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Iron-Modified Sepiolite for Ni^{2+} Sorption from Aqueous Solution: An Equilibrium, Kinetic, and Thermodynamic Study

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Sepiolite was used for the synthesis of the sepiolite−iron oxide system to obtain a sorbent suitable for the removal of Ni^{2+} from aqueous solution. The modified material, Fe-sepiolite, was characterized by X-ray diffraction analysis, Fourier transform infrared spectroscopy, differential thermal/thermogravimetric analysis, and point of zero charge (pH_{pzc}) determination. The sorption experiments were performed as a function of the initial metal concentration, equilibration time, and temperature using the batch method. The Fe-sepiolite had a higher sorption capacity than the natural sepiolite sample due to a higher specific sorption and a higher ion exchange with Mg^{2+} ions from the sepiolite surface. Thermodynamic parameters, such as enthalpy, Gibbs energy, and entropy, were calculated from the temperature-dependent sorption isotherms, and these values showed that the sorption of Ni^{2+} onto sepiolites was endothermic. Pseudo-second-order kinetic models provide the best correlation of the experimental kinetic data.

Introduction

Toxic nickel ions are frequently present in wastewater from industries such as steel, electroplating, and ceramic factories and battery and accumulator manufacture. Nickel is also present in nuclear wastes due to its use in actinide research. This heavy metal ion, even at low concentrations, has a damaging effect on human health because there are no adequate mechanisms for nickel elimination from the body. When incorporated into the organism, it accumulates in the lungs, kidneys, liver, intestines, and heart. Higher concentrations of nickel cause various diseases and disorders, including cancer of the lungs, nose, and bone, chronic headaches, sleeplessness, and diarrhea.[1]

Several treatment technologies, such as chemical precipitation, ion exchange, electrochemical removal, membrane separation, microbe separation, sorption by activated carbon, etc., have been developed for the removal of heavy metals from wastewaters. Clay minerals, such as kaolinite,[2,3] vermiculite,[4] montmorillonite,[5] bentonite,[6] and sepiolite,[7,8] are natural materials that have been investigated as heavy metal sorbents because they are abundant in nature, inexpensive, and environmentally friendly. The high sorption capacities of clays are mainly ascribed to their high specific surface area and high cation exchange capacity.

Sepiolite ($Mg_8Si_{12}O_{30}(OH)_4(H_2O)_4 \cdot 8H_2O$) presents a structure of needle-like particles, which can be described as an arrangement of talc-like layers (two layers of tetrahedral silica and a central octahedral magnesium layer) separated by channels running along the *c* axis of the particles. This unique fibrous structure with interior channels allows the penetration of organic and inorganic ions into the structure of sepiolite and assigns sepiolite important industrial applications. Sepiolite is used as a catalyst and catalyst support,[9] a filler in polymer composites,[10] a membrane for ultrafiltration,[11] and molecular sieves.[12] Sepiolite is an effective and economic sorbent material, a bleaching and clarifying agent, a filter aid, and an industrial sorbent, and the spectrum of its utilization ranges from cosmetics to paints and fertilizers.

In recent years, researchers have attempted to synthesize systems of iron oxides and clay minerals[13−16] or zeolites[17−19] to improve the sorption capacity or catalytic properties. These systems were able to sorb higher concentrations of species due to the presence of the iron oxides, which are also active sorbents.

The present work was aimed at the synthesis and characterization of the sepiolite−iron solid system and the determination of the effectiveness of the obtained sorbent and a natural sepiolite sample in the removal of Ni^{2+} from aqueous solutions. To our knowledge, iron-modified sepiolite was not previously used for heavy metal sorption from wastewaters. The sorption experiments were also performed to examine the dominant mechanisms of the interaction of Ni^{2+} ions and sepiolites, study the capability of the Langmuir, Freundlich, and Dubinin−Kaganer−Radushkevich (DKR) isotherm models to fit the experimental sorption data, investigate the influence of the equilibrium time and temperature on the sorption capacity of the sepiolites, and determine the thermodynamic functions of sorption (Gibbs energy change, enthalpy and entropy change).

For a better understanding of the sorption mechanism an important aspect of this study is the determination of the point of zero charge. The solution pH value at which the surface charge density of the solid phase is equal to zero ($\sigma_o = 0$, $pH = pH_{pzc}$) is called the point of zero charge (pH_{pzc}). The solid-phase surface is positively charged if $pH < pH_{pzc}$ and negatively if $pH > pH_{pzc}$. Sorption of cations is favored at $pH > pH_{pzc}$, while sorption of anions is favored at $pH < pH_{pzc}$. The point of zero charge is frequently taken to be equal to the isoelectric point (pH_{iep}), which is the pH value at which the electrokinetic potential is equal to zero. The point of zero charge, however, will be equal to the isoelectric point only if there is no specific sorption of ions at the surface of the solid phase. The specific sorption of cations, as known from the literature,[20−22] shifts

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the $\mathrm{pH_{pzc}}$ toward lower pH values, and the specific sorption of anions shifts the $\mathrm{pH_{pzc}}$ in the opposite direction.

Experimental Section

Materials. The natural sepiolite (SEP) used for the metal sorption experiments and for modification with iron came from Andrici (Serbia). The chemical composition, specific surface area, pore volume, pore radius, and X-ray diffraction and FTIR analyses of the sample were reported previously.[20]

The Fe-sepiolite (FeSEP) was prepared by mixing 20.0 g of sepiolite, 200 $\mathrm{cm^3}$ of freshly prepared 0.5 $\mathrm{mol \cdot dm^{-3}}$ $\mathrm{FeCl_3}$, and 360 $\mathrm{cm^3}$ of 1 $\mathrm{mol \cdot dm^{-3}}$ NaOH solution. The addition of NaOH solution was rapid and with stirring. The suspension was diluted to 1 $\mathrm{dm^3}$ with the water (18 MΩ) obtained from a Mill-Q water purification system and was kept in a closed polyethylene flask at 343 K for 48 h. The precipitate was then centrifuged and washed with distilled water until $\mathrm{Cl^-}$ ion free.

