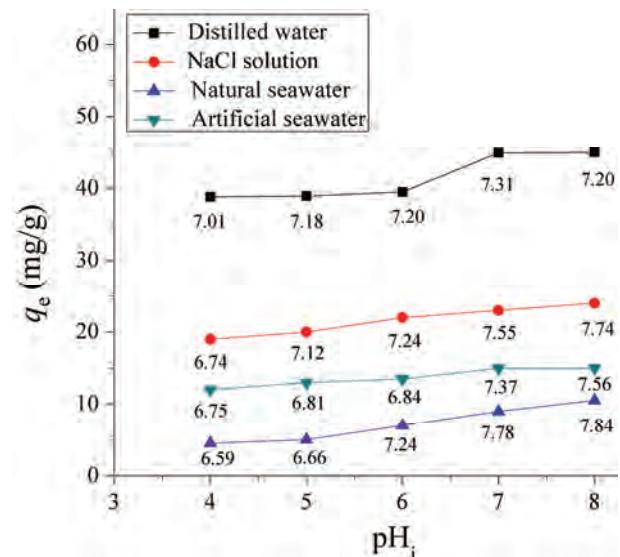


Figure 1. The comparison of the effect of the initial pH on the sorption capacity of Fe(III)-zeolite for Cd²⁺ from different types of water (the numbers in the figure indicate the final pH values). Concentration of Cd(II) solution was 50 mg/dm³.

According to Fig. 1, the cadmium sorption efficiency on Fe(III)-zeolite increased when the initial pH was increased. This appeared because Fe(III)-zeolite was highly selective to H₃O⁺ when the concentration of these ions was high. The values of pH_f, for pH_i ≤ 7, indicate that H₃O⁺ associates with the functional groups on the Fe(III)-zeolite surface. As pH_i was lower, the negative charge of the surface became lower and the positive charge higher, which decreased the sorption of positively charged cadmium ions. At pH_i 8, pH_f values

were lower than the initial ones, which indicates releasing of H_3O^+ into the solution because of the surface functional groups dissociation. Thus, the Cd^{2+} sorption at $\text{pH}_i = 8$ was higher than at lower pH_i . These results show that pH values at which the surface charge was changed from positive to negative and vice versa were lower than pH_{PZC} of Fe(III)-zeolite [14], which indicates that the specific sorption is included in the process of Cd^{2+} sorption, as it was shown in previous investigation for the solutions in distilled water [14].

It should be noted that there was no indication of $\text{Cd}(\text{OH})_2$ precipitation during adsorption at higher pH values. For the Cd^{2+} concentration of $50 \text{ mg}/\text{dm}^3$, the saturation for $\text{Cd}(\text{OH})_2$ precipitation is at $\text{pH} \approx 8.5$ (according to the value of the solubility product constant of $\text{Cd}(\text{OH})_2$). However, in order to start precipitation (nucleation of solid phase from liquid phase), super saturation is necessary [22], which means that $\text{Cd}(\text{OH})_2$ precipitation starts at pH higher than 8.5. If there are some dispersed particles in solution (like the sorbent in Cd^{2+} solution), a super saturation for nucleation is less than in solution without dispersed particle, but still pH value for the beginning of precipitation is higher than pH value for saturation. According to that, it can be said with certainty that there was no $\text{Cd}(\text{OH})_2$ precipitation during the experiments.

It can be seen from Fig. 1 that the order of sorption capacity of Fe(III)-zeolite for Cd^{2+} , at all pHs is: distilled water > NaCl solution > artificial seawater > natural seawater. Obviously, the ions from saline waters decrease sorption capacity of Fe(III)-zeolite for Cd^{2+} , because those ions compete with Cd^{2+} for the sorption sites at the surface of the sorbent. The higher-valence ions have more competitive effect than monovalence ions [23], which explains the lower sorption capacity of the sorbent in artificial and natural seawaters than in NaCl solution: besides Na^+ , both seawaters contain higher-valence ions, such as Ca^{2+} and Mg^{2+} . The lowest sorption capacity of the Fe(III)-zeolite in natural seawater can be explained by the presence of some other ions (carbonate and bicarbonate) and organic matter that are not present in artificial seawater.

Further investigations, the determination of sorption isotherms and kinetic analysis, were done at the initial pH 7.

