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Research paper

Insight into thiabendazole interaction with montmorillonite and organically modified montmorillonites

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ABSTRACT

The interactions of the fungicide, thiabendazole (TBZ) on montmorillonite (Mt) and organoclays synthesized from phosphatidylcholine (DSPC) and octadecyltrimethylammonium bromide (ODTMA) was investigated for water remediation. The affinity of TBZ on the surface of Mt and organoclays was evaluated by powder X-ray diffraction, X-ray photoelectron spectroscopy and the experimental results were also reinforced by molecular modelling in order to explore the surfaces arrangements. TBZ was protonated upon interaction with negative charged Mt and therefore this strong electrostatic interactions prevented it's desorption in water. Repulsive electrostatic interactions between the cationic surfactant ODTMA and the cationic form of TBZ on the outer surface of the ODTMA modified Mt resulted in high desorption values. In the DSPC modified Mt, TBZ was anchored within the surfactant chains and a small amount of interlayer water was released from the interlayer space.

1. Introduction

Thiabendazole (TBZ) is a benzimidazole derivative compound, used primarily in agriculture to control mould, blight and other fungi causing diseases in fruits and vegetables (Amin et al., 2011). A high amount of TBZ used as post-harvest fungicide leads to water contamination, with consequent concerns since it exhibits toxicity for animals causing liver and intestinal disorders (Groh et al., 2012; Price et al., 2004; Tada et al., 2001).

Adsorption is a widely studied process for removing contaminants from aqueous effluents where different types of porous materials were applied. In particular, the adsorption capacity of montmorillonite (Mt) towards different contaminants has been largely studied (Gamba et al., 2015; Guz et al., 2014; Hocine et al., 2004; Marco-Brown et al., 2014; Sen Gupta and Bhattacharyya, 2012; Zhu et al., 2014). The main reasons that turn Mt into important adsorbents are (i) its external negative charge, which makes them particularly useful for removing cationic compounds from water, and (ii) its large total specific surface area, which allows them to anchor and concentrate a high amount of molecules and ions on both outer and inner surfaces (Torres Sánchez et al., 2011). To improve the low adsorption capacity shown by montmorillonites with anionic or less polar matrices, they should be transformed to organo-montmorillonites (OMt), by intercalation of organic cations through cation exchange interaction, leading to both chemical and structural changes. The increase of interlayer distance originated by the entrance of surfactants depends on the concentration and their chain length (Bianchi et al., 2013; de Paiva et al., 2008; He et al., 2014; Ouellet-Plamondon et al., 2014; Patel et al., 2010, 2009; Xi et al., 2007). On the outer surface, a decrease of negative Mt charge is observed when using cationic surfactants (Pecini and Avena, 2013). The swelling behaviour and the specific surface area is also suppressed. These changes in properties of Mt lead to coagulation improvement, allowing an easy separation from water. Generally proposed mechanisms for the adsorption of organic compounds onto OMt samples are (i) organophilic partitioning, (ii) electrostatic interactions, and (iii) chemical adsorption between the adsorbate and the adsorbent. Although the modifications cause a conversion of the silicate surface from hydrophilic to organophilic, not always an important enhancement of adsorption has been observed (Gamba et al., 2015). Therefore, a deep and thorough understanding of the interactions between adsorbate and adsorbent is important to design the best relationship between them and the consequent effective adsorption. For this purpose, molecular modelling has become a fundamental tool that allows to elucidate both configurations and interactions of the adsorbate (surfactants or organic molecules) at adsorbent surfaces (Aristilde et al., 2013; Bardziński, 2014; Liao et al., 2016; Zhao and Burns, 2012; Zhou et al., 2014).

