

# Adsorption of Cd(II), Cr(III) and Mn(II) on natural sepiolite

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Received 21 June 2006; Accepted 7 April 2008

## Abstract

Heavy metals such as cadmium, chromium and manganese are toxic priority pollutants that commonly interfere with the beneficial use of wastewater for irrigation and industrial applications. The sorption of cadmium, chromium and manganese from aqueous solutions onto natural sepiolite has been studied. The efficiency of sepiolite as an adsorbent for the removal of these heavy metals from aqueous solutions has been determined. The adsorption was carried out using a batch method. Adsorption data have been interpreted in terms of Langmuir and Freundlich equations. The results were provided strong support for the adsorption of heavy metals into sepiolite. For investigation of exchange equilibria different amounts of sepiolite were contacted with a fixed volume of a heavy metal bearing solutions. Because the uptake of these heavy metals is mainly dominated by the pH of the liquid phase the pH value was varied between pH 0–3 and 0.5–5 g in each series of samples. The initial and final concentrations of heavy metals were determined by means of atomic absorption spectrophotometry. All the operations were conducted at room temperature ( $20 \pm 1$  °C). Exchange equilibria have been evaluated for sepiolite by means of the surface complex formation theory. For evaluation of equilibrium parameters the generalized separation factors were calculated from experimental data and plotted vs. the respective dimensionless sepiolite loadings. The experiments demonstrated that  $\text{Cr}^{3+}$  and  $\text{Cd}^{2+}$  ions were more efficiently adsorbed than  $\text{Mn}^{2+}$  ions by sepiolite.

*Keywords:* Cadmium; Chromium; Manganese; Sepiolite; Surface complexation theory

## 1. Introduction

Heavy metals are common pollutants found in various industrial effluents. Industrial and municipal wastewaters mostly contain metal ions. Heavy metals, especially Pb(II), Hg(II), Cd(II), Co(II), Ni(II), Cr(VI), etc., have become

prominent pollutants these days due to their toxic and lethal effects. The stricter environment regulation on the discharge of heavy metals makes it necessary to develop various technologies for the removal. Waste streams containing a low-to-medium level of heavy metals are often encoun-





surface. The majority of the other ions are located in Stern layers parallel to the surface and with individual distances from the surface. The remaining counterions and also coions are distributed across the diffuse layer, which normally can be neglected [23–25]. Thus, the values of the equilibrium parameters were obtained from the generalized separation factors. For evaluation of equilibrium parameters the generalized separation factors have to be determined from equilibrium concentrations and resin loadings and have to be plotted vs. the respective dimensionless resin loading of (algebraic) sum of resin loadings.

For evaluation of equilibrium parameters the generalised separation factors for Cd,

$$\log Q_{Cd}^H = \log \frac{y(H) \cdot C(Cd)}{y(Cd) \cdot C(H)^2} \quad (2)$$

were calculated from experimental data for all metals as given formulas and plotted vs. the respective dimensionless resin loadings. The parameters are obtained from the linear relationship

$$\log Q_{Cd}^H = \log K_{Cd}^H + m(H, Cd) \cdot y(Cd) \quad (3)$$

From this plot the two equilibrium parameters,  $K_{Cd}^H$  and  $m(H, Cd)$  can be deduced.  $y(Cd)$  is obtained from

$$y(Cd) = \frac{Q(Cd)}{Q_{max}} \quad (4)$$

and  $y(H)$  from the measured pH values. The same equations were also used for other metals. Considering local equilibria, logarithmic equilibrium parameters (generalized separation factors) can be obtained by measuring pH values and equilibrium concentrations. The surface complexation approach allows chemical reactions or equilibria in the liquid phase to be taken into account using the same set of equilibrium parameters for the ion

exchange part of the entire equilibrium. The major advantage of the theoretical approach is that these constants can be applied without any adaptation to the prediction of multicomponent systems. Evaluation of amphoteric data requires a more sophisticated method: the first step is the assumption of a certain sequence of layers. Evaluation of data starts with the evaluation of the equilibrium for the uptake of protons and ions in the first layer. The respective parameters are required for evaluation of the sorption of species in the next layer. Determination of parameters for the third layer requires both sets of parameters of the inner layers. This kind of evaluation has to be continued until all sets of binary parameters are derived. The sequence of layers was assumed correctly if both the  $\log K$  and  $m(H, metal)$  values show a steady increase with increasing distance. If this condition is not fulfilled, the calculation has to be repeated with a modified sequence [26].

