

## Removal of Co<sup>2+</sup> ions from aqueous solutions using iron-functionalized sepiolite

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### ABSTRACT

The efficiency of iron-functionalized sepiolite for the removal of Co<sup>2+</sup> ions from aqueous solutions was determined under different experimental conditions, using the batch method. The ionization constants of the surface functional groups of the sepiolite–iron system, determined from potentiometric titration data, were  $pK_{a1}^{int} = 6.7 \pm 0.1$  and  $pK_{a2}^{int} = 10.2 \pm 0.1$ . The sorption experiments were performed as a function of initial metal concentration, initial pH value, and the equilibration time. The equilibrium process was well described by the Langmuir isotherm model. The pseudo-second order kinetic model provides the best correlation of the experimental kinetic data. The iron–sepiolite system had a noticeably higher Co<sup>2+</sup> sorption capacity than the natural sepiolite sample as a result of higher specific sorption and a higher ion exchange capacity.

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### 1. Introduction

The growth of human population, urbanization and industries, including metallurgy, tannery, mining, battery-production, the manufacture of insecticides, fungicides, paints and coatings, etc., contribute to environmental contamination by hazardous metals, which is of very serious environmental concern for all living organisms, especially for humans. Heavy metal ions, such as cobalt, accumulated through the food chain; even at low concentrations, have damaging effects on human health. Cobalt has many toxic effects such as imparting neurotoxicological disorder, genotoxicity, carcinogenicity, cardiomyopathy and bronchial asthma [1].

The application of various types of clays, as low-cost adsorbents, for the control of environmental pollution in terms of heavy metals removal from aqueous media is currently of great interest. The employment of clay minerals, such as kaolinite [2,3], vermiculite [4], montmorillonite [5], bentonite [6] and sepiolite [7,8] has recently received increasing attention because they have shown high sorption capacities and are abundant in nature, inexpensive and environmental friendly. Chemical modifications on the surface of the clays with acids, bases, cationic surfactants, and metal oxides were also studied in order to improve their sorption capacity.

Sepiolite is a hydrous magnesium silicate (Si<sub>12</sub>O<sub>30</sub>Mg<sub>8</sub>(OH)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>·8H<sub>2</sub>O) characterized by its fibrous

morphology. It 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.

Due to its sorptive, rheological and catalytic properties, sepiolite is widely used in a variety of industrial applications. Sepiolite is applied as an effective and economical sorbent material in many fields of sorption technology, including interactions with amines [9], uptake of ammonium ions [10], access of cationic dye to the structural micropores [11], sorption of cationic surfactants [12] and heavy metal ions from wastewaters [13].

Recently, a low cost iron–sepiolite system was synthesized, characterized, and tested for its effectiveness in the removal of Ni<sup>2+</sup> from aqueous solutions [14]. The experimental results obtained revealed that the iron–sepiolite system has a noticeably higher Ni<sup>2+</sup> sorption capacity than the natural sepiolite sample.

In the following, the objective was to quantify the ability of a sepiolite–iron oxide sample to remove Co<sup>2+</sup> ions from aqueous solutions and to compare it with the affinity of the natural sepiolite sample. The influence of the initial solution pH, and equilibrium time on the amount of Co<sup>2+</sup> ions sorbed on the Fe–sepiolite and the capability of the Langmuir, Freundlich and Dubinin–Kaganer–Radushkevich (DKR) isotherm models to fit the experimental sorption data were also investigated. The sorption was studied based on shifts in the point of zero charge, determination of sorption isotherms and the correlation between quantity of Mg<sup>2+</sup> ions released and the amount of Co<sup>2+</sup> ions sorbed, with the aim of determining the dominant mechanism of the interaction of

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these ions in an aqueous medium with the Fe–sepiolite. The point of zero charge ( $\text{pH}_{\text{pzc}}$ ), surface charge, and ionization constants were determined as very important parameters of the acid–base characteristics of the surface functional groups and their interactions with ions from aqueous solutions.

## 2. Experimental

### 2.1. Materials

The Fe–sepiolite (Fe–SEP) was prepared by mixing 20.0 g of sepiolite, 200 cm<sup>3</sup> of freshly prepared 0.5 mol dm<sup>-3</sup> FeCl<sub>3</sub> and 360 cm<sup>3</sup> of 1 mol dm<sup>-3</sup> NaOH solution according to a previously described method [14].

The chemical composition, differential thermal analyses (DTA), X-ray diffraction, and FTIR analyses of the sample were reported previously [14].

Nitrogen adsorption–desorption isotherms were determined using a Thermo Finnigan/Sorptomatic 1990 instrument. Before the sorption measurement, the Fe–sepiolite sample was degassed at 150 °C for 18 h under reduced pressure (<1 torr). Various models and the appropriate software, *i.e.*, ADP Version 5.1 Thermo Electron, were used to analyze the obtained isotherms at –196 °C. The specific surface area of samples ( $S_{\text{BET}}$ ) was calculated according to the Brunauer, Emmett, Teller (BET) method from the linear part of the nitrogen adsorption isotherms [15]. The total pore volume ( $V_{\text{tot}}$ ) was given at  $p/p_0 = 0.998$ . The volume of the mesopores and pore size distribution was calculated according to the Barrett, Joyner and Halenda method from the desorption branch of isotherm [16]. The micropores were analyzed using the Dubinin–Radushkevich method [17].

### 2.2. Determination of Fe–sepiolite surface charge density

Surface charge density of the Fe–sepiolite was determined by potentiometric titration [18,19].

Two series of experiments were performed. In the first series, the titrations were performed in the pH range from  $\text{pH}_{\text{pzc}}$  (point of zero charge) to  $\text{pH} \approx 5$ . A 0.1 mol dm<sup>-3</sup> HNO<sub>3</sub> solution was used as the titrant. The titrations were performed in KNO<sub>3</sub> solutions of different concentrations (0.001, 0.01, and 0.1 mol dm<sup>-3</sup>). Suspensions were obtained by mixing 0.2 g of Fe–sepiolite in 200 cm<sup>3</sup> of the required KNO<sub>3</sub> solution. Solutions of the same concentrations, but without powder, were used as the blanks. Titrations were performed in PVC beakers at room temperature. During the titration, nitrogen was introduced into the solution to prevent CO<sub>2</sub> absorption from the air and change in pH. The samples were stirred on a magnetic stirrer. A dose of titrant was added successively every 5 min and pH values were recorded.

