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Smectite organofunctionalized with thiol groups for adsorption of heavy metal ions

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ABSTRACT

The structural characteristics as well as the binding capacity of the functionalized bentonite from Campina Grande (PB), Brazil, were investigated. The sample was modified by acid treatment followed by immobilization of ligands containing thiol (–SH) groups by covalent grafting with surface and interlayer silanol groups. The modification was carried out under anhydrous conditions with (3-mercaptopropyl) trimethoxysilane. The functionalization process changed the hydrophilic nature of the clay mineral into hydrophobic. X-ray diffraction indicated that their original structure had been preserved. The DRIFT spectra demonstrated the presence of organic chains and thiol groups. The BET results indicated decreased porosity and specific surface area after grafting. Organic loading, calculated from TG data was 1.76 mmol g^{-1} of bentonite. The thiol-functionalized bentonite presented binding capacity of Ag^+ ions about ten times higher compared to the ungrafted sample. These results support a mechanism of adsorption involving primarily ion complexation by the thiol groups (specific) instead of cation exchange (unspecific). The accessibility to the reactive centers was 60–75%. Thus, the adsorption capacity of bentonite can be enhanced by surface modification using organo-functional silane coupling agents. This new hybrid organic–inorganic material may be a good alternative for separation and pre-concentration of heavy metal ions.

1. Introduction

Silane coupling agents, used widely for the modification of silica surfaces, have also been employed more recently for modification of layered silicates (He et al, 2005; Prado et al., 2005; Walcarius et al., 2004; Celis et al., 2000). Modification with organosilane involves grafting reactions by establishing covalent bonds between the reactive groups of the layer, normally hydroxyl groups, and silane molecules. These reactions can be restricted to the external surface (the basal spacing remains unchanged) or to the interlayer surface, in which case an interlayer expansion occurs. The resulting material can be defined as a hybrid material or, more specifically, functionalized inorganic layered material (Wypych and Satyanarayana, 2004). Some recent works have shown that specific chemical activity can be created by the selection of adequate functional groups, such as amino, thiol, vinyl, long carbon chain and many others. Functionalized clay minerals may provide specific adsorption sites (Okutomo et al., 1999). Some of these modified clay minerals possess attractive features for various applications, such as the adsorption of organic and inorganic pollutants (Churchman et al, 2006, Sayilkan et al., 2004; Fonseca and Airoldi, 2000; Mercier and Pinnavaia, 1998); the manufacture of polymer/layered silicate nanocomposites (Herrera et al., 2006) as well as of modified electrodes (Tonle et al., 2004), of supports for catalysts (Kuzniarska-Biernacka et al., 2005), and of sensor and biosensors (Mousty, 2004); supports of drugs or enzymes (Park and Kwon, 2004); and adsorbents for heavy metal determination (Dias Filho et al., 2006).

The functionalization mechanism of organosilane on amorphous silica and alumina surfaces is reasonably well elucidated (Pavan et al. 2003; Bois et al, 2003; Mansur et al., 2000). Other studies have investigated the preparation of adsorbents by covalent attachment of organic molecules to synthetic layered materials obtained by the sol–gel process (Fonseca et al., 1999; Mori and Pinnavaia, 2001). More recently, chemical modification of natural clay minerals, mainly of smectites, especially by reactions involving the interlayer surfaces has been investigated. The smectites present a set of properties that make them attractive to the development of catalysts, adsorbents, supports of drugs or enzymes, and intercalation complexes (Bruce, 2006; Liu et al., 2004; Sayilkan et al, 2004; Pinnavaia et al, 1984; Occelli et al, 1987). Bentonite has been commonly studied as an adsorbent of heavy metal ions from soil and water due to high cation exchange capacity, high specific surface area associated with small particle size, low cost, and frequent occurrence in most soils (Bergaya et al., 2006; Abolino et al., 2003; Brigatti et al., 2004).