Effect of the initial cadmium ions concentration – sorption isotherms

Figure 2 shows the sorption isotherms for Cd^{2+} on Fe(III)-zeolite from different types of water. The equilibrium concentration and the uptake of Cd^{2+} increase as the initial Cd^{2+} concentration increases. This appeared since at lower initial concentration the ratio of the initial number of metal ions to the number of available surface sites of sorbent is low. With the increase in the

initial Cd^{2+} concentration, more Cd^{2+} were left in the solution due to the saturation of the binding sites.

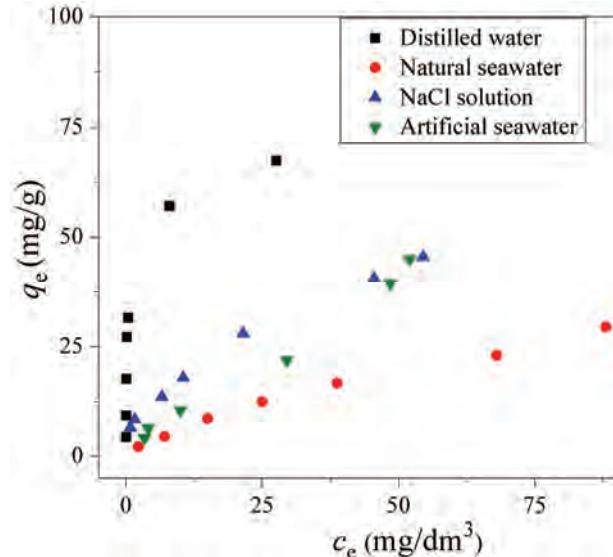


Figure 2. The comparison of sorption isotherms for Cd^{2+} on Fe(III)-zeolite from different types of water at initial pH 7.

The final pHs of the solutions in distilled water were between 8.98 (for $c_i = 5 \text{ mg}/\text{dm}^3$) and 7.02 (for $c_i = 100 \text{ mg}/\text{dm}^3$), which indicates that the specific sorption increased with c_i increase. In the case of NaCl solutions, pH_f was between 8.70 and 7.43. Lower pH_f for $c_i = 5 \text{ mg}/\text{dm}^3$ than for solution in distilled water can be explained by the specific sorption of Na^+ on the sorbent surface. Na^+ are generally indifferent ions, which mean that they can not be specifically sorbed, but that is possible when the concentration is very high. Higher pH_f in NaCl solution for $c_i = 100 \text{ mg}/\text{dm}^3$ than in the same solution in distilled water indicates lower specific sorption. Thus, the specific sorption is less pronounced in NaCl solution than in distilled water. The effect of ions in artificial seawater on the specific sorption is even more pronounced, because the pH_f changed from 7.89 to 7.48. Higher valence ions in artificial seawater can be specifically sorbed more than Na^+ , so pH_f for $c_i = 5 \text{ mg}/\text{dm}^3$ was much lower than in NaCl solution and distilled water. The final pHs in natural seawater were approximately 7.8 for all concentration, due to the buffering effect as a result of the presence of bicarbonates.

By comparing the sorption isotherms (Fig. 2) it is obvious that the order of sorption capacity of Fe(III)-zeolite for Cd^{2+} , at initial pH 7 is: distilled water > NaCl solution > artificial seawater > natural seawater. This order is the same as in the investigation of the effect of the initial pH value on Cd^{2+} sorption.

Isotherms modeling

The sorption equilibrium data were analyzed by linear form of the Langmuir and Freundlich models.

The Langmuir isotherm model assumes monolayer sorption, where the energy of sorption for each sorbate species is the same and independent of surface coverage. The sorption occurs only on localized sites and involves no interactions between sorbed species [16,24–28].

The Freundlich isotherm model describes sorption on heterogeneous surfaces where sorption sites have different energies of sorption. This empirical model can be applied to multilayer sorption, which can include chemisorption (if active sites are strong enough) followed by physisorption [17,24–28].

The corresponding Langmuir and Freundlich parameters for Cd²⁺ sorption onto Fe(III)-zeolite from different types of water are given in Table 2. The correlation coefficient values indicate the superiority of Langmuir over Freundlich model for the sorption from distilled water, while Freundlich model is better for modeling of the sorption from saline waters. According to this, it can be concluded that ions from saline waters influence not only sorption capacity, but also cause change of sorption mechanism. The sorbent surface was homogeneous during the sorption from distilled water and the sorption took place until monolayer was formed, while in the case of the sorption from saline waters, sorbent surface was heterogeneous and more than one layer of Cd²⁺ were formed.

