Sorption of Cu$^{2+}$ and Co$^{2+}$ from aqueous solutions onto sepiolite: an equilibrium, kinetic and thermodynamic study

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Abstract: The efficiency of natural sepiolite for the removal of Cu$^{2+}$ and Co$^{2+}$ from aqueous solution was determined using the batch method. The sorption experiments were performed as a function of the initial metal concentration, the equilibration time and temperature. Thermodynamic parameters, such as enthalpy, free energy and entropy, were calculated from the temperature dependent sorption isotherms and these values showed that the sorption of the investigated metals onto sepiolite was endothermic. The pseudo-second order kinetic model provides the best correlation of the experimental kinetic data.

Keywords: sepiolite; sorption; heavy metals; kinetics; thermodynamic.

INTRODUCTION

Wastewaters from many industries, such as metallurgy, tannery, mining, battery-production, insecticide, fungicide, paint and coating manufacture, etc., pollute the environment with heavy metals, which is of very serious environmental concern for all living organisms, especially for humans. Heavy metal ions, such as copper and cobalt, accumulated through the food chain; even at low concentrations, have damaging effects on human health because there are no adequate mechanisms for their elimination from the body.¹

The most important technologies developed to remove and recovery heavy metals from wastewaters include chemical precipitation, ion exchange, electro-chemical removal, membrane separation, microbe separation, sorption by activated carbon, etc. Heavy metals sorption by low-cost sorbents is currently of great interest. The employment of clay minerals, such as kaolinite,²,³ vermicu-

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lite, montmorillonite, bentonite and sepiolite has recently received increasing attention because they showed high sorption capacities and are abundant in nature, inexpensive and environmental friendly.

Sepiolite is a hydrous magnesium silicate characterized by its fibrous morphology and intracrystalline channels. Due to its sorptive, rheological and catalytic properties, sepiolite is widely used in a variety of industrial applications. Sepiolite is used as a catalyst and catalyst support, a filler in polymer composites, a membrane for ultrafiltration and as molecular sieves. Sepiolite is an effective and economical sorbent material, a bleaching and clarifying agent, a filter aid, an industrial sorbent and the spectrum of its utilization ranges from cosmetics to paints and fertilizers.

The aims of this study were: to investigate the effectiveness of natural sepiolite in the removal of Cu$^{2+}$ and Co$^{2+}$ by sorption from aqueous solution; to examine the dominant mechanisms of the interaction of these ions with sepiolite; to investigate the influence of the equilibrium time and temperature on the sorption capacity of sepiolite; to determine the thermodynamic parameters of sorption (free energy change, enthalpy and entropy change).

**EXPERIMENTAL**

The natural sepiolite sample was obtained from the deposit Andrići (Serbia). The chemical composition, X-ray diffraction, differential thermal and FTIR analyses of the sample and the point of zero charge of $7.4 \pm 0.1$ were reported previously.

Sorption procedure

The batch equilibration method was used to investigate the removal of Cu$^{2+}$ and Co$^{2+}$ by the natural sepiolite sample. The sorption of ions onto the sepiolite was studied based on the shift of the point of zero charge, determination of sorption isotherms and the correlation between the quantity of Mg$^{2+}$ released from, and the quantity of Cu$^{2+}$ and Co$^{2+}$ sorbed onto the sepiolite sample. The experiments were performed using solutions of Cu(NO$_3$)$_2$ and Co(NO$_3$)$_2$ in high quality water (18 MΩ) obtained from a Mill-Q water purification system.

The shift of the point of zero charge was investigated using 0.01 and 0.001 mol dm$^{-3}$ solutions of Cu(NO$_3$)$_2$ and Co(NO$_3$)$_2$. The measurements were performed using 25 cm$^3$ of metal ion solutions (concentration 0.01 or 0.001 mol dm$^{-3}$) in poly(vinyl chloride) (PVC) vessels. The initial pH value (pH$_i$) of the electrolytes was adjusted by the addition of small quantities of a 0.1 mol dm$^{-3}$ 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 (pH$_f$) was determined. The point of zero charge was found from a plot of pH$_f$ vs. pH$_i$. The sorption of Co$^{2+}$ was examined in the pH range from approx. 3.5 to approx. 8, whereas the sorption of Cu$^{2+}$ was investigated from approx. 3.5 to approx. 6 in order to avoid ion hydrolysis at higher pH values and the dissolution of sepiolite at lower pH values.