Most of the development of organic–inorganic hybrid compounds used American bentonite samples, whose properties and characteristics are well described (Mercier and Detellier, 1995; Celis et al., 2000;

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Madejová, 2003). The Brazilian bentonite from Campina Grande is polycationic and is usually activated by the addition of soda ash prior to application as a bonding material in the preparation of molding sand for metal casting, cat litter, the pelletizing of ore fines, the drilling mud, and in civil engineering. The authors are not aware of publications describing the functionalization of a Brazilian bentonite with organosilanes. We report here the possibility of utilizing the Brazilian bentonite for the preparation of an organic–inorganic hybrid material by grafting an organosilane containing the thiol group (SH) onto the surface of montmorillonite. The thiol group was chosen due its great affinity for some heavy metal ions such as Cd^{2+}, Hg^{2+}, Zn^{2+}, Cu^{2+}, Ag^+ and As(III).

The modification process used here is based on the strategy commonly used for silica gel functionalization. It consists of a direct condensation reaction between (3-mercaptopropyl) trimethoxysilane and the hydroxyl groups of the clay minerals. The strategy of functionalization used here differs from that proposed by Mercier and Detellier (1995) which involved the immobilization of (3-chloropropyl) trimethoxysilane followed by treatment with NaSH. The material was characterized by diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), X-ray diffraction (XRD), N_2 adsorption/desorption experiments (BET method), and thermogravimetric analysis (TG). The adsorption capacity as well as the accessibility to the binding sites was evaluated using a modified protocol of the Volhard silver nitrate method developed here for this purpose. Adsorption experiments have been performed to highlight the possible use of the grafted bentonite for heavy metal ions removal from dilute solutions.

2. Experimental

The bentonite with a predominance of Ca^{2+} as interlayer cation (sample BCa) from Campina Grande, Paraíba, Brazil was used. It was purified by sedimentation in aqueous dispersions, (2% w,w), for 4 h; the supernatant was centrifuged and freeze-dried. The purified fraction showed a size distribution of aggregated particles of 10%<0.7 μm, 50%<2.6 μm, and 90%<7.5 μm obtained by laser granulometer (Cilas, model 1064). The cation exchange capacity (CEC) of 0.80 meq/g freeze-dried bentonite was measured by ammonium acetate (Volzone and Garrido, 2001).

The organosilane grafting agent, the (3-mercaptopropyl)trimethoxysilane (MPTMS) ($Si(OCH_3)_3C_3H_6SH$), purity 98%, was purchased from Sigma-Aldrich and used without further purification. Toluene (99.8%) was also provided by Sigma-Aldrich. Reagent grade chemicals NaOH (>98%, pellets) and HCl (~37%) from Merck were used for acid treatment and pH adjustments during the adsorption experiments. The solutions of $AgNO_3$, KSCN, and $Fe(NH_4)(SO_4)_2$ used in the measurement of binding capacity were prepared with reagent grade chemicals (Merck). All solutions were prepared with high-purity water (18 MΩ cm^{-1}) obtained from a MilliQ water purification system.

The X-ray diffraction patterns were obtained with a Philips model PW1710 diffractometer, (CuKa; 40 kV, 20 mA, step size 0.06° 2θ, 5 s/step). Thermogravimetric curves were obtained in a TGA50 Shimadzu under N_2 environment, (20 mL/min), with a temperature ramp of 10 °C/min between 30 °C and 800 °C. DRIFT analyses were performed using a FT/IR-spectrophotometer, model SPECTRUM-1000, Perkin Elmer (64 scans of accumulation, resolution of 4 cm^{-1}). The IR measurements were taken at room temperature at 400–4000 cm^{-1}. The samples were mixed with KBr powder (5% w, w) and the KBr spectrum was used as a reference. The isotherms of adsorption–desorption of N_2 were obtained at 77 K. Before the adsorption experiments, the samples were outgassed under vacuum overnight at 60 °C. The specific surface area was obtained by a multipoint BET method using an Autosorb equipment from QUANTACHROME instruments.