The feasibility of Cd²⁺ sorption from distilled water in the investigated concentration range can be expressed in terms of a dimensionless constant R_L (Eq. (8)), called the constant separation factor or equilibrium parameter [24,25,27]:

$$R_L = \frac{1}{1 + k_L c_i} \quad (8)$$

where k_L is the Langmuir constant (dm³/mg), and c_i is the initial concentration (mg/dm³). According to the value of R_L it is possible to assess irreversibility of the sorption process: as the value of R_L closer to zero, the process is more irreversible. When the value of k_L is infinitely large, which means that the bond between a sorbent and a sorbate is infinitely strong, the sorption

process is irreversible ($R_L = 0$). The dependence of R_L on c_i in the investigated range of Cd²⁺ concentration in distilled water is presented in Fig. 3. It can be seen that R_L for the Cd²⁺ sorption from distilled water has very low values, which indicate favorable sorption and high degree of irreversibility.

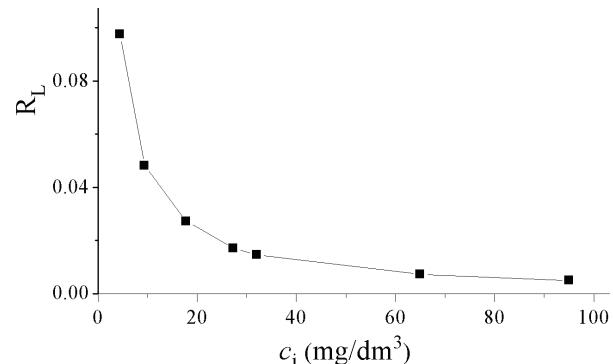


Figure 3. The dependence of R_L on the initial Cd²⁺ concentration.

In the case of the sorption from saline water, the Freundlich constant k_F had the lowest value for the seawater, slightly larger for the artificial seawater and the largest for the NaCl solution, meaning that the sorption capacity of Fe(III)-zeolite decreased in the following order: NaCl solution > artificial seawater > natural seawater. These results are in accordance with the conclusions made from studying the influence of pH_i value on sorption capacity and according to sorption isotherms obtained for different types of water.

The Freundlich parameter n is a sorption intensity parameter, where the strength of sorption bonds is higher when n is higher. In that way, the value of n is an indication of the favorability of adsorption. Values of $n > 1$ represent favorable nature of adsorption [24–28]. According to the values of n for Cd²⁺ sorption from saline water (Table 2) it can be concluded that the sorption was a favorable process and that bonds between Cd²⁺ and Fe-zeolite surface were stronger in NaCl solution than in natural and artificial seawater. Obviously, the presence of higher-valence ions in seawaters, such as Ca²⁺ and Mg²⁺ influenced the strength of bonds between Cd²⁺ and the surface sites on the adsorbent.

Table 2. The Langmuir and Freundlich parameters and the correlation coefficients for Cd²⁺ sorption onto Fe(III)-zeolite from different types of water

Type of water	Langmuir parameters			Freundlich parameters		
	q_m / mg g ⁻¹	k_L / dm ³ mg ⁻¹	R^2	k_F / ((mg/g) (mg/dm ³) ⁿ)	1/n	R^2
Distilled water	68.027	2.10	0.997	4.328	0.335	0.767
Natural seawater	43.478	0.017	0.864	1.090	0.702	0.993
NaCl solution	53.763	0.071	0.912	2.268	0.466	0.984
Artificial seawater	9.091	0.122	0.127	1.305	0.744	0.919

Effect of contact time

The effect of contact time on Cd^{2+} sorption onto Fe(III)-zeolite from different types of water is presented in Fig 4. As it was expected, the extent of Cd^{2+} removal increased with the contact time. The Cd^{2+} uptake was rapid at the beginning, then was slow in the case of the sorption from distilled water, NaCl solution, and artificial seawater, while the sorption from seawater was slow at the beginning, and then increased. Such difference in time-dependence of sorption from seawater and other types of water can be explained by the presence of some organic compounds in natural seawater which can influence the rate of sorption.

