

# Heavy Metal Adsorption by Montmorillonites Modified with Natural Organic Cations

M. Cruz-Guzmán, R. Celis, M. C. Hermosín, W. C. Koskinen, E. A. Nater, and J. Cornejo\*

## ABSTRACT

Agricultural and industrial pollution release large amounts of heavy metals into the atmosphere, surface water, soil, and plants. The protection and restoration of soils and water contaminated with heavy metals generate a great need to develop efficient adsorbents for these pollutants. This study reports the adsorption of Pb(II) and Hg(II) by two reference montmorillonites, Wyoming (SWy-2) and Arizona (SAZ-1), that were pretreated with various natural organic cations containing different functional groups (L-carnitine, L-cysteine ethyl ester, L-cystine dimethyl ester, and thiamine cations) and with synthetic, nonfunctionalized organic cations (hexadecyltrimethylammonium [HDTMA] and phenyltrimethylammonium [PTMA] cations). Most of the organoclays adsorbed less Pb(II) than the untreated montmorillonites, with the exception of the L-carnitine-treated montmorillonites. The carboxyl functional group on L-carnitine was apparently effective for complexing Pb. In contrast, Hg(II) adsorption was greatly increased by several of the organic cation pretreatments. Sulfur-containing organic functional groups enhanced Hg(II) adsorption. The synthetic organic cations PTMA and HDTMA suppressed adsorption of Pb(II) and Hg(II) because these organic cations competed with the metals for adsorption sites on the clay surfaces and lack organic functional groups capable of interacting with the heavy metals. These findings are consistent with prior understanding of organic functional group-metal complexation reactions but go further by demonstrating that organoclays can be selectively functionalized with natural organic cations to enhance their affinity for heavy metals.

**H**EAVY METALS are important environmental pollutants threatening the health of human populations and natural ecosystems. Metals contamination is a persistent problem in many contaminated soils. The most commonly occurring metals are Cd, Cu, Ni, Pb, Cr, Zn, and Hg (Tiller, 1989). The presence of metals in groundwater can also pose a significant threat to human health and ecological systems.

Different techniques have been proposed in the literature for the remediation of soils and water contaminated by heavy metals. General approaches to remediation of metal contamination include isolation, immobilization, toxicity reduction, physical separation, and extraction (Evanko and Dzombak, 1997). For the immobilization and separation of metal species by adsorptive techniques, the use of clay minerals has been extensively studied because of their high specific surface area, cation exchange capacity, and adsorption capacity

(Stadler and Schindler, 1993; Siantar et al., 1994; Brigatti et al., 1996; Undabeytia et al., 1996; Staunton and Roubaud, 1997).

The reactions with reagents containing metal-chelating functionalities have recently been explored in an effort to enhance the heavy metal binding capacities of clay minerals and their selectivity to the type of metal (Mercier and Detellier, 1995; Mercier and Pinnavaia, 1998; Celis et al., 2000). For instance, covalent grafting of ligands containing the thiol (-SH) functionality has been shown to improve the loading capacities and affinities of clay minerals for Hg(II) ions (Mercier and Detellier, 1995; Celis et al., 2000). A suitable selection of the functionalization mechanism to avoid clogging of the limited pore space of the clay mineral after functionalization has been stressed as important in improving the performance of functionalized clay minerals as adsorbents of heavy metals (Celis et al., 2000).

Organoclays (i.e., natural clay minerals with their original inorganic exchangeable cations replaced with organic cations) have been shown to be excellent adsorbents for different kinds of organic molecules. Accordingly, they have been proposed for decontamination of soils and water contaminated with organic pollutants (Hermosín and Cornejo, 1992; Celis et al., 1999; Carrizosa et al., 2001; Andrades et al., 2004). In contrast, organoclays have received limited interest as adsorbents of heavy metals, primarily because the organic cations most commonly used for their synthesis have been synthetic alkylammonium-type cations, which compete with metals for adsorption sites on the clay mineral surfaces and lack organic functional groups capable of interacting with heavy metals (Lee et al., 2002). Recent studies have shown that the presence of certain functionalities (-COOH, -SH) in the alkylammonium cation can provide the resulting organoclays with affinity for heavy metal ions (Sheng et al., 1999; Celis et al., 2000). Nevertheless, there is little prior work on how the presence of different functionalities influences the heavy metal adsorption capacity of organoclays.

The present work was designed to provide further insight into the heavy metal adsorption capacity of functionalized organoclays. The adsorption-desorption of Pb(II) and Hg(II) ions by two reference montmorillonites pretreated with four natural, functionalized organic cations (L-carnitine, L-cysteine ethyl ester, L-cystine dimethylester, and thiamine) was determined and compared with the adsorption behavior of organoclays prepared from classical alkylammonium cations without specific functional groups (phenyltrimethylammonium

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**Abbreviations:** AAS, atomic absorption spectroscopy; CAR, L-carnitine; CEC, cation exchange capacity; CYSTE, L-cysteine ethyl ester; CYSTI, L-cystine dimethyl ester; HDTMA, hexadecyltrimethylammonium; PTMA, phenyltrimethylammonium; SA, Arizona montmorillonite; SW, Wyoming montmorillonite; THIAM, thiamine.