For the determination of the sorption isotherms, solutions of Cu$^{2+}$ (initial concentrations from 30 to 250 mg dm$^{-3}$) and Co$^{2+}$ (initial concentrations from 30 to 200 mg dm$^{-3}$) in demineralized water were prepared. The initial pH values of the solutions were 5.6±0.1. Aliquot of 25 cm$^3$ of each solution was equilibrated for 24 h with 0.05 g of sepiolite, with shaking. The
metal ions remaining unabsorbed in the supernatant, as well as the concentration of Mg$^{2+}$, were determined using AAS (Perkin Elmer 730). All the sorption studies were repeated twice; the reported value is the average of two measurements.

**Effect of contact time**

The removal of Cu$^{2+}$ and Co$^{2+}$ by the sepiolite sample was also investigated as a function of the contact time. Solutions of the metal ions (25 cm$^3$) with an initial ion concentration of 100 mg dm$^{-3}$ and a pH value of 5.6$\pm$0.1 were equilibrated with 0.05 g sepiolite at a temperature of 298 K for contact times ranging from 1 h to 24 h. After separation of the solid from the liquid phase, the final concentration of Cu$^{2+}$, Co$^{2+}$ and Mg$^{2+}$ were measured as dependent variables of time.

**Effect of temperature**

In order to investigate the influence of the temperature on the sorption process, sorption experiments were also performed at temperatures of 318, 328 and 338 K. The M$^{2+}$ solutions with different initial concentrations were adjusted to a pH value of 5.6$\pm$0.1. Aliquot of 25 cm$^3$ of each solution was equilibrated for 24 h with 0.05 g of sepiolite, with shaking in a water bath thermostated at the desired temperature.

**RESULTS AND DISCUSSION**

**Sorption of Cu$^{2+}$ and Co$^{2+}$ onto sepiolite**

The specific sorption of cations onto a solid surface leads to a shift in the point of zero charge to lower values. This shift is more pronounced, the greater the amount of specifically sorbed ions is.$^{15}$

The results of the determination of the point of zero charge for sepiolite in Cu(NO$_3$)$_2$ and Co(NO$_3$)$_2$ solutions, of concentrations 0.01 and 0.001 mol dm$^{-3}$, are presented in Figs. 1 (for Cu$^{2+}$) and 2 (for Co$^{2+}$). From the dependences pH$_f$ vs. 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.

![Fig. 1. Dependences of pH$_f$ on pH$_i$ during the equilibration of sepiolite with 0.01 and 0.001 mol dm$^{-3}$ Cu(NO$_3$)$_2$ solutions.](Fig.1)
The pH of the point of zero charge, $pH_{pzc}$, values of the sepiolite determined in solutions of $M^{2+}$ of concentration 0.01 mol dm$^{-3}$ were 4.4±0.1 and 6.2±0.1 for the solutions of Cu$^{2+}$ and Co$^{2+}$, respectively, whereas the respective values obtained in solutions of concentration 0.001 mol dm$^{-3}$ were 4.6±0.1 and 6.5±0.1.

During the equilibration of sepiolite with Cu(NO$_3$)$_2$ and Co(NO$_3$)$_2$ solutions, the plateau position shifted towards lower pH values compared to the $pH_{pzc}$ of 7.4±0.1, obtained under the same conditions for KNO$_3$ solutions (concentration of 0.1, 0.01 and 0.001 mol dm$^{-3}$, in the pH range from approx. 3.5 to approx. 10), indicating that specific sorption of Cu$^{2+}$ and Co$^{2+}$ onto the sepiolite occurred. For the same initial ion concentration, the shift of the plateau was more pronounced with Cu$^{2+}$ than with Co$^{2+}$, suggesting that Cu$^{2+}$ have a higher affinity for specific sorption onto sepiolite sample than Co$^{2+}$. The shift of $pH_{pzc}$ in the solutions of $M^{2+}$ was higher when the initial concentration was 0.01 mol dm$^{-3}$ as a result of increased specific sorption.

