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# Kinetics of heavy-metal removal and recovery in sepiolite

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## Abstract

Fixed beds of Mg-enriched sepiolite were percolated through  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  single- and multicomponent heavy-metal solutions to study both the dynamic interactions between mineral and heavy-metal cations and the ion-sorption kinetics. The metal concentrations in the eluates were determined by atomic adsorption and/or inductively-coupled plasma and kinetics by the classical kinetic approach, using isothermal experiments at room temperature. The experimental results suggest that: (i) the amount of heavy metal sorbed by the mineral increases for smaller cations; ii) the sepiolite sorption efficiency sequence is, for single component solution,  $\text{Pb}^{2+} < \text{Cd}^{2+} < \text{Co}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+}$ , and, for multicomponent solution,  $\text{Pb}^{2+} = \text{Co}^{2+} < \text{Cd}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+}$ . Therefore, the ability of sepiolite to remove  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  is virtually independent of the competitive cation interactions, whereas its affinity for  $\text{Co}^{2+}$  is lower when other metals coexist in the solution. The cationic sorption-exchange equilibrium constants ( $k$ ), obtained by fitting the data with Langmuir equations are:  $k_{\text{Co}^{2+}} = 4.798 \times 10^{-3}$ ,  $k_{\text{Cu}^{2+}} = 3.424 \times 10^{-3}$ ,  $k_{\text{Zn}^{2+}} = 2.907 \times 10^{-3}$ ,  $k_{\text{Pb}^{2+}} = 1.009 \times 10^{-2}$  [meq min] $^{-1}$ ,  $k_{\text{Cd}^{2+}} = 1.187 \times 10^{-2}$  [meq min] $^{-1/2}$  for monocomponent solution experiment. The desorption study concerning the nature of eluting agents shows that  $\text{Mg}^{2+}$  is more effective than  $\text{Na}^{+}$  in removing heavy metals. Rapid kinetics and equilibrium of exchange of  $\text{Mg}^{2+}$  for heavy metals were observed; this is thought to indicate that the main process occurs at easily accessible sites at the outer and channel surface. Moreover, other processes can be assigned to the exchange of  $\text{Mg}^{2+}$  in the octahedral sites at the channel edges. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* sepiolite; heavy metal; dynamic interaction; kinetics

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## 1. Introduction

A thorough understanding of the capacity of clay minerals to adsorb heavy metal cations is essential in order to predict the fate of these pollutants in the environment and to interpret the interactions of heavy-metal ions with clays in aqueous media. In the last few years, the reaction mechanisms involving the transport of heavy metals in an aqueous phase in contact with minerals have been studied to predict the evolution and movement of groundwater contaminants. The mechanisms underlying the adsorption of solute on solid particles can be said to comprise the following main steps: (i) solute transfer from the bulk solution to the adsorbent surface; (ii) transfer from the surface to the structural active sites via exchange; (iii) uptake on the active site, via complexation, sorption, precipitation, hydrolysis (Thompson and Jackson, 1996). The type of sorption process which occurs is highly dependent on the quantity and type of mineral phase present. Solution conditions, such as pH, ionic strength, metal ion concentration and the presence and concentration of other sorbing species also play a major role in determining the extent and type of operative sorption process. Adsorption and complexation occur rapidly, whereas the exchange of the solute with cations inside the structure can be rapid or very slow.

Minerals, such as phyllosilicates, are often employed in environmental protection processes. They both have a large area and negative charge residual on the external surface; for this reason, they could be used in adsorption and/or exchange, especially in cation processes.

The objective of this work was to study the interaction between sepiolite and heavy-metal cation solutions by examining single- and multicomponent aqueous

Table 1

Composition and relevant mineralogical features of the sepiolite used in this study. The data were summarized by Brigatti et al. (1996)

Structural formula $[\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4] \cdot 8\text{H}_2\text{O}$		Unit cell parameters
$[\text{IV}]_{\text{Si}}$	11.62	$a = 13.463(2) \text{ \AA}$
$[\text{IV}]_{\text{Al}}$	0.38	$b = 26.98(1) \text{ \AA}$
$[\text{IV}]_{\text{total}}$	12.00	$c = 5.203(2) \text{ \AA}$
$[\text{VI}]_{\text{Ti}}$	0.02	$V = 1890 \text{ \AA}^3$
$[\text{VI}]_{\text{Fe}^{3+}}$	0.12	Space group
$[\text{VI}]_{\text{Al}}$	0.29	<i>Pnan</i>
$[\text{VI}]_{\text{Mn}}$	0.01	CEC [meq g <sup>-1</sup> ]
$[\text{VI}]_{\text{Mg}}$	7.12	0.095
$[\text{VI}]_{\text{total}}$	7.56	total weight loss
$[\text{XII}]_{\text{Ca}}$	0.25	$\Delta W_{25 \leq T^{\circ}\text{C} \leq 1000} [\%]$
$[\text{XII}]_{\text{Na}}$	0.19	21.43
$[\text{XII}]_{\text{K}}$	0.15	surface area <sup>a</sup>
$[\text{XII}]_{\text{total}}$	0.59	$S_{T=25^{\circ}\text{C}} [\text{m}^2 \text{ g}^{-1}]$
$[\text{XII}]_{\text{X}^{1+}}$	+0.84	246

