

Characterization of organo-modified bentonite sorbents: The effect of modification conditions on adsorption performance



María E. Parolo^{a,*}, Gisela R. Pettinari^a, Telma B. Musso^{a,c}, María P. Sánchez-Izquierdo^b, Laura G. Fernández^b

^a Instituto de Investigación y Desarrollo en Ingeniería de Procesos, Biotecnología y Energías Alternativas (PROBIEN), Facultad de Ingeniería, Universidad Nacional del Comahue, Neuquén 8300, Argentina

^b Facultad de Ingeniería, Universidad Nacional del Comahue, Neuquén 8300, Argentina

^c CONICET, Consejo Nacional de Investigaciones Científicas y Técnicas, Buenos Aires, Argentina

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ABSTRACT

The organic modification of a natural bentonite was evaluated using two methods: exchanging the interlayer cations by hexadecyltrimethylammonium (HDTMA) and grafting with vinyltrimethoxysilane (VTMS) and γ -methacryloyloxy propyl trimethoxysilane (TMSPMA) on montmorillonite surface. The physicochemical characterization of all materials was made by X-ray diffraction (XRD), IR spectroscopy, thermogravimetric analysis (TGA) and Brunauer–Emmett–Teller (BET) surface area techniques. HDTMA cations and organosilanes were intercalated into the interlayer space of montmorillonite, as deduced from the increase of the basal spacing. IR spectroscopy, TGA and BET area give evidence of successful organic modification. The studies show a decrease in the IR absorption band intensity at 3465 cm^{-1} with surfactant modification, and also a decrease of mass loss due to adsorbed water observed in two samples: the organoclay and functionalized bentonites, which are evidences of a lower interlayer hydrophilicity. The efficiency of aniline removal onto natural bentonite, organobentonite and functionalized bentonites from aqueous solutions was evaluated. Aniline sorption on natural bentonite was studied using batch experiments, XRD and IR spectroscopy. The hydrophobic surface of organobentonite and functionalized bentonites increased the retention capacity for nonionic organic substances such as aniline on bentonites. The sorption properties of modified bentonite, through different modification methods, enhanced the potential industrial applications of bentonites in water decontamination.

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1. Introduction

Bentonite is a clay mainly constituted by the clay mineral montmorillonite. Montmorillonites are swellable dioctahedral 2:1 layer silicates which consist of stacks of several so-called 2:1 layers. This clay mineral has a permanent negative charge that arises from isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet and Mg^{2+} for Al^{3+} in the octahedral sheet. This negative charge is naturally compensated by exchangeable cations (i.e. Na^+ , Ca^{2+}) located in the interlayer space [1]. Montmorillonite has a high cation exchange capacity (CEC), marked swelling and high specific surface area leading to a strong adsorption/absorption capacity of ionic or polar compounds [2]. Along the edges of this clay

mineral, another surface having variable charge is developed where Si–O–Si and Al–O–Al bonds are ‘broken’ and may convert into Si–OH and Al–OH groups [3]. The hydration of inorganic cations at the exchange sites causes its surface to be hydrophilic and provides appropriate properties for it to act as a natural adsorbent for several pollutants in the treatment of contaminated waters [4].

Sorption has an important effect on the transport, reactivity and bioavailability of contaminants in soils and sediments. There is great interest nowadays in the removal of organic compounds from water by sorption processes. A large number of effective sorbent clays have been developed for organic contaminants retention.

Montmorillonite surface is hydrophilic in character and has low affinity for nonpolar liquids. In order to enhance their applicability, this clay mineral has to be modified or functionalized. There are different ways to modify clay minerals, i.e., adsorption, ion exchange with organic/inorganic cations and grafting with organic compounds [5,6]. Montmorillonites can suffer ion exchange reactions with long-chain or short-chain quaternary amine cations to obtain

* Corresponding author. Tel.: +54 299 4490300x270; fax: +54 299 4485344.