In the second series of experiments, titrations were performed in the pH range from  $\text{pH}_{\text{pzc}}$  to  $\text{pH} \approx 11$  by the addition of a 0.1 mol dm<sup>-3</sup> KOH solution. Again, three titrations were performed in solutions of different KNO<sub>3</sub> concentrations ( $c_{\text{KNO}_3} = 0.001, 0.01$  and  $0.1$  mol dm<sup>-3</sup>) containing a suspension with Fe–sepiolite. Blanks were titrated for each of these KNO<sub>3</sub> concentrations.

All experiments were repeated two times.

Based on these results, potentiometric curves, pH values of the suspension/blank versus the titrant volume, were obtained for each concentration of KNO<sub>3</sub>.

Using the potentiometric titration results, the surface charge density,  $\sigma_o$ , can be calculated by the following equation [20]:

$$\sigma_o = \frac{100 \cdot \Delta V \cdot c \cdot F}{S \cdot m} \quad (\mu\text{C cm}^{-2}) \quad (1)$$

where  $\Delta V$  is the difference in titrant volumes of the suspension and the blank at the given pH value (dm<sup>3</sup>),  $c$  is the concentration

of the titrant used (mol dm<sup>-3</sup>),  $F$  is the Faraday constant, 96,500 (C mol<sup>-1</sup>),  $S$  is the specific surface area of the sepiolite (m<sup>2</sup> g<sup>-1</sup>) and  $m$  is mass of sepiolite in the suspension (g).

In this way, the dependences of the surface charge density on pH and electrolyte concentration were obtained.

### 2.3. Determination of ionization constants of the surface groups

Following the approach of some authors [21,22], the association–dissociation reactions of the surface functional groups of the Fe–sepiolite (S–OH) can be written as:



Eq. (2) represents the association of a proton with one surface site and relates to the pH range below the point of zero charge, whereas Eq. (3) represents the dissociation of one surface group (or adsorption of OH<sup>-</sup> ions) and relates to the pH range above  $\text{pH}_{\text{pzc}}$ . In the preceding equation, SOH<sub>2</sub><sup>+</sup>, SOH and SO<sup>-</sup> denote positive, neutral and negative sites on the sepiolite surface, respectively.

The intrinsic ionization constants,  $K_{a_1}^{\text{int}}$  and  $K_{a_2}^{\text{int}}$ , can be calculated using Eqs. (4) and (5):

$$\text{p}K_{a_1}^{\text{int}} = \text{pH} + \log \left[ \frac{\alpha_+}{1 - \alpha_+} \right] + e \frac{\Psi_o}{2.3kT} = \text{p}Q_{a_1} + e \frac{\Psi_o}{2.3kT} \quad (4)$$

$$\text{p}K_{a_2}^{\text{int}} = \text{pH} - \log \left[ \frac{\alpha_-}{1 - \alpha_-} \right] + e \frac{\Psi_o}{2.3kT} = \text{p}Q_{a_2} + e \frac{\Psi_o}{2.3kT} \quad (5)$$

where  $\alpha_+$  and  $\alpha_-$  denote the fractions of the charge sites,  $\Psi_o$  is the mean potential in the surface charge plane,  $k$  is the Boltzmann constant,  $Q_{a_1}$  and  $Q_{a_2}$  are apparent acidity and basicity quotient evaluated from bulk solution concentration.

The double-extrapolation technique proposed by James [23,24] was used to calculate  $\text{p}K_{a_1}^{\text{int}}$  whereas  $\text{p}K_{a_2}^{\text{int}}$ , was determined applying a single extrapolation procedure [25].

Since  $\sigma_o = 0$  at  $\text{pH}_{\text{pzc}}$ , the concentrations of SOH<sub>2</sub><sup>+</sup> and SO<sup>-</sup> are equal and Eqs. (2) and (3) can be used to express  $\text{pH}_{\text{pzc}}$  in terms of  $K_{a_1}^{\text{int}}$  and  $K_{a_2}^{\text{int}}$  alone:

$$\text{pH}_{\text{pzc}} = 0.5(\text{p}K_{a_1}^{\text{int}} + \text{p}K_{a_2}^{\text{int}}) \quad (6)$$

### 2.4. Sorption procedure

The batch equilibration method was used to investigate the removal of Co<sup>2+</sup> ions by Fe–sepiolite samples [26]. The sorption was studied based on the shift of the point of zero charge, determination of the sorption isotherms and the correlation between the quantity of Mg<sup>2+</sup> ions released from, and the quantity of Co<sup>2+</sup> ions sorbed onto the Fe–sepiolite sample. The experiments were performed using solutions of Co(NO<sub>3</sub>)<sub>2</sub> in millipore water.

The shift in the point of zero charge was investigated using 0.01 and 0.001 mol dm<sup>-3</sup> solutions of Co(NO<sub>3</sub>)<sub>2</sub> at different initial pH values by the batch method [26]. The measurements were performed using 25 cm<sup>3</sup> of metal ion solutions in poly(vinyl chloride) (PVC) vessels. The initial pH value ( $\text{pH}_i$ ) of the electrolytes was adjusted by the addition of small volumes of a 0.1 mol dm<sup>-3</sup> HCl or KOH solution. Then, 0.050 g of sepiolite was added to each sample. Equilibration was attained by shaking for 24 h in a water bath thermostated at 298 K. The dispersions were then filtered and the final pH of the solutions ( $\text{pH}_f$ ) was determined. From the dependences  $\text{pH}_f$  versus  $\text{pH}_i$ , the value of the point of zero charge was obtained as the pH value at which the plateau of the curve, *i.e.*, the inflexion point of the curve, appeared.

The sorption of Co<sup>2+</sup> ions was examined in the pH range from  $\approx 4$  to  $\approx 7.5$ , in order to avoid ion hydrolysis at higher pH values and the dissolution of the Fe–sepiolite at lower pH values.

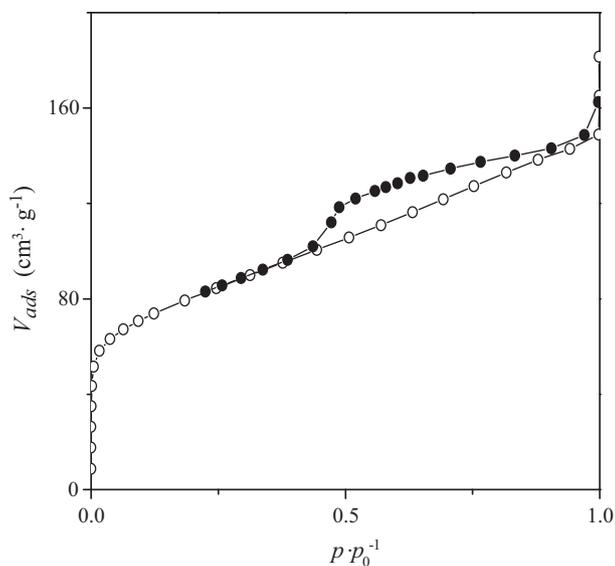


Fig. 1. Nitrogen adsorption (○) and desorption (●) isotherms of the Fe-sepiolite.