<sup>a</sup>Calculated following the method reported by Hibino et al. (1995).

systems. Owing to the sepiolite crystal-chemical features, heavy-metal retention by the mineral can occur by adsorption and/or cation exchange reactions. Adsorption can be seen as taking place on the oxygen ions of the tetrahedral sheets, on the water molecules at the edges of the octahedral sheet and on Si–OH groups along the direction of the fibres, whereas exchange occurs by substituting the solvated cations inside the channels and/or inside the octahedra at the edges of the channels (Serratos, 1979; Corma et al., 1985; Jones and Galán, 1988).

While the equilibrium properties (e.g., adsorption isotherms, adsorption edges, equilibrium constants) have been widely investigated, less information is available on the kinetics of such processes. Therefore, a further aim of this work is to investigate the ion exchange kinetics of divalent metal cations ( $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$ ) at sepiolite sites.

## 2. Materials

### 2.1. Sepiolite sample

The sepiolite was from Vallecas (Spain). Its composition and relevant mineralogical features have been amply described (Jones and Galán, 1988); the specific features of sample used have been previously reported (Brigatti et al., 1996) and are summarized in Table 1.

### 2.2. Solutions

Heavy-metal acetates [ $\text{Cd}(\text{CH}_3\text{COO})_2 \times 2\text{H}_2\text{O}$ ,  $\text{Co}(\text{CH}_3\text{COO})_2 \times 4\text{H}_2\text{O}$ ,  $\text{Pb}(\text{CH}_3\text{COO})_2 \times 3\text{H}_2\text{O}$ ,  $\text{Zn}(\text{CH}_3\text{COO})_2 \times 2\text{H}_2\text{O}$ ,  $\text{Cu}(\text{CH}_3\text{COO})_2 \times \text{H}_2\text{O}$ , Carlo Erba Chemicals, 99.9% pure] were used to obtain the following aqueous solutions: (i) five single-component solutions, i.e.,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$ , at a fixed concentration of  $10^{-2}$  N,  $\text{pH}_{T=21^\circ\text{C}} = 5.5$ ; (ii) a multicomponent solution containing  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  (total concentration,  $10^{-2}$  N; concentration of each species,  $2 \times 10^{-3}$  N;  $\text{pH}_{T=21^\circ\text{C}} = 5.5$ ). In order to investigate the effects of the ionic charge on the reversibility of exchange and/or adsorption reactions,  $\text{Na}(\text{CH}_3\text{COOH}) \times 3\text{H}_2\text{O}$  and  $\text{Mg}(\text{CH}_3\text{COOH})_2 \times 4\text{H}_2\text{O}$  were used to prepare single-component  $\text{Na}^+$  and  $\text{Mg}^{2+}$  solutions (concentration,  $10^{-2}$  N;  $\text{pH}_{T=20^\circ\text{C}} = 4.81$ ).

## 3. Experimental methods

### 3.1. Procedures

Chromatographic columns, one for each experiment, filled with distilled water (internal diameter 32 mm) were uniformly packed with 50 g of sepiolite (grain size 0.30–0.60 mm) to a bulk density of  $0.48 \text{ g cm}^{-3}$ ; the sample was

previously washed with deionized water and then dried overnight at constant temperature (35°C). Before starting percolation with heavy-metal solutions, the beds were thoroughly primed with  $\text{Mg}^{2+}$  by drenching with a 0.5 N  $\text{Mg}^{2+}$  solution until the concentrations of  $\text{Ca}^{2+}$ ,  $\text{Na}^{+}$  and  $\text{K}^{+}$  in the effluent were below the detection limit. The columns were washed with more diluted  $\text{Mg}^{2+}$ -solutions and finally with water, to remove excess of  $\text{Mg}^{2+}$ . Heavy-metal solutions were then percolated through the beds, the beds were eluted until exhausted (i.e., until the concentration of percolating and eluting solutions were the same within the standard deviation of the analytical determination) and then treated with  $10^{-2}$  N  $\text{Mg}^{2+}$  solution. In a separate set of experiments, the  $\text{Zn}^{2+}$ -exhausted bed was percolated with  $10^{-2}$  N  $\text{Na}^{+}$  solution. Actually, the ability of an adsorbent to remove and improve a solute is determined by both the sorption and the desorption characteristics of the sorbent. The study of both steps, using different species, is necessary to establish whether the operation is sufficiently non-destructive to allow the sorbent to be re-used. The following flow rates [ $\text{ml min}^{-1}$ ] were used: (i) single-component, heavy-metal treatments,  $\text{Co}^{2+} = 15.0$ ;  $\text{Cu}^{2+} = 18.7$ ;  $\text{Cd}^{2+} = 15.1$ ;  $\text{Pb}^{2+} = 16.5$ ;  $\text{Zn}^{2+} = 17.3$ ; (ii) multi-component heavy-metal treatment, 17.4.