TBZ adsorption into Mt has been deeply studied from an experimental point of view (Ennajih et al., 2012; Lombardi et al., 2003; Lombardi et

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al., 2006), and there is little knowledge about TBZ adsorption onto organoclays. In this work, a detailed characterization and comparison of TBZ behaviour adsorbed on a raw Mt and two organo-montmorillonites was performed from experimental and molecular simulations points of view. The widely used cationic surfactant octadecyltrimethylammonium (ODTMA) which can be considered to be toxic for environmental applications (Sarkar et al., 2013) and amphiphilic phospholipid surfactant phosphatidylcholine (DSPC), approved by Environmental Protection Agency, were used to obtain organo-montmorillonites. Adsorption-desorption experiments were performed, and products were characterized by X-ray diffraction analyses (XRD) to describe changes in the interlayer space (inner surface), X-ray photoelectron spectroscopy (XPS) to characterize changes on the outer surface, differential thermal analyses and thermogravimetric analyses (DTA-TG) to characterize bulk changes. Molecular modelling was used to obtain structural arrangement and description of mutual interactions between TBZ and $TBZH^+$ and Mt surface or organo-modified Mt surface which could influence and explain adsorption processes.

2. Experimental

2.1. Materials

The Wyoming Na-montmorillonite (Wy) obtained from the Source Clays Repository of Clay Minerals Society (Columbia, MO) was used in the experiments. Its cation exchange capacity (CEC) was 0.92 mmol g^{-1} (Tabak et al., 2007). The chemical composition of the montmorillonite is: SiO_2 62.9%, Al_2O_3 19.6%, Fe_2O_3 3.35%, MgO 3.05%, CaO 1.68%, Na_2O 1.53% (Xi et al., 2007).

The fungicide thiabendazole (TBZ) (Fig. S1), IUPAC chemical formula 2-(thiazol-4-yl) benzimidazole, was supplied by Fluka (Buchs, Switzerland) (98% purity) and used as received. It is a solid crystalline substance with molar mass (MM = 201.3 g mol^{-1}), solubility in water of 160 ppm at pH 4 and 30 ppm at pH 7–10, both at 20.0 ± 0.5 °C, (Tway and Love, 1982) and pK_as at 2.5; 4.7 and 12 (Roberts and Hudson, 1999). The maximum residue levels for TBZ in fruits are established in the range of 0.05 to 15 mg kg^{-1}, depending upon the type of crop. However, the more restrictive regulation for drinking water establishes the maximum admissible concentration for individual pesticides at 0.1 mg L^{-1} (Barahona et al., 2010).

Phosphatidylcholine (DSPC, Fig. S2, A) (74% distearoyl-PC and 26% 1-palmitoyl-stearoyl-PC, MM = 768 g mol^{-1}) was kindly provided by Lipold GmbH and used as received. Octadecyltrimethylammonium (ODTMA, Fig. S2, B) bromide [$C_{18}H_{37}N(CH_3)_3Br$] (≥98%, MM = 392.5 g mol^{-1}) was purchased from Fluka (Buchs, Switzerland) and used as received. All other chemical reagents were provided by Merck PA and used without any purification.

2.2. Sample preparations

Fractions of Wy were modified with the organic ODTMA cations and DSPC molecules through ion exchange reaction following the procedures described previously (Sánchez-Verdejo et al., 2008; Zhu et al., 2014). The samples obtained were denoted as WyODTMA and WyDSPC. The theoretical maximum and minimum ODTMA loading values were calculated from TG data (Boeva et al., 2013) being 140 and 115% of CEC, respectively, considering that none or all the Br^- ions remains in the sample. In case of WyDSPC sample, the amount of loaded DSPC corresponded to 140% CEC (Sánchez-Verdejo et al., 2008).