Characterization of Fe-Sepiolite. The chemical composition of the Fe-modified sepiolite was determined by atomic absorption spectroscopy (AAS; Perkin-Elmer 730). X-ray diffraction (XRD) analysis of the sample was realized with an Ital Structures APD 2000 diffractometer using Cu Kα radiation in the 2θ angle range from 3° to 50° with a 0.02° step. Fourier transform infrared (FTIR) analysis was done on an MB Bomem 100 Hartmann & Brown instrument in the wavenumber range from (4000 to 400) $\mathrm{cm^{-1}}$. The sample was prepared by the KBr method at a sample:KBr = 1:100 ratio. Thermal analysis was performed using an SDT Q-600 simultaneous differential scanning calorimetry−thermogravimetric analysis (DSC−TGA) instrument (TA Instruments). The samples were heated in a Pt pan under an oxygen atmosphere at a heating rate of 20 $\mathrm{°C \cdot min^{-1}}$. The cation exchange capacities (CECs) of the natural sepiolite and Fe-sepiolite were determined by the ammonium acetate method by extracting $\mathrm{NH_4^+}$ from the $\mathrm{NH_4^+}$-saturated samples obtained by treatment of sepiolites with 1 $\mathrm{mol \cdot dm^{-3}}$ ammonium acetate solution.

Determination of the Point of Zero Charge of the Fe-Sepiolite. The point of zero charge of the Fe-sepiolite was determined by the batch equilibration method[23] in $\mathrm{KNO_3}$ solutions (25 $\mathrm{cm^3}$ of solution) having concentrations of (0.1, 0.01, and 0.001) $\mathrm{mol \cdot dm^{-3}}$ with 0.05 g of Fe-sepiolite. The procedure for the determination of the point of zero charge has been described in previous papers.[20,22]

To determine the degree of dissolution of the Fe-sepiolite powder, the concentration of $\mathrm{Mg^{2+}}$, $\mathrm{Na^+}$, and $\mathrm{Fe^{3+}}$ ions in the solutions after equilibration with a 0.01 $\mathrm{mol \cdot dm^{-3}}$ $\mathrm{KNO_3}$ solution was measured by AAS.

Sorption Procedure. The batch equilibration method was used to investigate the removal of $\mathrm{Ni^{2+}}$ ions by the natural sepiolite and Fe-sepiolite samples.[23] The sorption was studied on the basis of the shift of the point of zero charge, determination of the sorption isotherms, and correlation between the quantity of $\mathrm{Mg^{2+}}$ ions released from and the quantity of $\mathrm{Ni^{2+}}$ ions sorbed onto the sepiolite samples. The experiments were performed using solutions of $\mathrm{Ni(NO_3)_2}$ in Millipore water.

The shift of the point of zero charge was investigated using (0.01 and 0.001) $\mathrm{mol \cdot dm^{-3}}$ solutions of $\mathrm{Ni(NO_3)_2}$ and 0.05 g of the sorbents. The sorption of $\mathrm{Ni^{2+}}$ ions was examined in the pH range from approximately 3.5 to approximately 8 to avoid ion hydrolysis at higher pH values and the dissolution of sepiolite at lower pH values.

For the purpose of determining the sorption isotherms, solutions of $\mathrm{Ni^{2+}}$ ions in demineralized water with different initial concentrations and an initial pH value of 5.6 ± 0.1 were prepared. An aliquot of 25 $\mathrm{cm^3}$ of each solution was equilibrated for 24 h with 0.05 g of sepiolite sample with shaking. The initial $\mathrm{Ni^{2+}}$ ion concentrations as well as the concentrations of $\mathrm{Ni^{2+}}$, $\mathrm{Mg^{2+}}$, $\mathrm{Na^+}$, and $\mathrm{Fe^{3+}}$ ions after the sorption were determined using AAS (Perkin-Elmer 730). All the sorption studies were repeated twice; the reported value is the average of two measurements.

Table 1. Chemical Analysis of the Fe-Modified Sepiolite

	$\mathrm{SiO_2}$	MgO	$\mathrm{Al_2O_3}$	$\mathrm{Fe_2O_3}$	CaO	$\mathrm{K_2O}$	$\mathrm{Na_2O}$	LOI
content, % (by weight)	38.5	18.8	0.53	31.45	0.25	0.04	0.70	9.73

The kinetic experiments were performed at a $\mathrm{Ni^{2+}}$ concentration of 100 $\mathrm{mg \cdot dm^{-3}}$ with 25 $\mathrm{cm^3}$ of the solution and 0.05 g of the sample at a pH value of 5.6 ± 0.1 and a temperature of 298 K for contact times ranging from (1 to 24) h. After separation of the solid from the liquid phase, the final concentrations of $\mathrm{Ni^{2+}}$ and $\mathrm{Mg^{2+}}$ ions were measured as variables dependent on time.

To investigate the influence of temperature on the sorption process, sorption experiments were also performed at temperatures of (318, 328, and 338) K in a thermostated water bath with shaking under the same conditions as those employed for the determination of the sorption isotherms at 298 K.

Desorption Experiments. The sepiolite samples separated by filtration from the sorption experiments at different initial metal concentrations were used to study the desorption behavior of sorbed $\mathrm{Ni^{2+}}$ with different extractants. The residual sepiolites of two replicates of the first sorption experiment were added to 25 $\mathrm{cm^3}$ of 0.001 $\mathrm{mol \cdot dm^{-3}}$ $\mathrm{HNO_3}$ solution in the first series of experiments or to 25 $\mathrm{cm^3}$ of demineralized water in the second series of experiments. After an equilibrium period of 24 h in a thermostated water bath with shaking at a temperature of 298 K, the dispersions were filtered and the final $\mathrm{Ni^{2+}}$ concentrations were measured.

Results and Discussion

Fe-Sepiolite Characterization. The Fe-sepiolite powder had a dark red color, and its elemental analysis, given in Table 1, revealed that the content of iron reached 22.2 %. Compared with the natural sepiolite sample,[20] there was no change in the $\mathrm{SiO_2}$:MgO ratio; i.e., the modification of sepiolite did not cause destruction of the sepiolite structure.

The CEC, determined by the ammonium acetate method, is 0.26 (mmol of $\mathrm{M^+}$)$\cdot \mathrm{g^{-1}}$ for natural sepiolite and 0.50 (mmol of $\mathrm{M^+}$)$\cdot \mathrm{g^{-1}}$ for the Fe-modified sample. The increase in the cation exchange capacity is a result of formation of additional −FeOH and −FeONa groups on the Fe-sepiolite surface during the treatment with $\mathrm{FeCl_3}$ and NaOH solutions.

