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Removal of pharmaceuticals from water by clay-cationic starch sorbents

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ABSTRACT

Significant concerns have been raised up due to the presence of organic micropollutants in surface waters. The ability of two polymer-clay sorbents based on a functionalized cationic starch was examined for the removal of three pharmaceuticals: atenolol, sulfamethoxazole and diclofenac sodium. In batch experiments, the complex which exhibited a planar conformation of the polymer on the clay surface and higher cationic charge density showed higher sorption of diclofenac and sulfamethoxazole over those of the composite with a loops and tails configuration, but similar with atenolol. The introduction of functional moieties on the polymers that are capable to create a network of hydrogen-bonds with the pollutants promoted their removal as revealed by thermal and infrared techniques: diclofenac molecules formed an ion pair including hydrogen bonds through their secondary amine groups; sulfamethoxazole sorbed by strong electrostatic interactions followed by proton transfer involving its sulphon-nitrogen group and the hydroxyl moieties of the composite. Filtration experiments showed a better performance of the columns made of the composite with higher cationic charge density on the removal of diclofenac and sulfamethoxazole over that of granular activated carbon. The filtration processes were successfully modeled by using an adsorption-convection model which enabled predictions under different operational conditions used in drinking water plants. Experimental removal of diclofenac by filtration within the range found in environmental concentrations was in good agreement with the predicted amounts.

1. Introduction

The occurrence of organic micropollutants or emerging contaminants (ECs) in surface waters and drinking water supply systems has been detected in the last few decades. A monitoring survey in untreated sources of drinking water in the United States revealed the occurrence of sixty three of the 100 targeted chemicals (Focazio et al., 2008). In another study in Canada by Kleywegt et al. (2011) on the ubiquity of emerging organic contaminants which included pharmaceuticals, hormones and bisphenol A, showed that 27 out of 48 of these contaminants were detected in source waters and finished drinking waters. Similarly, a survey for multi-class pharmaceuticals in drinking water sources of five major river watersheds in China conducted from 2012 to 2013 detected a total of 70 pharmaceuticals; the most frequent ones being sulfonamides, macrolides, antiepilepticdrugs, anti-inflammatory drugs, and β-blockers (Sun et al., 2015).

The ECs have a great potential risk for human health and environment, due to resistance to chemical, photolytic and biological degradation; high bioaccumulation and biomagnification potential in the food chain; great toxicity to wildlife; and long-range transport and distribution through the atmosphere and water bodies. The ECs comprise pharmaceuticals, personal care products, fluorinated surfactants, etc., which are not yet regulated contaminants.

Traditional water treatments were shown to be inefficient for the removal of quite a few of these ECs due to their high water solubility and often poor degradability, which enable them to persist through all natural filtration steps and man-made treatments of water purification. Specifically, coagulation-sedimentation and chlorination performed poorly in the removal of pharmaceuticals in drinking water treatment plants (Benotti et al., 2009; Simazaki et al., 2014). Therefore, there is a need to

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polish the treated water by implementing facilities based on the use of advanced water treatments such as ozonation (Feng et al., 2016), reverse osmosis (Radjenovic et al., 2008), advanced oxidation processes such as photo-Fenton system or photocatalysis using titanium dioxide (TiO_2), and adsorption onto activated carbons (Ahmed et al., 2014; Carrales-Alvarado et al., 2014). Zwiener (2007) observed a good correlation between the percentage of removal by activated carbon and the octanol/water partition coefficient (Kow) for chemicals with log Kow>3. Indeed, the latter treatment is incorporated in the vast majority of water treatment plants through the use of non-compressible filters made of granular activated carbon (GAC), but the removal of small polar molecules is usually unsatisfactory (Huerta-Fontela et al., 2011). Therefore, there is a growing interest in the development of composites that improve the performance of GAC or even can be an alternative to its use: micelle-clay (Nir et al., 2015), molecular imprinted polymers (Huang et al., 2015), nanotubes (Ji et al., 2009), magnetic particles (Álvarez et al., 2010), etc. In this context, clay-based composites have shown good sorbent properties for the retention of effluent dissolved organic matter (Kohay et al., 2015), pesticides (Gardi et al., 2015), inorganic anions (Taubert and Omorogie, 2017) and pharmaceuticals (Karaman et al., 2012; Mohd-Amin et al., 2016). The sorption of polymers on the planar surface of clay minerals can occur by entropic effects and electrostatic interactions (Theng, 2012). The conformations of cationic polymers on the clay surface can be tuned by varying the electrostatic charge density of the polymer with respect to the clay surface charge. A polymer with high charge density resulted in a planar conformation on the negatively charged clay surface, whereas lower electrostatic interactions yielded a loops-and-tails configuration with higher loading on the clay per surface unit (Claesson et al., 2005). Only a part of the negatively charge density of the clay mineral is neutralized by the cationic moieties of the polymer; the hydrophobic portions between adjoining cationic segments of the polymer screen the clay surface. Therefore, very small loading of the cationic polymer on the clay may easily yield charge reversal of the externally exposed surface, because the amount of adsorbed cationic monomers necessary for charge neutralization of the external surface of the clay is lower than the CEC (Zadaka et al., 2010).