The concentrations of  $\text{Co}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{Fe}^{3+}$  ions in the solutions after equilibration with  $0.001 \text{ mol dm}^{-3}$  solutions of  $\text{Co}(\text{NO}_3)_2$  were measured by atomic absorption spectroscopy, AAS (Perkin Elmer 730). The quantity of sorbed  $\text{Co}^{2+}$  ions was calculated in order to determine the effect of initial pH value on the sorption process.

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

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

### 3. Results and discussion

#### 3.1. Textural properties of Fe-sepiolite

Nitrogen adsorption-desorption isotherms on Fe-sepiolite are presented in Fig. 1. The measured BET surface area, volume of mesopores and micropores, the overall pore volume and  $D_{\text{max}}$ , the pore size at which density of pore size distribution achieve its maximum, and  $D$ , the average pore diameter, are presented in Table 1. It could be noticed from the data given in Table 1 and data obtained for a natural sepiolite sample [27] that modification of the sepiolite with iron caused negligible changes in the specific surface area, total pore volume and micropore volume, i.e., the sepiolite structure and high porosity were retained. The value of  $D_{\text{max}}$  is very similar to that of  $D$ , which means that the diameters of all pores are equally distributed around  $D_{\text{max}}$ .

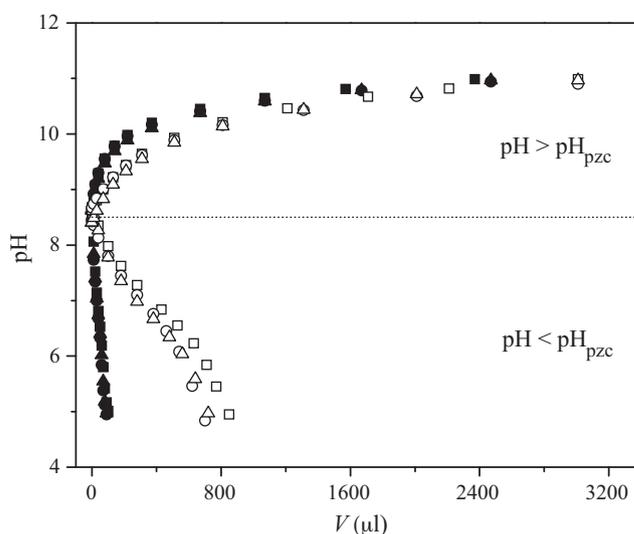


Fig. 2. Potentiometric titration curves for Fe-SEP in  $\text{KNO}_3$  solutions of different concentrations: (■)  $0.1 \text{ M KNO}_3$ , (●)  $0.01 \text{ M KNO}_3$ , (▲)  $0.001 \text{ M KNO}_3$ , (□)  $0.1 \text{ M KNO}_3 + \text{Fe-SEP}$ , (○)  $0.01 \text{ M KNO}_3 + \text{Fe-SEP}$ , (△)  $0.001 \text{ M KNO}_3 + \text{Fe-SEP}$ .

#### 3.2. Surface charge density and ionization constants of the surface functional groups of the Fe-sepiolite

Potentiometric curves and surface charge densities of the Fe-SEP as a function of pH above and below  $\text{pH}_{\text{pzc}}$  in  $\text{KNO}_3$  solutions of different concentrations are presented in Figs. 2–4, respectively. The value of  $\Delta V$  in the region  $\text{pH} < \text{pH}_{\text{pzc}}$  increased with increasing concentration of the  $\text{KNO}_3$  solution, while the value of  $\Delta V$  in the region  $\text{pH} > \text{pH}_{\text{pzc}}$  was constant for the different concentrations of the  $\text{KNO}_3$  solutions. These constant values of  $\Delta V$  resulted in the values for  $\sigma_0$  for the different  $\text{KNO}_3$  concentrations (Fig. 3) being constant. The surface charge density for the Fe-SEP in the region  $\text{pH} > \text{pH}_{\text{pzc}}$  did not depend on the concentration of the  $\text{KNO}_3$  solution, but only on the pH.

The intrinsic surface ionization constants,  $K_{a_1}^{\text{int}}$  and  $K_{a_2}^{\text{int}}$  for the Fe-SEP were calculated using Eqs. (4) and (5). The degrees of surface ionization,  $\alpha_+$  and  $\alpha_-$ , were determined as the ratio between the calculated surface charge density for a given concentration of the electrolyte solution (and pH value) and the maximum surface charge density. The assumed maximum surface charge density

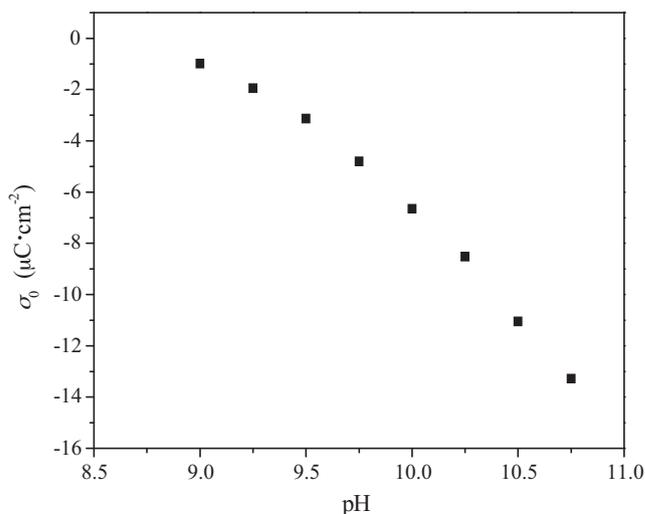
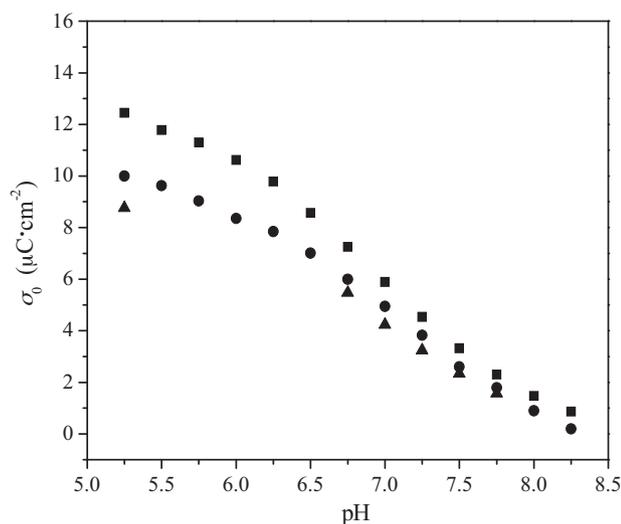


Fig. 3. Surface charge density of Fe-SEP as a function of pH (■) ( $\text{pH} > \text{pH}_{\text{pzc}}$ ).