### 3.2. Characterization

The metal concentrations in the eluates were determined by atomic adsorption and/or inductively-coupled plasma; the amount of heavy metal retained and eluted was estimated by integrating the areas above and below the breakthrough curves, respectively. The ion content standardized on 4.9 l of percolating solution was used to compare the yield of the mineral after each treatment.

It is well known that phyllosilicates are hydrolyzed by exchanging metal ions for hydronium ions in nearly neutral solutions, or even from deionised water (Glynn and Brown, 1996). In this study, the levels of hydronium ion exchange were closely monitored following a strict pH check on each eluate. The extent of  $\text{H}^{+}$  exchange was determined by inference from the chemical analyses of both the treated sepiolite and each eluate. Transition-metal ions tend to precipitate from solution even under weakly-acid conditions. Furthermore, many transition metal–salt solutions are sufficiently acid to gradually decompose a phyllosilicate structure. Sepiolite crystallinity was therefore monitored by analyzing maximally-exchanged samples of  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  prepared by exhaustively exchanging 5 g of sepiolite (grain size, 0.30–0.60 mm) with 100 ml portions of 2 N of the appropriate heavy metal acetate. The suspension was shaken at constant temperature (21°C) for 48 h; afterwards, the sepiolite was separated by filtration and washed. Exchange solutions were analysed for all the exchanging ions and for Si. The untreated sepiolite and the extensively-treated final products were analysed by: (i) X-ray powder diffraction (Philips 900 instrument, using  $\text{CuK}\alpha$  radiation and calibrated to the (101) reflection of low

quartz); (ii) infrared spectroscopy (FTIR Bruker IFS 113v), the band at 3720  $\text{cm}^{-1}$  being used as an index to detect changes in sepiolite structural order; (Serna and Van Socyoc, 1979); (iii) thermal analysis (TA Instrument Seiko SSC/5200), simultaneous TGA (thermal gravimetric analysis) and DTA (differential thermal analysis) in air with a heating rate of  $10^\circ\text{C min}^{-1}$ ; (iv) mineral chemical analyses by X-ray fluorescence (Philips PW 1400).

The results of maximally-exchanged sepiolite samples show that the  $A_z/Q$  ratio (where  $A_z$  is the equivalent fraction of the exchanging cation and  $Q$  is the theoretical sepiolite exchange capacity) was nearly equal to 1 for  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ , whereas it is greater than 1 for  $\text{Co}^{2+}$  ( $A_z/Q = 2.4$ ),  $\text{Cu}^{2+}$  ( $A_z/Q = 2.5$ ) and  $\text{Zn}^{2+}$  ( $A_z/Q = 2.3$ ). The water cation content decreases as cation size increases, which may be attributed to the restriction in the inter-crystalline space for water molecules inside the channels. In any event, the reactions produced by the loss of crystal water bonded to octahedra at the edge of the channels and of OH groups (Bellat and Simonot-Grange, 1990) do not seem affected by heavy-metals in the structure. Likewise, the IR band at  $1630 \text{ cm}^{-1}$ , associated with coordination water, observed by Corma et al. (1985) in studying Cu-exchange sepiolite, does not appear particularly affected by each treatment.

These results support the claim that the treatments do not markedly affect the mineral's structural features.

Kinetics were determined following the classical kinetic approach using isothermal experiments at room temperature. The best-fitting curve for each species was determined by calculating the vector which best fitted an overdetermined equation system  $Ax = b$  using the program MATLAB (Moler, 1992). To this end, we employed the least-square method, calculating the minimum for the function  $F(x) = R^T R$  ( $R = Ax - b$ ). The accuracy of the fit was evaluated by the  $Q$  parameter ( $Q = \|b - ax\|_2^2$ ).