[PTMA] and hexadecyltrimethylammonium [HDTMA]). In a previous paper, we reported that the presence of polar functionalities in the structure of several natural organic cations greatly influenced the capacity and selectivity of organoclays in adsorbing pesticides containing diverse polar functional groups (Cruz-Guzmán et al., 2005). Here, we assess how the presence of these organic functionalities in the organic cations influences the affinity of the resulting organoclays for heavy metal ions.

## MATERIALS AND METHODS

### Organic Cations and Heavy Metals

The four natural organic cations, L-carnitine, L-cysteine ethyl ester, L-cystine dimethyl ester, and thiamine (purity >98%) and the synthetic alkylammonium organic cations, PTMA and HDTMA, were purchased as high-purity chloride salts from Sigma (Germany). The chemical structures of the organic cations used are shown in Fig. 1. High-purity  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Hg}(\text{NO}_3)_2$  (purity = 99%) were supplied by Sigma, ACS reagent. Initial heavy metal solutions were prepared in 0.001 M  $\text{HNO}_3$  (pH 3) to avoid precipitation and to simulate a worst-case scenario of heavy metal mobilization.

### Synthesis of the Organoclays

SWy-2 Wyoming montmorillonite (SW) and SAz-1 Arizona montmorillonite (SA) from The Clay Minerals Society (Columbia, MO) were exchanged with the four natural organic cations through ion exchange reactions (Cruz-Guzmán et al., 2004). For the synthesis, the amount of L-carnitine, L-cysteine ethyl ester, L-cystine dimethyl ester, or thiamine (chloride salts) corresponding to 50%, 100%, or 150% of the cation exchange capacity of SW ( $\text{CEC}_{\text{SW}} = 764 \text{ mmol kg}^{-1}$ ) and SA ( $\text{CEC}_{\text{SA}} = 1200 \text{ mmol kg}^{-1}$ ) were dissolved in 50 mL of 1 mM  $\text{HNO}_3$  and added to 1 g of each type of montmorillonite.

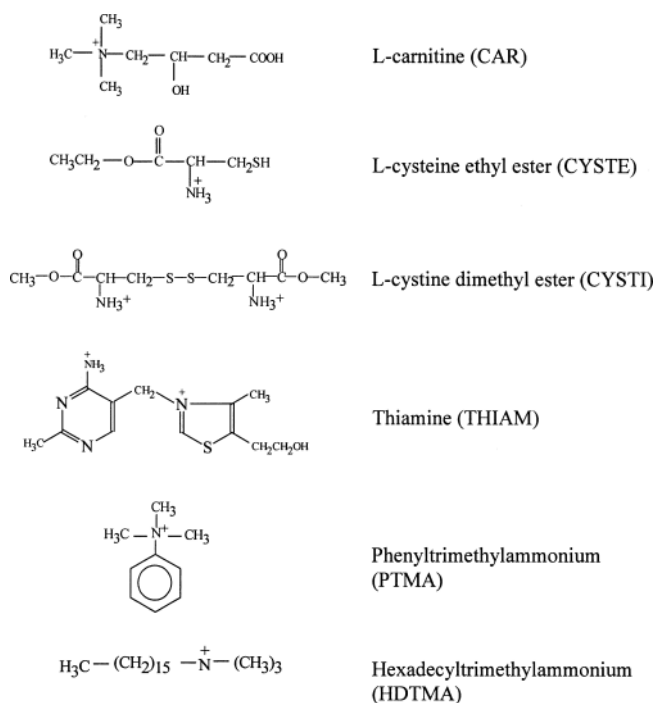


Fig. 1. Chemical structure of L-carnitine, L-cysteine ethyl ester, L-cystine dimethyl ester, thiamine, PTMA, and HDTMA cations.

Table 1. Nomenclature of the organoclays.