**Table 1**

The textural properties of the Fe–sepiolite.

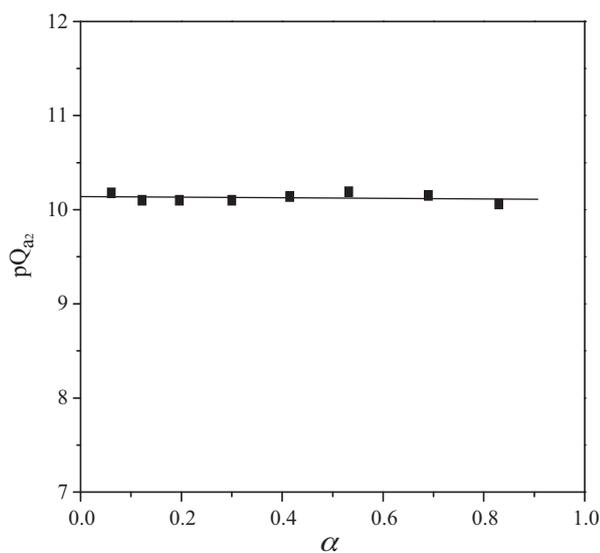
Sample	$S_{BET}$ ( $m^2 g^{-1}$ )	$V_{pore,total}$ ( $cm^3 g^{-1}$ )	$V_{micro,pore}$ ( $cm^3 g^{-1}$ )	$V_{meso,pore}$ ( $cm^3 g^{-1}$ )	$D_{max}$ (nm)	$D$ (nm)
Fe–SEP	285.6	0.227	0.111	0.1589	3.678	3.694

**Fig. 4.** Surface charge density of Fe–SEP as a function of pH ( $pH < pH_{pzc}$ ) for different  $KNO_3$  concentrations: (■)  $0.1 \text{ mol dm}^{-3}$ , (●)  $0.01 \text{ mol dm}^{-3}$  and (▲)  $0.001 \text{ mol dm}^{-3}$ .

for Fe–SEP was  $16 \mu\text{C cm}^{-2}$ , corresponding to a surface functional group density of  $1 \text{ group nm}^{-2}$  [20].

The intrinsic ionization constant of the surface functional groups of Fe–SEP,  $pK_{a_2}^{int}$ , was determined to be  $10.2 \pm 0.1$  from the dependence of  $pQ_{a_2}$  on  $\alpha_-$  (Fig. 5) applying a single extrapolation procedure [25]. The intrinsic ionization constant  $pK_{a_1}^{int}$  was determined from the dependence of  $pQ_{a_1}$  on  $\alpha_+ + c(KNO_3)^{1/2}$  (Fig. 6) applying the double extrapolation technique [23,24]. The experimental data were extrapolated to  $\alpha_- = 0$  and  $c_{KNO_3} = 0$ . The two extrapolation routes led to the same values of  $pK_{a_1}^{int} = 6.7 \pm 0.1$ .

From the values the ionization constants  $pK_{a_2}^{int}$  and  $pK_{a_1}^{int}$  obtained using Eq. (6), a value of the point of zero charge  $pH_{pzc}$  of  $8.45 \pm 0.1$  was calculated. This value is in excellent agreement with

**Fig. 5.** Dependence of  $pQ_{a_2}$  on  $\alpha_-$  (■) and the single extrapolation procedure.

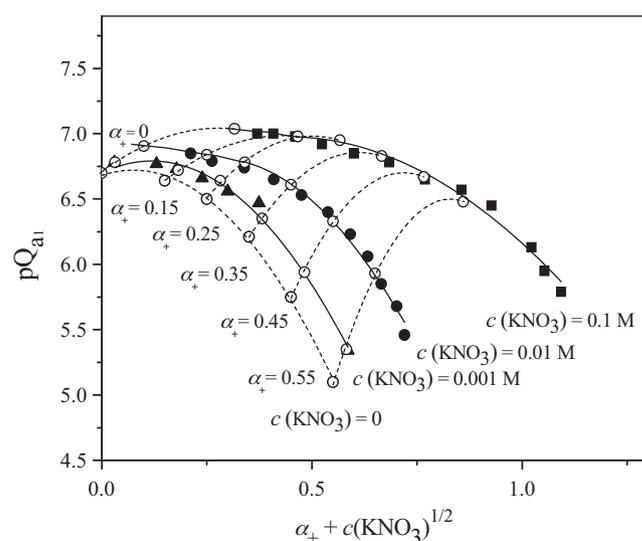
the value of  $pH_{pzc}$  determined for Fe–SEP using the batch method [14].

The relative acidity of the surface functional groups can be expressed by  $\Delta pK^{int} = pK_{a_2}^{int} - pK_{a_1}^{int}$ . The  $\Delta pK^{int}$  value for the Fe-modified sepiolite sample was  $3.5 \pm 0.1$ , which is higher than that for natural sepiolite of  $2.6 \pm 0.1$ . This value is similar to the values of  $\Delta pK^{int}$  for amorphous  $FeOOH$  of 3.9 and 3.6, determined by batch titrations in  $KNO_3$  and  $NaCl$  solutions [28], indicating that Fe oxyhydroxide particles were present and dominant on the surface of the modified material.

### 3.3. Determination of the point of zero charge of the Fe–sepiolite in solutions of $Co^{2+}$ ions

The results of the determination of the point of zero charge for the Fe–sepiolite in solutions of  $Co(NO_3)_2$  of concentrations  $0.01$  and  $0.001 \text{ mol dm}^{-3}$  are presented in Fig. 7. The plateaus, i.e., the curve inflexions, on the dependences  $pH_f$  versus  $pH_i$ , obtained at pH values of 6.2 for  $0.01 \text{ mol dm}^{-3}$  and 6.6 for  $0.001 \text{ mol dm}^{-3}$  correspond to the points of zero charge. This means that the points of zero charge in  $Co^{2+}$  solutions were shifted to the lower values compared with those obtained for Fe–sepiolite in  $KNO_3$  solutions of different concentrations under the same conditions [14]. The reason for such shifting is the specific sorption on the Fe–sepiolite surface, which 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. The shift of  $pH_{pzc}$  was higher when the initial concentration was  $0.01 \text{ mol dm}^{-3}$  as a result of the increased specific sorption.