The XRD diffractogram of the Fe-modified sample (presented in Figure 1) is similar to those of natural samples.[20] Figure 1 clearly shows the presence of the main characteristic peaks for sepiolite and reveals no notable change in the basic sepiolite diffraction peaks, indicating conservation of the sepiolite structure with some decrease in crystallinity. Although the presence of a new crystalline Fe phase was not detected by XRD, it is not possible to exclude its presence.

The FTIR spectra of the Fe-sepiolite (Figure 2) confirmed that the modified material maintained the basic structure of sepiolite:[24,25] bands in the (4000 to 3000) $\mathrm{cm^{-1}}$ range corresponding to the vibrations of the Mg−OH group (3690 $\mathrm{cm^{-1}}$), coordinated water (3568 $\mathrm{cm^{-1}}$), and zeolitic water (at 3422 $\mathrm{cm^{-1}}$), a band at 1659 $\mathrm{cm^{-1}}$ due to the vibration of zeolitic water, bands in the (1200 to 400) $\mathrm{cm^{-1}}$ range characteristic of silicate [bands centered at (1016 and 460) $\mathrm{cm^{-1}}$ due to Si−O−Si vibration, bands at (1215, 1076, and 973) $\mathrm{cm^{-1}}$ due to Si−O bonds, and a band at 437 $\mathrm{cm^{-1}}$ originating from octahedral−tetra-

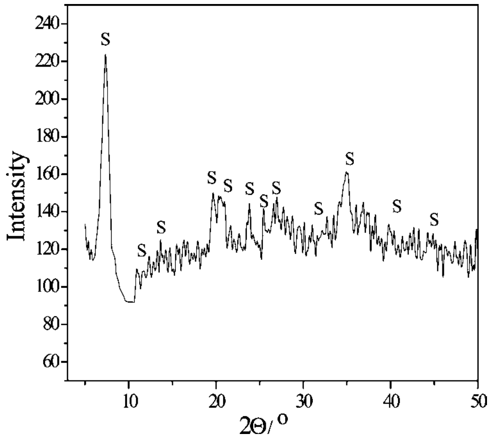

Figure 1. X-ray diffractogram of the FeSEP sample (S-sepiolite).

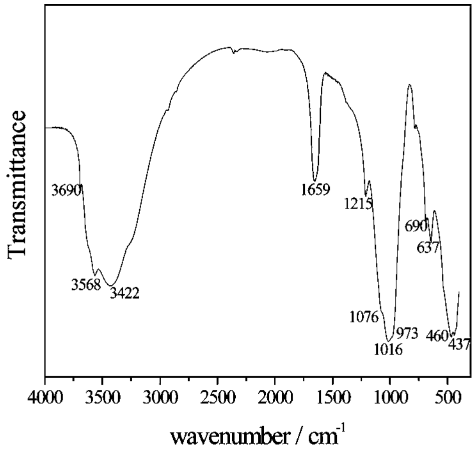

Figure 2. FTIR spectra of the FeSEP sample.

hedral bonds (Si−O−Mg bonds)], and bands at (690 and 637) cm^{-1} corresponding to vibrations of the Mg−OH bond.

The FTIR spectra do not reveal the existence of a new iron oxide phase or the formation of an Fe-sepiolite covalent bond. Due to the presence of the characteristic sepiolite bands, a peak at 606 cm^{-1}, assignable to the vibration of Fe−OH, could not be clearly identified.

The differential thermal analysis/thermogravimetric analysis (DTA/TGA) curves of the sepiolite samples, shown in Figure 3, present the loss of zeolite water and a double dehydration process corresponding to the loss of coordinated and structural (OH group) water (peaks in the temperature range from (200 to 600) °C). The exothermic peak at 840 °C for SEP and at 829 °C for FeSEP is assigned to the phase transformation of sepiolite into enstatite ($MgSiO_3$). The difference between the intensity of the exothermic peaks appears because the percentage of Mg^{2+} and Si^{4+} ions in the FeSEP is lower compared to the amount in the pure sepiolite. Therefore, the broadening of the exothermic peak indicates a hindering of phase transformation because of the presence of iron oxide on the Fe-sepiolite surface.

Determination of the Point of Zero Charge of the Fe-Sepiolite. From the dependence of pH_f on pH_i (Figure 4), a value of the point of zero charge of 8.5 ± 0.1 was obtained as the pH value at which the curve plateaus, i.e., the curve inflection appears. The pH value at the plateau remains constant with changing concentration of the KNO_3 electrolyte, indicating that KNO_3 is an inert electrolyte; i.e., the specific sorption of K^+ and NO_3^- ions did not occur at the Fe-sepiolite surface. The increase of the point of zero charge compared to the pH_{pzc} of the natural sepiolite sample $(7.4 \pm 0.1)^{20}$ indicates an increase in the basicity of the sepiolite surface.

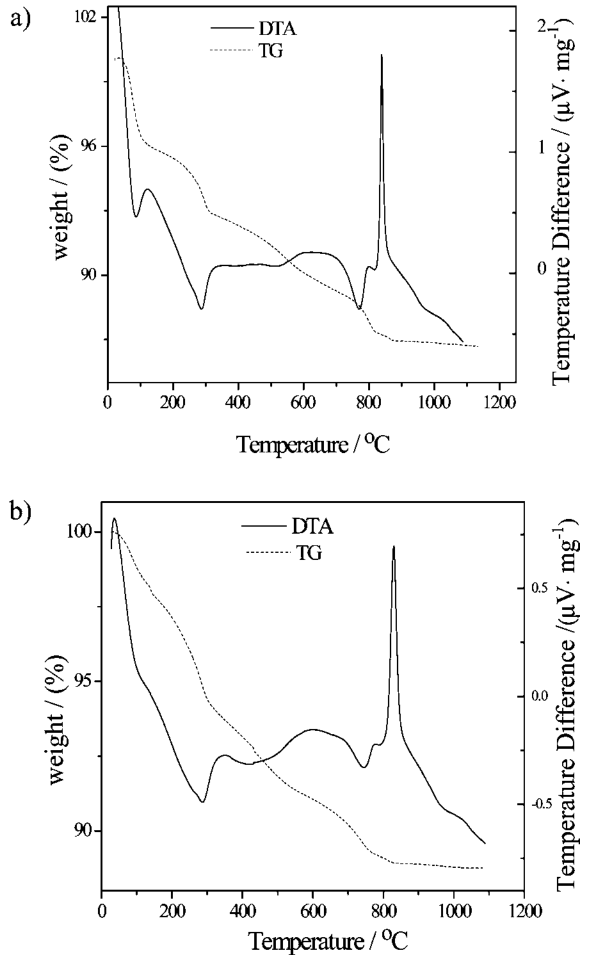

Figure 3. DTA and TGA curves of SEP (a) and FeSEP (b).

