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Tetracycline removal from water by adsorption/bioadsorption on activated carbons and sludge-derived adsorbents

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ABSTRACT

The objective of this study was to analyze the behavior of activated carbons with different chemical and textural natures in the adsorption of three tetracyclines (TCs) (tetracycline, oxytetracycline, and chlortetracycline). We also assessed the influence of the solution pH and ionic strength on the adsorption of these compounds and studied their removal by the combined use of microorganisms and activated carbon (bioadsorption). Sludge-derived materials were also used to remove TC from water. The capacity of these materials to adsorb TC was very high and was much greater than that of commercial activated carbon. This elevated adsorption capacity (512.1–672.0 mg/g) is explained by the high tendency of TC to form complex ions with some of the metal ions present in these materials. The medium pH and presence of electrolytes considerably affected TCs adsorption on commercial activated carbon. These results indicate that electrostatic adsorbent–adsorbate interactions play an important role in TC adsorption processes when conducted at pH values that produce TC deprotonation. The presence of bacteria during the TCs adsorption process decreases their adsorption/bioadsorption on the commercial activated carbon, weakening interactions between the adsorbate and the microfilm formed on the carbon surface. The adsorptive capacity was considerably lower in dynamic *versus* static regime, attributable to problems of TC diffusion into carbon pores and the shorter contact time between adsorbate and adsorbent.

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1. Introduction

Both granular (GAC) and powdered (PAC) activated carbons have been widely used for the adsorption of organic micropollutants in solution (Karanfil and Kilduff, 1999; Radovic et al., 2001; Moreno-Castilla, 2004; Dias et al., 2007; Rivera Utrilla et al., 2011). The capacity of activated carbon to adsorb pharmaceutical-related pollutants has attracted recent research interest (Fuerhacker et al., 2001; Adams et al., 2002; Snyder et al., 2007; Choi et al., 2008; Simazaki et al., 2008; Yu et al., 2008; Rivera Utrilla et al., 2009). An important advantage of using activated carbon to remove pharmaceuticals is that toxic or pharmacologically active products are not generated (Rivera Utrilla et al., 2009).

Snyder et al. (2007) assessed the mechanisms underlying the adsorption of various pharmaceuticals and hormones on GAC and PAC and obtained removal percentages of around 90% for most of the pharmaceuticals studied. Optimal performances were obtained for acetaminophen (73–84%), carbamazepine (74–86%), triclosan (90–96%), and fluoxetine (91%), but the removal percentage did not exceed 50% for naproxen, diclofenac, gemfibrozil, sulfamethoxazole, and ibuprofen, among other drugs. They observed that the effectiveness of activated carbon was markedly reduced in the presence of natural organic matter (NOM), which competes for the active sites on the carbon, blocking its porosity.

Various authors have studied the adsorption of tetracyclines (TCs), one of the most important antibiotic groups, using adsorbents other than carbon, including apatites (Misra, 1991), clays and soils (Kulshrestha et al., 2004; Figueroa et al., 2004; Jones et al., 2005; Başakçilardan-Kabakci et al., 2007; Turku et al., 2007; Gu and Karthikeyan, 2008; Parolo et al., 2008). However, fewer data are available on activated carbon as TC adsorbent. One study (Choi et al., 2008) found activated carbon columns to be highly effective for the adsorption of seven TCs in aqueous medium, obtaining percentage removal values of around 90% that varied according to the type of TC and characteristics of the water, especially the concentration of NOM. Choi et al. (2008) reported a higher adsorption on activated carbon for TCs than for sulfonamide, despite the greater hydrophobicity of the latter.

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With this background, it is clear that the adsorption of pharmaceuticals on carbon materials has yet to be fully elucidated. Thus, the objective of this study was to analyze and compare the behavior of carbon materials, both commercial activated carbons and sludge-derived materials, with different chemical and textural natures in the adsorption of three TCs (tetracycline [TC], oxytetracycline [OTC], chlorotetracycline [CTC]). This behavior was analyzed in both static and dynamic regime and using ultrapure water, surface water, groundwater, and urban wastewater. We also assessed the influence of solution chemical nature (pH and ionic strength) on the adsorption of these compounds analyzing the adsorbent–adsorbate interaction types, and evaluated the combined use of microorganisms and activated carbon (bioadsorption) in these processes.

2. Experimental

2.1. Tetracyclines characterization

Fig. 1 shows the chemical structure of tetracyclines and the pKa corresponding to the different deprotonations (Stephens et al., 1956; Leeson et al., 1963; Bhatt and Jee, 1985) and Table 1 summarizes their characteristics. The species distribution diagram of TCs as a function of solution pH is depicted in Fig. 2.