The quantity of specifically sorbed ions onto the surface of solids is strongly dependent of the radii of the hydrated ions, the electron charge, the metal electronegativity, the hydrolysis constant, etc. The electric charge of the investigated ions are the same and the radii of the hydrated ions (Co$^{2+}$, 0.423 nm and Cu$^{2+}$, 0.419 nm) and metal electronegativities (Cu, 1.90 and Co, 1.88) are similar. There are, however, differences in the hydrolysis constant: Cu$^{2+}$ (10$^{-7.53}$) > Co$^{2+}$ (10$^{-9.6}$). The higher the hydrolysis constant of a given ion is, the higher is the tendency of the ion to specific sorption.

The sorption isotherms (with the same solid/liquid ratio as in the determination of the $pH_{pzc}$) and the dependences of the quantity of Mg$^{2+}$ released into the solution as a result of the ion exchange process on the equilibration concentration of the sorbed ions, $c_e$, are presented in Figs. 3 (for Cu$^{2+}$) and 4 (for Co$^{2+}$).
The total amount of $\text{Mg}^{2+}$ present in the solution after equilibration of the solution with sepiolite is the result of two processes: the ion exchange of $\text{Mg}^{2+}$ from the sepiolite structure with $\text{Cu}^{2+}$ and $\text{Co}^{2+}$, and dissolution of the sepiolite. The exchangeable $\text{Mg}^{2+}$ were determined as the difference between the total amount and amount of $\text{Mg}^{2+}$ released into the solution due to dissolution of sepiolite (0.09 mmol g$^{-1}$, determined during the determination of the $\text{pH}_{\text{pzc}}$). The difference between the values of $q_e$ (mmol (M$^{2+}$) g$^{-1}$) and $q_e$ (mmol (M$^{2+}$) g$^{-1}$) corresponds to the quantity of M$^{2+}$ removed from the solution by other mechanisms: specific sorption, ion exchange with exchangeable ions from the sepiolite structure, etc. The mechanism of precipitation of hydroxides of these ions ($\text{M(OH)}_2$) could not be involved considering the pH values of the solutions. The occurrence of specific sorption of $\text{Cu}^{2+}$ and $\text{Co}^{2+}$ onto the sepiolite was con-
confirmed by the shifts of the pH_{pzc} towards lower pH values, proportional to the quantity of specifically sorbed ions.

During the ion exchange of Cu^{2+} and Co^{2+}, Mg^{2+} are displaced from the sepiolite lattice, releasing them into solution and replacing them within the structure. This process does not influence the change of the pH_{pzc} because H^{+} ions are not involved in the ion exchange process.

The process of ion exchange depends of the similarity of crystallographic radii of Mg^{2+} and the M^{2+}. The values of crystallographic radii of Cu^{2+}, Co^{2+} and Mg^{2+} of 0.073, 0.075 and 0.072 nm, respectively, suggest that the affinity of the investigated ions for ion exchange with Mg^{2+} should be very similar. The results of the present investigation showed that quantity of M^{2+} exchanged was almost the same for Cu^{2+} and Co^{2+}.

According to the results presented in Figs. 3 and 4, obtained at a temperature of 298 K, the sepiolite sample showed the higher sorption capacity for Cu^{2+} then for Co^{2+}.

Effect of contact time

The effect of contact time on the amounts of Cu^{2+} and Co^{2+} sorbed onto sepiolite is shown in Fig. 5. It can be seen that the removal of Cu^{2+} and Co^{2+} using sepiolite as the sorbent is a two-step process. Most of the metal ion sorption was achieved within 400 min for both investigated ions. The initial faster metal ion uptake may be explained by the high number of available active sites on the sepiolite surface. Thereafter, a slower increase of the amount of cations sorbed can be observed in the second stage, due to the gradual occupancy of the active sites and the decrease of the metal ion concentrations in the solutions; thus the sorption became less efficient.

