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THE EFFECT OF SALINITY ON THE SORPTION OF CADMIUM IONS FROM AQUEOUS MEDIUM ON Fe(III)-SEPIOLITE

Article Highlights

- Cadmium ions sorption from saline waters onto Fe(III)-sepiolite was studied
- Sorption capacities in saline waters were lower than in distilled water
- The bonds sorbate-sorbent were stronger in distilled water than in saline waters
- Sorption was well described by Sips isotherm and pseudo-second order kinetic models
- Desorption studies indicated strong sorbate-sorbent bonds, *i.e.*, chemisorption

Abstract

In this study, the sorption of cadmium ions onto sepiolite modified with hydrated iron(III) oxide, Fe(III)-sepiolite, has been investigated in natural seawater, artificial seawater, aqueous solution of NaCl of the same ionic strength as the seawater and distilled water. The sorption experiments were performed as a function of the initial solution pH value, initial metal concentration, and equilibration time, using the batch method. The equilibrium sorption data were analyzed by the Langmuir, Freundlich and Sips isotherm models and the kinetics of sorption was analyzed using the pseudo-first-order and the pseudo-second-order kinetic models. The maximum sorption capacity and the strength of the sorbate-sorbent bonds at initial pH 7 were found to decrease in the following order: distilled water > NaCl solution > artificial seawater > natural seawater. The values of parameter n_s in the Sips model, which fitted the equilibrium sorption results best, showed that heterogeneity of the sorbent surface was the highest in distilled water and the lowest in natural seawater. The sorption kinetic data fitted well with the pseudo-second-order kinetic model, which suggests that the rate-limiting step in Cd^{2+} sorption onto Fe(III)-sepiolite could be chemisorption. The low desorption percentage in both distilled water and 0.001 M HNO_3 indicated that sorption occurred mainly by chemisorption mechanisms.

Keywords: chemisorption, Cd^{2+} , modified sepiolite, seawater, modeling, desorption.

The contamination of natural waters by toxic heavy metals through the discharge of industry is a significant environmental problem. In particular, cadmium is a highly toxic element at relatively low dosages and causes serious health problems to human, animals and aquatic life [1,2]. Cadmium is released into natural waters mainly through a number of ind-

ustries such as smelting, metal plating and mining, nickel-cadmium battery manufacturing, phosphate fertilizers, pigments, stabilizer and alloys production [1,3]. To avoid significant toxic effects on aquatic ecosystems, a cost-effective method to remove Cd^{2+} from natural waters is needed. The sorption is an appropriate technology for cadmium removal from natural water systems, especially using low-cost sorbents such as zeolite [4], bentonite [5,6] and sepiolite [7,8].

Sepiolite is fibrous hydrated magnesium silicate clay with a unit cell formula $Mg_8Si_{12}O_{30}(OH)_4(OH_2)_4 \cdot 8H_2O$. In some aspects, sepiolite is similar to other 2:1 trioctahedral silicates, such as talc (two layers of tetrahedral silica and a central octahedral

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magnesium layer), but it has discontinuities and inversion in silica sheets, which give rise to structural channels filled with water molecules and running along the c-axis of fibrous particles. Due to its unique structure with micro channels and high surface area, sepiolite has received considerable attention as a sorbent for organic and inorganic compounds from water, as well as a support for catalysts [9-14].

Recently, research interest has increased in term of use of iron oxides for modification of clay minerals to improve their sorption capacity [10-13]. These systems, which are characterized by the presence of additional active sites, were applied as effective sorbents for metal ions removal from aqueous solutions.

A number of sorbents have shown high capacities for the removal of Cd²⁺ from aqueous solutions. However, these sorption capacities have been determined in deionized water, a simple matrix that fails to account for the effects of metal ion speciation, complexation, competing ions, and fouling of the sorbent materials by organic molecules often present in real waters [15]. In this study, the cadmium sorption on sepiolite modified with hydrated iron(III) oxide was investigated by using saline waters as an aquatic matrix. The cadmium sorption from different types of saline waters (natural seawater, artificial seawater and aqueous solution of NaCl of the same ionic strength as seawater) was compared with the sorption from distilled water. The influence of the initial solution pH value, initial Cd²⁺ concentration and the equilibration time on the amount of Cd²⁺ sorbed on the modified sepiolite and the capability of the Langmuir, Freundlich and Sips isotherm models to fit the experimental sorption data, were investigated.