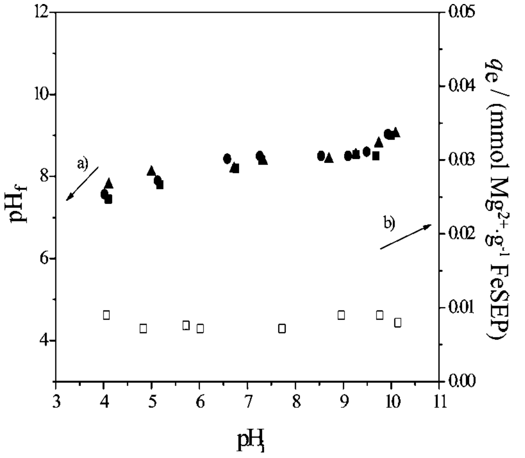

Figure 4. (a) pH_f vs pH_i during the equilibration of 0.05 g of FeSEP with 25 cm^3 of (●) 0.1 $mol\cdot dm^{-3}$ KNO_3, (■) 0.01 $mol\cdot dm^{-3}$ KNO_3, and (▲) 0.001 $mol\cdot dm^{-3}$ KNO_3. (b) Dependence of the quantity of Mg^{2+} ions released into the solution per unit mass of sepiolite on the pH_i values during the equilibration of 0.05 g of sepiolite sample with 0.01 $mol\cdot dm^{-3}$ KNO_3 solutions (□).

The dependence of the quantity of Mg^{2+} ions released into solution during the equilibration of 0.05 g of the Fe-sepiolite sample with 25 cm^3 of 0.01 $mol\cdot dm^{-3}$ KNO_3 solution is also shown in Figure 4. According to this figure, in the investigated pH range, the quantity of Mg^{2+} ions present in the solution as a result of the dissolution of Fe-sepiolite was almost constant and was equal to 0.008 $mmol\cdot(g\ of\ FeSEP)^{-1}$.

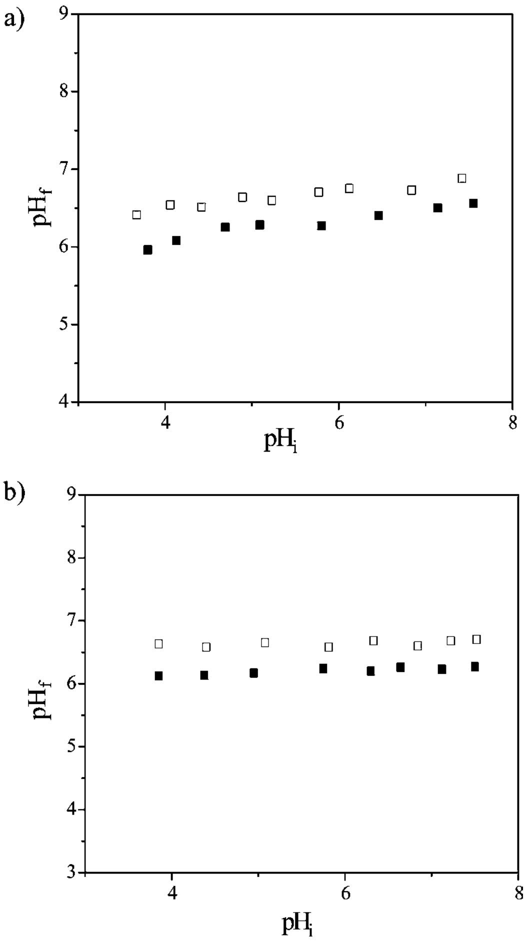

Figure 5. pH$_f$ vs pH$_i$ during the equilibration of 0.05 g of SEP (a) and FeSEP (b) with 25 cm^3 of (■) 0.01 mol·dm^{-3} Ni(NO$_3$)$_2$ and (□) 0.001 mol·dm^{-3} Ni(NO$_3$)$_2$ solutions.

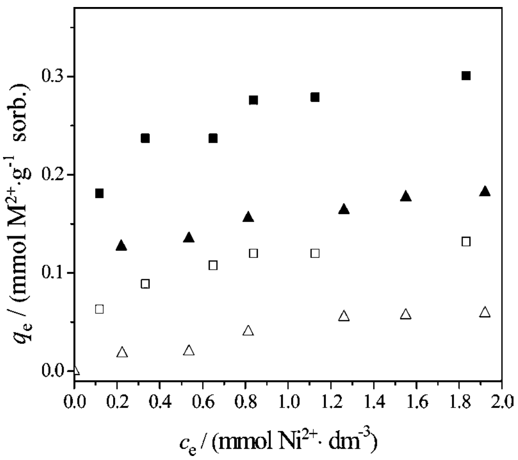

Figure 6. Sorption isotherms for Ni^{2+} ions onto SEP (▲) and FeSEP (■) and the dependences of q_e [(mmol of Mg^{2+})·(g of sorbent)$^{-1}$] on c_e [(mmol of Ni^{2+})·dm^{-3}] for SEP (△) and FeSEP (□).

A high release of Na$^+$ for Fe-sepiolite was registered, which was a result of the synthesis procedure: the material was in contact with 1 mol·dm^{-3} NaOH and FeCl$_3$ solutions for 48 h. The high concentration of Na$^+$ ions released could be because of the presence of NaCl on the system sites, which was not totally washed out and was dissolved during equilibrium and sorption. The amount of Na$^+$ ions released remained constant in the investigated pH range. The presence of Fe^{3+} in the solutions was not evident.

Sorption of Ni^{2+} onto the Sepiolites. Specific sorption of cations lowers the number of sites available for the sorption of H$^+$ ions; hence, a larger number of H$^+$ ions remain in the solution, which leads to lower pH$_{pzc}$ values.[21] This shift will be more pronounced the greater the amount of specifically adsorbed ions.

During the equilibration of sepiolites with Ni(NO$_3$)$_2$ solutions of concentrations of (0.01 and 0.001) mol·dm^{-3} (results presented in parts a and b of Figure 5 for SEP and FeSEP, respectively), the plateau position shifted toward lower pH values compared to the pH obtained under the same conditions for a KNO$_3$ solution, indicating that specific sorption of Ni^{2+} ions onto both natural sepiolite and Fe-sepiolite occurred.