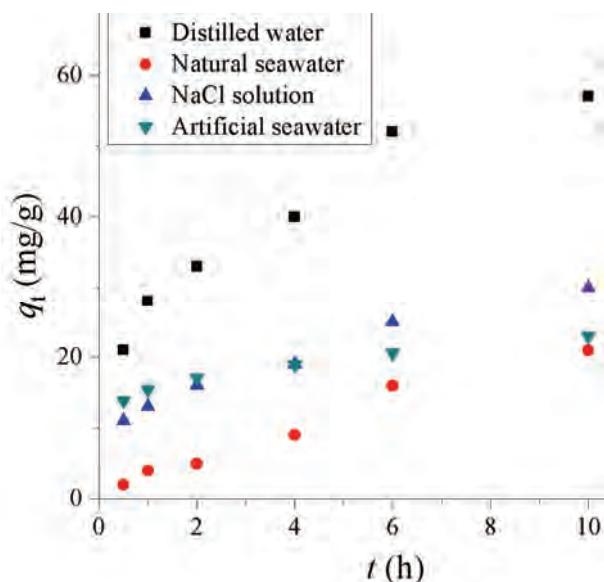


Figure 4. The effect of contact time on the Cd^{2+} sorption onto Fe(III)-zeolite from different types of water. Concentration of Cd^{2+} solution was 100 mg/dm^3 .

Kinetics models

The sorption kinetics data were analyzed by three, most widely used kinetics models, *i.e.*, the pseudo-first order, pseudo-second order, and intra-particle diffusion models. The kinetic constants and correlation coefficients of these models are given in Table 3.

The pseudo-first order model is based on the assumption that the sorption rate is proportional to the number of free sites, while in the case of the pseudo-

-second-order kinetic model, the rate of sorption is proportional to the square of the number of unoccupied sites. According to the values of correlation coefficients (Table 3), it can be seen that pseudo-first order model can be applied for all the types of water, but for distilled water a slightly higher correlation coefficient was obtained for the pseudo second order model. In addition, pseudo-second-order model fits well the kinetics data of the Cd^{2+} adsorption from NaCl solution and artificial seawater, while in the case of natural seawater the correlation coefficient is very low. In that way, kinetics analysis showed that the mechanism of Cd^{2+} sorption from natural seawater differs from the sorption mechanism out of distilled water, NaCl solution and artificial seawater.

Sorption of any metal ion from aqueous phase onto porous materials proceeds by a multi-step process, and the rate of the sorption is controlled by either the film diffusion (external mass transfer) or the intra-particle diffusion rate or both [24,25,29–32]. In order to identify the diffusion mechanism, the intra-particle diffusion model (Eq. (7)) was applied and dependences q_t versus $t^{0.5}$ for all types of water are presented in Fig. 5. All the dependences consisted of two linear portions, indicating that the two stages occurred during sorption. The first portion is attributed to the boundary layer diffusion and the second one to the region where the intra-particle diffusion is involved in the sorption process [24,25,29–32]. Figure 5 shows differences between natural seawater and other types of water: the first linear part is longer for natural seawater than for other types of water, which means that boundary layer diffusion was included in sorption from seawater more than from other types of water. It can be supposed that some components from natural seawater, for example organic components, sorb at the surface of the sorbent, block some active sites at the outer surface of the sorbent and increase boundary layer.

The values of intra-particle diffusion rate constant, k_{td} , calculated from the second linear part of the dependence q_t versus $t^{0.5}$ (Fig. 5) are presented in Table 3. The highest value of k_{td} was obtained for distilled water, probably because there are no other dissolved substances that could slow down the Cd^{2+} diffusion in the pores.

Table 3. The kinetic parameters and correlation coefficients for the Cd^{2+} sorption onto Fe(III)-zeolite from different types of water

Type of water	Pseudo-first order constants		Pseudo-second order constants		Intra-particle diffusion model constants		
	$k_1 \times 10^3 / \text{min}^{-1}$	R^2	$q_e / \text{mg g}^{-1}$	$k_2 / \text{g mg}^{-1} \cdot \text{min}^{-1}$	R^2	$k_{td} / \text{g mg}^{-1} \text{min}^{-0.5}$	
Distilled water	4.61	0.90	64.27	$1.67 \cdot 10^{-4}$	0.98	1.82	0.96
Seawater	3.90	0.96	47.62	$2.59 \cdot 10^{-5}$	0.52	1.29	0.90
NaCl solution	3.68	0.93	33.33	$2.67 \cdot 10^{-4}$	0.95	1.01	0.98
Artificial seawater	3.23	0.99	23.92	$1.01 \cdot 10^{-3}$	0.99	0.50	0.99