EXPERIMENTAL PROCEDURE

Materials

Sorbent

The natural sepiolite used for the modification with hydrated iron(III) oxide was sampled from Andrici (Serbia). The chemical composition, specific surface area, pore size, X-ray diffraction and FTIR analyses of the sepiolite were reported previously [14]. The Fe(III)-sepiolite was prepared by mixing 20.0 g of sepiolite, 200 cm³ of freshly prepared 0.5 mol/dm³ FeCl₃ aqueous solution, and 360 cm³ of 1 mol/dm³ NaOH aqueous solution [11]. The addition of NaOH solution was rapid and with stirring. The suspension was diluted to 1 dm³ by distilled water and was kept in closed polyethylene flask at 70 °C for 48 h. Then, the precipitate was centrifuged and washed by distilled water until it was Cl⁻-free. The Fe(III)-sepiolite powder

had a dark red color, and its elemental analysis revealed that the content of iron reached 22.2 wt. % [11]. The characterization of the modified sepiolite showed that Fe(III)-sepiolite maintained the basic structure of the natural sepiolite, which contained pure sepiolite, without impurities [11]. The presence of new crystalline Fe phases was not observed by X-ray diffraction analysis, indicating that an amorphous Fe compound was formed. The pH_{pzc} of Fe(III)-sepiolite (8.5±0.1) was higher than the pH_{pzc} of the natural sepiolite (7.4±0.1), which means that the basicity of the sepiolite surface was increased [11]. In addition, it was showed that modification of the sepiolite with hydrated iron(III) oxide caused negligible change of the specific surface area (from 280.0 to 285.6 m²/g) and small decrease of the pore volume (from 0.311 to 0.227 cm³/g) [12,13].

Types of water

The four types of aquatic systems were used for Cd²⁺ solutions preparation:

1. Natural seawater (NSW) obtained from Greece, which contained Cl⁻ (564.13 mmol/dm³), Na⁺ (488.9 mmol/dm³), K⁺ (8.74 mmol/dm³), Mg²⁺ (45.22 mmol/dm³), Ca²⁺ (8.56 mmol/dm³), SO₄²⁻ (27.91 mmol/dm³) and Br⁻ (0.62 mmol/dm³); the concentration of the major cations and anions in NSW was determined on a Metrohm ion chromatography instrument, 861 Advanced Compact IC MSM II.

2. Artificial seawater (ASW), prepared according to analysis of the seawater; the quantities of salts used for the artificial seawater preparation were: 488.9 mmol/dm³ NaCl, 8.74 mmol/dm³ KCl, 25.88 mmol/dm³ MgCl₂, 19.34 mmol/dm³ MgSO₄, 8.56 mmol/dm³ CaSO₄ and 0.62 mmol/dm³ NaBr.

3. Distilled water (DW);

4. Aqueous solution of NaCl (NCS) of the same ionic strength as the seawater, prepared by dissolution of 40.2 g NaCl(s) in 1 dm³ of distilled water; ionic strength of NSW, *I*, was calculated according to the equation:

$$I = \frac{1}{2} \sum c_i z_i \quad (1)$$

where: *c_i* is the concentration of the ion and *z_i* is the charge of the ion.

Sorbate

The Cd²⁺ solutions were prepared by using cadmium nitrate (Cd(NO₃)₂·4H₂O) produced by Zorka, Šabac (Serbia).

Sorption experiments

The batch equilibration method was used to investigate the removal of Cd²⁺ from the solutions by

Fe(III)-sepiolite at 25±1 °C. The equilibrations of samples with 0.04 g Fe(III)-sepiolite and 20 cm³ of the solution were performed in a thermostated water bath with shaking. The sorption experiments were performed as a function of the initial metal concentration, the initial solution pH and the equilibration time. The initial Cd²⁺ concentrations as well as the concentration of Cd²⁺ after the sorption were determined using atomic absorption spectroscopy (AAS, Perkin-Elmer 730; detection limit for Cd²⁺ was 0.3 mg/dm³). All the sorption studies were repeated twice; the reported values are the average of two measurements.

Influence of the initial solution pH

The influence of the initial solution pH value (pH_i) on the sorption capacity was investigated using Cd²⁺ solution of 50 mg/dm³ concentration. The starting pH value was adjusted by HNO₃ or KOH at 4, 5, 6, 7 and 8. The suspensions were equilibrated for 24 h and then filtrated through a filter paper (retention of particles larger than 11 μm). The final solution pH (pH_f) was measured using a pH meter InoLab WTW series pH 720.

The amount of cadmium sorbed per unit mass of Fe(III)-sepiolite at equilibrium, q_e (mg/g), was calculated using the equation:

$$q_e = \frac{c_o - c_e}{m} V \quad (2)$$

where c_o and c_e are the initial and the equilibrium concentrations (mg/dm³), m is the mass of the sorbent (g), and V is the volume of the solution (dm³).

