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Research paper

Effect of the Al/clay ratio on the thiabendazol removal by aluminum pillared clays

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ABSTRACT

In this work, four aluminum pillared clays (Al-PILC) with different Al/clay ratios were synthesized and evaluated for the removal of thiabendazole (TB) (a fungicide widely used in agricultural activities) from aqueous media. The Al-PILC were thoroughly characterized by different techniques, such as X-ray diffraction (XRD), thermogravimetric analysis (DTA-TG), adsorption–desorption of N_2 at 77 K, NH_3-temperature programmed desorption (NH_3-TPD) and transmission electron microscopy (TEM). The TB-adsorption studies were carried out in batch, at room temperature, at pH = 6 (natural pH, without additional control) and with different concentrations of TB (2–100 ppm). The measured TB adsorption capacities varied from 11.78 to 17.50 mg TB per gram of clay. The TB–Al PILC complexes obtained after the adsorption process were studied by X-ray photoelectron spectroscopy (XPS). The results suggested that the molecules of TB were adsorbed on the Al-PILC by two different phenomena: by physisorption in their porous structure and by chemisorption on their pillars, showing a concordance between the amounts of incorporated aluminum in the pillared clays and their fungicide adsorption capacity.

1. Introduction

During the last years, the presence of organic compounds as pesticides, antibiotics, hormones and dyes in the environment has become a matter of growing interest. Pesticides have been found in soils and watercourses as a result of agricultural practices. The majority of these pesticides are not biodegradable and their adsorption from solution has been proven to be a feasible methodology to remove these pesticides from aqueous courses.

Many natural adsorbents have been studied; among them, the natural clay minerals are a good option because of their abundance. Natural clay minerals have showed optimal adsorption capabilities with various organic and inorganic pollutants due to their surface area and their cation-exchange capacity (Crini, 2006). However, these materials are highly hydrophilic and their separation from aqueous dispersions is difficult. In consequence, additional techniques like flocculation are required to separate these adsorbents from aqueous media.

The pillared interlayered clay minerals (PILC) are laminar solids with a permanent porous structure commonly obtained from natural clay minerals as montmorillonite (Mt). These materials are synthesized through a cationic exchange process that involves the displacement of the cations from the natural material by hydroxyl-metal polycations. After a thermal treatment, polycations become oxide species within the interlayer, keeping the layers separated and avoiding the collapse of the structure, such oxides are the so-called pillars of the PILC. The pillars provide new acid sites to the material and a permanent microporous structure within the interlayer that produces a considerable increase of the specific surface area (Cool and Vansant, 1998; Gil et al., 2008; Kloprogge, 1998; Vicente et al., 2013). The studies with PILC began during the oil crisis in the 70's as optional catalysts to zeolites. Nowadays, due to their features, the PILC are used as catalysts or catalyst support in several reactions (Gil et al., 2008; Oliveira et al., 2008; Romero-Pérez et al., 2012; Vicente et al., 2013) and as adsorbents for organic (Gil et al., 2011; Hou et al., 2011; Konstantinou et al., 2000; Molu and Yurdakoc, 2010; Polubesova et al., 2002) and inorganic (Manohar et al., 2005; Tian et al., 2009) pollutants.

The adsorption mechanism of different organic compounds from aqueous solution on natural clay minerals is generally related to cation exchange or van der Waals interactions (Wang et al., 2011). In particular, previous studies have shown that TB adsorption is related to cation exchange of the protonated fungicide by the interlayer cations of the

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natural clay mineral (Lombardi et al., 2003, 2006). However, in Al-PILC the interlayer cations of the natural clay mineral were replaced by aluminum oligocations, which are transformed into pillars of aluminum oxides when they are subjected to thermal treatment. These aluminum pillars can give rise to different adsorption mechanisms of organic species on PILC. In fact, PILC have two main differences with natural clay mineral: the porous structure and the presence of acid surface sites. The porous structure is important because it can give rise to steric effects depending on the adsorptive molecular size as was showed by Mishael et al. (1999). In addition, the presence of aluminum in the pillars produces new Lewis acid sites that can contribute to the adsorption of organic molecules with Lewis basic character (Undabeytia et al., 2000). In spite of the fact that PILC are widely studied as adsorbents, there are a few exhaustive studies about the concordance between their porous structure and their removal capacity.

Thiabendazole (TB) is a fungicide widely used in the production of different species such as sugar cane, tobacco, rice, apple and other products, as well as a post-harvest fungicide before fruit packing. The *Alto Valle de Río Negro-Neuquén* region (Argentine) is the major producer of apples and pears of the country. In this region, TB is one of the most used post-harvest fungicides and is found in the main waterways, where its concentration is superior to the advisable values for drinking water. Although thiabendazole does not have a high risk of toxicity, its accumulation in the environment causes the increasing resistance of some microorganisms. A previous study has showed that natural clays, abundant in this region, are suitable as TB adsorbents in spite of the inconveniences mentioned above (Lombardi et al., 2003). Recently, Roca Jalil et al. (2013) reported an aluminum PILC (synthesized from one of these natural clay minerals) as TB adsorbent in aqueous medium, obtaining better TB adsorption capacities than the former natural clay mineral with the advantage of being more easily separated from the adsorption medium due to its hydrophilicity.

