



Hexadimethrine-montmorillonite nanocomposite: Characterization and application as a pesticide adsorbent



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ABSTRACT

The goal of this work was to prepare and characterize a novel functional material by the modification of SAz-1 montmorillonite with the cationic polymer hexadimethrine (SA-HEXAD), and to explore the potential use of this nanocomposite as a pesticide adsorbent. Comparative preparation and characterization with the well-known hexadecyltrimethylammonium-modified SAz-1 montmorillonite (SA-HDTMA) was also assessed. The characterization was performed by elemental analysis, X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), physisorption of N₂, scanning electron microscopy (SEM) and Z potential measurements. The characterization and adsorption experiments showed that the extent of pesticide adsorption was markedly subjected to the structure and features of the surface of each organo-clay and also to the nature of the considered pesticide. SA-HEXAD displayed a high affinity for anionic pesticides which, presumably, were adsorbed by electrostatic attraction on positively-charged ammonium groups of the polymer not directly interacting with the clay. In contrast, SA-HDTMA displayed great adsorption of both uncharged and anionic pesticides with predominance of hydrophobic interactions. This work provided information about the surface properties of a new organic–inorganic nanohybrid material, SA-HEXAD, and its potential as an adsorbent for the removal of anionic organic pollutants from aqueous solutions.

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1. Introduction

Clay minerals have attracted attention over the last decades for being naturally occurring and versatile materials. The importance of these materials lies on their peculiar properties such as small particle size, swelling capacity, anisotropic shape, reactive surfaces, and high cation exchange capacity (CEC) [1,2]. As a consequence, a vast number of applications have been projected for clay minerals; among others, their use as adsorbents of pollutants in order to reduce their environmental impact [3]. The interest in clay minerals has grown as the development of nanoscience and nanotechnology has progressed, due to their nano-sized layers and interlayer space [4–6].

Expandable clay minerals (i.e., smectites) have a marked hydrophilic character caused by the strong hydration of the inorganic counter ions present in the interlayer space. Indeed, they are rarely good adsorbents for hydrophobic organic compounds [7–10]. Nevertheless, the modification of the nature of the clay mineral surface from hydrophilic to hydrophobic, through ion-exchange

reactions replacing the inorganic cation with an organic cation, can dramatically alter the affinity of smectites toward hydrophobic organic compounds. The resulting so-called organo-clays have been extensively proposed as adsorbents for poorly water soluble, highly hydrophobic compounds [3,11–15].

Alkylammonium-exchanged smectites have been the most common organo-clays proposed for adsorption of pesticides [3,16]. Celis et al. [17] found that the adsorption of the neutral fungicide triadimefon reached values higher than 90% after the modification of SAz-1 montmorillonite with hexadecyltrimethylammonium (HDTMA) cations, and a similar behavior was observed for neutral phenylureas pesticides [18,19]. Noticeable increases in adsorption of SAz-1 after its modification with HDTMA cations have also been reported for acidic pesticides, such as 2,4-D [13], imazamox [20], bentazone and dicamba [21], picloram [22] and MCPA [23,24]. However, several studies have pointed out that quaternary alkylammonium ions such as HDTMA may have undesirable toxicological properties which may limit their usefulness for environmental applications. Several studies reported antimicrobial properties for this type of organo-clays, which can thus be toxic for natural xenobiotic degraders and hinder natural attenuation of pollutants in the environment [25,26]. Hence, new strategies to circumvent the limitations of traditional alkylammonium-modified

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clay minerals are needed. Alternative methods involve, for instance, preparation of clay-organic nanohybrid or nanocomposite materials using more friendly organic cations, capable of reducing the impact of the adsorbent once it is incorporated into natural environments for practical applications [18,24,27–30].

It is well-known that the leading mechanism in the adsorption of organic solutes by organo-clays will depend, for a given clay mineral, on the properties of the organic modifier and those of the selected solute [3,6]. The principal mechanism for the adsorption of organic pollutants on the traditional HDTMA-modified Arizona montmorillonite (SA-HDTMA) is the solute partitioning into the paraffinic-like organic phase formed by the vertical arrangement of HDTMA cations in the interlayer space of the clay mineral, which provides an excellent medium for the adsorption of hydrophobic organic compounds [11,31–33]. In the interaction of SA-HDTMA with anionic pesticides, including those of the phenoxyacetic group, polar interactions have also been proposed, in addition to hydrophobic interactions, as long as free polar space exists between alkylammonium groups in the organo-clay interlayer to host the pesticide [13,20,34–36].

