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Research paper

Evaluation of thiol-modified vermiculite for removal of Hg(II) from aqueous solutions

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ABSTRACT

Aiming the removal of Hg(II) from waters, Na^+ exchanged vermiculite (Na-VT) was modified with L-cysteine (CYS-VT), cysteamine hydrochloride (CTA-VT) and (3-mercaptopropyl) trimethoxysilane (3-MPS-VT). Modification with CTA and CYS was made at pH 6.0 ± 0.1 to facilitate ion exchange of Na^+ in the interlayer with the protonated amines. Modification with 3-MPS was made by silylation, covalently binding the modifier to the silanols. Initial adsorption rate (μmol g^{-1} min^{-1}) on Na-VT and 3-MPS-VT was very fast and obeyed a pseudo second order kinetics. Intraparticle diffusion controlled the initial adsorption rate in CTA-VT and CYS-VT. Adsorption isotherms constructed at pH 6.0 ± 0.1 and 25.0 ± 0.5 °C fitted to Langmuir and Freundlich equations. The adsorption capacities of CTA-VT, CYS-VT, 3-MPS-VT and Na-VT were 83 ± 30, 57 ± 4, 21 ± 2 and 18 ± 1 μmol g^{-1} ($n = 3$), respectively. The adsorption capacity in columns followed the order: 3-MPS-VT > CTA-VT > CYS-VT > Na-VT, which is consistent with the instantaneous adsorption on 3-MPS-VT and the intraparticle diffusion control in CTA-VT and CYS-VT. The modifications afforded materials with adsorption capacities less affected by variation of ionic strength and pH as a consequence of the strong binding of Hg(II) to the incorporated thiols.

1. Introduction

Industrial activities increased the load of potentially toxic compounds in all environmental compartments. Mercury species deserve special attention because of their high toxicity and accumulation in food chains (Mil-Homens et al., 2013; Ottesen et al., 2013). Nowadays, there is a growing demand for development of materials and methods to remove mercury compounds from aqueous solutions (Kolya et al., 2014).

Removal of Hg(II) is based on chemical precipitation, coagulation, ion exchange, membrane filtration, electrolysis, reverse osmosis, solvent extraction, adsorption, etc. (Kolya et al., 2014; Zhou et al., 2014). Among these processes, adsorption is the cheapest and the easiest to operate (Zhou et al., 2014). Adsorption on clay minerals such as smectites has gained interest because of their low cost and abundance. The large surface area (montmorillonite) and the high cation exchange capacity (vermiculite) of clay minerals enable their use as adsorbents (dos Anjos et al., 2014). Additionally, the reactivity of the silanol and aluminol groups enables easy chemical modifications to enhance their affinity towards different pollutants (Abate and Masini, 2005; Konya and Nagy, 2011).

Vermiculite is a 2:1 clay mineral with permanent diffuse negative charges generated by isomorphic substitution of Si(IV) by Al(III) in the tetrahedral sheets (McBride, 1994). These negative charges confer high cation exchange capacity to the mineral, with exchangeable Na^+, Ca^{2+} and Mg^{2+} in the interlayer. Adsorption of heavy metal cations on vermiculite occurs by cation exchange in the interlayer and formation of inner- and outer-sphere complexes with Si–O and Al–O groups at the particle edges (Abollino et al., 2008; Brigatti et al., 2005; Kongchum et al., 2011). According to the Hard and Soft Acid Base (HSAB) theory of Pearson (Pearson, 1963), the silicate 2:1 layers and the hydrated interlayer cations can be considered as Lewis bases and acids, respectively. Vermiculite behaves as a hard base because the layer charge derives from tetrahedral substitutions, affecting the charge of coordinating oxygen atoms (Malferrari et al., 2007; Xu and Harsh, 1992). Because hard bases form stronger complexes with hard acids, vermiculite adsorbs more strongly Pb(II) and Cu(II) (intermediate acids) than Cd(II) and Hg(II) (soft acids) (dos Santos and Masini, 2007).

Enhancement of the adsorption capacity and affinity of smectites by Hg(II) is achieved by ion exchange with alkyl ammonium cations followed by interaction with thiol or amine organosilanes (Celis et al., 2000; Guerra et al., 2009; Guimaraes et al., 2009; Jaber et al., 2005; Lagadic et al., 2001; Mercier and Detellier, 1995; Tchinda et al., 2009; Tonle et al., 2003, 2005). Exchange of interlayer inorganic cations in vermiculite by sulfur-containing amines such as cysteamine hydrochloride was recently described by Lytuong et al. (2015). Malferrari et al. (2007) studied the adsorption of Cd(II) on cysteine-exchanged and non-exchanged vermiculite and montmorillonite by synchrotron-based X-ray absorption spectroscopy via extended X-ray absorption fine

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structure (EXAFS) verifying that Cd–S bonding prevailed in the cysteine treated clay mineral, whereas Cd–O was the main bonding in the untreated adsorbents.

In this work the adsorption of Hg(II) on Na^+-homoionic vermiculite was compared with that of the vermiculite exchanged with cysteine and cysteamine hydrochloride. Additionally, modification with (3-mercaptopropyl) trimethoxysilane was also made by covalently binding the thiol compound to silanol groups at the particle edges of the clay mineral. Adsorption isotherms and kinetic curves were constructed for all materials and the effect of different conditions of pH and ionic strength was evaluated.