Tetracycline concentration was determined with a Genesys 5 spectrophotometer. Wavelength scanning at different TC concentrations yielded the respective adsorption spectra, with maxima at $\lambda = 350$ nm for the determination of TC, OTC, and CTC.

2.2. Adsorbents

A previous article (Gómez-Pacheco et al., 2012) described in detail the techniques and methods applied to prepare and characterize the sludge-derived adsorbent materials used in this study (surface area, pore size distribution, elemental analysis, metal compound content, surface oxygenated groups, and pH_{pzc}). Tables SM-1, SM-2, SM-3, and SM-4, in Supplementary materials, show the results obtained from the characterization of the adsorbents prepared from treatment plant sludge: (i) non-activated sludge (CL), (ii) NaOH-activated sludge (C2), (iii) sludge activated in the presence of humic acid (CH), iv) sludge activated in the presence of clayey soil (CAR), v) sludge activated in the presence of phenolic resin 1 (CR1), (vi) sludge activated in the presence of phenolic resin 2 (CR2), and Sorbo (S) and Merck (M) commercial activated carbons, with a particle diameter ranging between 0.6 and 1 mm. The experimental methods followed to characterize the adsorbents were described in detail elsewhere (Sánchez-Polo and Rivera-Utrilla, 2003; Rivera-Utrilla and Sánchez-Polo, 2004; Bautista-Toledo et al., 2008; Gómez-Pacheco et al., 2012).

2.3. Adsorption isotherms

For this purpose, 100 mL aqueous TC, OTC or CTC solution at increasing concentrations (100–1000 mg/L) was placed in contact with 0.1 g adsorbent. The flasks were maintained in thermostatic bath at 298 K and, after equilibrium time had elapsed, 8 days, as determined from adsorption kinetics (Ocampo-Pérez et al., 2012), the TCs concentration was determined. Adsorption isotherms, representing the amount adsorbed as a function of the equilibrium concentration, were obtained at pH values between 7 and 8 for sludge-derived materials and between 4 and 5 for commercial activated carbons. These pH values were the natural solution pHs without adding any buffer solution.

2.4. Influence of solution chemical nature on tetracycline adsorption

The influence of the medium pH on TCs adsorption was studied by adding 0.1 g adsorbent to Erlenmeyer flasks of 100 mL TC solution at 700 mg/L concentration using different pH values (2–11). Working pH was obtained by adding the appropriate volume of HCl (0.1 N) and/or NaOH (0.1 N) to the corresponding TC solution. After reaching equilibrium, the TC concentration in solution and amount adsorbed were determined.

The effect of electrolyte presence in the TCs adsorption process was analyzed by placing 100 mL of a solution of the corresponding TC (700 mg/L) and NaCl (concentrations between 0.0001 and 1 M) in contact with 0.1 g adsorbent. The amount of TC adsorbed in each system was determined by obtaining the equilibrium concentration.

In order to study the influence of water with different chemical composition, samples of natural water (surface water and groundwater) and wastewater from the Drinking Water Treatment Plant (DWTP) and Wastewater Treatment Plant (WWTP) of Motril (Granada, Spain), respectively, were supplied by *Aguas y Servicios de la Costa Tropical de Granada*. Table 2 shows the characteristics of these types water. The concentration of total organic carbon (TOC) in water was determined using a Shimadzu V-CSH equipment. The methodology used to determine water alkalinity and hardness is reported in detail in Normalized Methods for the Analysis of Drinking Waters and Wastewaters of APHA–AWWA–WPCF (1998).

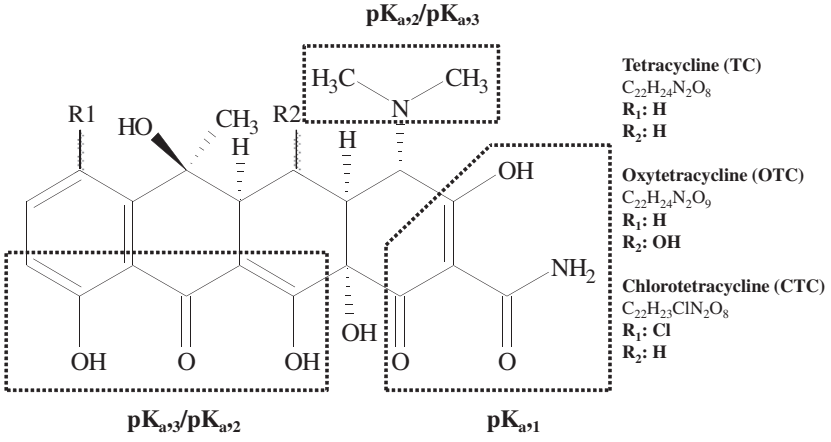

Fig. 1. Chemical structure of tetracyclines.

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