



Reactive adsorption of pharmaceuticals on tin oxide pillared montmorillonite: Effect of visible light exposure

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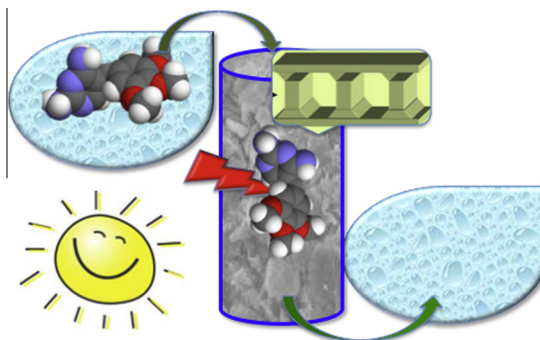
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HIGHLIGHTS

- Montmorillonite was pillared with tin oxide.
- As increase in the surface area was found owing to the deposition of SnO₂.
- The pillared clay was used for adsorption of trimethoprim and sulfamethoxazole.
- As increase in the adsorption was found compared to the initial clay.
- Solar light decomposes trimethoprim and thus increases its adsorption in small pores.

GRAPHICAL ABSTRACT



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ABSTRACT

Montmorillonite (Mt) clay was pillared with SnO₂ and tested as an adsorbent for the removal pharmaceuticals trimethoprim (TMP) and sulfamethoxazole (SMX) frequently present in wastewaters. Adsorption process was carried out in dynamic conditions and the effects of light exposure were investigated. The initial and modified clays were characterized using XRD, FTIR, SEM, potentiometric titration, TA/MS and adsorption of nitrogen. The XRD analysis revealed an enlargement of the clay's interlayer space as a consequence of SnO₂ particles intercalation into the clay interlayer spaces. A marked increase in the volume of mesopores was also noticed. It indicated the precipitation of tin species on the flake surface. These changes resulted in a five-fold increase in TMP adsorption. Upon exposure to light a 30% increase in TMP adsorption was found in comparison to the performance in the dark. The good performance of the modified clay was linked to specific acid–base and electrostatic interactions of TMP with the Lewis acid sites of SnO₂. Since exposure to solar light resulted in the decomposition of some TMP adsorbed on the surface, those smaller molecules formed were able to relocate to small pores of higher adsorption energy, which were initially inaccessible for TMP. SMX was not adsorbed on the surface of the modified clay owing mainly to its acidic character.

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1. Introduction

The presence of pharmaceuticals and their metabolites in water have caught global attention due to its environmental and health

hazards [1]. Among the various types of pollutants, pharmaceuticals are of particular concern because they can interfere with the function of the endocrine system in wildlife and humans [2]. The majority of pharmaceuticals that has been reported as dangerous to living organisms can be found in municipal wastewater. These compounds usually are not completely removed by conventional wastewater treatment due to their high resistance

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to biodegradation [3,4]. Moreover, various pharmaceuticals have been also detected in seawater. Their presence in such ecosystems is attributed to the transport of contaminated wastewater effluents by rivers into larger water bodies such as oceans and seas, which indicates that they can be quite persistent to natural biotransformation [5]. To reduce the potential risk caused by these compounds in treated wastewater discharged to aquatic environments, their removal in water treatment plants is considered as an important technological challenge.

Adsorption is one of the most promising techniques used to remove pharmaceuticals from water [4]. Among the adsorbents used for water decontamination clay minerals are often selected, owing to their low cost and selectivity to adsorb specific contaminants [6–8].

Montmorillonite (Mt) is an abundant clay mineral, consisting of two layers of tetrahedral silica sheets sandwiching one octahedral alumina sheet [9]. Its interlayer charge is neutralized by the presence of cations such as sodium or calcium. The cationic layered clays can be transformed into highly porous structures by a three-step synthesis procedure: (1) polymerization of a multivalent cation (such as Al^{3+} , Ga^{3+} , Ti^{4+} , Zr^{4+} , Sn^{4+} , Fe^{3+} , and Cr^{3+} , among others) leading to polycations; (2) intercalation of these hydroxy-metal polycations into the interlayer space of clays, involving the substitution of natural exchangeable charge-compensating cations; and (3) calcination at moderate temperatures [10,11]. The latter step is necessary because the solids obtained after the second step, usually called intercalated clays, are metastable, like the polycations themselves. Calcination transforms the polycations into stable oxy-hydroxide phases referred to as pillars, which contribute significantly to the porosity development in such materials [12].

Over the past few years various nanostructures of tin oxide such as nano-wire, nano-tubes, nano-rods, nano-sheets, nano-particles and nano-pillars have been reported with their diversifying properties and, hence, functionalities [13–15]. Even though tin oxide has been studied as an adsorbent from a gas phase [16–18], there are few studies in the literature using it in the clay pillaring process [13,19–21] or analyzing in details its beneficial effects for the separation of pollutants.

