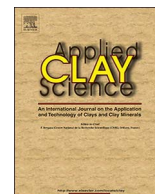




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Research paper

Individual and simultaneous degradation of antibiotics sulfamethoxazole and trimethoprim by UV and solar radiation in aqueous solution using bentonite and vermiculite as photocatalysts

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ABSTRACT

This work is aimed at studying the utilization of bentonite and vermiculite as a photocatalyst in the individual and simultaneous degradation of sulfamethoxazole (SMX) and trimethoprim (TMP) by UV and solar light radiation. The clays were characterized by various analytical techniques, and it was corroborated that the photoactivity and textural properties of clays remained unaffected by the UV radiation. The band gap energy (E_g) of both clays was less than 4 eV, revealing that they could behave as semiconductor materials and could act as photoactive materials in the presence of UV radiation. The photodegradation rate and the maximum percentage of degradation for SMX and TMP were markedly enhanced by the presence of the clays. The reaction rate constant for SMX and TMP degradation in UV radiation was increased 11.4 and 46.4 times, respectively, when 10 mg of vermiculite were added to the UV system. Better degradation results were observed by using vermiculite, and this trend could be attributed to the higher percentage of doping ions in the vermiculite. In the UV radiation and UV/Clay systems, the rate constants for single degradation were faster than those for simultaneous degradation of SMX and TMP; this was due to the competition of SMX and TMP for the generated oxidant radicals. The photoactivity of the reutilized clays was similar to that of the original clays.

1. Introduction

The most commonly used drugs for the treatment of infectious diseases are antibiotics. More specifically, sulfamethoxazole (SMX) and trimethoprim (TMP) are usually prescribed together in veterinary and human medical treatment for respiratory, urinal, and gastrointestinal diseases (de Paula et al., 2008; Nguyen Dang Giang et al., 2015). Both antibiotics have been identified as emerging contaminants and have been found in underground and superficial water resources, as well as in the effluents of hospitals and municipal wastewater treatment plants at concentrations ranging from ng L^{-1} to $\mu\text{g L}^{-1}$ (Bueno et al., 2012; Johnson et al., 2015; Ngumba et al., 2016).

Both antibiotics can be removed from aqueous solutions by different processes, such as separation by membrane (Hylton et al., 2009), electro-oxidation (Carlesi Jara et al., 2007), electrocoagulation (Martins et al., 2011), adsorption (Mailler et al., 2015; Sheng et al., 2016) and advanced oxidation processes (AOPs) (Dias et al., 2014; Moreira et al., 2015). Some of these methods are not always efficient, resulting in the discharging of pollutants to surface waters (Petrović et al., 2005). AOPs

could be a promising technology for the elimination of the antibiotics SMX and TMP because they have several advantages such as a high mineralization of pharmaceuticals, treatment of contaminants at trace concentrations and generation of degradable byproducts, which are not usually harmful to the environment (Klavarioti et al., 2009).

Various AOPs are based upon photocatalytic processes that involve the use of radiation to promote the electronic activation of the catalyst, generating e^-/h^+ pairs, which subsequently produce reactive species that degrade the antibiotics. One of the most commonly used catalysts is titanium dioxide (Vorontsov et al., 2001) due to its high stability at a wide range of pH and its low cost (Ferrer, 2004). However, titanium dioxide presents some disadvantages such as its reduced absorption percentage of the solar spectrum, a high level of recombination of the electron-hole pairs, its aggregation and the difficulty to remove it from the treated effluents, as well as the difficulty to re-utilization (Velo-Gala et al., 2013).

The use of clays as photocatalysts in heterogeneous reactions is a promising alternative for the treatment of aqueous effluents, due to these minerals are abundant, cheap, chemically stable and friendly to

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the environment. Additionally, one outstanding advantage of clays is their structure stability during the degradation of pharmaceuticals by AOPs. The amount of iron present in these materials, either in natural or synthetic forms, can promote a Fenton reaction which would produce radical oxidants for the degradation of contaminants (Hofstetter et al., 2003). Specifically, clays are some of the minerals with the highest chemical activity in soils and are usually pillared with oxides of iron or copper to carry out Fenton-like heterogeneous reactions (Azmi et al., 2014; Bel Hadjtaief et al., 2014; Garrido-Ramírez et al., 2013).

Few studies have been reported on the photocatalytic activity of clays per se, for the degradation of pollutants in aqueous solutions (Cheng et al., 2008; Jia et al., 2012). The use of clays as photocatalysts can be a feasible option because they are inexpensive and non-toxic, and they have very good mechanical, thermal and chemical stability (Jia et al., 2012). Bentonite is a clay that belongs to the group of the smectites and is mainly composed of montmorillonite (Chaves and Tito, 2011; Galindo et al., 2013; Zhu et al., 2008). On the other hand, the vermiculite is formed by weathering or hydrothermal alteration of biotite. The vermiculite structure consists of sheets of trioctahedral mica separated by layers of water molecules (Badawy et al., 2010; Padilla-Ortega et al., 2014).

The principal aim of this work was to examine the photocatalytic properties of bentonite and vermiculite for the degradation of the emerging contaminants SMX and TMP in aqueous solutions. The photocatalytic degradation of SMX and TMP was carried out in UV and solar radiation and UV/clay systems to analyze the role of the electronic, chemical and textural properties of clays in the degradation of both antibiotics. Additionally, the effect doping ions in the clays on the photocatalytic process was argued, and the acting mechanism of clays in the photodegradation of SMX and TMP was proposed.