Sorption isotherms

Sorption isotherms were determined using Cd²⁺ solutions of different concentration (5, 10, 20, 30, 45, 75, 100 and 150 mg/dm³) at pH_i 7.0±0.1. The samples were equilibrated for 24 h. The amount of Cd²⁺ sorbed per unit mass of Fe(III)-sepiolite at equilibrium, q_e (mg/g), was calculated using Eq. (2).

Sorption kinetics

The kinetic experiments were performed at the Cd²⁺ initial concentration of 50 mg/dm³ (c_o), at the initial pH 7.0±0.1, for the contact time of ½, 1, 2, 4, 8, 16 and 24 h.

The quantity of Cd²⁺ ions sorbed per unit mass of Fe(III)-sepiolite after the period of time t (q_t) was calculated according to the equation:

$$q_t = \frac{c_o - c_t}{m} V \quad (3)$$

where c_t is the concentration of Cd²⁺ after the period of time t .

Desorption studies

Desorption studies were performed with the sorbent samples obtained by the sorption from the solutions in DW, NCL, ASW and NSW at the initial concentration of 150 mg/dm³. The loaded sorbent samples were dried at 100 °C for 24 h and used in batch desorption experiments. Test flasks were filled with 20 cm³ of desorbing solution (distilled water or 0.001 M HNO₃), and 0.04 g of the loaded sorbent sample was added. After an equilibration for 24 h in a thermostated water bath with shaking at a temperature of 25 °C, the dispersions were filtered and the filtrates were analyzed to check the desorbed Cd²⁺, using AAS. The desorption efficiency was defined as the ratio between the amount of Cd²⁺ desorbed and the amount of Cd²⁺ sorbed on the sorbent. In addition, concentration of Fe³⁺ in the filtrates after desorption, as well as in solution after the sorption at the initial concentration of 150 mg/dm³, was determined in order to check stability of hydrated iron(III) oxide on the sepiolite surface.

RESULTS AND DISCUSSION

Influence of initial solution pH on the sorption capacity

Metal sorption from aqueous solutions can be greatly affected by the solution pH that influences not only the binding sites (*e.g.*, degree of protonation or deprotonation of functional groups at the sorbent surface), but also the metal chemistry (*e.g.* speciation and precipitation). At pH below 8, Cd²⁺ is a dominant and soluble form, while precipitate is formed at higher pH values [16]. In general, the precipitate formation depends on the Cd²⁺ concentration, other present cations concentration, types and concentrations of anions, temperature, and presence of solids.

The influences of the initial solution pH value on the sorption capacity of Fe(III)-sepiolite in distilled water, seawater, artificial seawater and NaCl solution are presented in Figure 1. The effect of pH_i was studied in the pH range from 4 to 8 in order to avoid the occurrence of the precipitation of cadmium hydroxide at higher pH values. According to the value of the solubility product constant of Cd(OH)₂ and Cd²⁺ initial concentration, Cd(OH)₂ precipitation starts at pH > 8.5. The final pH values, pH_f, for each sample are also given in Figure 1.

According to Figure 1, the sorption capacity generally increased with the initial pH increase for all types of water systems that can be explained by decrease in number of H⁺ that compete with Cd²⁺ for the sorption sites. The values of pH_f show that H⁺ ions associated with the surface functional groups of Fe(III)-sepiolite at pH_i ≤ 7 (pH_f > pH_i), while at pH 8 they were released into the solution due to disso-

ciation of the functional groups ($\text{pH}_i < \text{pH}_i$). Thus, the pH value at which the surface charge changed from positive to negative and vice versa is between pH 7 and pH 8 for all types of water, which is lower than the pH_{pzc} of Fe(III)-sepiolite (8.5 ± 0.1). This indicates the specific sorption of Cd²⁺, *i.e.*, formation of inner-sphere complexes with the surface functional groups. Such bonds are stronger than electrostatic interactions between charged surface and oppositely charged ions (outer-sphere complexes). As pH_i decreased from 7 to 4, more H⁺ were bonded to the surface functional groups, leaving a smaller number of groups for Cd²⁺ binding, so the sorption capacity decreased with the pH_i decrease. In addition, as pH_i was lower, the negative charge of the surface became lower and the positive charge higher, which also decreased the sorption of positively charged cadmium ions by electrostatic interactions.