Sample	Organic cation	OCtS†	
		Theoretical	Actual
		%	
SW	–	–	–
SW-CAR <sub>100</sub>	L-Carnitine	100	43
SW-CAR <sub>150</sub>	L-Carnitine	150	72
SW-CYSTI <sub>50</sub>	L-Cystine dimethyl ester	50	42
SW-CYSTI <sub>100</sub>	L-Cystine dimethyl ester	100	93
SW-CYSTE <sub>50</sub>	L-Cysteine ethyl ester	50	50
SW-CYSTE <sub>100</sub>	L-Cysteine ethyl ester	100	83
SW-THIAM <sub>50</sub>	Thiamine	50	48
SW-THIAM <sub>100</sub>	Thiamine	100	98
SW-HDTMA <sub>50</sub>	HDTMA	50	55
SW-HDTMA <sub>100</sub>	HDTMA	100	83
SW-PTMA <sub>50</sub>	PTMA	50	56
SW-PTMA <sub>100</sub>	PTMA	100	85
SA	–	–	–
SA-CAR <sub>50</sub>	L-Carnitine	50	23
SA-CAR <sub>100</sub>	L-Carnitine	100	39
SA-CAR <sub>150</sub>	L-Carnitine	150	48
SA-CYSTI <sub>50</sub>	L-Cystine dimethyl ester	50	54
SA-CYSTI <sub>100</sub>	L-Cystine dimethyl ester	100	77
SA-CYSTE <sub>50</sub>	L-Cysteine ethyl ester	50	22
SA-CYSTE <sub>100</sub>	L-Cysteine ethyl ester	100	32
SA-THIAM <sub>50</sub>	Thiamine	50	50
SA-THIAM <sub>100</sub>	Thiamine	100	84
SA-HDTMA <sub>50</sub>	HDTMA	50	53
SA-HDTMA <sub>100</sub>	HDTMA	100	75
SA-PTMA <sub>50</sub>	PTMA	50	54
SA-PTMA <sub>100</sub>	PTMA	100	83

† Organic cation saturation: percentage of the CEC compensated by organic cations.

Acidic conditions were used to ensure the protonation of the biomolecules, thus favoring the exchange reaction.

The suspensions were shaken for 24 h, centrifuged, washed three times with 100 mL of distilled water, and freeze-dried. Blank clay samples, SW(Blank) and SA(Blank), were prepared by shaking 1 g of clay in 50 mL of 1 mM  $\text{HNO}_3$  for 24 h, washing three times with 100 mL of distilled water, and freeze-drying. These samples, free of organic cations, served as a control and helped evaluate the effects of the acid treatment on the clay mineral during the synthesis procedure.

The nomenclature of the different samples prepared in this work is summarized in Table 1. Methods for characterization of these organoclays have been reported previously (Cruz-Guzmán et al., 2004; 2005). The two alkylammonium-exchanged clays used as reference materials in the adsorption–desorption experiments were HDTMA- and PTMA-montmorillonite, containing an amount of alkylammonium cation equal to 50% and 100% of the CEC of SW and SA. The preparation and characteristics of these samples have been reported elsewhere (Celis et al., 2002).

### Heavy Metal Adsorption–Desorption Experiments

Pb(II) and Hg(II) adsorption–desorption isotherms were obtained using the batch equilibration procedure. Duplicate 10-mg adsorbent samples were equilibrated for 24 h at  $20 \pm 2^\circ\text{C}$  with 10 mL of aqueous solutions (pH 3) of  $\text{Pb}(\text{NO}_3)_2$  or  $\text{Hg}(\text{NO}_3)_2$  (Sigma, ACS reagent) with metal ion concentrations ranging from 0.2–1.5  $\text{mmol L}^{-1}$ . For all adsorbents, the pH of the suspensions remained  $3.0 \pm 0.3$  after a 24-h equilibration. After equilibration, the suspensions were centrifuged, and 5 mL of the supernatant solution was removed for analysis. The concentration of heavy metal in the supernatant was determined by atomic absorption spectroscopy (AAS) using a PerkinElmer 1100B atomic absorption spectrometer. The amount of metal adsorbed was calculated as the difference between the initial and final solution concentrations. Metal solutions without

adsorbent were also shaken for 24 h and served as controls. For the experimental conditions used, the sensitivity of AAS for Pb(II) and Hg(II) analysis was about 0.002 and 0.025 mmol L<sup>-1</sup>, respectively. Due to the high concentrations used in the adsorption experiments (initial concentrations ≥0.25 mmol L<sup>-1</sup>), errors associated with metal analysis were generally <10%. The behavior of selected adsorbents at high Hg concentrations was confirmed at a lower concentration range (0.01–0.1 mmol L<sup>-1</sup>) by the use of the Cold Vapor Atomic Fluorescence Spectrometry (CVAS) technique, according to the method of Bloom and Creclius (1983).

Desorption was measured immediately after adsorption from the 1.5 mmol L<sup>-1</sup> initial concentration point of the adsorption isotherms. The 5 mL of supernatant removed for the adsorption analysis were replaced with 5 mL of HNO<sub>3</sub>, NaNO<sub>3</sub>, or Ca(NO<sub>3</sub>)<sub>2</sub> at different concentrations. The suspensions were shaken at 20 ± 2°C for 24 h and centrifuged, and the metal concentration determined in the supernatant. This desorption procedure was repeated three times. All adsorption and desorption studies were conducted in duplicate.

