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Adsorption of Mercury(II) from Aqueous Solutions by the Clay Mineral Montmorillonite

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The input of mercury into the environment from natural and anthropogenic sources (Morel *et al*., 1998; Boening, 2000), in addition to its high toxicity and availability to be accumulated by organisms, has led to critical localized mercury pollution sites around the world and the risk for the environment and the health of organisms, including humans, has been increased. Thus, clean-up technologies for the treatment of huge volumes of water, sediments and soils contaminated with this metal are needed. Mechanical, chemical and biological methods have been developed for water purification and mercury recovery operations from wastewater (Wagner-Döbler *et al*., 2000; King *et al*., 2002; Manohar *et al*., 2002). Because of the physical and chemical characteristics of clay minerals such as large surface area, moderate to high cation exchange capacity and high negative surface charge (Horowitz, 1991), the use of these materials for adsorbing heavy metals can be an effective technology for the treatment of industrial wastewaters and can become a good tool for the remediation of coastal ecosystems impacted with mercury. Hirst (1962) suggested that clay minerals concentrate trace elements in the sequence: montmorillonite > vermiculite > illite = chlorite > kaolinite. In this study, montmorillonite, which is considered as a suitable adsorbent for mercury removal, has been used in adsorption experiments in order to learn the effects of mercury concentration and pH on the ability of this mineral to trap the metal.

MATERIALS AND METHODS

Untreated calcic montmorillonite was obtained from Fluka (Sigma-Aldrich Co.). The chemical composition of this mineral was obtained by an X-Ray Fluorescence sequential system (Siemens SRS300), and the specific surface area (SSA) and total pore volume (TPV) were calculated by applying the BET method (Celis et al., 2000). This montmorillonite was employed directly for mercury(II) batch adsorption experiments. One gram of montmorillonite was put into 250 ml polypropylene flasks containing 100 mL of Hg(II) solution with variable initial concentration (0.25, 0.5, 1.0, 2.5, 5.0 and 10.0 mg L^{-1}), and agitated on an oscillating shaker at 100 rpm for a period of 2 h at room temperature (25 ºC). Mercury(II) solutions were prepared from mercuric chloride ($HgCl_2$) and Milli-Q purified water. Hydrochloric acid or sodium hydroxide were used for adjusting

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(increasing or decreasing, respectively) the initial pH of all the metal solutions to pH 6. No more pH measurements were made during the experiment. Three-ml samples were taken from each flask at the beginning and the end of the experiments. The samples were filtered through 0.22 μm-nitrocellulose filters and filtrates were analyzed for Hg concentration by using a cold vapor mercury analyzer Buck Scientific Model 400A. In addition, the effect of the pH on the mercury removal capacity of montmorillonite was investigated in the pH range 3.0 – 9.0, following the same procedure, but only using a solution with 10 mg Hg L^{-1}. All the experiments were conducted in triplicate and the averages of the measurements for each treatment were used. Metal solutions without montmorillonite were also shaken for 2 h (controls) and no decrease of Hg concentrations in solutions was observed.

Langmuir and Freundlich adsorption isotherms were constructed from the experimental data. For Langmuir isotherms the following equation was used:

$$q_{eq} = q_m C_{eq}/(K_d + C_{eq})$$

where q_{eq} and C_{eq} correspond to the milligrams of Hg adsorbed per gram of montmorillonite and the equilibrium Hg concentration in the solution (in this case, after 120 min), respectively, and K_d and q_m are the Langmuir constant and the maximum adsorption capacity for this model. Freundlich isotherm constants were calculated with the equation:

$$q_{eq} = K_F (C_{eq})^{1/n}$$

where K_F and n are the Freundlich constants characteristic of the experimental system (Volesky 1990).

RESULTS AND DISCUSSION

The average chemical composition of the montmorillonite used here (Table 1) is similar to that of natural calcic bentonites from Guayaquil, Ecuador (Morales-Carrera et al., 2004) and Cheto, USA (Van Olphen and Fripiat, 1979). Magnesium and Ca mainly compose these three clays, followed by K and Na. The value of the specific surface area for the Fluka Montmorillonite (117 m^2 g^{-1}) was greater than those for calcic bentonites from Guayaquil and Cheto, and for natural (20 m^2 g^{-1}) and functionalized sodic montmorillonite from Wyoming, USA, by replacement of the interlayer inorganic cation (Na^+) by 2-mercaptoethylammonium cations at 50 (19 m^2 g^{-1}) and 100 % (61 m^2 g^{-1}) of its cation exchange capacity (Celis et al., 2000). However, the specific surface area for the Fluka Montmorillonite is lower than that for functionalized sodic montmorillonite from Wyoming, USA, at 150 % (153 m^2 g^{-1}) of its cation exchange capacity (Celis et al., 2000). On the other hand, the total volume of pores of Fluka Montmorillonite was higher than that found for the clay mineral from Guayaquil, Ecuador (Morales-Carrera et al., 2004).