The specific sorption of  $Co^{2+}$  ions on Fe–sepiolite ( $\Delta pH_{Fe-SEP} = 8.5 - 6.5 = 2.0$ , for  $0.001 \text{ mol dm}^{-3}$   $Co(NO_3)_2$  and  $\Delta pH_{Fe-SEP} = 8.5 - 6.1 = 2.4$ , for  $0.01 \text{ mol dm}^{-3}$   $Co(NO_3)_2$ ) was higher than on the natural sepiolite sample [29] due to the presence of Fe-species located on the external sites of the sepiolite, additional  $-Fe-OH$  groups, which interact with the  $Co^{2+}$  ions by forming stable surface complexes.

**Fig. 6.** Dependence of  $pQ_{a_1}$  on  $\alpha_+ + c(KNO_3)^{1/2}$  and the double extrapolation procedure.

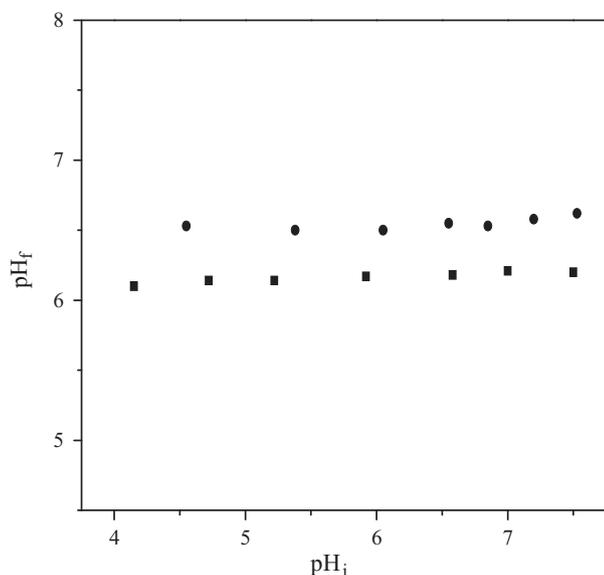


Fig. 7. Dependences of  $\text{pH}_f$  on  $\text{pH}_i$  during the equilibration of Fe-sepiolite with  $0.01 \text{ mol dm}^{-3}$  (■) and  $0.001 \text{ mol dm}^{-3}$  (●)  $\text{Co}(\text{NO}_3)_2$  solutions.

### 3.4. Effect of the initial pH value

The pH value affects the surface charge of an adsorbent, the protonation and deprotonation of surface functional groups, chemical species of metal ions present in the solution and the interaction between sorbents and sorbates. Therefore, the quantities of sorbed  $\text{Co}^{2+}$  ions at different pH ranging from 4 to 7.5 and amounts of  $\text{Mg}^{2+}$  ions present in the solutions as result of ion exchange are shown in Fig. 8. In the investigated pH range, the  $\text{M}^{2+}$  ions were the only metal species present in the solutions. From Fig. 8, it can be seen that the amount of metal ion sorbed per unit mass of Fe-sepiolite was almost constant, amounting to  $\approx 0.35 \text{ mmol Co}^{2+} (\text{g Fe-SEP})^{-1}$ . It is obvious that the change in the initial pH value of the metal ion solutions from 4 to 7.5 did not affect a change in the sorption capacity.

The change in  $\text{H}^+$  and  $\text{OH}^-$  in the solution will cause protonation and deprotonation of the surface functional groups of Fe-sepiolite ( $\equiv\text{S-OH}$ ) which are a main centers for the process of specific

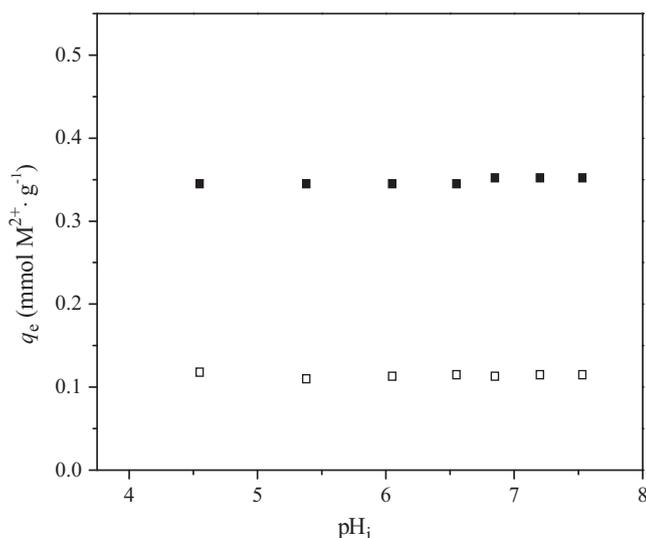


Fig. 8. Effect of initial pH on the amount of  $\text{Co}^{2+}$  sorbed on Fe-sepiolite (■) and quantity of ion exchanged  $\text{Mg}^{2+}$  ions (□) ( $c_i = 0.001 \text{ mol dm}^{-3}$ ).

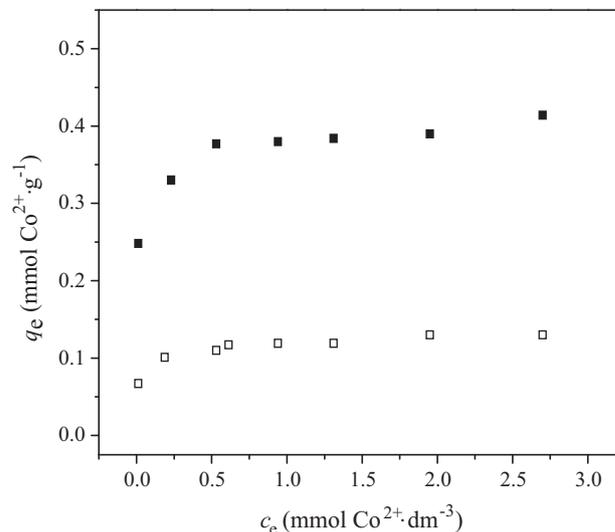


Fig. 9. Sorption isotherm for  $\text{Co}^{2+}$  ions on Fe-sepiolite (■) and the dependence of  $q_e$  ( $\text{mmol Mg}^{2+} \text{ g}^{-1}$ ) on  $c_e$  ( $\text{mmol Co}^{2+} \text{ dm}^{-3}$ ) (□).