## 4. Results and discussion

Heavy metals, which are priority pollutants, tend to concentrate in minerals and groundwater. Factors influencing adsorption of metal ion include the nature of the substrate, the nature and concentration of the adsorbate, the residence time of the metal ion at the surface and the presence of competing or complexing ions or ligands (Winkels et al., 1998). Thus, the affinity of each heavy metal for sepiolite was evaluated by single component heavy-metal solutions, whereas a multicomponent solution was used to verify the affinity of each metal in the presence of competing pollutants.

### 4.1. Experiment with single-component, heavy-metal solutions

Fig. 1a shows the breakthrough curves resulting from the runs performed by percolating  $\text{Mg}^{2+}$ -exchanged sepiolite with single-component, heavy-metal solu-

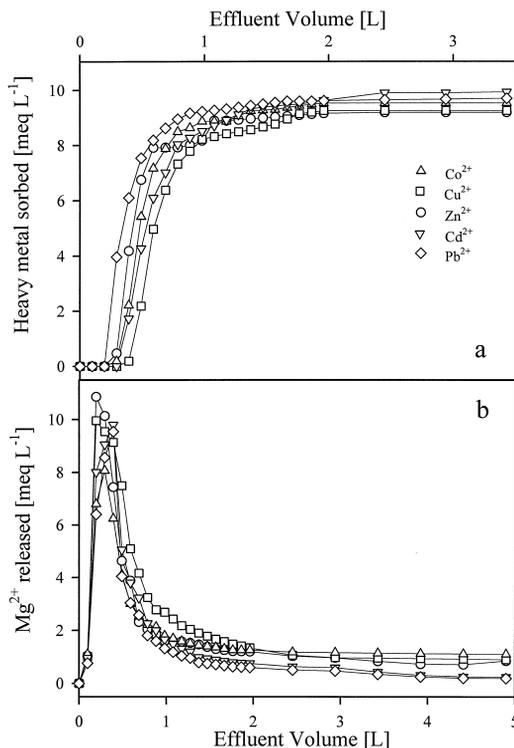


Fig. 1. (a) Breakthrough curves of sepiolite treated with heavy-metal, single-component solutions ( $10^{-2}$  N). The curves refer to the estimated heavy metal content ( $\text{meq l}^{-1}$ ) in the effluent solutions at each percolation. The abscissa was truncated at 3.5 l in order to clarify the trends in the range 0–2 l. (b) Elution curves of  $\text{Mg}^{2+}$  released by each sepiolite bed with single heavy-metal component solutions. The ordinate is the amount of  $\text{Mg}^{2+}$  in each volume of eluate ( $\text{meq l}^{-1}$ ).

tions. The amount of heavy-metal cation removed [ $\text{meq g}^{-1}$ ] by the mineral during each experiment was  $\text{Pb}^{2+}$  (0.099) <  $\text{Cd}^{2+}$  (0.128) <  $\text{Co}^{2+}$  (0.141) <  $\text{Zn}^{2+}$  (0.159) <  $\text{Cu}^{2+}$  (0.190). Hence, apart from  $\text{Pb}^{2+}$ , the experimental sorption values are slightly higher than for the sepiolite CEC. In the mass transfer zone (MTZ), which is the fraction of the bed in which sorption reactions are supposed to occur under dynamic conditions,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  deplete quickly; the trend of the breakthrough curve indicates that  $C_s/C_0$  (where  $C_s$  and  $C_0$  are the solute concentrations in the effluent and in the influent solution, respectively) changes from 0 to nearly 1 for a relatively low volume of solution.

On the other hand,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Co}^{2+}$  were not completely exhausted in MTZ at the end of the standardised experiment. Breakthrough curves show a steep slope at the beginning,  $C_s/C_0$  changing from 0 to  $\sim 0.8$  for  $\sim 1$  liter of effluent, whereafter a slow trend is observed. Also, the  $\text{Cu}^{2+}$  curve shows two broad peaks at the  $C_s/C_0$  ratio of nearly 0.8 and 0.9, respectively.

The experimental results indicate that the quantity of heavy metal sorbed by the sepiolite layer increases for smaller cations. This increase is consistent with the hypothesis that small cations can diffuse both into channels and into additional structural sites, such as some Mg octahedra at the edges of the channels.