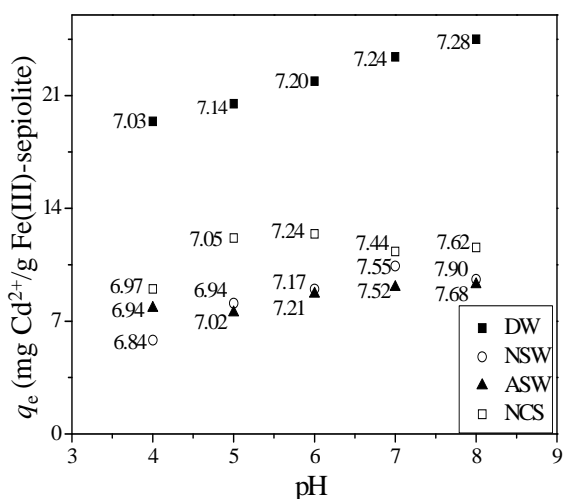


Figure 1. The effect of the initial pH on Cd²⁺ sorption by Fe(III)-sepiolite from DW, NCS, ASW and NSW for the initial Cd²⁺ concentration of 50 mg/dm³ (the numbers in the figure indicate the final pH values).

The sorption capacity of Fe(III)-sepiolite is significantly higher in the case of sorption from distilled water than from the saline waters, which can be explained by competitive effect of ions from saline waters for active sites at the surface of the sorbent. NSW and ASW contain higher-valence ions (Ca²⁺ and Mg²⁺), which have more competitive effect than monovalence ions, so sorption capacity was lower in NSW and ASW than in NaCl solution. Moreover, high concentration of ions in water, like in all types of saline waters, caused decreasing of surface charge of the sorbent [17] and consequently, sorption capacity decreasing. Comparison of the sorption capacity of Fe(III)-sepiolite in different types of water was done further by sorption isotherm determination at pH_i 7.0 ± 0.1 .

Sorption isotherms studies and modeling

The experimental sorption isotherms as the dependence of mass of Cd²⁺ sorbed per unit mass of Fe(III)-sepiolite at equilibrium on the Cd²⁺ equilibrium concentration, for distilled water, natural seawater, artificial seawater and NaCl solution at pH_i 7.0 ± 0.1 are presented in Figure 2. The equilibrium sorption data were fitted to the Langmuir, Freundlich and Sips isotherms, and the model fits are presented with the experimental data in Figure 2. The sorption isotherms constants, determined by non-linear regression analysis using the Easy Plot, are summarized in Table 1, where: q_m is the maximum adsorption capacity, K_L is the Langmuir constant related to the energy of adsorption, K_f is the Freundlich constant related to the adsorption capacity, n is the dimensionless sorption intensity parameter, K_s is the Sips equilibrium constant and n_s is the index of heterogeneity.

According to Figure 2, the Fe(III)-sepiolite showed the highest sorption capacity for Cd²⁺ in distilled water, then in NaCl solution, followed by sorption capacity in artificial seawater and the lowest in natural seawater. Such order of sorption capacity, which is the same as in the investigation of the effect of pH_i on Cd²⁺ sorption, confirmed strong influence of salinity on the sorption properties of Fe(III)-sepiolite. Salinity was also observed to limit performance of different organic and inorganic chemisorbents for the collection of a diverse range of fission and activation product elements of the nuclear fuel cycle including Co, Zr, Nb, Ru, Ag, Te, Sb, Ba and Cs [18]. Salinity dependence was most significant for hard cations, *i.e.*, Cs⁺ and Ba²⁺. Likewise, sorption capacities of three nanoporous sorbents containing chelating diamine functionalities [15] for Cu²⁺ were lower in saline water than in river water.

The saline waters used in this research had the same ionic strength, but Fe(III)-sepiolite had lower sorption capacity in NSW and ASW than in NaCl solution because Ca²⁺ and Mg²⁺ from seawaters compete with Cd²⁺ more effectively than Na⁺. The similar results were observed for the sorption of Cd²⁺ onto amorphous hydrous manganese dioxide [19], where sorption has been studied in 0.5 M NaCl solution and major ion seawater: sorption capacity was lower in seawater than in 0.5 M NaCl solution. Lower sorption capacity of Fe(III)-sepiolite in the NSW than in ASW may result from the presence of natural organic matter (NOM) and other ions that are not present in ASW. NOM might have occupied some binding sites of Fe(III)-sepiolite, which led to the reduction of Cd²⁺ sorption. It was shown also that the presence of natural organic matter had little effect on the ability of different chemisorbents to extract target elements [18].