E-mail addresses: maria.parolo@fain.uncoma.edu.ar, meparolo@gmail.com (M.E. Parolo).

organobentonites [2,7,8]. Cation surfactant retention occurs within the interlayer space of clay minerals with a consequent increase of the basal spacing which provides an optimal hydrophobic environment for the retention of organic molecules. The increment of the basal spacing depends on the surfactant chain length and the charge density of the clay mineral [9,10]. X-ray diffraction (XRD) analyses are mostly conducted to elucidate the structural and mineralogical aspect of intercalated clay minerals [11–14]. The interaction between hydrophobic molecules and clay surfaces can also be greatly enhanced by simple grafting of hydrophobic groups onto the layer surfaces [15], which leads to a well-organized inorganic/organic structural layer material. In previous studies of the interaction between silane derivatives and swelling clay materials, three grafting sites (interlayer, external surface and “broken” edge) have been proposed [16]. The silane compounds interact with the hydroxylated surface groups and the organic moieties are covalently grafted to the mineral [17]. Several other authors have carried out clay modification studies to improve their ability as barriers to isolate organic compounds from gasoline storage tanks [18], landfill waste sites [19] and in the area of nanotechnology to develop polymer nanocomposites from natural clays [20,21].

Phenolic compounds and aniline are common contaminants, particularly found in effluents from pesticides, pharmaceuticals, petrochemicals and other industries. A variety of organobentonites and organosilane grafted bentonites have been applied for the removal of hydrophobic organic compounds, such as phenolic compounds and toxic metals in aquatic environments [10,22–24]. Majdan et al. [25] investigated the relationship between different structures and arrangements of hexadecyltrimethylammonium (HDTMA) and benzyldimethylhexadecylammonium (BDMHDA) surfactant cations in the interlayer space of bentonite and their phenol sorption properties. Liu et al. [26], using IR spectroscopy and X-ray diffraction (XRD) analyses, have demonstrated that phenol is adsorbed and penetrates the interlayer space of the surfactant-modified montmorillonite. Organosilane grafted clays are obtained for the removal of heavy metals and neutral and anionic pollutants from water [24]. Also, alachlor and imazquin removal by clay grafted with 3-chloropropyl-trimethoxysilane and octyltrimethoxysilane was previously studied [23].

The applications of these materials in the waste water treatment is an emerging area of interest [4], however, there are few studies that address the effects of the type of bentonite modification, organic or grafting, on the structural/surface characteristics and organic contaminant sorption performance of the resulting clay adsorbent materials.

In the North Patagonia region (Argentina) it is possible to identify numerous outcrops of commercially available sodium bentonite. Technological applications of raw clay materials mainly depend on total mineral composition, particle size distribution, processing conditions and particularly the state and distribution of the electrostatic charge of the structural layers of the clay minerals [27]. Numerous studies have been performed in our laboratory to investigate environmental applications of North Patagonian bentonites, i.e. pesticide retention [28], pharmaceutical formulation [29–31] and as liners in landfills [32,33].

The main objective of this work is to compare two methods for producing mineral surface variations in montmorillonites, and the potential of the resulting materials for hydrophobic contaminant sorption. In this study, two approaches were adopted for the organic modification of bentonite. The first is based on exchanging the interlayer cations with different concentrations of HDTMA. The other strategy is the grafting of either vinyltrimethoxysilane (VTMS) or γ -methacryloyloxy propyl trimethoxysilane (TMSPMA) on the montmorillonite surface (Fig. 1). The physicochemical characterization of all materials was made by X-ray diffraction (XRD), IR spectroscopy, thermogravimetric analysis (TGA) and

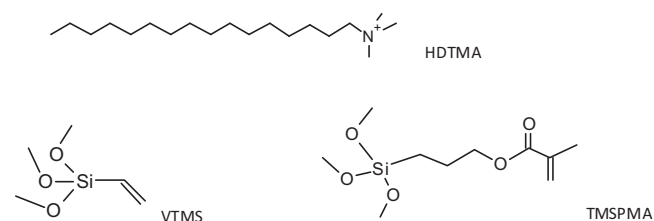


Fig. 1. Structural formulae of the surfactant cation (HDTMA) and silane compounds (VTMS and TMSPMA) used as modifiers for the Na–B.