The shift in the plateau position was greater for the Fe-modified sample ($\Delta pH_{SEP} = 7.4 - 6.8 = 0.6$ and $\Delta pH_{FeSEP} = 8.5 - 6.6 = 1.9$ for 0.001 mol·dm^{-3} Ni(NO$_3$)$_2$; $\Delta pH_{SEP} = 7.4 - 6.5 = 0.9$ and $\Delta pH_{FeSEP} = 8.5 - 6.2 = 2.3$ for 0.01 mol·dm^{-3} Ni(NO$_3$)$_2$. The higher affinity of the iron-modified sepiolite for specific sorption may be ascribed to the increase in the number of surface groups (SOH) available for specific sorption. The modified material, due to the presence of Fe species located on the external sites of the sepiolite, has additional −FeOH groups which interact with the Ni^{2+} ions by forming stable surface complexes.

The shift of pH$_{pzc}$ in the solutions of Ni^{2+} ions was higher when the initial concentration was 0.01 mol·dm^{-3} as a result of increased specific sorption.

The sorption isotherms as q_e [(mmol of Ni^{2+})·(g of sorbent)$^{-1}$] vs c_e [(mmol of Ni^{2+})·dm^{-3}] for SEP and FeSEP are presented in Figure 6, as are the dependences of the quantity of ion-exchangeable Mg^{2+} ions on c_e. The total amount of Mg^{2+} ions present in the solution after equilibration is the result of two processes: the ion exchange of Mg^{2+} from the sepiolite structure with Ni^{2+} ions and the dissolution of the sepiolites. Therefore, the quantity of exchangeable Mg^{2+} ions was determined as the difference between the total amount and the amount of Mg^{2+} ions released into the solution by the dissolution of the sepiolite (0.09 mmol·g^{-1} for SEP and 0.008 mmol·g^{-1} for FeSEP). The amount of Mg released in the equilibrium solutions of clay suspensions increased with increasing amount of Ni^{2+} sorbed onto the minerals as a result of ion exchange, i.e., replacement of Mg^{2+} in the edges of the octahedral layer of sepiolites with Ni^{2+} ions. According to Figure 5, the Fe-sepiolite had a higher ion exchange capacity.

The Fe-sepiolite had a higher sorption capacity than the natural sepiolite sample due to a higher specific sorption and higher ion exchange capacity.

Each sepiolite structural block is made up of two tetrahedral silica sheets and a central octahedral magnesium sheet. The silanol SiOH groups present on the external surface are more acidic than the MgOH groups and act as Lewis acid centers. Considering that deposition of Fe species on the tetrahedral silica sheets can be assumed, the presence of additional −FeOH groups increases the number of base groups on the sepiolite surface, which results in a higher specific sorption. Furthermore, the decreased crystallinity of Fe-sepiolite and increased basicity make the Mg^{2+} ions located at the edges of the internal channels of the sepiolite more available for ion exchange with Ni^{2+} ions, leading to an increase in the sorption capacity.

No Fe^{3+} ions were observed in the final solutions; however, significant amounts of Na$^+$ ions were observed in the final solutions after treatment with FeSEP, but they did not vary as a function of Ni^{2+} sorption and were similar to the amounts of this ion released into the solution as a result of the dissolution of FeSEP determined during the determination of the point of zero charge. Thus, the sorption process was not affected by the

Table 2. Sorption Parameters and Coefficients of Determination According to the Langmuir, Freundlich, and DKR Models for the Sorption of Ni^{2+} Ions onto SEP and FeSEP at 298 K

	Langmuir			Freundlich			DKR		
	$c_e/q_e = 1/K_Lq_m + c_e/q_m$			$\ln q_e = \ln K_f + (1/n) \ln c_e$			$\ln q_e = \ln q_m - \beta\varepsilon^2$, where $\varepsilon = RT \ln(1 + 1/c_e)$		
	K_L	q_m		K_f			q_m	β	
	$dm^3 \cdot mmol^{-1}$	$mmol \cdot g^{-1}$	R^2	$mmol^{1-1/n} \cdot dm^{3/n} \cdot g^{-1}$	n	R^2	$mmol \cdot g^{-1}$	$mol^2 \cdot J^{-2}$	R^2
SEP	4.14	0.210	0.992	0.163	5.26	0.940	0.181	$2.45 \cdot 10^{-8}$	0.752
FeSEP	7.49	0.317	0.994	0.273	5.55	0.941	0.286	$1.50 \cdot 10^{-8}$	0.897

presence of Na^+ ions in the new solid system, and the retention of Ni^{2+} ions by the two examined sorbents occurred by the ion exchange process with the release of sepiolite Mg^{2+} ions and by the process of specific sorption, i.e., inner-sphere complexation of Ni^{2+} on the functional groups on the broken edges of the mineral and subsequent release of H^+.

Equilibrium Data Modeling. The sorption data obtained for equilibrium conditions were analyzed using the linear forms of the Langmuir, Freundlich,[26,27] and DKR models (Table 2). The sorption parameters are as follows: q_m is the maximum sorption capacity ($mmol \cdot g^{-1}$), K_L is the Langmuir constant related to the energy of sorption ($dm^3 \cdot mmol^{-1}$), K_f and n are Freundlich constants related to the sorption ($mmol^{1-1/n} \cdot dm^{3/n} \cdot g^{-1}$) capacity and intensity (dimensionless), β ($mol^2 \cdot J^{-2}$) is the DKR activity coefficient related to the sorption energy, and ε is the Polanyi potential. Graphical illustrations of the linear data fitting for the SEP and FeSEP are given in Figures 7, 8, and 9 for the Langmuir, Freundlich, and DKR models, respectively.

According to the results presented in Table 2, the Langmuir isotherm equation represents the sorption process very well; the R^2 values were all higher than 0.99, indicating a very good mathematical fit. Furthermore, the Langmuir constants related to the maximum sorption capacity, q_m, were close to the value obtained from the q_e–c_e dependence. The fact that the Langmuir isotherm fitted the experimental data very well indicates monolayer coverage by Ni^{2+} ions of the SEP and FeSEP and a homogeneous distribution of the active sites on the surface of the sepiolites.