The amount of  $Mg^{2+}$  measured in the effluent is reflected in the shape of the heavy-metal breakthrough curves (Fig. 1b): in all cases, it is released readily at first, the elution curve peaks always occurring at  $\sim 0.5$ – $0.6$  l; subsequently, the  $Mg^{2+}$  values decrease and stabilize at a plateau near zero for  $Cd^{2+}$  and  $Pb^{2+}$  and at  $\sim 1$  [meq  $l^{-1}$ ], for  $Co^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$ . It is noteworthy that  $Co^{2+}$ ,  $Zn^{2+}$  and  $Cu^{2+}$  are not completely exhausted in the MTZ. For each experiment, the  $Mg^{2+}$  released [meq  $g^{-1}$ ] is:  $Mg_{Pb}^{2+}$  (0.114)  $<$   $Mg_{Cd}^{2+}$  (0.135)  $<$   $Mg_{Zn}^{2+}$  (0.168)  $\cong$   $Mg_{Co}^{2+}$  (0.169)  $<$   $Mg_{Cu}^{2+}$  (0.200). It can be clearly seen that  $Mg^{2+}$  increases with the amount of heavy metal sorbed, and in all cases the values are slightly higher than those of heavy metal retained, indicating that the degree of hydronium ion exchange is slight. Kinetic behaviour (Fig. 2a) was investigated by plotting the heavy metal increment ( $\Delta M^{2+}$ ) in the mineral at different times. For each metal, the isotherms in the range 0–350 min show a different trend:  $Cd^{2+}$  reaches an equilibrium value at  $\sim 130$  min and  $Pb^{2+}$  at 250 min, whereas  $Co^{2+}$ ,  $Zn^{2+}$  and  $Cu^{2+}$  increase at a different rate and reach equilibrium values at 500, 600 and 750 min, respectively (these values are not reported in Fig. 2a, because they do not add any further information about the trends of the curves and would only clutter up the figure). The sorption and/or exchange-reaction rate constants ( $k_{M^{2+}}$ ) were obtained from angular coefficients of the linearized form of each Langmuir isotherm (Fig. 2a) using Eqs. (1) and (2):  $k_{Co^{2+}} = 4.798 \times 10^{-3}$ ,  $k_{Cu^{2+}} = 3.424 \times 10^{-3}$ ,  $k_{Zn^{2+}} = 2.907 \times 10^{-3}$ ,  $k_{Pb^{2+}} = 1.009 \times 10^{-2}$  [meq min] $^{-1}$ ,  $k_{Cd^{2+}} = 1.187 \times 10^{-2}$  [meq min] $^{-1/2}$ . Actually, the reactions of  $Co^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$  and  $Pb^{2+}$  with sepiolite proceed according to the kinetic law described by Eq. (1); this model, however, fails for the  $Cd^{2+}$  isotherm, which is better described by Eq. (2):

$$\frac{1}{(C_{eq} - C_t)} - \alpha = kt \quad (1)$$

$$\left( \frac{1}{(C_{eq} - C_t)} - \alpha \right)^{1/2} = kt \quad (2)$$

where  $C_{eq}$  (meq) is the heavy-metal concentration at equilibrium,  $C_t$  (meq) is the amount of the sorbed metal at time  $t$  and  $\alpha$  is a constant equal to  $1/C_{eq}$  (Fig. 2b).

#### 4.2. Experiment with multicomponent heavy-metal solution

Fig. 3 shows the breakthrough curves obtained by treating the sepiolite with the multicomponent solution. The slope of the breakthrough curves depends on

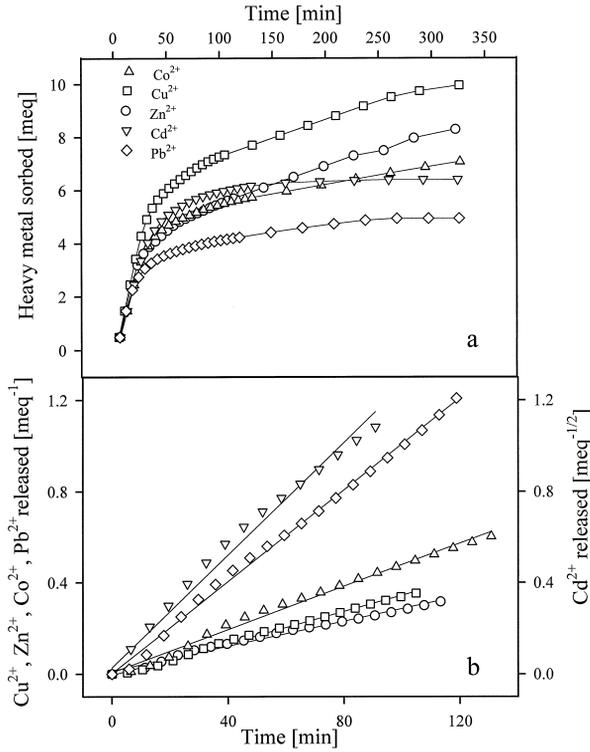


Fig. 2. (a) Adsorption isotherms of heavy metals on sepiolite beds. (b) Linearization of the adsorption isotherms following Eq. (1) for  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and Eq. (2) for  $\text{Cd}^{2+}$ .