2. Materials and methods

2.1. Materials

The antibiotics SMX [4-amino-N-(5-methyl-3-isoxazolyl)benzenesulfonamide] and TMP [2,4-diamino-5-(3,4,5-trimethoxybenzyl)pyrimidine], formic acid, sulfuric acid, sodium bisulfite, ferrous sulfate, ferric chloride and humic acid were supplied by Sigma-Aldrich. Acetonitrile was provided by Fisher Chemical. All the solutions were prepared using ultrapure water obtained from a Milli-Q® equipment. The clays used throughout this work were a calcium bentonite from a deposit located in San Luis Potosi, Mexico, and a vermiculite that was collected in a mine in Virginia, United States. The average diameter of the clay particles was 0.272 μm .

2.2. Chemical and textural characterization of natural clays

The iron content of the clays was quantified using an inductively coupled plasma emission spectrometer (Thermo Jarrell Ash, IRIS/AP). An X-ray fluorescence spectrometer (THERMO, ARL ADVANT XP+) provided the chemical composition of the clays.

The adsorption-desorption isotherms of N_2 on bentonite and vermiculite at 77 K were determined in a surface area and porosimetry analyzer (Micromeritics, ASAP 2020). The textural properties of both clays were estimated by analyzing the adsorption-desorption isotherms of N_2 . The X-ray patterns and diffuse reflectance spectra of both clays were obtained using an X-ray diffractometer (Rigaku, D-MAX) and a spectrophotometer with a dual camera (Varian, Cary-5E). The latter was equipped with a spherical diffuse reflectance accessory. Further details of the analytical procedures can be found elsewhere (Siraj et al., 2011; Velo-Gala et al., 2013).

2.3. Determination the concentration of SMX and TMP in a water solution

The concentrations of SMX and TMP in water solution were

quantified using a high-performance liquid chromatograph (HPLC) (Thermo-Fisher), equipped with a visible UV detector and an automatic sampler for 120 vials. The dimensions of the chromatographic column (Phenomenex C_{18}) were 150×4.6 mm, and the particle size was 4.6 μm . The mobile phase was 30% acetonitrile and 70% of acid water (0.1% formic acid), and a volumetric flow rate of 0.55 mL/min in isocratic mode. The UV-visible detector was set up at a wavelength of 270 nm, and the injection volume was 100 μL .

2.4. Degradation of SMX and TMP by direct photolysis

The photodegradation experiments of SMX and TMP were carried out in two photoreactors. The first photoreactor consisted of six quartz reaction tubes (diameter of 1.5 cm and height of 20 cm) and a low-pressure Hg lamp (Heraeus Nobelight, TNN 15/32,) with a working power of 15 W (795.8 W/m^2) that emits UV radiation at $\lambda = 254$ nm. The solution in the reaction tubes was stirred continuously by magnetic agitation, and the solution temperature was kept constant at 25 ± 0.2 °C using an ultrathermostat (Frigiterm). The other photoreactor was a solar simulator SOLARBOX 1500 (Neurtek) having a 1500 W Xenon lamp (Philips XOP-15-OF). The Xenon lamp supplied a radiant energy in a spectral range from 280 to 825 nm and the irradiance was set up at 450 W/m^2 . The operating power of the Xenon lamp was 1.77 times less than that of the UV lamp. Also, the solar simulator included a fan for circulating cooled air to maintain constant the temperature in the photoreactor at 25 °C. The reaction quartz tubes had an inner diameter of 22 mm and a height of 220 mm, and the solution inside the quartz tubes was continuously mixed by recirculating the solution using a peristaltic pump (Fischer Scientific, FH100).

The degradation of SMX and TMP antibiotics by direct photolysis were carried out by adding 40 mL of an antibiotic solution with an initial concentration of 40 mg L^{-1} and pH of 3, 8 and 12 to a reaction tube, and then placing the reaction tube inside the photo-reactor. The solutions were kept in constant agitation throughout the experiment. The experiment lasted for 30 min and at regular intervals, samples of the solution were taken out for the subsequent determination of the concentrations of antibiotics. All solutions were prepared with deionized water.

2.5. Photodegradation of SMX and TMP by the radiation/clay

Experimental data for photodegradation of SMX and TMP in the presence of vermiculite or bentonite were obtained as described in Section 2.4, except that 5 or 10 mg of clay were poured into the solution at pH = 7. This pH value was chosen to avoid that the clays can lose aluminum (dealuminize) and affect its crystalline structure. Subsequently, samples were filtered through Millipore disk filters (0.45 μm), to remove the clay. These experimental conditions were chosen in order to be able to follow the degradation kinetics properly and observe the effect of the operating conditions on the degradation rate.

2.6. Adsorption of SMX and TMP on the bentonite and vermiculite

The adsorption equilibrium data of SMX and TMP on the clays were obtained in a reaction tube, which served as a batch adsorber. A mass of 0.1 g of bentonite or vermiculite and 40 mL of a solution having a particular initial concentration of SMX or TMP were added to the batch adsorber. The adsorber was placed inside the photo-reactor, but the light was off. The initial concentration of the antibiotic varied from 20 to 400 mg L^{-1} and the operating conditions were $T = 25$ °C and pH = 7.0. The solution was continuously stirred, and its temperature was kept constant. The solution was sampled to determine the antibiotic concentration.

The mass of SMX and TMP adsorbed on each clay was computed by a mass balance represented by the following expression:

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