2. Experimental

2.1. Reagents and procedures

Free concentrations of Hg(II) were determined by stripping chronopotentiometry using a PalmSens potentiostat (Palm Instrument BV, Houten, The Netherlands) and the PSTrace 2.4 software for instrument control and data acquisition. The electrochemical flow cell was assembled with screen printed sensors (PalmSens), and consisted of an Au film working electrode (7.06 mm^2), an Ag pseudo-reference and a graphite counter electrode (Laschi et al., 2006). Solution handling was made by Sequential Injection Analysis (SIA) and the complete procedure has been described elsewhere (do Nascimento and Masini, 2012, 2014, in press).

Batch adsorption/desorption experiments were made in a thermostatic orbital shaker from Marconi (Piracicaba, SP, Brazil), set at 25.0 ± 0.5 °C. Unless stated elsewhere, all the adsorption/desorption experiments were done inside polypropylene centrifuge tubes from Cornning® (capacity of 15 mL), which were accommodated horizontally inside the shaker. Dispersions were filtered through 0.45 μm syringe filters (hydrophilic Minisart®, Sartorius Stedim Biotech GmbH, Germany).

Determinations of sulfur were made by inductively coupled plasma–atomic emission spectrometry (ICP-AES) using a Spectro Arcos instrument (Spectro Analytical Instruments GmbH, Kleve, Germany) after digesting the samples with concentrated HNO_3 at 80 °C in closed flasks in a dry block digester. Fourier transform infrared (FTIR) spectra were obtained in a Perkin-Elmer–Frontier spectrometer using KBr pellets over the spectral range from 4000 to 400 cm^{-1} with resolution of 1 cm^{-1}. Elemental analysis was made with a Perkin Elmer 2400 series II (Waltham, MA, USA) elemental analyzer.

Scanning electron microscopy (SEM) was made with a Fesem Jeol JSM − 740 1 F instrument (Jeol Ltda, Tokyo, Japan). X-ray diffraction (XRD) experiments were done in a Rigaku Miniflex instrument using Cu Kα radiation source at voltage = 30 kV, current = 15 mA, scattering slit = 4.2° and receiving slit = 0.3 mm. Continuous scan mode was used at scan speed = $1.000° \cdot min^{-1}$, sampling width = 0.020° and scan range from 2.0 to 50.000°.

Cysteamine hydrochloride, L-cysteine and (3-mercaptopropyl) trimethoxysilane (3-MPS) were purchased from Sigma-Aldrich (Table 1). Suprapur® hydrochloric acid from Merck-Millipore (0.05 mol L^{-1}) was used as carrier in the SIA procedure and to acidify the Hg(II) solutions after the adsorption/desorption processes. Calibration for quantification of Hg(II) was made with solutions prepared by dilution of a 1000 mg L^{-1} ICP standard (in 10% v v^{-1} HNO_3) from Merck. Determination of the total surface area was made with ethylene glycol monoethyl ether (EGME) purchased form Merck. Adsorption media was buffered at pH 6.0 ± 0.1 using 2-(*N*-morpholino) ethanesulfonic acid (MES). Solutions were prepared with deionized water (resistivity > 18.2 MΩ cm) obtained from a Millipore (Billerica, MA, USA) system. Ionic strength was adjusted with analytical grade $NaNO_3$ from Merck.

2.2. Vermiculite

The crude vermiculite sample from the Massapê mine (Paulistana, PI, Brazil) was milled with mortar and pistil, and sieved. A granulometric fraction between 212 and 300 μm was chosen for the adsorption studies. This sieved sample (80 g) was treated with 1.0 mol L^{-1} HCl (250 mL) for 3 h. The dispersion was centrifuged (15 min, 3000 r.p.m.) and the solid phase was washed with deionized water until the washing water had no detectable chloride (<10^{-5} mol L^{-1}) (do Nascimento and Masini, 2014). To obtain the Na^+ exchanged vermiculite, the protonated form was brought in contact with 1 mol L^{-1} $NaNO_3$ for 24 h under continuous agitation. The Na^+-vermiculite (Na-VT) was washed with deionised water, filtered through 0.45 μm, and dried in a vacuum oven at 45 °C until constant weight.

2.3. Modification with CTA and CYS

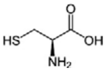
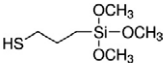
Amounts of CYS and CTA were added to a dispersion of 10.0 g of Na-VT in 70 mL of water, adjusted to pH 6.0, to provide 1:1 M ratio of the thiol and the cation exchange capacity (CEC) of Na-VT (1.154 ± 0.006 mmol g^{-1}). The dispersion was agitated in an orbital shaker (180 r.p.m., 25.0 ± 0.5 °C) for 72 h, the time needed for the system reach the equilibrium, which was verified by determining the free concentration of thiol (Chagas et al., 2009).

The solid phases were washed with portions of 50 mL of deionized water (three times) under agitation for 5 min. After that the solid materials were dried in a vacuum oven (40 °C) until constant weight. The resulting materials were named as CYS-VT and CTA-VT for the vermiculites exchanged with L-cysteine and cysteamine hydrochloride, respectively.

2.4. Modification with 3-MPS

Na-VT was modified with 3-MPS following the procedure of Guerra et al. (2009). In short, 5.0 g of Na-VT were dispersed in dry toluene

Table 1
Thiol containing substances used to modify the Na^+-vermiculite.

Organothiol	Structure	Molar mass ($g\ mol^{-1}$)	pKa		
			Carboxylic	Thiol	Amine
CYS[a]		121.15	1.71	8.33	10.78
CTA[b]		77.15	–	8.19	10.75
3-MPS[c]		196.34	–	–[d]	–

[a] L-cysteine

[b] Cysteamine.

[c] (3-mercaptopropyl)trimethoxysilane.

[d] There is no pKa reported for the thiol group of 3-MPS in aqueous medium.