2.3. Adsorption and desorption experiments

TBZ solution for adsorption experiments was prepared by dissolving the pure fungicide in water, to achieve a concentration of 25 ppm. A Wy dispersion of 1 g L^{-1} was used and a contact time of 24 h under stirring was applied until the equilibrium state was reached. The pH of the dispersions was measured at $t = 0$ and $t = 24$ h, being 6.5 at $t = 0$ for all samples and 8.5 and 7 at $t = 24$ h for Wy and OMt, respectively. After the equilibration time at 20 °C the dispersion were centrifuged at 14000 rpm for 15 min and the solid phases were rinsed with distilled water, air dried and stored for further analyses. Solids obtained were denoted as Wy-TBZ, WyODTMA-TBZ and WyDSPC-TBZ, respectively. The supernatants were stored to determine the TBZ concentration, and fractions of the solids followed three successive desorption steps by replacing half of the supernatant with water, re-equilibrating for 24 h and the last procedure was repeated twice. The concentration of TBZ in the supernatants was analysed by High Performance Liquid Chromatography (HPLC) coupled with UV–visible detection ($\lambda = 298$ nm) using a Shimadzu HPLC. The mobile phase was 70/30 methanol/ammonium acetate mixture flowing at 1 mL min^{-1}. The linear range of TBZ concentrations was within 0.5–25 ppm ($R^2 = 0.999$). All solutions and dispersions were prepared using Milli-Q water. The TBZ adsorption amounts were determined as the difference between initial concentration and that of the supernatant in equilibrium.

2.4. Characterization of the adsorbents and adsorption products

The X-ray diffraction patterns were obtained using semi-oriented samples in a Philips PW 1710 diffractometer with Ni-filtered CuKα radiation (35 kV, 40 mA). Step-scan data were collected from 3 to 30° 2θ, with a step width of 0.02° and a counting time of 10 s $step^{-1}$. The divergence, receiving, and scattering slits were 1, 0.2 and 1°, and no monochromator was used.

XPS analyses were performed on a computer equipped with a Multitechnic Specs with dual X-ray source of Mg/Al and XR50 model Phoibos 150 hemispherical analyser, in transmission mode fixed analyser (FAT). The spectra were obtained using a not monochromatic Al K_α radiation (h = 1486.6 eV) operated at 100 W and 10 kV. The pass energy for the survey scan was 30 eV. The survey scan range was 1200–10 eV and dwell time 100 ms. The pressure during measurement was <2.10^{-6} Pa. Samples were supported on double sided Cu tape and then subjected to ultra-high vacuum evacuation for 12 h prior to the XPS analysis. To minimize the effects of surface charge the experiments were carried out with Flood Gun 1 eV ignition energy. The C-(C, H) component of the C 1s peak of carbon has been fixed to 285 eV to set the binding energy scale. Molar fractions were calculated using peak areas normalized on the basis of acquisition parameters after a Shirley background subtraction, sensitivity factors, Mean Free Path, and transmission factors were provided by the manufacturer.

ATD and TG experiments were conducted using a NETZSCH STA 409 PC/PG with alumina as a reference. Samples of 20 mg were placed in Al_2O_3 crucibles and heated from 30 to 1000 °C at a scanning rate of 10 °C min^{-1} in nitrogen/air atmosphere.

2.5. Molecular modelling

For purposes of molecular modelling a Wyoming Na-Mt with the composition $[(Si_{3.89}Al_{0.11})(Al_{1.70}Mg_{0.30})O_{10}(OH)_2]Na^+_{0.41}$ was used. Lattice parameters were the following: $a = 5.21$ Å, $b = 9.02$ Å. The space group was *C2/m* (Tsipursky and Drits, 1984). The layer charge of Wy used in the calculations corresponded to that used in the experiments. Molecular modelling was used for 2 types of calculations:

(i) the structure of the interlayer space of Wy intercalated with ODTMA and DSPC cations. In case of WyODTMA a $5a \times 3b \times 1c$ supercell with the total charge of −12 el. was built. The composition of the layer of the supercell was $[(Si_{117}Al_3)(Al_{51}Mg_9)O_{300}(OH)_{60}]^{-12}$. The c parameter was taken from XRD measurements. Its value was the same before and after TBZ adsorption and was of 19.7 Å. The model contained 12 ODTMA cations in the interlayer space. For WyDSPC model a $10a \times 3b \times 1c$ supercell with the total charge of −24 el. was