Heavy metal adsorption isotherms were fit to the Langmuir equation:  $C_e/C_s = C_e/C_m + 1/C_m \cdot L$ , where  $C_s$  (mmol kg<sup>-1</sup>) is the amount of heavy metal adsorbed at the equilibrium concentration  $C_e$  (mmol L<sup>-1</sup>),  $C_m$  (mmol kg<sup>-1</sup>) is the maximum adsorption capacity of the adsorbent, and  $L$  (L mmol<sup>-1</sup>) is the Langmuir constant, which is related to the free energy of adsorption (Gu et al., 1995).  $C_m$  and  $L$  can be calculated from the linear plot of  $C_e/C_s$  versus  $C_e$ .

## RESULTS AND DISCUSSION

### Pb(II) and Hg(II) Adsorption Studies

We fit the Pb(II) and Hg(II) adsorption isotherms to the Langmuir equation to obtain coefficients  $C_m$  and  $L$  (Table 2). The adsorption coefficients for blank clay

samples are not shown because they were similar to the values for the untreated clay samples. All adsorption isotherms, except Pb(II) on SW-alkylammonium and SA-HDTMA samples and Hg(II) on SA-HDTMA samples, fit the Langmuir equation with  $R^2 > 0.93$ .

### Pb(II) Adsorption

With the exception of SW-CAR, SA-CAR, and SA-CYSTE, the organoclays had lower adsorption coefficients,  $K_d$  and  $C_m$ , as compared with the untreated clay minerals (Table 2). Therefore, replacement of the inorganic exchangeable cations by the organic cations produced, in most cases, a decrease in the adsorbent capacity of the montmorillonites for Pb(II), similar to the results obtained by Celis et al. (2000). Only the clays treated with CAR and SA treated with CYSTE had an adsorption behavior similar to that of the untreated clay mineral. For clay-CAR samples, although CAR occupies a Pb(II) retention site on the clay surface (i.e., a cation exchange site) it contains also a carboxylic functional group, for which Pb(II) has a high affinity (Table 2, Fig. 2). The higher  $L$  Langmuir coefficients for the SW clays exchanged with CAR, as compared with values for the untreated clay, support the high affinity of Pb(II) for the carboxylic group of carnitine (Table 2).

For SA-CYSTE, the low amount of organic cation in the organoclay (22–32%) (Table 1) could explain the high capacity of available active sites for the retention of Pb(II), similar to that in the original SA clay (Table 2). In addition, the -SH group of CYSTE could complex this metal (Tofan and Paduraru, 2004).

Table 2.  $K_d$  and Langmuir coefficients for Pb(II) and Hg(II) adsorption on unexchanged and exchanged clays.

Sample	Pb(II)			Hg(II)		
	$K_d$ †	$C_m$ ‡	L	$K_d$ †	$C_m$ ‡	L
SW	356 ± 15§	393 (363–429)§	1 (1–1)	210 ± 84	294 (265–331)	3 (2–4)
SW-CAR <sub>100</sub>	327 ± 23	198 (175–228)	9 (6–38)	1019 ± 108	402 (362–452)	4 (3–6)
SW-CAR <sub>50</sub>	274 ± 6	207 (188–229)	6 (4–9)	n.d.	398 (355–410)	4 (5–7)
SW-CYSTI <sub>50</sub>	131 ± 5	n.d.¶	n.d.	2 838 ± 456	738 (693–789)	12 (9–20)
SW-CYSTI <sub>100</sub>	70 ± 4	n.d.	n.d.	13 893 ± 5176	805 (762–853)	26 (16–96)
SW-CYSTE <sub>50</sub>	82 ± 10	n.d.	n.d.	1 511 ± 76	430 (409–454)	13 (9–24)
SW-CYSTE <sub>100</sub>	66 ± 4	n.d.	n.d.	862 ± 45	261 (257–266)	26 (19–42)
SW-THIAM <sub>50</sub>	153 ± 7	n.d.	n.d.	5 194 ± 1071	372 (359–387)	67 (22–84)
SW-THIAM <sub>100</sub>	27 ± 6	n.d.	n.d.	1 046 ± 44	248 (239–258)	44 (19–55)
SW-HDTMA <sub>50</sub>	217 ± 35	195 (162–246)	2 (1–3)	67 ± 26	n.d.	n.d.
SW-HDTMA <sub>100</sub>	67 ± 22	0#	–	19 ± 6	n.d.	n.d.
SW-PTMA <sub>50</sub>	304 ± 17	241 (197–311)	2 (1–4)	160 ± 5	n.d.	n.d.
SW-PTMA <sub>100</sub>	200 ± 45	136 (101–207)	3 (1–10)	49 ± 19	n.d.	n.d.
SA	930 ± 0	413 (382–450)	6 (4–8)	543 ± 23	339 (319–360)	3 (2–4)
SA-CAR <sub>50</sub>	1190 ± 22	436 (387–499)	5 (3–8)	1 108 ± 90	439 (411–470)	5 (4–7)
SA-CAR <sub>100</sub>	1161 ± 7	364 (354–374)	8 (7–9)	1 220 ± 192	473 (443–508)	6 (5–8)
SA-CAR <sub>150</sub>	1242 ± 45	428 (372–505)	5 (3–10)	1 560 ± 148	451 (411–499)	8 (5–16)
SA-CYSTI <sub>50</sub>	396 ± 16	n.d.	n.d.	23 985 ± 4997	947 (894–1007)	24 (17–38)
SA-CYSTI <sub>100</sub>	241 ± 26	n.d.	n.d.	39 067 ± 1908	991 (957–1028)	53 (38–82)
SA-CYSTE <sub>50</sub>	831 ± 156	n.d.	n.d.	4 998 ± 86	642 (604–686)	16 (11–28)
SA-CYSTE <sub>100</sub>	1191 ± 130	n.d.	n.d.	41 399 ± 4240	819 (770–874)	35 (21–91)
SA-THIAM <sub>50</sub>	346 ± 3	n.d.	n.d.	4 254 ± 197	455 (423–492)	25 (12–50)
SA-THIAM <sub>100</sub>	62 ± 26	n.d.	n.d.	63 961 ± 4997	574 (535–619)	42 (18–82)
SA-HDTMA <sub>50</sub>	121 ± 14	96 (82–115)	4 (2–13)	89 ± 15	66 (52–91)	7 (2–102)
SA-HDTMA <sub>100</sub>	0 ± 0	0	–	14 ± 14	0	–
SA-PTMA <sub>50</sub>	455 ± 12	222 (209–236)	6 (5–9)	304 ± 69	130 (113–153)	15 (6–708)
SA-PTMA <sub>100</sub>	276 ± 18	201 (176–235)	4 (2–8)	178 ± 17	117 (99–141)	6 (3–28)