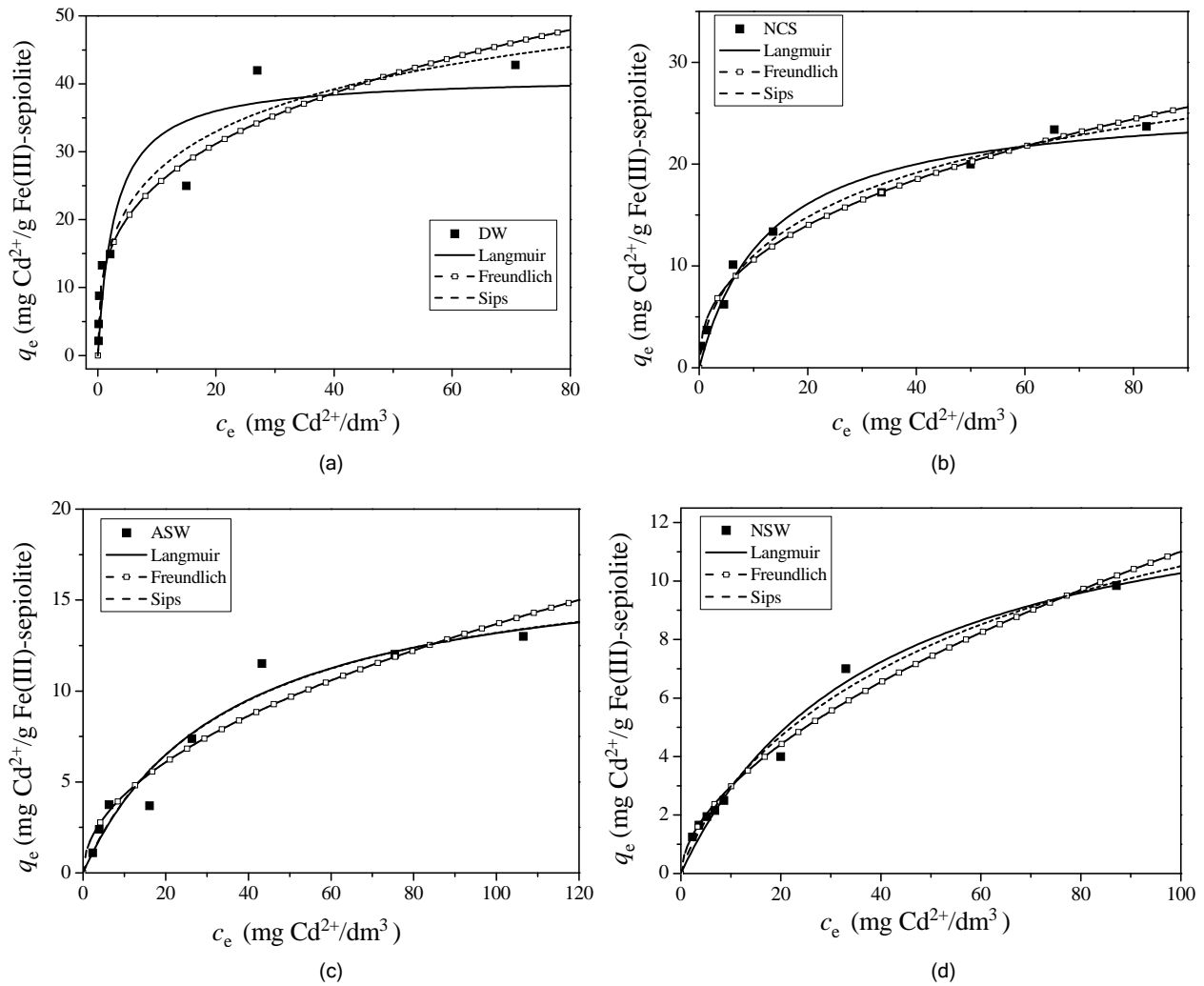


Figure 2. The sorption isotherms for Cd²⁺ onto Fe(III)-sepiolite in DW (a), NCS (b), ASW (c) and NSW (d) at pH, 7.