sorption. At the  $\text{pH}_{\text{pzc}}$  of the Fe-sepiolite sample ( $8.5 \pm 0.1$ ), the net proton charge is zero, *i.e.*, the number of positively charged sites  $\equiv\text{SOH}_2^+$  is equal to the number of negatively charged sites  $\equiv\text{SO}^-$ . As the solution pH increases, in the pH range above  $\text{pH}_{\text{pzc}}$ , the number of  $\equiv\text{SO}^-$  sites increases. If the solution pH decreases below 8.5, the concentration of surface species will become different, *i.e.*, the number of  $\equiv\text{SOH}_2^+$  groups increases. In such a system,  $\text{M}^{2+}$  ions compete with the  $\text{H}^+$  ions for the same active site ( $\equiv\text{S-OH}$ ), resulting in surface complexation or protonation of the active surface site. At higher  $\text{H}^+$  concentrations, *i.e.*, low pH values, the surface active sites become protonated, the surface becomes more positively charged reducing the attraction between surface and metal cations [30]. The effect of the pH value on the sorption on the sepiolite was not investigated at  $\text{pH} > 8.5$ ,  $\text{pH} > \text{pH}_{\text{pzc}}$ , to avoid the precipitation of  $\text{M}(\text{OH})_2$ , which would be the dominant process for the removal of metal ions at higher pH values, or at  $\text{pH} < 4$ , to avoid the dissolution of the Fe-sepiolite.

In the region  $\text{pH} < 7$ , surface complexation or the specific sorption of cations lowers the number of sites available for the sorption of  $\text{H}^+$  ions, hence a larger number of  $\text{H}^+$  ions remain in the solution, which leads to lower  $\text{pH}_{\text{pzc}}$  values (Fig. 7). This shift was the same of all the investigated initial pH values, meaning that the specific sorption in this pH range was the same. The quantity of  $\text{Mg}^{2+}$  ions released into the solution during the ion exchange process with  $\text{Co}^{2+}$  ions was also the same and as the result of these simultaneously occurring processes, the total amount of metal ion sorbed per unit mass of Fe-sepiolite remained almost constant.

### 3.5. Sorption isotherm

The sorption isotherm as  $q_e$  ( $\text{mmol Co}^{2+} \text{ g}^{-1}$  sorbent) versus  $c_e$  ( $\text{mmol Co}^{2+} \text{ dm}^{-3}$ ) for the Fe-SEP is presented in Fig. 9, together with the dependence of the quantity of ion exchangeable  $\text{Mg}^{2+}$  ions on  $c_e$ . The quantity of exchangeable  $\text{Mg}^{2+}$  ions was determined as the difference between the total amount and the amount of  $\text{Mg}^{2+}$  ions released into the solution by the dissolution of the Fe-sepiolite ( $0.008 \text{ mmol g}^{-1}$ ) [14] because the total amount of  $\text{Mg}^{2+}$  ions present in the solution after equilibration is the result of these two processes. The amount of  $\text{Mg}^{2+}$  increased with increasing amount of  $\text{Co}^{2+}$  sorbed on the mineral, which corroborates the occurrence of ion exchange, *i.e.*, the replacement of  $\text{Mg}^{2+}$  on the edges of the octahedral layer of sepiolites with  $\text{Co}^{2+}$  ions as one of main mechanisms of sorption. From Fig. 9, it can be seen that the

Fe-sepiolite had a slightly higher ion exchange capacity for  $\text{Co}^{2+}$  ions than the natural sepiolite sample [29].

The sorption of  $\text{Co}^{2+}$  ions occurred by the ion exchange process and by the process of specific sorption, *i.e.*, inner-sphere complexation of  $\text{Co}^{2+}$  on the functional groups on the broken edges of the mineral and subsequent release of  $\text{H}^+$ , which was proved by the shift in the point of zero charge. The sorption process was not affected by the presence of  $\text{Na}^+$  ions in the modified material. Amounts of  $\text{Na}^+$  ions observed in the solutions after sorption, did not vary as a function of  $\text{Co}^{2+}$  sorption and were similar to the amounts released into the solution as a result of dissolution of Fe-sepiolite [14]. In the final solutions presents of  $\text{Fe}^{3+}$  ions were not observed.

The equilibrium sorption data were analyzed using the linear forms of the Langmuir, Freundlich [31,32] and Dubinin–Kaganer–Radushkevich (DKR) models presented by the following equations:

$$\frac{c_e}{q_e} = \frac{1}{K_L q_m} + \frac{c_e}{q_m} \quad (7)$$

$$\log q_e = \log K_f + \frac{1}{n} \log c_e \quad (8)$$

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (9)$$

The sorption parameters are as follows:  $q_m$  is the maximum sorption capacity ( $\text{mmol g}^{-1}$ ),  $K_L$  the Langmuir constant related to energy of sorption ( $\text{dm}^3 \text{mmol}^{-1}$ ),  $K_f$  and  $n$  are Freundlich constants related to the sorption capacity and intensity, respectively,  $\beta$  ( $\text{mol}^2 \text{J}^{-2}$ ) is the DKR activity coefficient related to the sorption energy and  $\varepsilon$  is the Polanyi potential.

The sorption parameters (Table 2) were determined from the linear slope and intercept of the graphs:  $q_m$  and  $K_L$  from the graphs  $c_e/q_e$  versus  $c_e$ ,  $K_f$  and  $1/n$  from the graphs  $\log q_e$  versus  $\log c_e$  and  $\beta$  and  $\varepsilon$  from the graphs  $\ln q_e$  versus  $\varepsilon^2$ .

The Langmuir isotherm equation represents the sorption process very well; the  $R^2$  values were all higher than 0.99, and the Langmuir constants related to the maximum sorption capacity,  $q_m$ , were similar to the value obtained from the  $q_e - c_e$  dependence. The maximum sorption capacity of metal ions onto the Fe-sepiolite, according to the evaluation using the Langmuir equation, was  $0.413 \text{ mmol Co}^{2+} (\text{g Fe-SEP})^{-1}$ . The applicability of Langmuir isotherm indicates monolayer coverage by  $\text{Co}^{2+}$  ions of the Fe-SEP and a homogenous distribution of the active sites on the surface of the Fe-sepiolite.

