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Thiabendazole adsorption on montmorillonite, octadecyltrimethylammonium- and *Acremonium* sp.-loaded products and their copper complexes

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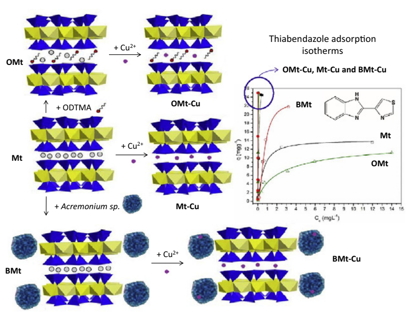
HIGHLIGHTS

- Cu^{2+}-loaded bio and organo-montmorillonites were efficient TBZ adsorbents.
- Cu^{2+}-thiabendazole complexes were formed in the interlayer of montmorillonite.
- Low leaching values attained from Cu^{2+} and TBZ, suggested its use in wastewater treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

This study is a preliminary approach to develop novel montmorillonite (Mt) based adsorbents for removing inorganic and organic contaminants in a step-like process. Biomass (fungi) and surfactant (octadecyltrimethylammonium bromide) modified montmorillonites (BMt and OMt, respectively) were obtained. In a prior step, Cu^{2+} was loaded into Mt, BMt and OMt. In a second step, the materials (Mt, Mt-Cu, BMt, BMt-Cu, OMt, OMt-Cu) were used as thiabendazole (TBZ) adsorbents. TBZ adsorption isotherms were performed, and Langmuir, Freundlich and Langmuir-Freundlich mathematical models were evaluated. TBZ removal efficiency of the materials was also tested using three adsorbent dosages.

The adsorbents and TBZ-adsorbed products were characterized by X-ray diffraction and thermal analysis, and by electron paramagnetic resonance (EPR) and solid-state nuclear magnetic resonance measurements (ss-NMR). To determine the subsequent arrangement of the adsorption products, leaching experiments were also conducted.

In the BMt sample, TBZ adsorption was enhanced compared to the raw Mt sample. An opposite behaviour was observed for OMt samples. All the Cu^{2+}-loaded materials showed better TBZ removal efficiencies than the same materials without Cu^{2+}. Furthermore, Cu^{2+} chelation through the imidazolic and thiazolic nitrogen atoms of TBZ in all Cu^{2+}-loaded samples allowed TBZ and Cu^{2+} to be resistant to migration in environmental leaching conditions.

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1. Introduction

Thiabendazole (TBZ) is a benzimidazolic derivate compound, used mainly in agriculture to control mould, blight and other fungi that cause diseases in fruits and vegetables [1]. The high amount of TBZ used as post-harvest fungicide leads to water pollution through effluents from fruit packing plants. It represents a major environmental concern since it exhibits toxicity to animals, causing liver and intestinal disorders [2].

Adsorption is a widely studied process used to remove contaminants from aqueous effluents, where montmorillonite (Mt) clays have been largely studied as adsorbent of different contaminants [3–6]. The main reasons that turn Mt into an important adsorbent are its external negative surface charge – which makes it particularly useful to remove cationic compounds from water – and its large total specific surface – which allows concentrating a high amount of molecules and ions at both outer and inner surfaces. These surfaces use two different mechanisms to adsorb cationic compounds; for the inner surface, the cation exchange mechanism with Na^+ or Ca^{2+} raw interlayer cations has been indicated, while for the outer surface a pH dependent electrostatic mechanism with silanol and aluminol groups has been inferred by electrostatic measurements [7].

Organic intercalation into montmorillonite is usually proposed to enhance its adsorption capacity towards organic compounds [8–10]. Specially, when organic cations such as alkylammonium salts are used to exchange the inorganic cations of the raw clay interlayer, organo-montmorillonites are generated, promoting both chemical and structural changes. For instance, the basal space increases by entrance of organic cations in the interlayer space. The organophilic character becomes organophobic due to the disappearance of the hydration sphere related to the interlayer inorganic cations, evidenced by thermal analysis [11]. Besides, the negative external electric charge of Mt decreases or reverses to positive, trough the partial neutralization of permanent charges due to organic cations loading [12]. Furthermore, the swelling behaviour and the specific surface area of the clay decrease, which would allow an easier separation of the adsorbent from water by coagulation. These advantages have made organo-montmorillonites a material widely tested for the removal of organic pollutants from wastewater [7–8].

There is a lack of reports about TBZ adsorption onto organo-montmorillonites, while its adsorption onto Mt and pillared Mt clays has been already studied [13,14]. Roca Jalil et al. [10] reported maximum TBZ amounts (Langmuir parameter) of 11.91 mg/g adsorbed onto Mt and an improvement of up to 63.87 mg/g for those adsorbed onto the respective aluminium pillared sample [14]. The ability of thiabendazole to coordinate transition metal ions through the imidazolic and thiazolic nitrogen atoms [15,16] suggests that the incorporation of a transition metal cation in the adsorbent structure would further improve TBZ removal efficiency.