solute concentration and interfering cations (Pansini et al., 1996). Thus, using the five divalent metal cations in combination, we can expect the results of the experiment to be quite different from those obtained when using the cations singly. The total amount of metals removed was  $0.12 \text{ [meq g}^{-1}\text{]}$ , in the

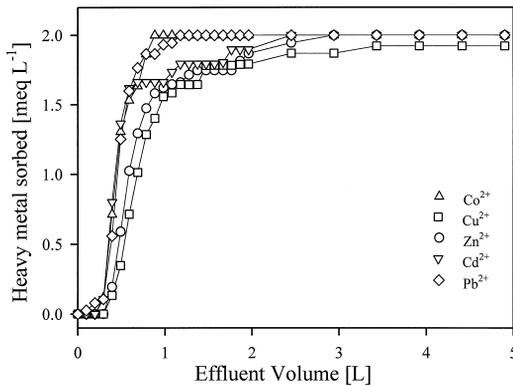


Fig. 3. Breakthrough curves of sepiolite treated with heavy-metal, multicomponent solutions. The curves refer to the estimated heavy-metal content ( $\text{meq l}^{-1}$ ) in the eluates at each percolation.

following proportions:  $\text{Co}^{2+}$  (0.017) =  $\text{Pb}^{2+}$  (0.017) <  $\text{Cd}^{2+}$  (0.022) <  $\text{Zn}^{2+}$  (0.029) <  $\text{Cu}^{2+}$  (0.038) [meq  $\text{g}^{-1}$ ]. Apart from  $\text{Cu}^{2+}$  (MTZ exhaustion after 5.8 l of the influent) the material quickly became saturated. For all other metals, the adsorption zone was reduced, and exhausted at 3 l. The total amount of heavy metals sorbed is slightly lower than the mean value obtained for the single-component treatments. Furthermore, the  $\text{Co}^{2+}$  MTZ was nearly completely exhausted at 1 l, indicating that, when it coexists with  $\text{Cu}^{2+}$ , sepiolite affinity is greater for the latter. The difference in the degree of exchange of  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  can be attributed only to differences in the diffusion mechanism of the ions within the crystal structure. Actually,  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  form similar cation–water complexes, thus the mobility of these ions, which depends on the size of the hydrated cation in aqueous solution, is very similar (Robinson and Stokes, 1968).

After Sherry (1993), the metal efficiency or the efficiency of the exchange process may be defined by:

$$M^{q+} = (\text{equiv } BM^{q+}) / (\text{equiv } AM^{q+}) \quad (3)$$

where  $M^{q+}$  represents the in-going metal cation and  $A$  and  $B$  the metal concentration in the influent and mineral, respectively. The sepiolite sorption and/or exchange efficiency sequence was: (i) single component solutions:  $\text{Pb}^{2+}(0.49) < \text{Cd}^{2+}(0.64) < \text{Co}^{2+}(0.71) < \text{Zn}^{2+}(0.80) < \text{Cu}^{2+}(0.95)$ ; (ii) multi-component solution  $\text{Pb}^{2+}(0.44) = \text{Co}^{2+}(0.44) < \text{Cd}^{2+}(0.56) < \text{Zn}^{2+}(0.74) < \text{Cu}^{2+}(0.95)$ . This may indicate that sepiolite's ability to remove  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  is virtually independent of the competitive cation interactions, whereas its affinity for  $\text{Co}^{2+}$  is much lower when other metals coexist in the solution.

With respect to the single component experiments, a similar pattern of kinetic behaviour was found only for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  in the time range 0–100 min. Beyond 100 min, and for other coexisting metals, the data reveal a different kinetic character.

#### 4.3. Desorption experiments

Firstly, the beds treated with single component solutions were eluted with a  $\text{Mg}^{2+}$  solution. This cation was chosen as the eluting ion owing to its trioctahedral mineral character (Jones and Galán, 1988), which should ensure that the in-going  $\text{Mg}^{2+}$  ions effectively exchange with heavy metals even in octahedral sites (Fig. 4a). In Fig. 4b, the  $\text{Mg}^{2+}$  desorption efficiency was evaluated in accordance with the expression:

$$\text{DE}(\%) = (AM^{q+} - R_i) / AM^{q+} \times 100. \quad (4)$$

Where  $R_i = \sum_{l=0}^{i-1} B_l \times \Delta V_l$  indicates the heavy-metal fraction released during the elution experiment, ( $B_l$  was the amount of heavy-metal released per volume