The characteristics of the Langmuir isotherm can be used to predict the affinity between the sorbate and sorbent using the separation factor or dimensionless equilibrium parameter, R_L, expressed as

$$R_L = \frac{1}{1 + K_L c_o} \tag{1}$$

where c_o ($mol \cdot dm^{-3}$) is the initial metal ion concentration.

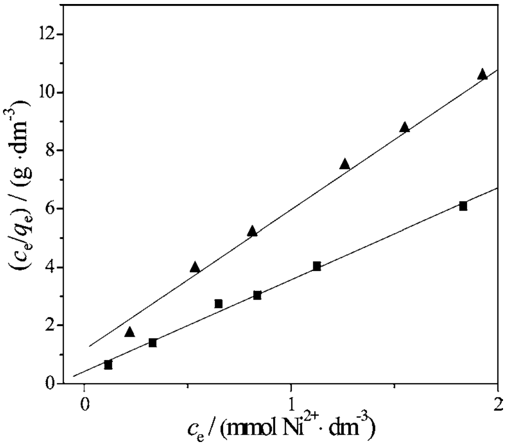

Figure 7. Experimental data fitting for Ni^{2+} sorption onto SEP (▲) and FeSEP (■) using the linear form of the Langmuir isotherm.

The R_L value indicates that the sorption process is unfavorable when $R_L > 1$, linear when $R_L = 1$, favorable when $0 < R_L < 1$, or irreversible when $R_L = 0$.

The calculated R_L values for initial metal ion concentrations of Ni^{2+} ions in the range of (10^{-4} to 10^{-2}) $mol \cdot dm^{-3}$ were between 0.321 and 0.095 for SEP and 0.213 and 0.052 for FeSEP, which indicates that the sorption of Ni^{2+} ions onto both sepiolite samples was favorable.

Effect of the Contact Time. The effects of the contact time on the amount of Ni^{2+} sorbed onto natural sepiolite and sepiolite modified with iron are shown in Figure 10. It can be seen that the removal of Ni^{2+} ions using sepiolites as sorbents is a two-step process. Nickel sorption on the minerals was initially rapid and then continued slowly until a pseudo-equilibrium condition was reached. The initial faster metal ion uptake may be explained by the high number of active sites available on the sepiolite surface. Thereafter, a slower increase of the amount of cation sorbed can be observed in the second stage, due to

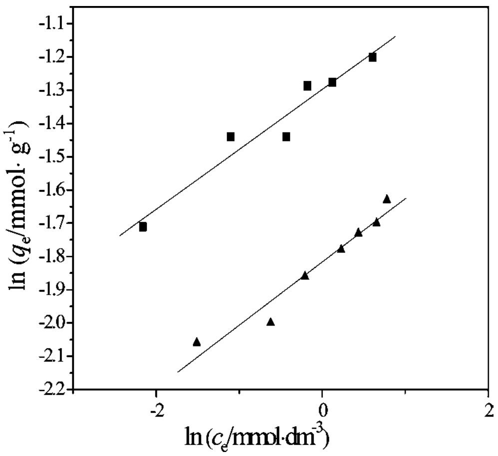

Figure 8. Experimental data fitting for Ni^{2+} sorption onto SEP (▲) and FeSEP (■) using the linear form of the Freundlich isotherm.

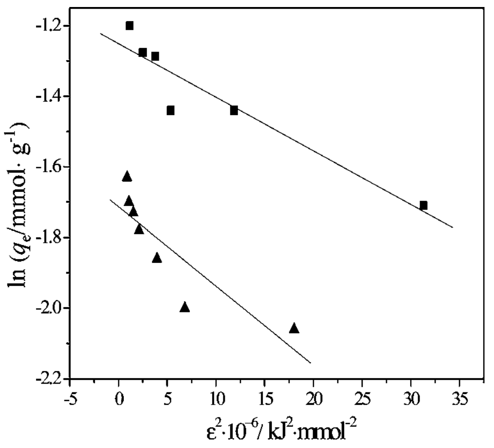

Figure 9. Experimental data fitting onto SEP (▲) and FeSEP (■) using the linear form of the DKR isotherm.

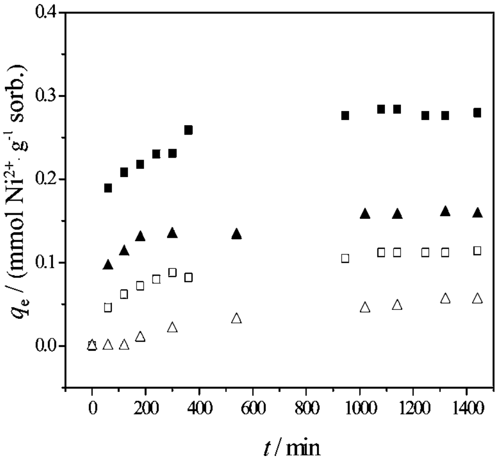

Figure 10. Effect of the contact time on the amounts of Ni^{2+} sorbed onto SEP (▲) and FeSEP (■) and Mg^{2+} ion exchanged (initial ion concentration of 100 mg·dm^{-3} at a temperature of 298 K and pH of 5.6 ± 0.1) for SEP (△) and FeSEP (□).

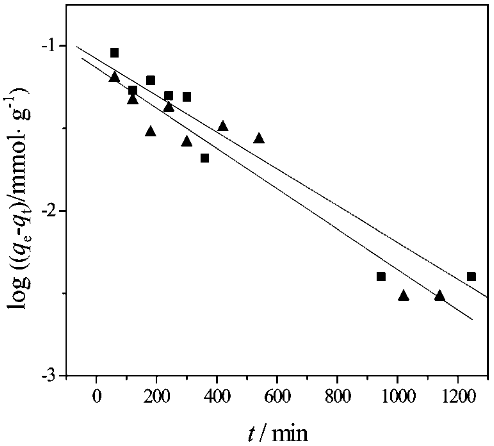

Figure 11. Linear fitting of the kinetic data for Ni^{2+} sorption onto SEP (▲) and FeSEP (■) by the pseudo-first-order kinetic model.