Brunauer–Emmett–Teller (BET) surface area techniques. Subsequently, the removal efficiency of aniline from aqueous solutions onto natural bentonite, organobentonite and silane grafted bentonite was evaluated.

2. Materials and methods

2.1. Materials

The bentonite sample (Na–B) was obtained from deposits located close to the margin of the Pellegrini Lake, Río Negro province, North Patagonia, Argentina. The mineralogical composition, determined by XRD, is mainly montmorillonite (90%), with quartz, feldspars and zeolites (heulandite–clinoptilolite) as secondary phases. The structural formula, calculated from $<2\ \mu\text{m}$ fraction, can be expressed as $((\text{Si}_{3.85}, \text{Al}_{0.15})(\text{Al}_{1.43}, \text{Fe}^{3+}_{0.26}, \text{Mg}_{0.28}, \text{Ti}_{0.02})\text{O}_{10}(\text{OH})_2) \text{M}^{+}_{0.21}$, where M^{+} is predominantly Na^{+} . Its cationic exchange capacity is $105\ \text{cmol}_c/\text{kg}$ as measured by the AgNO_3 /thiourea method and it has a specific surface of $755\ \text{m}^2/\text{g}$ ($0.755\ \text{m}^2/\text{kg}$) as measured by the adsorption of ethylene glycol monoethyl ether [32] (identified as sample CATAE).

Hexadecyltrimethylammonium bromide (HDTMA) was purchased from SIGMA (purity of 98%). The silane coupling agents were vinyltrimethoxysilane (VTMS) (FLUKA) and 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) (ALDRICH). The reaction solvent was a mixture of isomeric xylenes (FLUKA). Aniline, used as an organic contaminant model of analytical grade with an octanol–water partition coefficient ($\log K_{ow}$) of 0.9 and aqueous solubility of $36,000\ \text{mg}/\text{L}$ at $25\ ^\circ\text{C}$. The pK_a value at $25\ ^\circ\text{C}$ for the deprotonation of anilinium was 4.58 [34]. The molecule is therefore present primarily as a neutral species at slightly acidic pH values and higher.

2.2. Synthesis of organic modified bentonites

HDTMA intercalated montmorillonite (organobentonite) was synthesized as follows: hexadecyltrimethylammonium bromide amounts equivalent to various percentages of the CEC (0.20, 0.50, 0.70, 1.00, 1.50, $2.00 \times \text{CEC}$) were dissolved in deionized water. 1 g of Na–B was added to the surfactant solutions at $60\ ^\circ\text{C}$. The dispersions were stirred for 4 h at $60\ ^\circ\text{C}$ and then centrifuged at 3600 rpm during 1 h. The samples collected were washed with deionized water by centrifugation (3600 rpm, 30 min) several times until Br^- free. Na–B with various HDTMA loading amounts were denoted as $x\text{CEC-HDTMA}$ (x means the added amount of HDTMA).

Reactive groups were introduced onto the montmorillonite surfaces by the reaction of silane with hydroxyl groups of the mineral in an anhydrous environment, following Fernández et al. [35]. The silylation reactor system consisted of a 500 mL glass reaction flask that was heated and stirred using a heating/magnetic stirring device placed in an oil bath. The Na–B loading of the solution was $80\ \text{g}/\text{L}$. Silylation was carried out using 10% v/v VTMS or TMSPMA solution in xylene. The reaction proceeded for 5 h at $130\ ^\circ\text{C}$. The temperature of the condenser was kept at $75\ ^\circ\text{C}$ to reflux the

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