Recently, new composites with good anti-microbial properties were described based on starch, functionalized with quaternary ammonium groups adsorbed on a commercial bentonite (Undabeytia et al., 2014). In the current work, the retention of three pharmaceuticals (PhAcs) with different physico-chemical properties by two selected composites differing in the conformation of the polymer, loading on the clay surface and surface charge, were examined. The nonsteroidal anti-inflammatory drug diclofenac (DC), the beta blocker atenolol (AT) and the sulfonamide antibiotic sulfamethoxazole (SMX) were removed from water in suspension and filtration columns.

2. Materials and methods

2.1. Materials

Two cationic starches with different degree of substitution (DS), Topcat L-98 (DS = 0.22) (denoted hereafter as Tpt) and Penbond 1000 (DS = 0.05) (denoted as Pen), were supplied by Penford Co. (Centennial, CO) and are based on the reaction of hydroxyl groups of pristine starch with 3-chloro-2-hydroxypropyltrimethylammonium. Atenolol, sulfamethoxazole, and diclofenac sodium were obtained from Sigma-Aldrich (Sigma Chemical Co., St Louis, MO). Their solubilities in water are 300 mg/L for AT, 610 mg/L for SMX and 50000 mg/L for DC. The chemical structure of the pharmaceuticals and the cationic starch are shown in Fig. 1. A commercial bentonite (bent) (Bentonil A, CEC 0.8 $mmol_c$/g) was kindly supplied from Süd-Chemie Spain. Granular activated carbon (GAC) (NUSORB GC60, 12 × 30 mesh) was purchased from NUCON International, Inc. (Columbus, OH). HPLC grade -acetonitrile and −methanol were obtained from Teknokroma S.A. (Barcelona, Spain).

2.2. Preparation of polymer-clay composites

Clay powder was added to a polymer solution of either Tpt or Pen; the suspension was shaken for 24 h and centrifuged; the pellet was dry-frozen yielding the clay-polymer composite. The concentrations used were 10 g/L of polymer and 4.25 g/L of clay. The sorbed amounts of the polymers on the clay were 0.80 g/g clay for Tpt and 1.72 g/g clay for Pen.

2.3. Sorption of the pharmaceuticals

Sorption isotherms of AT, SMX and DC onto the commercial bentonite and the polymer-clay composites were carried out in triplicate by mixing 15 mL of solutions of each one (1–50 mg/L) prepared in distilled water with 24 mg of clay or composite. The sorbent concentration was 1.6 g/L. After shaking for 24 h at 20 °C, the suspensions were centrifuged at 12,000 g for 10 min, and the analyte in the supernatants measured by HPLC. A particular case was performed by using equimolar solutions (4–170 μM) of DC with either AT or SMX.

Pharmaceuticals sorption was modeled by using the Langmuir-Scatchard equation:

$$\frac{Lo - L}{L} = \frac{Ro^*\, K}{1 + K^* L}, \qquad (1)$$

in which Lo and L denote the molar concentration of total and free surfactant, respectively, Ro is the molar concentration of sorption sites and K is the binding coefficient. The determination of Ro was performed by saturation of the bentonite and polymer-clay complexes with solutions of the pharmaceuticals whose concentrations

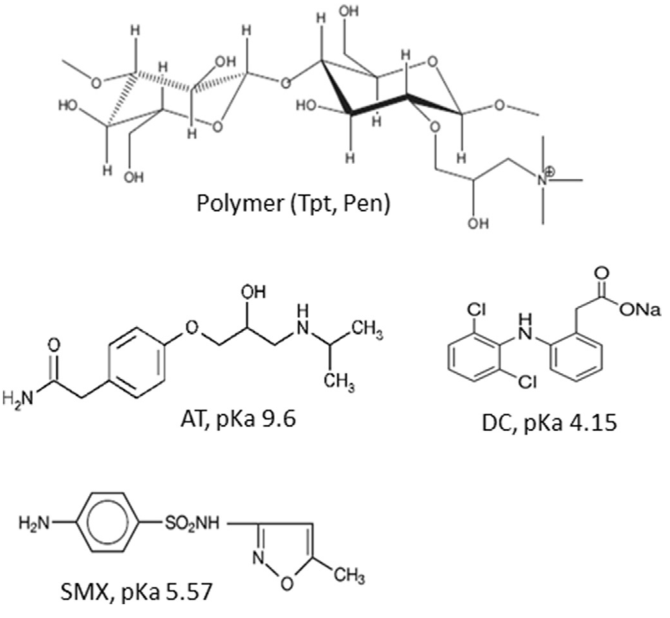

Fig. 1. Molecular structures of the PhAcs and structural monomer units in the polymers.