### 3. Results and discussion

Equilibrium experiments were done and adsorption isotherms were obtained and are presented in Fig. 1. It can be seen that equilibrium is strongly favorable for  $Cr^{3+}$ . According to the equilibrium isotherms, the selectivity series is  $Cr^{3+} > Cd^{2+} > Mn^{2+}$ . Sorption data have been interpreted in terms of Langmuir and Freundlich equations. The results are given in Figs. 2 and 3. The plots have good linearity in both cases (Freundlich plots:  $R^2 = 0.948, 0.960$  and  $0.969$ ; Langmuir plots:  $R^2 = 0.940, 0.957$  and  $0.988$ ) at room temperature.

The parameters of Freundlich and Langmuir isotherms are given in Table 2. It can be seen that the Langmuir model yields a little better linearity than the Freundlich model when  $R^2$  values are compared. The Langmuir isotherm models the monolayer coverage of the adsorption surface. This model assumes that adsorption occurs at specific homogeneous adsorption sites within the

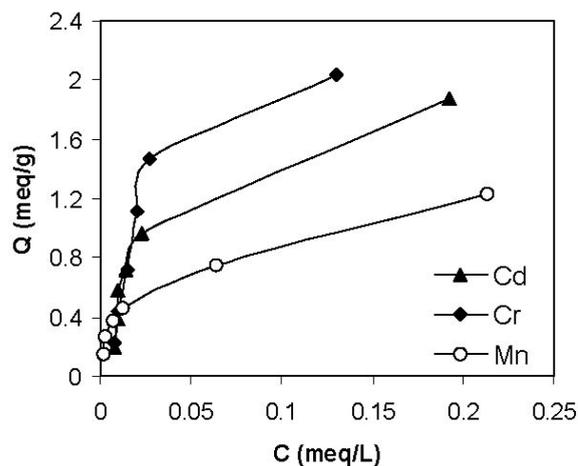


Fig. 1. Isotherms of the uptake of metals by sepiolite.

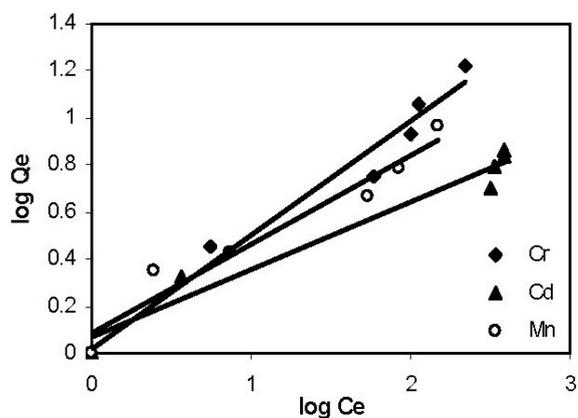


Fig. 2. Freundlich sorption isotherm of metal ions by sepiolite.

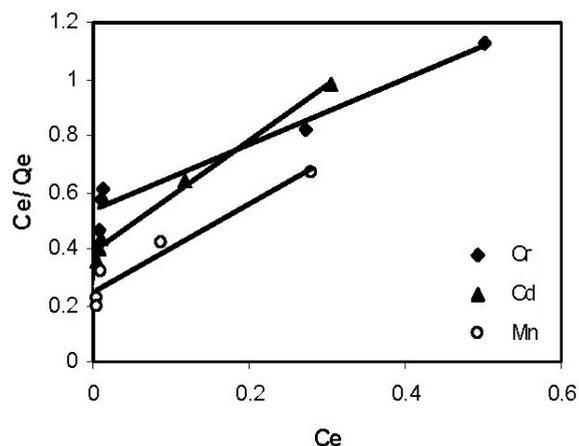


Fig. 3. Langmuir sorption isotherm of metal ions by sepiolite.

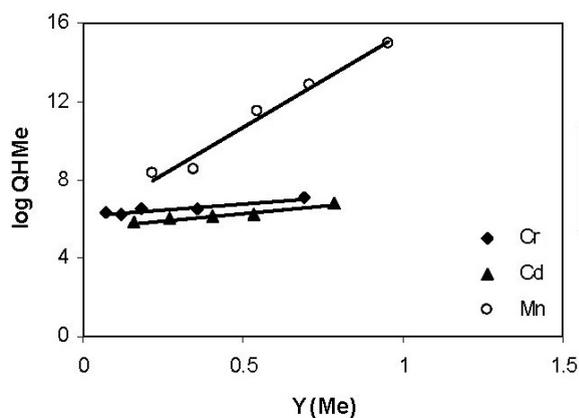


Fig. 4. Generalized separation factor for metals.

Table 2

Parameters of Langmuir and Freundlich isotherms for sorption of metal ions on sepiolite

Metal ion	Langmuir isotherm method			Freundlich isotherm method		
	$b$	$Q_0$	$R^2$	$K_f$	$n$	$R^2$
$Cr^{3+}$	1.1604	0.5341	0.957	0.4826	0.0187	0.969
$Cd^{2+}$	1.9778	0.3876	0.988	0.2871	0.0701	0.960
$Mn^{2+}$	1.5648	0.2465	0.940	0.3785	0.0866	0.948

adsorbent and intermolecular forces decrease rapidly with the distance from the adsorption surface. The Langmuir adsorption model further

based on the assumption that all the adsorption sites are energetically identical and adsorption occurs on a structurally homogeneous adsorbent.