† The concentration at which  $K_d$  was determined was 0.4 mmol L<sup>-1</sup>.

‡ The metal concentration range was 0.2–1.5 mmol L<sup>-1</sup>.

§ Standard error of the coefficients.

¶ Not determined.

# Very low or negligible adsorption.

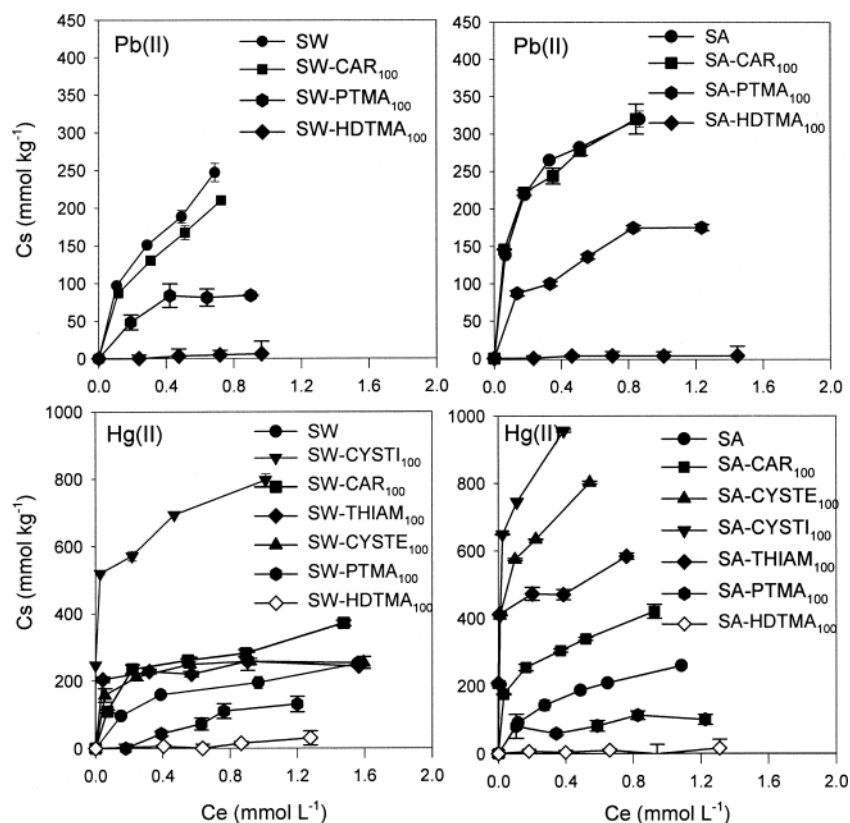


Fig. 2. Pb(II) and Hg(II) adsorption isotherms on selected organoclays.