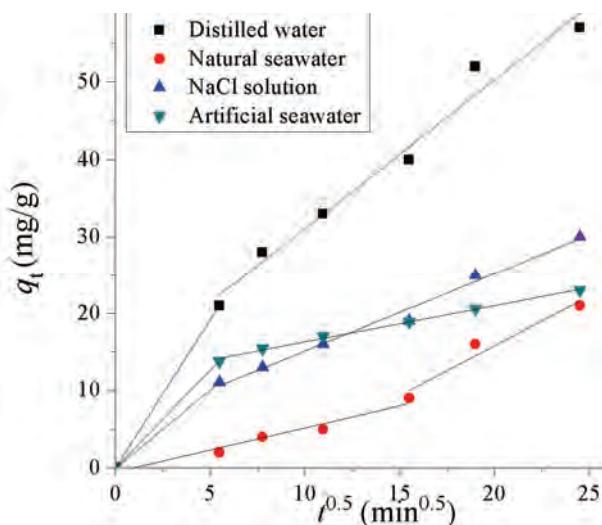


Figure 5. Weber–Morris intraparticle diffusion model plot for the Cd^{2+} sorption onto Fe(III)-zeolite from different types of water.

CONCLUSIONS

The sorption potential of zeolite modified by iron(III) oxide to cadmium ions from different types of water was evaluated. It was shown that the sorbent capacity and sorption mechanisms are highly influenced by the presence of competitive ions in water. The sorbent capacity at initial pH 7 decreased in the following order: distilled water > NaCl solution > artificial seawater > natural seawater. The Freundlich isotherm model provides the best fit to the sorption equilibrium data obtained from saline waters, which indicates heterogeneity of the sorbent surface and the multilayer adsorption. The sorption was a favorable process and bonds between cadmium ions and Fe(III)-zeolite surface were stronger in NaCl solution than in natural and artificial seawater. In the case of sorption from distilled water, the sorption equilibrium data were best fitted by the Langmuir model, indicating homogeneous and monolayer sorption. Kinetics analysis showed that both boundary layer diffusion and intra-particle diffusion influenced the rate of the sorption from all types of water. In the case of the sorption from natural seawater, the intraparticle diffusion was significant at longer contact times than in the case of other types of water.

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IZVOD

SORPCIJA JONA KADMIJUMA IZ SLANIH VODA NA Fe(III)-ZEOLITU

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(Naučni rad)

U ovom radu je ispitivana sorpcija Cd²⁺ iz prirodne morske vode, laboratorijski pripremljene morske vode, destilovane vode i rastvora NaCl, iste jonske jačine kao morska voda, na zeolitu modifikovanom gvožđe(III)-oksidom. Pokazano je da sorpcija zavisi od vremena, početne koncentracije Cd²⁺ i pH vrednosti. Sorpcioni kapacitet Fe(III)-zeolita za Cd²⁺ pri početnoj pH 7 opada u sledećem nizu: destilovana voda > NaCl rastvor > laboratorijski pripremljena morska voda > prirodna morska voda. Modelovanje rezultata ispitivanja sorpcije u ravnotežnim uslovima je pokazalo da se adsorpcija iz destilovane vode može opisati Langmirovim modelom, što ukazuje na homogenu sorpciju i formiranje monosloja na površini Fe(III)-zeolita. Rezultati sorpcije iz slanih voda se bolje opisuju Frojndlihovim nego Langmirovim modelom, što ukazuje na višeslojnu sorpciju na heterogenoj površini sorbenta. Vrednosti Frojndlihovog parametra *n* pokazuju da je sorpcija Cd²⁺ na Fe(III)-zeolitu favorizovan proces i da su veze između Cd²⁺ i površine Fe(III)-zeolita jače u NaCl rastvoru nego u prirodnoj i laboratorijski pripremljenoj morskoj vodi. Kinetička analiza sorpcije je pokazala da se mehanizam sorpcije iz prirodne morske vode razlikuje od mehanizma sorpcije iz ostalih ispitivanih tipova vode. Kinetički model unutarčestične difuzije je pokazao da i difuzija kroz granični sloj i unutarčestična difuzija određuju brzinu sorpcije. Difuzija kroz granični sloj je u većoj meri zastupljena kod sorpcije iz morske vode nego u slučaju sorpcije iz drugih ispitivanih tipova vode.

Ključne reči: Sorpcija • Kadmijum ion • Fe(III)-zeolit • Morska voda • Modelovanje