The Langmuir constant  $b$  and maximum adsorption capacity  $Q_0$  of adsorbent were calculated and these are also shown in Table 2. The Langmuir monolayer adsorption capacity,  $Q_0$ , is between 0.246 and 0.534 meq/g. The Langmuir equilibrium coefficient,  $b$ , has values of 1.160 and 1.978. The Freundlich equation predicts that the metal ion concentration on the sorbent will increase as long as there is an increase in the metal ion concentration while experimental results showed a plateau indicating a limiting value of the sorption.

The coefficients  $K_f$  and  $n$  can be estimated from the slopes. Both  $K_f$  and  $n$  are empirical constants, being indicative of the extent of adsorption and the degree of nonlinearity between solution and concentration, respectively. The Freundlich plots yielded values for the coefficients  $K_f$  and  $n$  in the ranges from 0.287 to 0.483 and from 0.019 to 0.087. These values signify the sorption intensity and sorption capacity, respectively. The numerical value of  $1/n < 1$  indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentration. The Freundlich isotherms do not yield any concrete information about the mechanism of adsorption, but they are applicable to non-specific adsorption on heterogeneous solid surfaces.

Some other studies showed that Freundlich and Langmuir isotherms correspond well with the experimental results of some heavy metals [22, 27–30].

For evaluation of equilibrium parameters the generalized separation factors have to be determined from equilibrium concentrations and resin loadings and have to be plotted vs. the respective dimensionless resin loading of (algebraic) sum of sepiolite loadings. In the case of binary systems and pure cation exchange the respective graphical representations directly yield the equilibrium parameters: the intersection of the linear relationship leads to  $\log K$  whereas the slope of the straight line yields  $m$  (H, metal). It was shown that with increasing  $\log K$  more and more

Table 3  
Equilibrium parameters of sepiolite for the exchange of protons

$\log K_{Me}^H$	(Cr)	6.177
$\log K_{Me}^H$	(Cd)	5.520
$\log K_{Me}^H$	(Mn)	5.895
$m(H, Me)$	(Cr)	1.244
$m(H, Me)$	(Cd)	1.525
$m(H, Me)$	(Mn)	9.620

counterions were fixed in Stern layers, whereas at stronger dissociation values an increasingly large fraction of the counterion was located in the diffuse layer. Greater deviation from linear development of  $\log Q$  values relative to  $y$  (metal) is due to this effect as well.

Fig. 4 gives the generalized separation factors for each metals. It can be seen that the numerical values of the separation factors follow a straight line, from which the equilibrium parameters were derived. The developments of  $Q_{Me}^H$  data show that the exchange of Me against  $H^+$ , straight lines with positive slopes are obtained for  $y(H) \geq 1$ . The straight line has a positive slope indicating that the Stern layer for the metal ions is some distance from the surface, whereas protons undergo specific interactions with the functional sites and are located directly in the surface plane. The sorption process can be mathematically described by the surface complexation theory after determining the equilibrium parameters,  $\log K_{Me}^H$  and  $m(H, Me)$  for the binary system (H/Me), where Me is any metal ion. The respective numerical values of  $\log K_{Me}^H$  and  $m(H, Me)$  are summarized in Table 3. The amount of sorbed metal was increased with increasing pH.

The results demonstrate that linear relationships are obtained in most cases. Systematic deviations are found for small loadings. This has to be credited to the neglect of counterions in the diffuse layer.

#### 4. Conclusions

The results of this study indicate that sepiolite, a natural low-cost adsorbent, can be successfully used for the removal of  $\text{Cr}^{3+}$ ,  $\text{Cd}^{2+}$  and  $\text{Mn}^{2+}$  from aqueous solutions.

Adsorption on sepiolite can be expressed better with Langmuir-type adsorption isotherms and adsorption capacities order was found as  $\text{Cr}^{3+} > \text{Cd}^{2+} > \text{Mn}^{2+}$ . Correlation coefficients for the isotherm models indicate that the Langmuir model best describes the metal adsorption process and experimental data are better fitted to the Langmuir isotherm. The observed metal ion uptake is thought not only a simple ion-exchange process but also ion exchange, complex formation and surface adsorption mechanisms play an important role in the whole adsorption process of sepiolite.

Equilibrium parameters for the different kinds of resins were obtained from a number of binary experiments. The surface complexation model provides an excellent description and prediction of counterion equilibria with sepiolite and facilitates the accurate anticipation of their distribution in the sepiolite and liquid phases.

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