The original SW and SA clays decreased their adsorption capacity when they were exchanged with alkylammonium cations, HDTMA, and PTMA. These cations provide no functionalities with affinity for Pb(II) but block the exchange sites of the clay mineral. In general, HDTMA, being larger than PTMA, resulted in greater blockage of exchanged sites than PTMA. The residual adsorption in SW-PTMA<sub>100</sub> and SA-PTMA<sub>100</sub> can be due to the heavy metal retention by the edges of the clay. HDTMA cation covered these edges, producing an almost total blockage (Fig. 2).

### Hg(II) Adsorption

The Hg(II) adsorption isotherms (Fig. 2, Table 2) showed a great increase in the Hg(II) adsorption after treatment of the clays with the functionalized organic cations, whereas the adsorption capacity of the clays exchanged with alkylammonium cations decreased similar to that observed for Pb(II). The greatest increase in the Hg(II) adsorption was observed in the clays exchanged with CYSTI, CYSTE, and THIAM cations, which can be attributed to the high affinity of Hg(II) for S-containing groups of these cations (Mercier and Detellier, 1995; Mercier and Pinnavaia, 1998; Feng et al., 1997; Celis et al., 2000).

In general, Hg(II) retention increased with the amount of CYSTE and CYSTI cations, most likely due to the increase in the number of S-containing groups present in the exchanged clays (Mercier and Detellier, 1995; Xia et al., 1999; Celis et al., 2000; Lagadic et al., 2001), which also

produced an increase in the separation of the sheets of the clay (Cruz-Guzmán et al., 2004). According to the higher *L* values for the functionalized organoclays than for the original clays SW and SA, the clays exchanged with functionalized organic cations seem to have higher affinity for Hg(II) than the pure clays (Table 2) (Celis et al., 2000).

It is important to note how SW-CYSTE and SW-THIAM organoclays exchanged at 50% of the CEC displayed greater Hg(II) adsorption than the same organoclays exchanged at 100% of the CEC (Table 2). Although at low Hg(II) concentrations SW-CYSTE<sub>100</sub> and SW-THIAM<sub>100</sub> retained more Hg(II) than the original clay SW, at high Hg(II) levels they had a behavior similar to that of SW (Fig. 2). In this regard, Celis et al. (2000) suggested the congestion of the internal porosity of clay minerals as a main obstacle to heavy metal adsorption by functionalized clays.

The clays exchanged with the alkylammonium cations HDTMA and PTMA had less Hg(II) adsorption capacity than the untreated clay (Fig. 2, Table 2), possibly due to the absence of functional groups with affinity for the metal in these alkylammonium cations and the blockage of the clay exchange sites. In general, HDTMA, with a larger size than PTMA, resulted in greater blockage of adsorption sites for the heavy metal than PTMA, as was observed for Pb(II).

The amount of Hg(II) retained by the functionalized organoclays was higher than the retained amount of Pb(II) (Table 2), except in the case of SA-CAR samples, which had similar values of *C<sub>m</sub>* for Pb and Hg (Table 2). It seems that Hg(II) has an affinity for the COOH group

similar to that of Pb(II), although Hg(II) has a higher affinity for the sulfur of the organic cations CYSTE, CYSTI, and THIAM. Brown et al. (1999) explained the low affinity of Pb(II) for -SH groups of functionalized organoclays by the thermodynamic inability of this metal ion to be coordinated inside the internal porosity of the adsorbents.

Other authors have studied the interaction between -SH groups and the heavy metals Pb(II) and Hg(II). Celis et al. (2000) used a montmorillonite exchanged with 2-mercaptoethylammonium cations and observed a greater Hg(II) adsorption capacity than that of Pb(II). Lagadic et al. (2001) studied the Pb(II), Hg(II), and Cd(II) adsorption on a thiol-functionalized layered magnesium phyllosilicate material. The amounts of adsorbed metal decreased in the following order: Hg(II) > Pb(II) > Cd(II). Bois et al. (2003) prepared functionalized silica with amine and mercapto groups for heavy metal ions adsorption. Krishnan and Anirudhan (2002) studied the uptake of heavy metals as Pb(II), Hg(II), Cd(II), and Co(II), in batch systems by sulfurized steam activated carbon, obtaining high-affinity adsorption isotherms in all cases (Giles et al., 1960).

### Hg(II) Adsorption at Low Heavy Metal Concentrations

The behavior of the adsorbents at high Hg concentrations was confirmed at a lower concentration range by the use of the CVAS technique, according to the method of Bloom and Crecelius (1983). The Hg(II) adsorption isotherms on SA, SA-CYSTE<sub>100</sub> and SA-CYSTI<sub>100</sub>, at high and low concentration ranges are compared in Fig. 3. The results obtained with CVAS at low Hg concentrations (Fig. 3a) are consistent with those obtained at higher concentrations measured using Atomic Absorption Spectroscopy (Fig. 3b).