![Fig. 5. Effect of contact time on the amounts of Cu^{2+} and Co^{2+} sorbed and Mg^{2+} exchanged (initial ion concentration of 100 mg dm^{-3}, at a temperature of 298 K and pH of 5.6±0.1).](image-url)
In addition to Cu$^{2+}$ and Co$^{2+}$ sorption, the quantity of Mg$^{2+}$ released into the solution as result of the ion exchange process was also examined (Fig. 5). The obtained data confirmed that the affinity for ion exchange was similar for Cu$^{2+}$ and Co$^{2+}$, and that sorption of the investigated ions included a high amount of specific sorption on the sepiolite surface.

In order 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\textsuperscript{20} and the pseudo-second-order kinetic model proposed by Ho and G. McKay\textsuperscript{21}. The linear forms of the pseudo-first-order and pseudo-second-order equations are given by the following equations:

\[
\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{1}
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}
\]

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

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

\[
h = k_2 q_e^2 \tag{3}
\]

The pseudo-first-order and pseudo-second-order model for the sorption of Cu$^{2+}$ and Co$^{2+}$ onto sepiolite are shown in Figs. 6 and 7, respectively. Based on
the above two kinetic models, the obtained parameters for the sorption kinetics are given in Table I.

![Fig. 7. Linear fitting of the kinetic data by the pseudo-second-order kinetic model.](image)

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.

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>$k_1$ (min$^{-1}$)</th>
<th>$q_e$ (mmol g$^{-1}$)</th>
<th>$R^2$</th>
<th>$k_2$ (g mmol$^{-1}$ min$^{-1}$)</th>
<th>$q_e$ (mmol g$^{-1}$)</th>
<th>$R^2$</th>
<th>$h$ (mmol g$^{-1}$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>0.00322</td>
<td>0.184</td>
<td>0.972</td>
<td>0.025</td>
<td>0.352</td>
<td>0.995</td>
<td>0.0031</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>0.00398</td>
<td>0.147</td>
<td>0.947</td>
<td>0.078</td>
<td>0.201</td>
<td>0.997</td>
<td>0.0030</td>
</tr>
</tbody>
</table>

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 the sorbate and that the sorption rate depends on the concentration of sorbate at the sorbent surface.\(^{21,22}\) As the correlation coefficients are very high (Table I), it may also be assumed that sorption of Cu$^{2+}$ and Co$^{2+}$ onto sepiolite occurs through chemisorption, which confirms that the main mechanisms of sorption onto the sepiolite sample are specific sorption and ion exchange of Mg$^{2+}$ from the sepiolite structure with Cu$^{2+}$ and Co$^{2+}$ from the solutions.

**Effect of temperature**

The relationship between the amount of Cu$^{2+}$ and Co$^{2+}$ sorbed per unit mass of sepiolite $q_e$ (mmol (M$^{2+}$) g$^{-1}$) and the equilibrium concentration $c_e$ (mmol
(M^{2+})\ dm^{-3})\ for\ four\ series\ of\ experiments\ at\ different\ temperatures\ are\ shown\ in\ Figs.\ 8\ and\ 9.\ The\ quantity\ of\ sorbed\ ions\ increased\ with\ increasing\ temperature.\ This\ indicates\ that\ a\ higher\ temperature\ favors\ metal\ ion\ removal\ by\ sepiolite,\ i.e.,\ that\ the\ sorption\ of\ Cu^{2+}\ and\ Co^{2+}\ onto\ sepiolite\ are\ endothermic\ processes.\ 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;\ hence\ the\ mass\ transfer\ resistance\ of\ the\ sorbate\ in\ the\ boundary\ layer\ decreases.\ 23
Thermodynamics of sorption

In order to investigate the effect of temperature on the sorption of Cu$^{2+}$ and Co$^{2+}$ onto sepiolite, the distribution coefficient, $K_d$, was calculated at the temperatures 298, 318, 328 and 338 K using the equation:

$$ K_d = \frac{q_c}{c_e} \quad (4) $$

The thermodynamic parameters, the enthalpy change ($\Delta H$), the entropy change ($\Delta S$), and the Gibbs free energy change ($\Delta G$) were calculated using the following equations:

$$ \ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (5) $$

$$ \Delta G = \Delta H - T\Delta S \quad (6) $$

The enthalpy change and the entropy change were determined graphically from the slope and intercept of the straight line plots of $\ln K_d$ versus $1/T$ (Fig. 10). The values of the thermodynamic parameters are presented in Table II.