Equilibration times for adsorption of Hg(II) on montmorillonite at three different initial metal concentration (1, 5 and 10 mg Hg L^{-1}) .were studied. Mercury

Table 1. Average chemical composition (± standard deviation), specific surface area and total volume of pores of montmorillonites.

	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MgO (%)	CaO (%)	K_2O (%)	Na_2O (%)	SSA[1] ($m^2\ g^{-1}$)	TVP[2] ($cm^3\ g^{-1}$)
Fluka	59.9 ± 0.49	17.45 ± 0.35	4.69 ± 0.02	3.09 ± 0.01	2.22 ± 0.02	1.41 ± 0.04	0.24 ± 0.03	117	0.220
Guayaquil[3]	65.8 ± 2.05	15.3 ± 0.97	5.25 ± 0.42	2.00 ± 0.15	1.68 ± 0.44	1.12 ± 0.11	0.84 ± 0.12	17 – 30	0.039
Cheto[4]	60.4	17.6	1.42	6.46	2.82	0.19	0.06	50	

[1]Specific surface area; [2]Total volume of pores; [3]Morales-Carrera et al. (2004); [4]Van Olphen and Fripiat (1979)

concentration was measured at different contact times (0, 20, 40, 60, 90 and 120 min) and the adsorbed amount of Hg was calculated by difference among the initial concentration (0 min) and the concentrations that correspond to the other times. Fig. 1 shows the effect of the initial concentration of mercury(II) on the adsorption rate. For the three treatments, the rate of adsorption was highest during the first 20 – 40 min, probably due to the relatively high availability of adsorption sites on montmorillonite. As these sites were occupied by Hg ions, the mineral surface began to be saturated and equilibrium was reached about 60 min after beginning the experiments. Equilibrium occurred relatively earlier (within 40 min) in the solution with the lowest Hg concentration (1 mg L^{-1}). Similar behavior was reported for removal of mercury (II) by a 2-mercaptobenzimidazole-clay (Manohar *et al.*, 2002), as well as for different organic and inorganic adsorbents and metal sorbates (Zhuang and Yu, 2002; Acar and Malkoc, 2004); however it is difficult to compare these studies because multiple parameters, such as the inherent characteristics of the adsorbent and experimental conditions, play a role in the adsorption mechanism (Kaçar *et al.*, 2002).

The effect of six different initial mercury concentrations on the adsorption of Hg(II) on montmorillonite was evaluated experimentally. The amount of mercury adsorbed per gram of montmorillonite was calculated by difference between the initial metal concentration (0 min) and the metal concentration after 120 min. This amount ranged from 0.242 mg g^{-1} for an initial concentration of 0.250 mg L^{-1}, to 8.000 mg g^{-1} when the concentration of Hg was 10.000 mg L^{-1} at the beginning of the experiment. The observed increase in Hg(II) adsorption as the initial concentration increased (Table 2) is possibly due to the higher Hg(II)-ionic strength of the more concentrated solutions. Nevertheless, if calculated as the percent of the initial Hg, adsorption decreased from 97 to 80 % when the initial Hg(II) concentration increased (Table 2). These observations agree with the results obtained by Bajpai (1999) for Ni(II) adsorption by illite at different initial metal concentration.

There are several isotherm models described in the literature, however the two

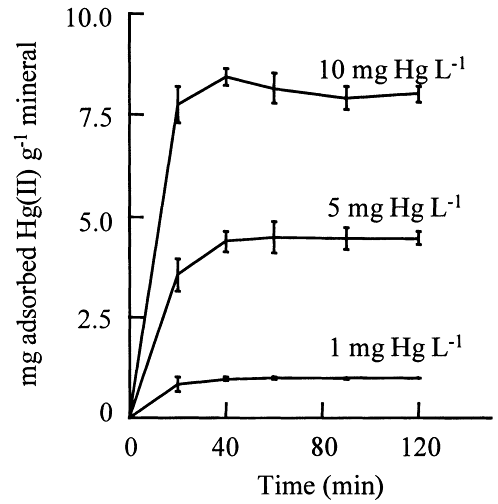

Figure 1. Adsorption rate of Hg(II) by montmorillonite as a function of initial metal concentration at 25 °C and pH = 6.