Table 1. Langmuir, Freundlich and Sips isotherms constants for the sorption of Cd²⁺ onto Fe(III)-sepiolite at pH, 7

Model		Type of water			
		DW	NCS	ASW	NSW
Langmuir model	$K_L / \text{dm}^3 \text{mg}^{-1}$	0.349	0.0784	0.0289	0.0257
	$q_m / \text{mg g}^{-1}$	41.1	26.4	17.7	14.3
	R^2	0.888	0.976	0.949	0.979
Freundlich model	$K_f / \text{mg}^{(1-1/n)} \text{dm}^{3/n} \text{g}^{-1}$	12.3	4.20	1.35	0.804
	n	3.22	2.49	1.98	1.76
	R^2	0.938	0.983	0.924	0.974
Sips model	$q_m / \text{mg g}^{-1}$	79.3	44.0	18.1	19.1
	$K_a / (\text{dm}^3 \text{mg}^{-1})^{n_s}$	0.181	0.0836	0.0299	0.0279
	n_s	0.457	0.602	0.978	0.821
	R^2	0.948	0.988	0.949	0.982

The study of equilibrium sorption isotherms provides important data for understanding the mechanism of the sorption. The different sorption isotherms are characterized by their constants, the values of

which suggest the surface properties and affinity of the sorbent to the sorbate. The Langmuir model [20,21] assumes monolayer sorption at specific homogeneous sites, without any interactions between sor-

bed species. The Freundlich equation [21,22] describes sorption (possibly multilayer in nature) on a heterogeneous surface consisting of non-identical and energetically non-uniform sites. A combined form of Langmuir and Freundlich expressions, the Sips model [21,23], deduced for predicting the heterogeneous sorption systems and circumventing the limitation of the rising sorbate concentration associated with the Freundlich isotherm model. At low sorbate concentrations (when the sorbate content is much lower than the sorbent capacity), the model reduces to Freundlich isotherm, while at high concentrations (when the sorbate content is higher than the sorbent capacity), it predicts a monolayer sorption capacity, characteristic of the Langmuir isotherm.

The results presented in Table 1 show that the Sips model is the best model to explain the sorption behavior of Cd²⁺ onto Fe(III)-sepiolite, but also both Langmuir and Freundlich fit the results well.

The maximum sorption capacity obtained by Langmuir equation, q_m , and the affinity parameter, K_L , were found to decrease in the following order: DW > NCS > ASW > NSW. The higher values of K_L imply stronger sorbate-sorbent interactions, so the strongest bonds were formed in distilled water and the weakest in natural seawater [21]. The Freundlich constant K_f , which is an approximate indicator of adsorption capacity, and intensity parameter n , which is an indicator of the strength of sorption [21], decrease in the same order as q_m and K_L .

The values of the maximal sorption capacity obtained by the Sips model were higher than those obtained by the Langmuir model. The Sips constant K_a , similarly to the Langmuir constant K_L , could be regarded as representative of the strength of sorption: higher value of K_a implies stronger bonds between sorbate species and sorbent active sites [21,23]. According to the values of K_a in Table 1, the strength of sorbate-sorbent bonds decreases in the order: DW > NCS > ASW > NSW. The parameter n_s in Sips model is the heterogeneity factor, which shows the deviation from the Langmuir model. The value of n_s for a homogeneous material is 1, and it is less than one for heterogeneous materials [24,25]. According to the values of n_s for Cd²⁺ sorption onto Fe(III)-sepiolite (Table 1), the heterogeneity of the sorbent is the highest in distilled water, lower in NaCl solution and the lowest in seawaters. Heterogeneity of a sorbent surface is a result of existence of different active sites for sorption. In the case of sorption from NaCl solution, it can be supposed that Na⁺ and Cl⁻ blocked some active sites for Cd²⁺ sorption at the surface of Fe(III)-sepiolite and thus the surface had less different active sites than in the case of the sorption from distilled

water, meaning lower heterogeneity of the surface. Having in mind that sorbate-sorbent bonds were stronger in distilled water than in NaCl solution, it can be supposed that Na⁺ and Cl⁻ blocked active sites of higher energy, leaving active sites of lower energy for Cd²⁺ sorption. In seawaters, where there were Ca²⁺ and Mg²⁺, the heterogeneity was even lower and sorbate-sorbent bonds were weaker than in NaCl solution.

The results of the isotherm modeling showed that Cd²⁺ sorbed onto heterogeneous surface of Fe(III)-sepiolite until the monolayer is formed, but sorption capacity and surface heterogeneity were highly influenced by the presence of ions in saline waters.

Sorption kinetics and modeling

The influence of the contact time t on the amount of Cd²⁺ sorbed onto Fe(III)-sepiolite, q_t , is shown in Figure 3. It can be seen that the removal of Cd²⁺ from different water systems by sorption onto Fe(III)-sepiolite is comprised of three steps: the rapid sorption in the first 0.5 h, then slightly decreased sorption, followed by its slow increase after 2 h, until the equilibrium was reached. The high number of active sites available at the beginning of the sorption may explain the fast initial Cd²⁺ uptake at the Fe(III)-sepiolite surface. However, some rapidly sorbed ions were desorbed in the next step. After that, a slow increase of the amount of sorbed Cd²⁺ can be observed, since the most sorption sites were occupied and Cd²⁺ concentration in the solutions decreased; thus, the sorption became less efficient.