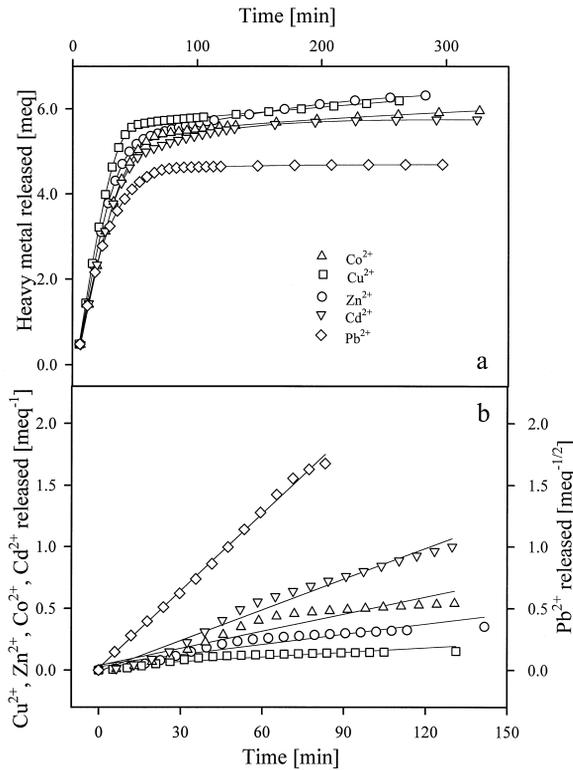


Fig. 5. (a) Desorption isotherms of heavy metals on sepiolite beds. (b) Linearization of the desorption isotherms following Eq. (1) for  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and Eq. (2) for  $\text{Pb}^{2+}$ . (c) Desorption curves obtained treating two  $\text{Zn}^{2+}$ -exhausted beds with  $\text{Mg}^{2+}$  and  $\text{Na}^+$  ( $10^{-2}$  N).

sorption ( $k_{\text{Co}^{2+}} = 5.031 \times 10^{-3}$ ,  $k_{\text{Cu}^{2+}} = 1.645 \times 10^{-3}$ ,  $k_{\text{Zn}^{2+}} = 3.255 \times 10^{-3}$ ,  $k_{\text{Cd}^{2+}} = 8.177 \times 10^{-3}$  [meq min]<sup>-1</sup>,  $k_{\text{Pb}^{2+}} = 1.569 \times 10^{-2}$  [meq min]<sup>-1/2</sup>).

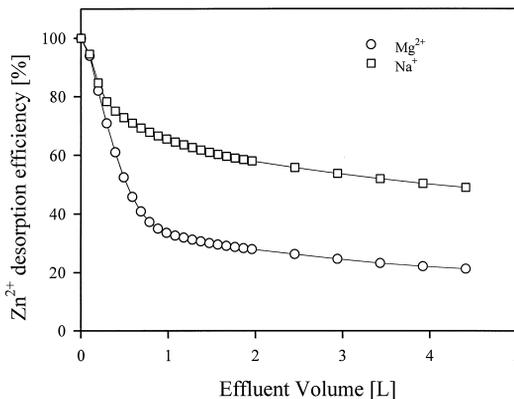


Fig. 6. Desorption curves obtained treating two  $\text{Zn}^{2+}$ -exhausted beds with  $\text{Mg}^{2+}$  and  $\text{Na}^+$  ( $10^{-2}$  N).

In a separate set of experiments, the effects of ion species in the influent on heavy-metal desorption were compared. The effectiveness of  $10^{-2}$  N  $\text{Mg}^{2+}$  and  $\text{Na}^+$  solutions to elute  $\text{Zn}^{2+}$  cations from exhausted  $\text{Zn}^{2+}$  beds was assessed (Fig. 6). As in the case of the  $\text{Mg}^{2+}$  ion-regeneration system, most  $\text{Zn}^{2+}$  is removed at the beginning, which suggests that there are accessible  $\text{Zn}^{2+}$  positions for both  $\text{Mg}^{2+}$  and  $\text{Na}^+$  cations. However, the amount of  $\text{Zn}^{2+}$  eluted with  $\text{Na}^+$  is lower than that for  $\text{Mg}^{2+}$ , which indicates that some  $\text{Zn}^{2+}$  positions resist exchange by the eluting agent.

## 5. Conclusions

Accurate, reliable laboratory measurements of heavy-metal ( $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ) adsorption and desorption on a fixed mineral substrate, and under controlled conditions, are essential for the prediction of the mobilization and accumulative reduction of these contaminants in the environment.

We have demonstrated in this paper that heavy-metal ion sorption by sepiolite is fast at the beginning and then proceeds slowly, mostly for cations with a cation–water coordination sphere similar to that of  $\text{Mg}^{2+}$ . Most importantly, except for  $\text{Co}^{2+}$ , the rate and efficiency of sorption seem to be independent of interfering ions. Heavy-metal sorption by sepiolite decreases in the order  $\text{Pb}^{2+} \approx \text{Cd}^{2+} < \text{Co}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+}$ , and depends roughly on the size of the cation. Actually, small ions are preferred as elution proceeds, indicating that not only the structural channels but also octahedral sites at the edges of the channels can be involved in the sorption.