Table 2. Effect of initial Hg(II) concentration on its adsorption on montmorillonite after 120 min at 25 °C and pH= 6.

Initial Hg (mg L^{-1})	Final Hg (mg L^{-1})	Adsorption (mg g^{-1})	Adsorption (%)
0.250	0.008 ± 0.007	0.242 ± 0.007	96.8 ± 2.8
0.500	0.007 ± 0.009	0.493 ± 0.009	98.6 ± 1.8
1.000	0.012 ± 0.012	0.988 ± 0.012	98.8 ± 1.2
2.500	0.297 ± 0.070	2.203 ± 0.070	88.1 ± 2.8
5.000	0.517 ± 0.152	4.483 ± 0.152	89.7 ± 3.0
10.000	2.007 ± 0.193	7.993 ± 0.193	79.9 ± 1.9

most used are the Langmuir and Freundlich models. The Langmuir model is valid for modeling monolayer adsorption onto a homogeneous surface with constant adsorption energy, while the Freundlich equation considers a heterogeneous surface with molecules attached to a surface site influencing neighboring sites (Volesky 1990). The adsorption data from the experiments varying the initial Hg(II) concentration were analyzed in terms of both Langmuir and Freundlich equations at pH = 6 and 25 °C. The values obtained for the respective model constants are shown in Table 3. According to the correlation coefficient (r^2), used to describe the goodness of fit between the experimental data and the theoretical models, the Freundlich isotherm equation (r^2 = 0.90) better described the adsorption process of mercury(II) by montmorillonite as compared to the Langmuir equation (r^2 = 0.86). This fact suggests that heterogeneous conditions (i. e., the heterogeneity of the montmorillonite surface and its internal structure) prevail for monolayer adsorption under the experimental conditions used here. According to Acar and Malkoc (2004), if $0.1 < 1/n < 1.0$, the adsorption of an adsorbate on the anion exchanger is favorable. In this study, 1/n was 0.51,

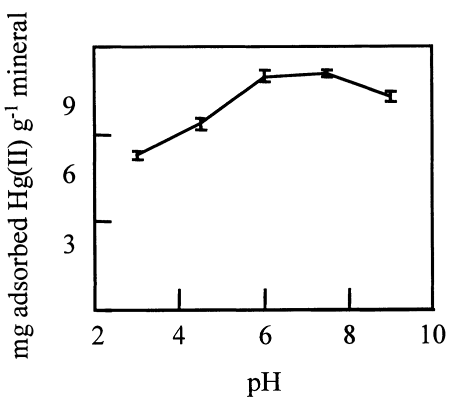

Figure 2. Effect of pH on Hg(II) adsorption by montmorillonite after 120 min at 25 °C and an initial metal concentration of 10 mg L^{-1}.

Table 3. Langmuir and Freundlich constants for Hg(II) adsorption by montmorillonite at 25 °C and pH = 6.

Model	q_m (mg g^{-1})	K_d (mg L^{-1})	1/n (L g^{-1})	K_F (mg g^{-1})	r^2
Langmuir	0.86	0.28	-	-	0.86
Freundlich			0.51	0.54	0.90

indicating that montmorillonite can be used effectively for the removal of Hg(II) from aqueous solutions.

With respect to the effect of pH on Hg adsorption, according to Abollino *et al.* (2003), it is expected that the adsorption of metals by montmorillonite would decrease with decreasing pH as the result of protonation of aluminol and silanol groups, leaving less available sites for adsorption of other cations. In contrast, at pH ≥ 7, hydroxo species of the metals can form and do not bind to the adsorption sites on the surface of the adsorbent (Kaçar *et al.*, 2002). The results shown in Figure 2 suggest that these two processes occur in the mercury – montmorillonite systems studied here. Thus, changes in pH have a significant effect on the Hg(II) adsorption capacity of the montmorillonite, with the optimal pH value between 6.0 and 7.5.

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