The positive enthalpy change indicates that the process of Cu$^{2+}$ and Co$^{2+}$ removal from solution by sepiolite is endothermic. The free 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 $\Delta G$ values will be negative if the solution temperature becomes higher than 338 K. This indicates the presence of an energy barrier in the sorption process.\(^{24}\) Considering the positive values of $\Delta G$, it has been suggested that this is quite common with the sorption of metal ions by the ion-exchange mechanism because of the activated complexation of the metal ion formed with the sorbent in the excited state.\(^{25}\)
TABLE II. Thermodynamic parameters of the sorption of Cu$^{2+}$ and Co$^{2+}$ by sepiolite

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>$\Delta H$ / kJ mol$^{-1}$</th>
<th>$\Delta S$ / J mol$^{-1}$ K$^{-1}$</th>
<th>$\Delta G$ / kJ mol$^{-1}$</th>
<th>$T$ / K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>13.45</td>
<td>37.77</td>
<td>2.24</td>
<td>298</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>19.34</td>
<td>48.80</td>
<td>4.80</td>
<td>318</td>
</tr>
</tbody>
</table>

The positive values of entropy change may be explained by structural changes of both the sorbates and sorbents during the sorption process. According to some authors, the positive values of $\Delta S$ indicate an increase in randomness at the solid/liquid interface during the sorption of metal ions by clays.

CONCLUSIONS

The sorption capacity shown by the sepiolite suggests that this mineral, as a natural low-cost sorbent, can be successfully employed for the removal of Cu$^{2+}$ and Co$^{2+}$ from highly polluted waters.

The retention occurred dominantly by specific sorption and exchange of Mg$^{2+}$ from the sepiolite structure. The occurrence of specific sorption was confirmed by shifts of the pH$_{pzc}$ towards lower pH values, proportional to the quantity of specifically sorbed ions.

The sorption kinetic study showed that the pseudo-second-order model described best the experimental data, indicating that the sorption may be controlled by chemical sorption.

The thermodynamic analysis showed that the process of sorption of Cu$^{2+}$ and Co$^{2+}$ onto sepiolite was endothermic. The small and positive $\Delta G$ values suggest that the sorption process requires a small amount of energy.

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ИЗВОД

СОРПЦИЈА ЈОНА БАКРА И КОБАЛТА ИЗ ВОДЕНИХ РАСТВОРА НА СЕПИОЛИТУ, ИСПИТИВАЊЕ РАВНОТЕЖЕ, КИНЕТИКЕ И ТЕРМОДИНАМИКЕ СОРПЦИЈЕ

СЛАВИЦА ЛАЗАРЕВИЋ, ИВОНА ЈАНКОВИЋ-ЧАСТВАН, ЖЕЉКО РАДОВАНОВИЋ, БРАНИСЛАВ ПОТКОЊАК И РАДА ПЕТРОВИЋ

У раду је испитана ефикасност уклањања јона бакра и кобалта из водених раствора на природном сепиолиту применом методе уравнотежавања посебних проба. Испитан је утицај почетних концентрација Cu$^{2+}$ и Co$^{2+}$, као и времена уравнотежавања и температуре на процес сорпције. Вредности термодинамичких параметара сорпције (промене ентаплије, промене ентропије, промене слободне енергије сорпције), одређене на основу зависности сорпциононог капацитета од температуре, указују на то да је процес сорпције Cu$^{2+}$ и Co$^{2+}$ на сепиолиту...
ендотерман. Поређењем експерименталних резултата са кинетичким моделима утврђено је да се кинетика сорпције Cu²⁺ и Co²⁺ на сепиолиту може описати кинетичким моделом псеудо-другог реда.

(Примљено 18. јануара, ревидирано 10. септембра 2010)

REFERENCES
20. S. Lagergren, K. Sven, *Vetenskapsakad. Handl.* **24** (1898) 1

Available online at www.shd.org.rs/JSCS/