To determine if an adsorption process is favorable or unfavorable, for a Langmuir type sorption process, the isotherm can be classified by a term  $R_L$ , a dimensionless constant separation factor, which is defined as:

$$R_L = \frac{1}{1 + K_L c_0} \quad (10)$$

where  $c_0$  ( $\text{mol dm}^{-3}$ ) is the initial metal ion concentration.

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  $\text{Co}^{2+}$  ions in the range  $10^{-4}$  to  $10^{-2} \text{ mol dm}^{-3}$  were between 0.10 and 0.016, which indicates that the sorption of  $\text{Co}^{2+}$  ions onto Fe-sepiolite samples was favorable.

### 3.6. Sorption kinetics

The effects of contact time on the amounts of  $\text{Co}^{2+}$  sorbed onto sepiolite modified with iron, and the quantity of  $\text{Mg}^{2+}$  ions released into the solution as a result of the ion exchange process are shown in Fig. 10. The sorption showed a rapid increase during

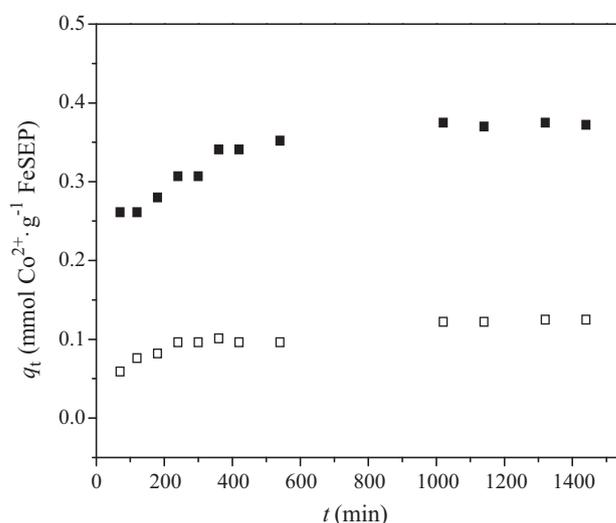


Fig. 10. Effect of contact time on the amounts of  $\text{Co}^{2+}$  sorbed on Fe-SEP (■) and  $\text{Mg}^{2+}$  ions exchanged (□) ( $c_i = 100 \text{ mg dm}^{-3}$ , at a temperature of 298 K and a pH of  $5.6 \pm 0.1$ ).

the first 400 min and then continued slowly until a pseudo equilibrium condition was reached. The initial faster metal ion uptake may be explained by the large number of active sites available on the Fe-sepiolite surface. A slower increase in the amount of cations sorbed was observed in the second stage, due to the gradual occupancy of the active sites and a decrease of the metal ion concentrations in the solutions.

In order to investigate the mechanism of sorption and the potential rate-controlling steps, three kinetic models were used to test the experimental data: the pseudo-first-order equation proposed by Lagergren [33], the pseudo-second-order kinetic model proposed by Ho and G. McKay [34], and the intraparticle diffusion model proposed by Weber and Morris [35]. The respective linear forms of the equations are given by:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (11)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (12)$$

$$q_t = k_i t^{1/2} + C \quad (13)$$

where  $t$  (min) is the contact time,  $q_e$  and  $q_t$  ( $\text{mmol g}^{-1}$ ) are the amounts of sorbed  $\text{Co}^{2+}$  at equilibrium and time  $t$ , respectively, and  $k_1$  ( $\text{min}^{-1}$ ),  $k_2$  ( $\text{g mmol}^{-1} \text{min}^{-1}$ ), and  $k_i$  ( $\text{mmol g}^{-1} \text{min}^{-1/2}$ ) are the rate constants of the pseudo-first-order, pseudo-second-order and the intraparticle diffusion model, respectively.

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

$$h = k_2 \cdot q_e^2 \quad (14)$$

Figs. 11 and 12 show the curve fitting plots of the pseudo-first-order and pseudo-second-order model for the sorption of  $\text{Co}^{2+}$  onto Fe-SEP, respectively. Based on the above kinetic models, the corresponding kinetic parameters are listed in Table 3.

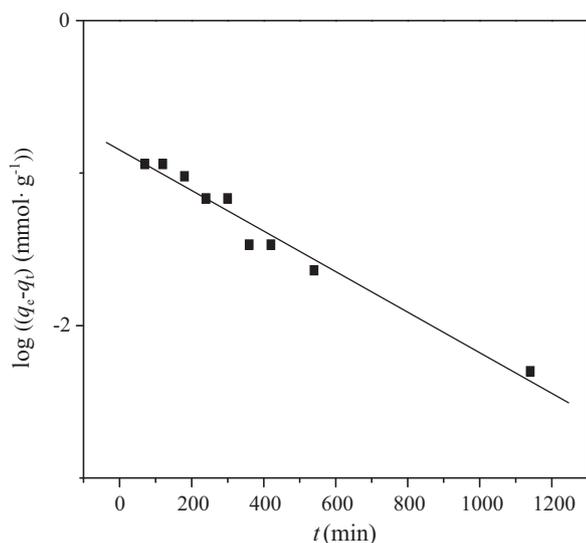
As seen from Table 3, the sorption data of  $\text{Co}^{2+}$  can be satisfactorily described by the pseudo-second-order equation, since the  $q_e$  values estimated by this model are in good agreement with the experimental results, and the values of the correlation coefficient is close to 1. Since the pseudo-second-order kinetic model is based on the assumption that the rate-limiting step may be chemical sorption or chemisorption [34,36], it may also be assumed that sorption

**Table 2**  
Sorption parameters and coefficients of determination according to the Langmuir, Freundlich and DKR model for the sorption of  $\text{Co}^{2+}$  ions onto Fe-SEP at 298 K.