### Pb(II) and Hg(II) Desorption Studies

Pb(II) and Hg(II) desorption curves, representing the percentage of adsorbed metal versus the number of desorption treatments, for the selected organoclays are shown in Fig. 4 and 5. In all cases, the desorption process was performed using different solutions with pH 3: 0.001 M HNO<sub>3</sub>, 0.1 M NaNO<sub>3</sub>, and 0.1 M Ca(NO<sub>3</sub>)<sub>2</sub>.

Pb(II) desorption curves from SW, SA, SW-CAR<sub>100</sub>, and SA-CAR<sub>100</sub> samples are shown in Fig. 4. With

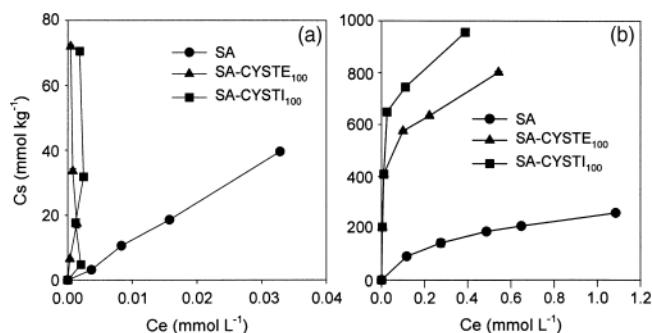


Fig. 3. Hg(II) adsorption isotherms at low (a) and high (b) metal ion concentrations.

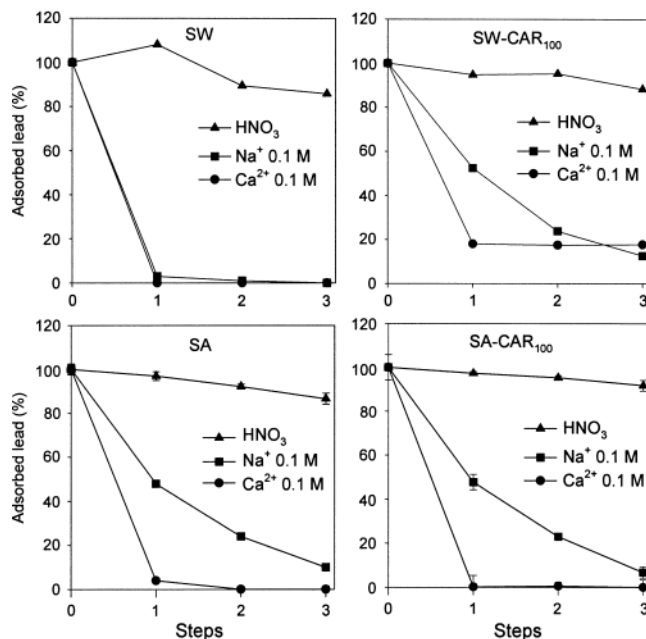


Fig. 4. Pb(II) desorption from unexchanged and exchanged clays.

similar solutions for the desorption process, we observed a more irreversible Pb(II) adsorption on SW-CAR than that on SW. It seems that the COOH group of carnitine in SW-CAR<sub>100</sub> increased the strength of the retention of Pb(II) as compared with the metal retention on SW. This fact was not observed for SA and SA-CAR<sub>100</sub> samples, possibly due to the high layer charge of SA, which increased the strength of the Pb(II) retention on SA. For all adsorbents, the degree of metal desorption increased with the ionic strength of the solution used, following the order Ca<sup>2+</sup> > Na<sup>+</sup> > HNO<sub>3</sub>.

Figure 5 shows the Hg(II) desorption curves from SW, SA, SW-CYSTE<sub>100</sub>, SW-THIAM<sub>100</sub>, SA-CYSTE<sub>100</sub>, and SA-THIAM<sub>100</sub> samples. The Hg(II) adsorption irreversibility followed the order SW < SW-CYSTE<sub>100</sub> < SW-THIAM<sub>100</sub>. Irreversibility was observed in the Hg(II) adsorption on SW-THIAM<sub>100</sub> with the use of solutions of low ionic strength (HNO<sub>3</sub> or Na<sup>+</sup>). Although the Hg(II) retention by SW-CYSTE<sub>100</sub> was greater than that by SW-THIAM<sub>100</sub> (Fig. 2), it seems that the metal retention strength was higher for SW-THIAM<sub>100</sub> than for SW-CYSTE<sub>100</sub>.

For SA-CYSTE<sub>100</sub> and SA-THIAM<sub>100</sub> organoclays, the desorption process was practically negligible, even using Na<sup>+</sup> and Ca<sup>2+</sup> solutions. In contrast, desorption was reversible for the original clay SA.