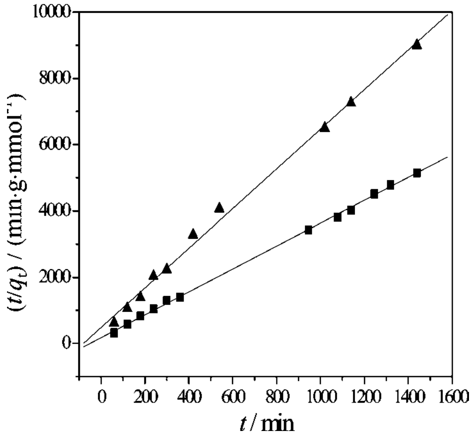

Figure 12. Linear fitting of the kinetic data for Ni^{2+} sorption onto SEP (▲) and FeSEP (■) by the pseudo-second-order kinetic model.

the gradual occupancy of the active sites and a decrease of the metal ion concentrations in the solutions; thus, the sorption became less efficient.

In addition to Ni^{2+} sorption, the quantity of Mg^{2+} ions released into the solution as a result of the ion exchange process was also examined (Figure 10). The obtained data confirmed that the affinity for ion exchange with Ni^{2+} ions was higher for FeSEP than for SEP.

Kinetic Modeling. To investigate the mechanism of sorption and the potential rate-controlling steps, the two most widely applied kinetic models were used to fit the experimental data: the pseudo-first-order equation proposed by Lagergren[28] and the pseudo-second-order kinetic model proposed by Ho and McKay.[29] The linear forms of the pseudo-first-order and pseudo-second-order equations are given by the following equations, respectively:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \qquad (3)$$

where t (min) is the contact time, q_e and q_t (mmol·g^{-1}) are the amounts of sorbed Ni^{2+} at equilibrium and time t, and k_1 (min^{-1}) and k_2 (g·mmol^{-1}·min^{-1}) are the rate constants of the pseudo-first-order and pseudo-second-order kinetics, respectively.

The initial sorption rate, h (mmol·g^{-1}·min^{-1}), can be obtained using the calculated values of the pseudo-second-order rate constant and the equilibrium sorbed amounts employing the following expression:

$$h = k_2 {q_e}^2 \qquad (4)$$

The pseudo-first-order and pseudo-second-order models for the sorption of Ni^{2+} onto SEP and FeSEP are shown in Figures 11 and 12, respectively. On the basis of the above two kinetic models, the obtained parameters for the sorption kinetics are given in Table 3.

It can be concluded that 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. According to the literature, the pseudo-second-order kinetic model includes different sorption mechanisms, such as surface complexation, ion exchange, etc. The model is based on the assumption that the rate-limiting step may be chemical sorption or chemisorption involving valence forces through the sharing or exchange of electrons between the sorbent and sorbate and that the sorption rate depends on the concentration of sorbate at the sorbent surface.[29,30] As the correlation coefficients are very high (Table 3), it may also be assumed that sorption of Ni^{2+} ions onto sepiolites occurred through chemisorption, which confirms that the main mechanisms of sorption onto the sepiolite samples are specific sorption and ion exchange of Mg^{2+} from the sepiolite structure with Ni^{2+} ions from the solutions.

Effect of the Temperature. The sorption isotherms for Ni^{2+} sorption onto SEP and FeSEP at different temperatures are shown in Figures 13 and 14, respectively. The quantity of sorbed ions increased with increasing temperature. This indicates that a higher temperature favors metal ion removal by sepiolites, i.e., that the sorption of Ni^{2+} ions onto sepiolites is an endothermic process. The increase of sorption with increasing temperature may be attributed to either an increase in the number of active surface sites on the sorbent surface or the desolvation of the sorbing species and a decrease in the thickness of the boundary layer surrounding the sorbent, so that the mass transfer resistance of the sorbate in the boundary layer decreases.[31]

Thermodynamics of Sorption. To investigate the effect of the temperature on the sorption of Ni^{2+} ions onto sepiolites,

Table 3. Kinetic Parameters for Ni^{2+} Sorption onto SEP and FeSEP

	pseudo-first-order			pseudo-second-order			
	k_1	q_e		k_2	q_e		h
sample	min^{-1}	$mmol \cdot g^{-1}$	R^2	$g \cdot mmol^{-1} \cdot min^{-1}$	$mmol \cdot g^{-1}$	R^2	$mmol \cdot g^{-1} \cdot min^{-1}$
SEP	0.00281	0.074	0.929	0.092	0.166	0.997	0.0025
FeSEP	0.00433	0.124	0.917	0.069	0.290	0.999	0.0058

the distribution coefficient, K_d, was calculated at temperatures of (298, 318, 328, and 338) K using the equation:

$$K_d = \frac{q_e}{c_e} \tag{5}$$

The thermodynamic parameters, the enthalpy change (ΔH^o), the entropy change (ΔS^o), and the Gibbs energy change (ΔG^o), were calculated using the following equations:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{6}$$

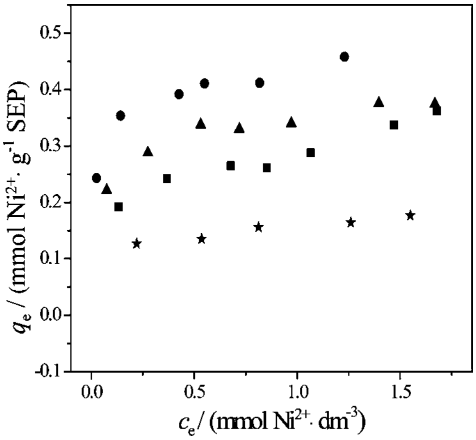

Figure 13. Sorption isotherms of Ni^{2+} ions onto SEP at 298 K (★), 318 K (■), 328 K (▲), and 338 K (●).

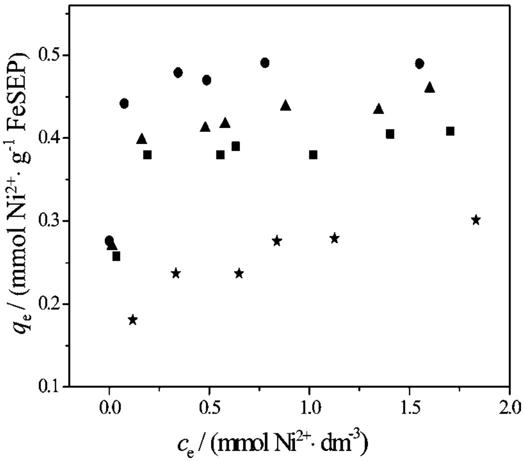

Figure 14. Sorption isotherms of Ni^{2+} ions onto FeSEP at 298 K (★), 318 K (■), 328 K (▲), and 338 K (●).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

By plotting $\ln K_d$ vs $1/T$, the enthalpy change (ΔH°) and the entropy change (ΔS°) were determined graphically from the slope and intercept of the straight line, respectively (Figure 15). The values of the obtained thermodynamic parameters are presented in Table 4.