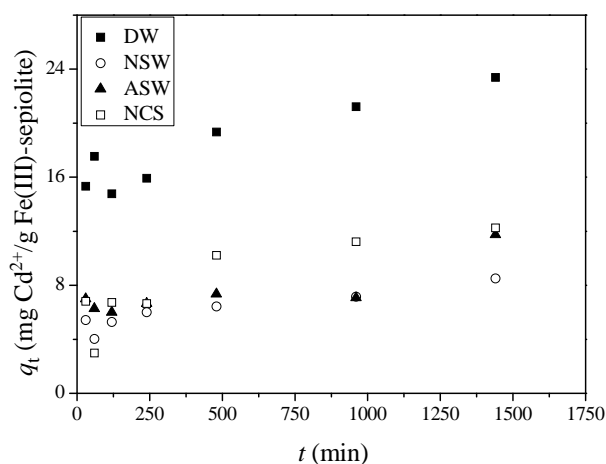


Figure 3. The effect of contact time on Cd²⁺ sorption onto Fe(III)-sepiolite in DW, NCS, ASW and NSW at pH_i 7, for initial Cd²⁺ concentration of 50 mg/dm³.

The kinetics of Cd²⁺ sorption onto Fe(III)-sepiolite was analyzed using the pseudo-first-order equation proposed by Lagergren [26] and the pseudo-

second-order kinetic model proposed by Ho and McKay [27], and the results are presented in Table 2. Accordingly, the pseudo-second-order equation is the model that best describes the experimental data, since the q_e values estimated by this model are in good agreement with the experimental results and the values of the correlation coefficients are close to 1. The fact that the pseudo-second-order model gave better agreement with the experimental data than the pseudo-first-order model is not surprising, since this seems to be a generally prevalent observation in heavy metal sorption studies [27,28]. Further, this trend suggests that the rate-limiting step in heavy metal sorption is chemisorption, which involves valence forces through sharing or exchange of electrons between sorbent and sorbate, complexation, coordination and/or chelation, rather than physisorption [28]. As the correlation coefficients for the pseudo-second-order model are high (Table 2), it may be assumed that the sorption of Cd²⁺ onto Fe(III)-sepiolite occurs mainly through chemisorption mechanisms, *e.g.*, specific sorption, as it was shown during investigation of pH_i influence on the sorption capacity, and ion exchange of Mg²⁺ from the sepiolite structure by Cd²⁺ from the solutions [14]. Similarly, sorption of Ni²⁺ [11] and Co²⁺ [12] from solution in distilled water onto Fe(III)-sepiolite was mainly governed by chemisorption and was best described by the pseudo-second-order model.

Table 2. Kinetic parameters for Cd²⁺ sorption onto Fe(III)-sepiolite at pH_i 7, for the initial Cd²⁺ concentration of 50 mg/dm³ (k_1 is the rate constant of pseudo-first-order model; and k_2 is the rate constant of the pseudo-second-order model)

Kinetics		Type of water			
		DW	NCS	ASW	NSW
Pseudo-first-order	k_1 / min^{-1}	13.772	21.913	10.840	0.0085
$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$	$q_e / \text{mg g}^{-1}$	8.2	7.7	3.6	0.19
	R^2	0.888	0.886	0.841	0.530
Pseudo-second-order	$k_2 / \text{g mg}^{-1} \cdot \text{min}^{-1}$	0.0016	0.00035	0.0029	0.0123
$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	$q_e / \text{mg g}^{-1}$	25.0	14.3	7.7	7.7
	R^2	0.991	0.991	0.995	0.998

Kinetic analysis confirmed that sorption capacity of Fe(III)-sepiolite is the highest in distilled water, and that capacity in saline waters (natural and artificial) with higher valence ions present, is lower than in NaCl solution. Salinity influenced not just sorption capacity, but also rate of the sorption: according to the values of the kinetic constant, the rate of sorption was the highest in natural seawater, lower in artificial and distilled water and the lowest in NaCl solution.

Desorption studies

Desorption studies were conducted to better understand the mechanism of Cd²⁺ sorption, *i.e.*, to investigate the strength of sorbate-sorbent bonds. The results of desorption studies are given in Table 3.