Heavy-metal desorption reactions from used sepiolite show a pattern of metal extractability similar to that obtained for sorption experiments, i.e., it is governed by the size of the heavy-metal cation with  $\text{Cu}^{2+} < \text{Zn}^{2+} < \text{Co}^{2+}$ .  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  desorption is fast and their release is virtually complete by the end of the experiment. Comparison of  $\text{Zn}^{2+}$  release reactions using  $\text{Na}^+$  and  $\text{Mg}^{2+}$  solutions indicates that affinity is always in favour of the indigenous  $\text{Mg}^{2+}$  ions; the site number available for  $\text{Mg}^{2+}$  ions is therefore greater than that for  $\text{Na}^+$ .

Finally, the calculation of the kinetic constants ( $k_{\text{M}^{2+}}$ ) for the sorption and desorption reactions provides further insight into the availability of heavy metals to the environment: these constants are usually higher for large cations, which further confirms that different sites and bonding types are involved in exchange reactions.

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## References

- Bellat, J.P., Simonot-Grange, M.H., 1990. Adsorption–desorption of water by sepiolite. Characterization of zeolitic water. In: Farmer, V.C., Tardy, Y. (Eds.), *Proc. of the 9th Int. Clay Conf.*, Strasbourg, Vol. 87, No. 15. *Sci. Geol. Mem. Strasbourg*, pp. 15–23.
- Brigatti, M.F., Medici, L., Poppi, L., 1996. Sepiolite and industrial waste water purification: removal of  $Zn^{2+}$  and  $Pb^{2+}$  from aqueous solutions. *Appl. Clay Sci.* 11, 43–54.
- Corma, A., Perez Pariente, J., Soria, J., 1985. Physico-chemical characterization of  $Cu^{2+}$  exchanged sepiolite. *Clay Miner.* 20, 467–475.
- Glynn, P., Brown, J., 1996. Reactive transport modelling of acidic metal-contaminated ground water at a site with spatial information. In: Lichtner, P.C., Steefel, C.I., Oelkes, E.H. (Eds.), *Reactive transport in porous media*, Vol. 34. Mineralogical Society of America, pp. 269–310.
- Hibino, T., Tsunashima, A., Yamazaki, A., Otsuka, R., 1995. Model calculation of sepiolite surface areas. *Clays Clay Miner.* 43, 391–396.
- Jones, B.F., Galán, E., 1988. Sepiolite and palygorskite. In: Bailey, S.W. (Ed.), *Review in Mineralogy*, Vol. 19. Mineralogical Society of America, Washington DC, pp. 631–674.
- Moler, C., 1992. The student edition of MATLAB. The Math. Works, Prentice Hall, Englewood Cliff, NY, 495 pp.
- Pansini, M., Colella, C., Caputo, D., Di Gennaro, M., Langella, A., 1996. Evaluation of phillipsite as cation exchanger in lead removal from water. *Microporous Materials* 5, 357–364.
- Robinson, R.A., Stokes, R.H., 1968. *Electrolyte solutions*, 2nd edn., Vol. 14A. Butterworth, London, pp. 22–34.
- Serna, C., Van Socyoc, G.E., 1979. Infrared study of sepiolite and palygorskite surfaces. Mortland, M.M., Farmer, V.C. (Eds.), *Proc. of the Int. Clay Conf.* 1978. Elsevier, Amsterdam, pp. 197–206.
- Serratosa, J.M., 1979. Surface property of fibrous clay minerals (palygorskite and sepiolite). In: Mortland, M.M., Farmer, V.C. (Eds.), *Proc. of the Int. Clay Conf.* 1978. Elsevier, Amsterdam, pp. 99–109.
- Sherry, H., 1993. The design of ion exchange processes. *Zeolites* 13, 377–383.
- Thompson, A.F.B., Jackson, K.J., 1996. Reactive transport in heterogeneous system: an overview. In: Lichtner, P.C., Steefel, C.I., Oelkes, E.H. (Eds.), *Reactive transport of porous media*, Vol. 34. Mineralogical Society of America, pp. 269–310.
- Winkels, H.J., Kroonenberg, S.B., Lychagin, M.Y., Marin, G., Rusakov, G.V., Kasimov, N.S., 1998. Geochronology of priority pollutants in sedimentation zones of the Volga and Danube delta in comparison with the Rhine delta. *Applied Geochemistry* 13, 581–591.