Prior to the grafting process, the bentonite (BCa) samples were acid-activated with 0.15 mol dm^{-3} HCl solution to avoid the dissolution of the octahedral sheet and the collapse of the structure. This dispersion was maintained under agitation overnight, rinsed in deionized water until a neutral pH was achieved, then centrifuged and freeze-dried (Mercier and Detellier, 1995). The resulting samples were designated as BH. In a next step, 1 g of acid-activated bentonite dried at 140 °C for 2 h, was dispersed in 50 cm^3 of 0.2 mol dm^{-3} MPTMS in dry toluene. The dispersion was refluxed and agitated for 24 h in N_2 atmosphere to avoid the oxidation of the SH groups. The obtained solid was sequentially washed three times with toluene to remove the non-bonded silane, ethyl alcohol; filtered; and dried for 2 h at 120 °C in nitrogen atmosphere. The functionalized samples were termed BCASH and BHSH. The modification method is similar to that described by Walcarius et al. (2004) for the functionalization of silica gel.

Table 1
Chemical analysis of acid-activated (BH) and raw bentonite (BCa) (wt.%)

Sample	SiO_2	Al_2O_3	FeO	Fe_2O_3	MgO	CaO	TiO_2	Na_2O	K_2O	L.O.I
BCa	55.43	15.45	0.28	9.56	0.93	0.40	0.92	0.15	0.23	16.64
BH	55.17	14.75	0.25	9.40	0.67	0.00	1.12	0.02	0.09	17.78

L.O.I=loss on ignition 950 °C.

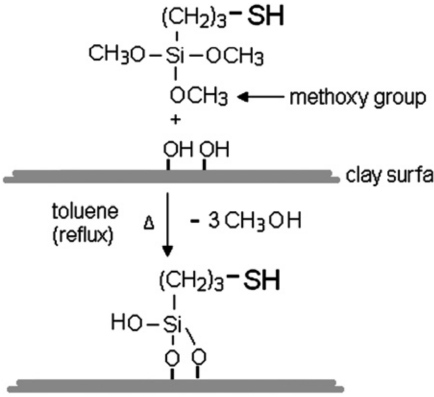

Fig. 1. Schematic illustration of functionalization.

In the present investigation, the amount of the immobilized and accessible thiol groups was determined according to a protocol based on the Volhard silver nitrate method (Dominguez et al., 2002). This protocol was, for the first time, applied to a thiol-modified inorganic substrate. The determination is based on the thiol groups' chemical affinity toward silver ions. 25 cm^3 of 0.01 mol dm^{-3} silver nitrate solution were added to flasks containing 100 mg of dried modified bentonite. The flasks were covered to avoid exposure to light and shaken for 12 h. The remaining silver nitrate was titrated with a standardized 0.01 mol dm^{-3} potassium thiocyanate (KSCN), using iron ammonium sulfate hexahydrate as an indicator. The endpoint was detected when an excess of thiocyanate formed a red colored iron complex. The binding capacity of the thiol-modified bentonite was expressed in mmol g^{-1} of bentonite dried at 120 °C.

3. Results and discussion

Acid activation was used to increase the number of active sites on the clay mineral surfaces by creation of structural defects in the Si–O tetrahedral sheet and also by replacing exchangeable cations by protons. The chemical composition of the natural (BCa) and its acid-activated form (BH) is summarized in Table 1. Using the described procedure, the interlayer cations were replaced by protons without leaching significant amount of Al from the clay mineral structure.

The functionalization of the clay mineral involves a direct condensation reaction between the terminal (OH) groups from the silicate surface

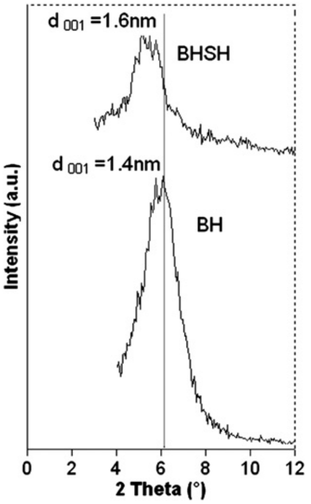

Fig. 2. XRD pattern of the bentonite before (BH) and after functionalization (BHSH).