Table 3. Percentage desorption of Cd²⁺ from Fe(III)-sepiolite loaded in different types of water

Fe(III)-sepiolite loaded in:	Percentage desorption in:	
	Distilled water	0.001 M HNO ₃
DW	0.36	2.54
NCL	0.40	2.80
ASW	2.24	3.61
NSW	3.30	4.67

Very low desorption percentage in both desorbing media suggests that the sorption of Cd²⁺ onto Fe(III)-sepiolite occurred significantly via chemisorption mechanisms, as it was found according to dependences pH_f-pH_i and kinetics modeling. Desorption was slightly more intense in 0.001 M HNO₃ than in distilled water, as it was expected, because the acid solution is a stronger desorbing agent than water due to higher concentration of H⁺. In both desorbing media, percentage desorption was the lowest for the sorbent loaded in DW and the highest for the sorbent loaded in NSW (Table 3). These results indicate that the strongest sorbate-sorbent bonds were formed in

DW, than in NCL, followed by ASW and the weakest in NSW, as it was found according to isotherm modeling.

The concentration of Fe³⁺ in solution after sorption, as well as after desorption in both distilled water and 0.001 M HNO₃, was below detection limit of the AAS ($\leq 0.3 \text{ mg/dm}^3$), which indicate high stability of hydrated iron(III) oxide on the sepiolite surface, *i.e.* low Fe³⁺ releasing from Fe(III)-sepiolite, even in acid solution.

CONCLUSIONS

In this study, sepiolite modified with hydrated iron(III) oxide, Fe(III)-sepiolite, was used as a sorbent for Cd²⁺ from different types of water and aqueous solutions. It was shown that the sorption capacity was highly influenced by the ions presented in aqueous media: the highest capacity was in distilled water, where there were no other ions except Cd²⁺, than in NaCl solution, followed by artificial seawater and the lowest capacity was in natural seawater. The equilibrium sorption data modeling with the Langmuir, Freundlich and Sips models showed that the Sips model was the best to explain the sorption behavior of Cd²⁺ onto Fe(III)-sepiolite at initial pH 7, which indicates the sorption onto heterogeneous surface until the monolayer is formed. According to the values of Sips parameters, it was concluded that the strength of sorbate-sorbent bonds and heterogeneity of the sorbent surface decreased in the following order: distilled water > NaCl solution > artificial seawater > natural seawater. The sorption kinetic data fitted well with the pseudo-second-order kinetic model, which suggested that the rate-limiting step in Cd²⁺ sorption onto Fe(III)-sepiolite could be chemisorption. The desorption studies in distilled water and 0.001 M HNO₃, as well as dependence of final pH on initial pH, suggested that the sorption of Cd²⁺ onto Fe(III)-sepiolite occurred significantly via chemisorption mechanisms.

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NAUČNI RAD

UTICAJ SALINITETA VODE NA SORPCIJU JONA KADMIJUMA NA Fe(III)-SEPIOLITU

U ovom radu je proučavana sorpcija jona kadmijuma iz prirodne morske vode, laboratorijski pripremljene morske vode, vodenog rastvora NaCl iste jonske jačine kao morska voda i destilovane vode, na sepiolitu modifikovanom hidratiziranim gvožđe(III)-oksidom. Eksperimenti su izvedeni u šaržnim uslovima, pri različitim početnim pH vrednostima, početnim koncentracijama jona kadmijuma i vremenima uravnotežavanja. Rezultati sorpcije u ravnotežnim uslovima su analizirani primenom modela Langmira, Frojndliha i Sipsa, a kinetika sorpcije je analizirana kinetičkim modelima pseudo-prvog i pseudo-drugog reda. Utvrđeno je da maksimalni adsorpcioni kapacitet i jačina veza sorbat-sorbent pri početnoj pH 7 opadaju u nizu: destilovana voda > NaCl rastvor > laboratorijski pripremljena morska voda > prirodna morska voda. Vrednosti parametra n_s u modelu Sipsa, koji najbolje opisuje eksperimentalne rezultate, pokazuju da je heterogenost površine sorbenta najveća u destilovanoj vodi i najmanja u prirodnoj morskoj vodi. Rezultati ispitivanja kinetike sorpcije se bolje fituju modelom pseudo-drugog reda, što sugerise da stupanj koji određuje brzinu sorpcije može biti hemisorpcija. Mali stepen desorpcije i u destilovanoj vodi i u 0.001 M HNO₃ je potvrdio da se joni kadmijuma vezuju za modifikovani sepiolit uglavnom hemisorpcijom.

Ključne reči: hemisorpcija, Cd²⁺, modifikovani sepiolit, morska voda, modelovanje, desorpcija.