## CONCLUSIONS

The results of this work show that the presence of functional groups in the organic cation influences the adsorption capacity and selectivity of organoclays for heavy metals. Consequently, a suitable selection of the chemical characteristics of the organic cation can optimize the adsorbent properties of the organoclays as compared with the use of alkylammonium cations, which lack heavy

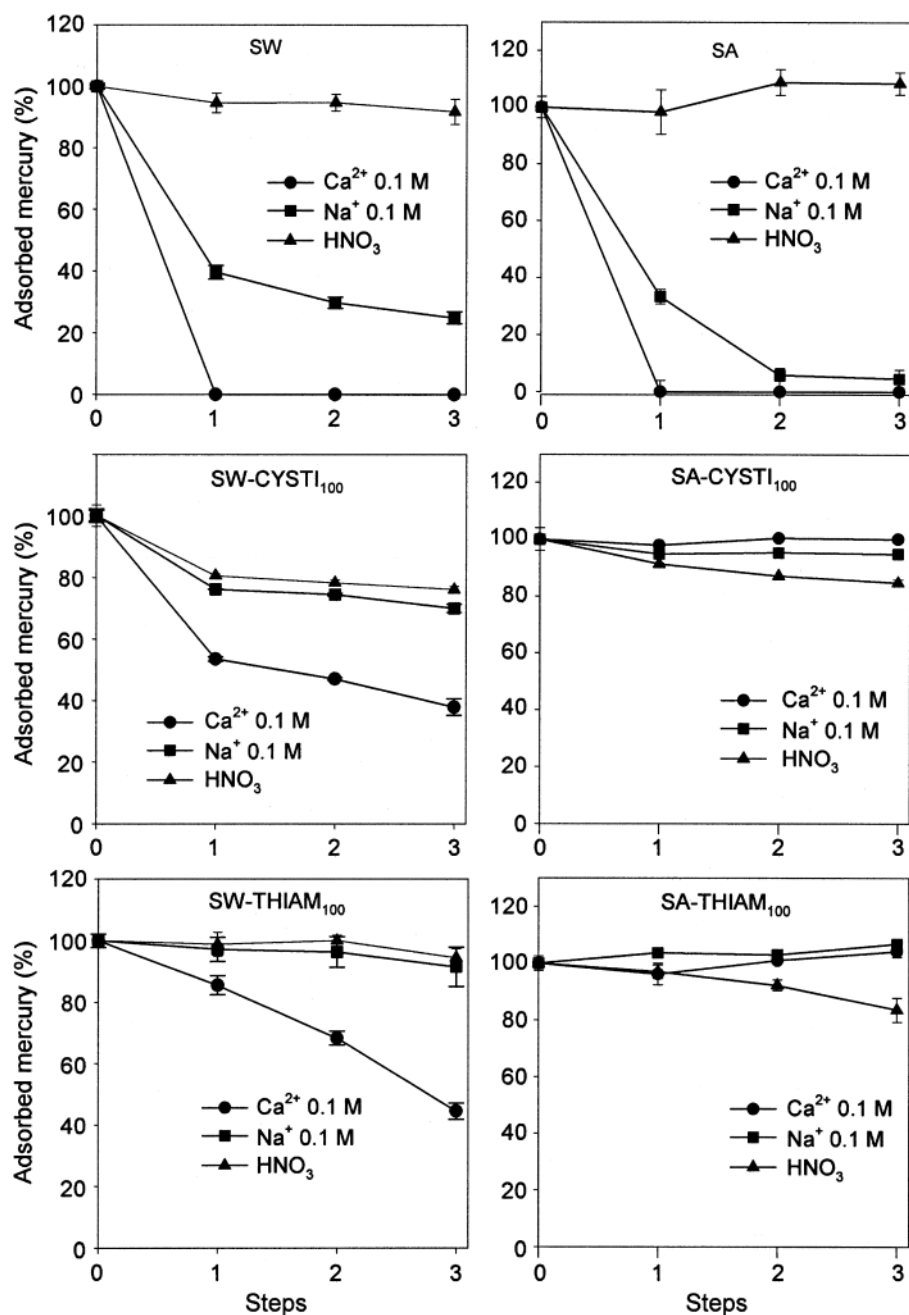


Fig. 5. Hg(II) desorption from unexchanged and exchanged clays.

metal adsorption capacity. In general, organoclays with high affinity for Pb(II) and Hg(II) showed a greater resistance to desorption as compared with organoclays with a lower affinity for heavy metals. These results reveal that functionalized organoclays could be useful as agents to selectively remove heavy metals from contaminated water. On the basis of previous work showing the usefulness of organoclays for adsorbing organic pollutants, functionalized organoclays could find application for the treatment of water contaminated with heavy metals and organic pollutants. The viability of using natural functionalized organic cations to prepare organoclays is interesting for minimizing the impact of the adsorbent once introduced into the environment.

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