The positive enthalpy change indicates that the process of removal of Ni^{2+} ions from solution by sepiolites was endothermic. The Gibbs energy values are small and positive and decrease with increasing temperature. This indicates that the sorption is more efficient at higher temperatures and that the reaction requires a small amount of energy. The ΔG° values would become negative if the solution temperature became higher than 338 K. This indicates the presence of an energy barrier in the sorption process.[32] Considering the positive values of ΔG°, it has been suggested that this is quite common for the sorption of metal ions by the ion exchange mechanism, because an activated complex of a metal ion is formed with the sorbent in the excited state.[33]

A positive value of the entropy change may be explained by structural changes in both the sorbates and sorbents during the sorption process.[3,34] According to some authors, positive values of ΔS° indicate an increase in randomness at the solid/liquid interface during the sorption of metal ions by clays.[35]

Desorption. The results of desorption of sorbed Ni^{2+} from SEP and FeSEP are presented in Table 5.

Desorption of Ni^{2+} from the metal-sorbed sepiolites using demineralized water was negligible. In the case of acid (0.001

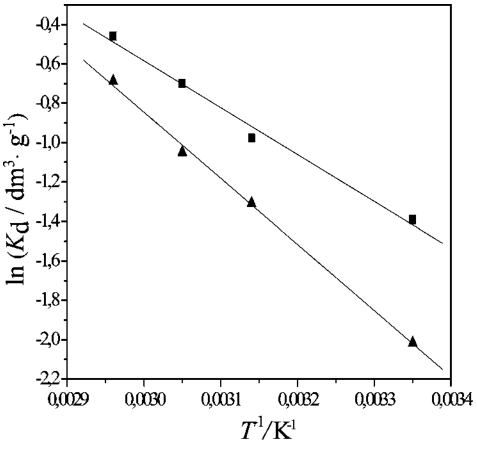

Figure 15. Effect of the temperature on the distribution coefficients of Ni^{2+} sorption onto SEP (▲) and FeSEP (■).

Table 4. Thermodynamic Parameters of the Sorption of Ni^{2+} Ions by SEP and FeSEP

	ΔH°	ΔS°	ΔG°			
			$kJ \cdot mol^{-1}$			
sample	$kJ \cdot mol^{-1}$	$J \cdot mol^{-1} \cdot K^{-1}$	298 K	318 K	328 K	338 K
SEP	27.93	76.75	5.05	3.51	2.74	1.98
FeSEP	19.81	54.60	3.53	2.44	1.89	1.35

Table 5. Ni^{2+} Desorption from SEP and FeSEP

	initial concn of Ni^{2+}	sorption	percentage of desorption	
sorbent	$mg \cdot dm^{-3}$	$mg \cdot g^{-1}$	$0.001\ mol \cdot dm^{-3}\ HNO_3$	demineralized water
SEP	28.20	8.050	26.46	< 0.25
	52.00	9.500	27.56	< 0.21
	72.10	10.05	31.34	< 0.20
	78.20	10.06	31.35	< 0.20
	95.40	10.07	33.27	< 0.20
	120.0	10.08	34.58	< 0.20
	130.0	10.08	34.70	< 0.20
FeSEP	28.20	12.18	32.40	< 0.16
	52.00	15.85	32.80	< 0.12
	72.10	17.10	34.10	< 0.12
	78.20	17.10	34.10	< 0.12
	95.40	17.20	34.33	< 0.11
	120.0	17.50	34.52	< 0.11
	130.0	18.30	34.83	< 0.11

$mol \cdot dm^{-3}\ HNO_3$) the removal of Ni^{2+} sorbed depends on the amount of metal cation previously sorbed, and the percentage of Ni^{2+} released was from (26.46 to 34.70) % for natural sepiolite and from (32.40 to 34.83) % for FeSEP. The amount of the metal desorbed would probably be higher if a stronger acid (0.1 $mol \cdot dm^{-3}\ HNO_3$ or 0.1 $mol \cdot dm^{-3}$ HCl) was used as the extractant. Decreasing the pH value of the solution to below pH 3 leads to dissolution of sepiolite, i.e., an increase of the quantity of Mg^{2+} ions in the solution. Hence, the number of MgOH groups, as main centers for specific sorption, and the number of Mg^{2+} ions available for ion exchange with M^{2+} ions would be lower, and the crystallinity and surface properties of the sorbents would be changed.[20] Considering this, the experiments were not performed with a stronger acid.

Conclusions

The sorption capacity of sepiolite suggests that this mineral, as a natural, low-cost sorbent, can be successfully employed for the removal of Ni^{2+} ions from highly polluted waters. Modification of natural sepiolite by iron resulted in the formation of a sorbent with a noticeably larger Ni^{2+} sorption capacity than the natural sepiolite.

Specific sorption, i.e., surface complexation, and ion exchange with Mg^{2+} are the main mechanisms of sorption of Ni^{2+} ions onto sepiolites. The increase in the content of Mg^{2+} released to equilibrium conditions with increasing amount of Ni^{2+} sorbed supported the suggestion of Mg^{2+} substitution on the edges of the octahedral sheet by Ni^{2+} ions. Specific sorption of Ni^{2+} on surface functional groups of the clay minerals was confirmed by shifts of the pH_{pzc} toward lower pH values, proportional to the quantity of the specifically sorbed ions.

XRD, FTIR, and DTA/TGA spectra confirmed that the modified material maintained the basic structure of sepiolite. The presence of new crystalline Fe phases was not observed, indicating that an amorphous Fe species was formed.

The experimental equilibrium data obtained at 298 K, for both sepiolite samples, correlated well with the Langmuir adsorption isotherm. The sorption kinetic study showed that the pseudo-second-order model best described the experimental data, indicating that the sorption may be controlled by chemical sorption.

Thermodynamic analysis showed that the process of Ni^{2+} sorption onto sepiolites was endothermic. The small and positive $\Delta G°$ values suggest that the sorption process requires a small amount of energy.

The amount desorbed from sepiolites by demineralized water was negligible, whereas desorption by acid (0.001 $mol \cdot dm^{-3}\ HNO_3$) was around 34 % of the sorbed nickel.

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