Tin oxide exists in two different forms; as stannous oxide/tin monoxide (SnO) and as stannic oxide/tin dioxide (SnO_2). The existence of these two oxides reflects the dual valency of tin with valence states of 2^+ and 4^+ , respectively. During the pillaring processes SnO is easily oxidized to SnO_2 [21,22].

SnO_2 is a well-known semiconductor oxide, which has received considerable attention due to its photocatalytic properties in the degradation of organic pollutants [23,24]. Wang and co-workers [25] synthesized and studied the photocatalytic properties of mesoporous SnO_2 -hexaniobate layered nanocomposites and they found that the nanocomposite demonstrates a high photocatalytic activity in the degradation of acid red G under UV-light irradiation, which can be ascribed to its high surface area, mesoporosity and the synergistic effect of the two components (SnO_2 and hexaniobate). Bandara and co-workers [26] studied composites of tin and zinc oxide nanocrystalline particles for enhanced charge separation in sensitized degradation of dyes. Improved photocatalytic activity was observed in the case of ZnO/SnO_2 composite catalyst compared to the catalytic activity of ZnO , SnO_2 or TiO_2 powder. A novel preparation method for nanosized $\text{ZnO}-\text{SnO}_2$ with high photocatalytic activity for methyl orange by homogeneous co-precipitation was proposed by Zhang and co-workers [27]. Fresno and co-workers [28] compared the photocatalytic activity of Sn-doped TiO_2 with P25 TiO_2 for the degradation of chlorsulfuron (ChS). Their results showed a beneficial effect of the presence of Sn^{4+} in the TiO_2 lattice. Bisphenol photodegradation on nanoporous SnO_2 and TiO_2 was investigated by Kim and co-workers [29] who also found an improvement when two materials were combined.

Based on the above, the objective of this paper is to investigate the effect of SnO_2 treatment on the properties of a montmorillonite from Brazil and to evaluate the modified montmorillonite as an adsorbent/reactive adsorbent for the removal of TMP and SMX frequently present in raw and treated wastewaters. We focus on the examination of the effect of the tin species surface location on the adsorption and photodegradation processes. To derive the mechanism of surface interactions and elucidate the role of tin oxide in the separation process. An extensive characterization of the initial clay, its tin oxide modified counterpart and the exhausted samples with TMP and SMX has been carried out. Finally, adsorption experiments were conducted in light and in dark conditions in order to investigate the photoactivity effect.

2. Materials and methods

2.1. Materials/adsorbents

Montmorillonite (Mt) was supplied by Bentonisa (Campina Grande, Brazil). Its cation exchange capacity (CEC) is 0.108 mol/100 g. It was estimated using the ammonium acetate method [30].

The pillaring agent was prepared by adding dropwise 50 mL of tin chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (II) 0.4 mol L^{-1} to 50 mL of 0.4 mol L^{-1} KOH with continuous steering at 70°C . No precipitation was observed. The final pH was 2. Previous studies have shown that the trimer $\text{Sn}_3(\text{OH})_4^{2+}$ is one of the predominant species when Sn(II) salts undergo hydrolysis under controlled conditions [21], but at that pH, the SnOH^+ , $\text{Sn}_2(\text{OH})_2^{2+}$ species are also expected in the solution. Hydra/Medusa Chemical Equilibrium Database and Plotting Software were used to predict the polycations present in the pillaring agent solution (Fig. 1S of Supplementary Information). Mt (5.0 g) was well dispersed in 400 mL of deionized and then 100 mL of pillaring agent was added into the clay suspension. The mixture reaction was stirred at 60°C for 24 h. The resulting suspension was centrifuged and washed several times with deionized water, dried at 80°C and calcined at 500°C for 3 h. During this process in the presence of air oxidation of Sn^{2+} to Sn^{4+} is expected to take place [21,22]. The modified clay is referred to as SnO_2 -Mt. The exhausted samples after adsorption have a name of a specific adsorbate added.

2.2. Adsorbates

The pharmaceuticals used, trimethoprim (TMP) and sulfamethoxazole (SMX), were purchased from VWR (USA). Then, working solutions for the adsorption tests were prepared by diluting the adsorbate in distilled water to a concentration of 10 mg L^{-1} using an ultrasonic cleaner (Brason 1510) to improve the dissolution of the compounds. The physicochemical properties for the pharmaceuticals selected are shown in Table 1. Their structural formulas are given below.

2.3. Methods

X-Ray powder diffraction (XRD) patterns were recorded at XRD diffractometer (Philips X'Pert X-Ray diffractometer) with a $\text{CuK}\alpha$ radiation for crystalline phase with a routine power of 1600 W (40 kV, 40 mA).

The X-Ray fluorescence spectra were obtained using a wavelength dispersive X-Ray fluorescence spectrometer (model ZMS Mini II, Rigaku).

Scanning electron microscopy (SEM) was performed on Zeiss Supra 55 instrument with a resolution of 5 nm at 30 kV. Analyses were performed on a sample powder previously dried. A sputter coating of a thin layer of gold was performed to avoid specimen charging.

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