Copper is a transition metal usually found in mining, industrial and agricultural effluents. The International Programme on Chemical Safety (IPCS) stated that although the acceptable upper limit of copper for oral intake in adults is uncertain, it is likely to be in the range of several mg per day [17]. In order to obtain the acceptable limit of copper in the mentioned effluents, different physical or chemical treatment processes have been used. Among them, copper adsorption on clays, and particularly on montmorillonites, is a deeply studied method to remove it from aqueous media [18–21] taking advantage of copper species bonding capability on permanent (interlayer or inner) and pH dependent (edge or outer) charge sites [22]. In addition, biosorption technology is recognized as a potential alternative method among conventional metal retention techniques where the main interactions involved in adsorption are those of functional groups on the cell wall structure of microorganisms with the contaminants. This process uses living, dead, pretreated or immobilized forms of biological cells such as bacteria, fungi, yeasts and algae as sorbent materials. In particular, the immobilized forms of biosorbent materials are more convenient in practical applications because of their mechanical strength, anti-degradability, physical morphology and chemical stability, as well as regeneration capacity [23].

The aim of this work was to evaluate different materials derived from Mt as TBZ adsorbents and study whether their performance changed when Cu^{2+} was present in their structure. The Mt derived materials were an octadecyltrimethylammonium (ODTMA) exchanged Mt (OMt) and an immobilized biosorbent material (fungi-loaded Mt, BMt). Organo-montmorillonites were chosen due to the possible improvement of organic species adsorption and their ease of separation from water [12], whereas BMt was selected taking into account its ability to remove heavy metal cations from water [24]. These materials (OMt, BMt and Mt) were first loaded with Cu^{2+} (OMt-Cu, BMt-Cu and Mt-Cu) and their TBZ adsorption capacity was evaluated. The successful use of these materials and methodology would also allow consecutive adsorption steps for wastewater treatments where metal cations and fungicides coexist. Although thiabendazole is one of the most widely used post-harvest fungicides in fruit production, there are other imidazole or benzimidazole fungicides (eg imazalil, carbendazim, methyl thiophanate, etc.) that could also be coordinated with Cu^{2+}, to which the results of this work could be extended.

In order to compare the adsorbent performance, adsorption isotherms were done, and removal efficiency was evaluated at different solid dosages. To identify the surface adsorption sites involved, the adsorbents and TBZ-adsorbed products were characterized by X-ray diffraction (XRD), thermal analysis, electron paramagnetic resonance (EPR), and solid-state nuclear magnetic resonance measurements (*ss*-NMR). Furthermore, in order to establish the subsequent disposal of the adsorption products, leaching experiments were performed.

2. Materials and methods

2.1. Materials

A Patagonian (Rio Negro province, Argentina) montmorillonite (Mt) sample, provided by Castiglioni Pes y Cia., was used as received. The main properties of Mt are: isoelectric point (IEP) = 2.7, specific surface area (SSA) = 34.0 m^2/g, total specific surface area (TSSA) = 621 m^2/g [25], and cation exchange capacity (CEC) = 0.8250 ± 0.0007 mmol/g clay [12]. The XRD and chemical analyses indicated that the raw sample contained Na-Mt (>86%) with quartz and feldspars as minor phases. The structural formula obtained from the chemical analysis of purified Mt was: $[(Si_{3.89}Al_{0.11})(Al_{1.43}Fe^{3+}_{0.28}Mg_{0.30})O_{10}(OH)_2]\ Na^{+}_{0.41}$ [25].

Octadecyltrimethylammonium (ODTMA) bromide (≥97%), molecular weight (MW) = 392.5, $CuSO_4{\cdot}5H_2O$ (≥97%), MW = 249.7, and thiabendazole [2-(thiazol-4-yl) benzimidazole] (TBZ), MW = 201.3, pK_a values = 2.5, 4.7 and 12.0, and solubility in water at 20 ± 0.5 °C = 0.16 g/L at pH 4 and 0.03 g/L at pH 7–10 [26], were supplied by Fluka (Buchs, Switzerland). All chemicals were of analytical grade and used without further purification.

The organo-Mt sample (OMt) with ODTMA exchanged at 55% CEC was obtained and characterized previously [12].

The *Acremonium*-clay biocomposite was generated by growing *Acremonium* sp. (*Acre* sp.) biomass on Mt clay as indicated in former study [22]: the biomass was grown axenically in aerobic batch cultures, on the Mt clay 1% (w/v) in the presence of the culture medium P5. The biocomposite (denoted BMt) was isolated by centrifugation (20 min, 15,000 rpm), water rinsed and dried at 80 °C