Model	Langmuir			Freundlich			DKR		
	$K_L/\text{dm}^3 \text{ mmol}^{-1}$	$q_m/\text{mmol g}^{-1}$	$R^2$	$K_f/\text{mmol}^{1-1/n} \text{ dm}^{3/n} \text{ g}^{-1}$	$n$	$R^2$	$q_m/\text{mmol g}^{-1}$	$\beta/\text{mol}^2 \text{ J}^{-2}$	$R^2$
Fe-SEP	17.67	0.413	0.998	0.380	10.98	0.972	0.386	$3.873 \times 10^{-9}$	0.918

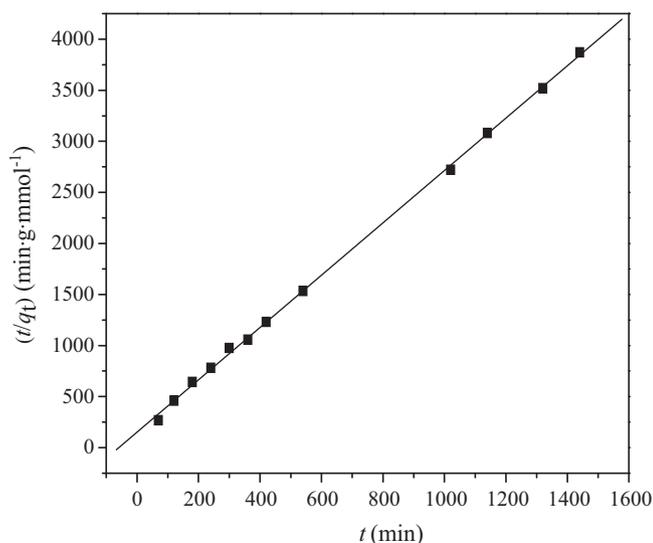
**Table 3**  
Kinetic parameters for  $\text{Co}^{2+}$  sorption onto Fe-SEP.

Sample	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion			
	$k_1/\text{min}^{-1}$	$q_e/\text{mmol g}^{-1}$	$R^2$	$k_2/\text{g mmol}^{-1} \text{ min}^{-1}$	$q_e/\text{mmol g}^{-1}$	$R^2$	$h/\text{mmol g}^{-1} \text{ min}^{-1/2}$	$k_i/\text{mmol g}^{-1} \text{ min}^{-1/2}$	$C/\text{mmol g}^{-1}$	$R^2$
Fe-SEP	0.0031	0.142	0.966	0.0432	0.142	0.999	0.0066	0.192	0.0071	0.941

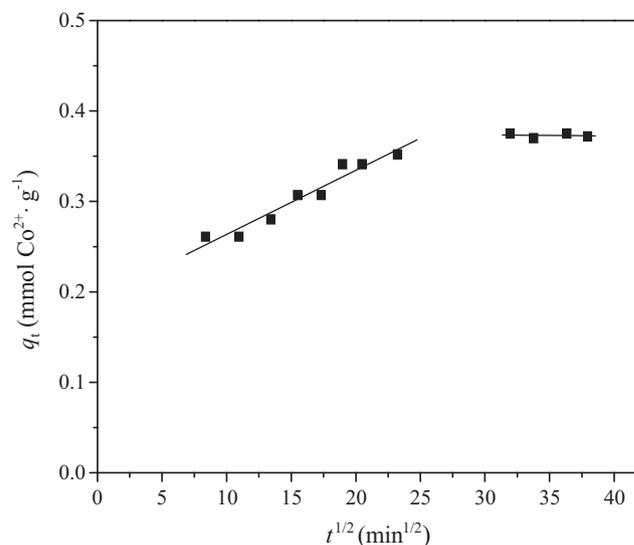


**Fig. 11.** Linear fitting of the kinetic data for  $\text{Co}^{2+}$  sorption onto Fe-SEP by the pseudo-first-order kinetic model (■).

of  $\text{Co}^{2+}$  ions onto Fe-sepiolite occurs through chemisorptions, *i.e.*, that the main mechanisms of sorption are specific sorption and ion exchange of  $\text{Mg}^{2+}$  from the sepiolite structure with  $\text{Co}^{2+}$  ions from the solutions.



**Fig. 12.** Linear fitting of the kinetic data for  $\text{Co}^{2+}$  sorption onto Fe-SEP by the pseudo-second-order kinetic model (■).



**Fig. 13.** Intraparticle diffusion plot for  $\text{Co}^{2+}$  sorption onto Fe-SEP (■).

The sorption of metal ions from an aqueous phase onto a solid phase is multi-step process involving: transport of metal ions from the aqueous phase to the surface of the solid particles (bulk diffusion); diffusion of metal ions through the boundary layer to the surface of the sorbent (film diffusion); transport of the metal ions from the surface to interior pores of the particle (intraparticle diffusion or pore diffusion), and sorption of metal ions at an active sites on the surface of the material by chemical reaction, such as ion exchange, complexation, and chelation [37,38]. The dependence described by Weber and Morris, expressed by Eq. (13), can be used to determine if particle diffusion is the rate-limiting step. According to this model, a plot of  $q_t$  versus  $t^{1/2}$  should be linear if intraparticle diffusion is involved in the sorption process and if the plot passes through the origin then intraparticle diffusion is the sole rate-limiting step. Such a plot for the sorption  $\text{Co}^{2+}$  ions onto the modified sepiolite (Fig. 13) suggests that the sorption occurred in a multi-step process. The values of  $k_i$  and  $C$ , reported in Table 3, were calculated according to the first linear part of the curves. As the plot did not pass through the origin, intraparticle diffusion was not the only rate-limiting step. This confirmed that sorption mechanism was a multi-step process, involving sorption onto the surface, diffusion into the interior and ion exchange or complex formation.

#### 4. Conclusions

An effective retention of  $\text{Co}^{2+}$  ions from aqueous solutions was realized using sepiolite functionalized with iron oxide. The removal of  $\text{Co}^{2+}$  occurred dominantly by specific sorption and exchange of  $\text{Mg}^{2+}$  ions from the Fe-sepiolite structure. The points of zero charge

in  $\text{Co}^{2+}$  solutions were shifted to the lower values as a result of specifically sorbed  $\text{Co}^{2+}$  ions. The observed increase in the content of  $\text{Mg}^{2+}$  released to equilibrium solutions with increasing amount of  $\text{Co}^{2+}$  sorbed supported the suggestion of  $\text{Mg}^{2+}$  substitution.

The equilibrium sorption data of  $\text{Co}^{2+}$  on Fe–sepiolite was adequately described by the Langmuir isotherm equation. The experimental results obtained revealed that the iron–sepiolite system has a noticeably higher  $\text{Co}^{2+}$  sorption capacity than that of the natural sepiolite sample.

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 and that chemisorption might be the rate-limiting step that controls the sorption process. It was observed that intraparticle diffusion was involved in the sorption process.

Using surface charge data, obtained by the potentiometric titration method, the intrinsic equilibrium constants  $\text{p}K_{a1}^{\text{int}}$  and  $\text{p}K_{a2}^{\text{int}}$  of Fe–sepiolite were calculated to be  $6.7 \pm 0.1$  and  $10.2 \pm 0.1$ , respectively.

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