In a preceding work, we found that the modification of SAz-1 Arizona montmorillonite with the cationic polymer hexadimethrine rendered a nanocomposite which displayed an affinity for the anionic pesticide MCPA comparable to that of the traditional SA-HDTMA organo-clay [24]. Given that the full potential of clay-organic nanohybrid materials has not been achieved due to limited understanding of the interaction mechanisms between different target compounds and the clay matrix [16], we aimed in this work at getting further insight into the interaction mechanisms governing the adsorption of a number of structurally different pesticides, as representatives of widely spread pollutants in the environment, and the novel hexadimethrine-montmorillonite (SA-HEXAD) nanohybrid material, comparing its behavior with that of the well-known SA-HDTMA organo-clay. For the purpose of this work, HDTMA and HEXAD are excellent models of monomeric versus polymeric alkylammonium-type modifiers lacking additional specific functional groups for the adsorption of pesticides. The specific objectives of this work were: (i) a detailed and comparative characterization of the SA-HEXAD and SA-HDTMA systems, and (ii) a comparative assessment of the adsorption of a suite of structurally different pesticides by SA-HEXAD and SA-HDTMA, to get further insight into the mechanisms governing the affinity of these nanohybrids for selected pesticides. The information reported in this paper should be useful for the implementation of the assayed materials in specific applications, such as the removal of pesticides from contaminated water, their immobilization in soil, or the preparation of slow release formulations.

2. Experimental

2.1. Montmorillonite, organic cations and pesticides

The reference Ca-rich Arizona montmorillonite (SAz-1) from the Source Clays Repository of the Clay Minerals Society (Purdue University, West Lafayette, IN), with CEC equal to 1200 mmol/kg, was used for the preparation of the organo-clays. The properties of SAz-1 montmorillonite have been reported elsewhere [37].

Hexadimethrine (HEXAD) bromide (purity > 95%) and hexadecyltrimethylammonium (HDTMA) chloride (purity \geq 98%) (Fig. S1) were purchased from Sigma–Aldrich. Hexadimethrine is an agglutinant blood cell polycation employed as heparin-neutralizing in pharmaceutical industry [38]. Hexadecyltrimethylammonium is a cationic surfactant which has been widely used, among other applications, for the preparation of organo-clays [3,39].

Selected analytical-grade (purity > 99.9%) pesticides (fluometuron, diuron, terbuthylazine, simazine, mecoprop, MCPA, and clopyralid) supplied by Sigma–Aldrich were used for adsorption experiments. The structures of the pesticides are shown in Fig. 1.

2.2. Preparation of SA-HEXAD and SA-HDTMA nanohybrids

Preparation of SA-HEXAD and SA-HDTMA was accomplished through a cation exchange reaction, following the procedures described in Celis et al. [24,40]. Briefly, raw SAz-1 was treated with an aqueous solution containing an amount of organic cation (HEXAD or HDTMA) equivalent to 100% of the cation exchange capacity (CEC) of the clay mineral. The suspensions were shaken for 24 h, centrifuged, and the resulting solid was washed three times with deionized water, freeze-dried, and stored at room temperature until used.

2.3. Characterization of the unmodified and modified-montmorillonite samples

The C and N contents of the unmodified and modified-montmorillonite samples were determined by the combustion method using a Perkin–Elmer, model 1106 elemental analyzer (Perkin–Elmer Corp., Norwalk, CT). The basal spacings (d_{001}) of oriented clay specimens were determined with a Siemens D-5000 diffractometer (Siemens, Stuttgart) with $\text{CuK}\alpha$ radiation. A Jasco FT/IR 6300 spectrometer (Jasco Europe s.r.l.) provided with a diffuse reflectance accessory was employed to record the Fourier-transform infrared (FTIR) spectra. Physisorption of N_2 at 77 K, using a Carlo Erba Sorptomatic 1900 (Fisons Instruments, Milan) gas adsorption analyzer, was used to obtain the specific surface area (SSA) by applying the BET method. Zeta potential distribution curves for SAz-1, SA-HEXAD and SA-HDTMA suspensions (1.4 mg mL^{-1}) were measured with a Zetasizer Nano ZS equipment (Malvern Instrument). Z potential (ξ) values were obtained at the pH of the suspension, previously dipped into an ultra-sound bath to disperse aggregates before analysis. Finally, scanning electron microscopy (SEM) was used to get insight into the morphology of the samples using a Hitachi S5200 microscope.

2.4. Adsorption studies

Adsorption experiments were conducted to determine the performance of SA-HEXAD as an adsorbent of a number of structurally different pesticides and to compare its behavior with that of SA-HDTMA, particularly with regard to different adsorption mechanisms possibly involved.

2.4.1. Preliminary adsorption study

A preliminary adsorption study with seven different pesticides (Fig. 1) was performed at a single initial pesticide concentration of 1 mg L^{-1} , using the batch equilibration technique. Triplicate 20 mg of SAz-1, SA-HEXAD or SA-HDTMA were placed in glass centrifuge tubes lined with screw caps. Subsequently, the clay samples were equilibrated with 8 mL of separate aqueous solutions of each pesticide with an initial concentration $C_i = 1 \text{ mg L}^{-1}$ by shaking at $20 \pm 2^\circ \text{C}$ for 24 h. After equilibration, the suspensions were centrifuged and 4 mL of the supernatant solution was removed, filtered, and analyzed by high performance liquid chromatography (HPLC) to determine the pesticide equilibrium concentration in solution, C_e (mg L^{-1}). Triplicate initial pesticide solutions of pesticides without adsorbent were also shaken for 24 h and served as controls. The percentage of pesticide adsorbed (% Ads) was calculated as: $\% \text{ Ads} = [(C_i - C_e)/C_i] \times 100$.

The HPLC system used for the determination of the initial and equilibrium pesticide concentrations was a Waters 600E

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