In this work, four aluminum PILC (Al-PILC) with different Al–clay ratios were synthesized and characterized by different techniques. Their structural, textural and surface properties were contrasted with their TB removal capacity, in order to establish a relationship between the Al-PILC properties and TB adsorption. Also, the adsorbate–adsorbent interaction was studied by XPS, with the aim of proposing a possible mechanism of TB adsorption on PILC materials.

2. Materials and methods

2.1. Synthesis of materials

The natural clay used in this work is a bentonite from the Pellegrini Lake, in *Rio Negro* province, Argentina. This clay has been described in a previous work (Roca Jalil et al., 2013). The PILC were prepared following the previously described methodology in which the oligocations were synthesized from a 0.2 M of $AlCl_3 \cdot 6H_2O$ solution and 0.5 M of NaOH solution, with a basicity relationship $OH^-/Al^{3+} = 2$, under stirring at 60 °C (Roca Jalil et al., 2013; Sapag and Mendioroz, 2001). The resultant solutions were aged under stirring for 12 h at room temperature and the oligocation obtained was added drop wise to a 3 mass% dispersion of natural clay in deionized water. Four PILC were prepared with different quantities of aluminum: 5, 10, 15 and 20 meq of aluminum per gram of clay, according to previous work (Romero-Pérez et al., 2012). The samples were washed using dialysis membranes until no chloride ions were found. Subsequently, the precursors obtained were dried at 60 °C and calcined at 500 °C for 1 h, with a heating rate of 10 °C min^{-1}. The PILC obtained were named: *Al-PILC 5*, *Al-PILC 10*, *Al-PILC 15* and *Al-PILC 20*, respectively.

2.2. Adsorptive: thiabendazole (TB)

A product commercialized as TECTO by Syngenta where the active agent is the TB in a 48.5% mass/mass aqueous dispersion, was used as

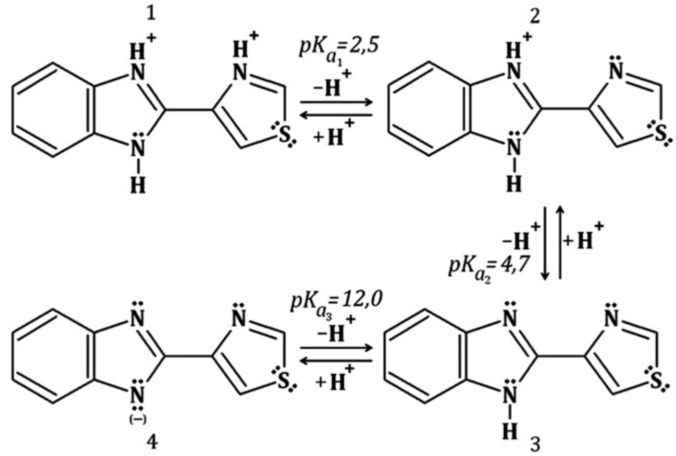

Fig. 1. Protonated–deprotonated species of TB.

adsorptive for the adsorption studies. The TB has a molecular mass of 201.3 g mol^{-1} and its solubility in water is 0.16 g L^{-1} at pH 4 and 0.03 g L^{-1} at pH 7–10, both at 20 ± 0.5 °C (Tway and Love, 1982). The dimensions of the TB molecule are 9.89 Å of length and 4.97 Å of width, estimated by using the software Gaussian03Rw. The TB thickness is below 2 Å due to this molecule is flat (Lombardi et al., 2003; Roca Jalil, 2010). TB has three pK_a values in aqueous solution, which are 2.5, 4.7 and 12.0; four different species can be generated by protonation–deprotonation reactions according to the pH of the solution. The molecular structure of TB and the protonated–deprotonated species are shown in Fig. 1. Fig. 2 shows the distribution of TB species at different pH obtained with the method reported by Del Piero et al. (2006).

2.3. Characterization of the adsorbents

Structural properties were analyzed by X-ray diffraction (XRD) using a RIGAKU Geigerflex X-ray diffractometer with Cu Kα radiation at 20 mA and 40 kV. The scans were recorded between 2° and 70° (2θ) with a step size of 0.02° and a scanning speed of 2°min^{-1}. Thermogravimetric analyses (TGA) were performed using a Shimadzu TG-51 equipment. The analyses were carried out by heating approximately 0.015 g of sample up to 1000 °C with a rate of 10 °C min^{-1}, in a dynamic air atmosphere.

Textural properties were obtained from nitrogen adsorption–desorption isotherms at 77 K using an ASAP 2000 (*Micromeritics*

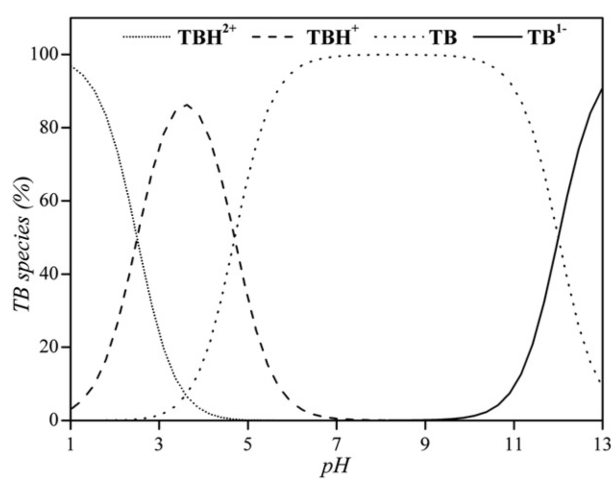

Fig. 2. Distribution of TB species as a function of pH.