



Adsorptive removal of pharmaceuticals from water by commercial and waste-based carbons



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ABSTRACT

This work describes the single adsorption of seven pharmaceuticals (carbamazepine, oxazepam, sulfamethoxazole, piroxicam, cetirizine, venlafaxine and paroxetine) from water onto a commercially available activated carbon and a non-activated carbon produced by pyrolysis of primary paper mill sludge. Kinetics and equilibrium adsorption studies were performed using a batch experimental approach. For all pharmaceuticals, both carbons presented fast kinetics (equilibrium times varying from less than 5 min to 120 min), mainly described by a pseudo-second order model. Equilibrium data were appropriately described by the Langmuir and Freundlich isotherm models, the last one giving slightly higher correlation coefficients. The fitted parameters obtained for both models were quite different for the seven pharmaceuticals under study. In order to evaluate the influence of water solubility, $\log K_{ow}$, pK_a , polar surface area and number of hydrogen bond acceptors of pharmaceuticals on the adsorption parameters, multiple linear regression analysis was performed. The variability is mainly due to $\log K_{ow}$ followed by water solubility, in the case of the waste-based carbon, and due to water solubility in the case of the commercial activated carbon.

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1. Introduction

The current knowledge about the contamination levels of water resources with anthropogenic organic pollutants alerts for the huge necessity of developing economically and environmentally sustainable remediation methods. Within organic contaminants, pharmaceutically active ingredients are a vast class of compounds with enormous impact in the environment, mainly due to their resistance and persistence in aquatic ecosystems (Calisto and Esteves, 2009; Kümmerer, 2009; Calisto et al., 2011b) and the biological effects they might exert on non-target organisms (Calisto and Esteves, 2009; Guler and Ford, 2010; Brodin et al., 2013).

During the last decade, there was a significant amount of research focusing on the removal of pharmaceuticals from wastewaters revealing that the most commonly available treatment options (such as flocculation, filtration, activated sludge, chlorination) are not effective in the elimination of these compounds (Ternes

et al., 2005; Rivera-Utrilla et al., 2013). In this context, removal of organic contaminants by adsorption is a very interesting solution due to its versatility and efficiency (Yu et al., 2008, 2009). Activated carbons (AC) are the most commonly used adsorbents which can be either in granular or powdered form (GAC or PAC, respectively) (Kyriakopoulos and Doulia, 2006). GAC and PAC are both applicable to wastewater treatment; however, PAC is usually more efficient with faster adsorption kinetics (due to smaller particle size) and GAC has the main advantage of regeneration/reuse after saturation (Altmann et al., 2014). Although there is a high availability of ACs in the market, a considerable amount of research has been published concerning the production of carbons using alternative starting materials (such as industrial and agriculture residues) with a view of lowering the production costs and of promoting waste's valorization (Kyriakopoulos and Doulia, 2006; Antunes et al., 2012; Yao et al., 2012; Jung et al., 2013; Calisto et al., 2014; Mestre et al., 2014). Some examples of residues used to produce carbons include sewage sludge, peanut shells, rice husk and pine wood (Ahmad et al., 2014; Mohan et al., 2014). Very few examples describe the production of carbons using paper mill sludge (Li et al., 2011). In fact, the use of paper mill sludge in this context has the

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extra advantage of contributing to implement new strategies for the management of such residues which is a critical issue for paper mills.

The adsorption process is a rather complex spontaneous phenomenon which is mostly governed by electrostatic interactions (relevant when the adsorbate is an electrolyte and can be of attractive or repulsive nature) and by non-electrostatic interactions (such as van der Waals or hydrogen bonding, always of attractive nature) (Moreno-Castilla, 2004). The influence of these interactions on the adsorption process is directly dictated by the adsorbent's and adsorbate's characteristics. Concerning the adsorbent, the two main features to consider are the porosity and pore morphology (Kyriakopoulos and Doulia, 2007) (it is desirable to have a well developed microporosity, enhancing its surface area, but also to have some meso and macroporosity which function as channels to allow easy access to the micropores) and the surface chemistry (which defines the nature of the attractive/repulsive interactions between the functional groups of the adsorbate and the adsorbent and its largely influenced by the heteroatom content of the carbon). Relatively to the adsorbate, the most relevant characteristics are the octanol–water partition coefficient ($\log K_{ow}$), water solubility (closely related to the adsorbate's hydrophobicity), pK_a (which defines the charged/neutral speciation of the adsorbate) and molecular size (Moreno-Castilla, 2004; Tascón, 2008; Baccar et al., 2012). Inferring about the effectiveness of adsorption for a given adsorbent/adsorbate system is not always straightforward due to the high complexity involved in balancing all of these variables.

This manuscript describes the single adsorption of seven pharmaceuticals with distinct physico-chemical characteristics onto a commercially available powdered activated carbon and onto a non-activated carbon produced from primary paper mill sludge. With the aim of relating the adsorption coefficients with the pharmaceuticals' properties, the following parameters were considered: water solubility, $\log K_{ow}$ and polar surface area (all related to the hydrophobicity of the compounds), number of H-bond acceptors (describing the ability of the adsorbate to establish H-bonding with water or with functional groups of the carbon surface) and pK_a (related to the neutral/charged speciation). The selected pharmaceuticals for this study were: carbamazepine (CBZ, anti-epileptic), oxazepam (OXZ, anxiolytic), sulfamethoxazole (SMX, antibiotic), piroxicam (PIR, non-steroidal anti-inflammatory), cetirizine (CTRZ, antihistaminic), venlafaxine (VEN, antidepressant, serotonin-norepinephrine reuptake inhibitor) and paroxetine (PAR, antidepressant, selective serotonin re-uptake inhibitor). All these pharmaceuticals have high consumption patterns and have already been found in the environment (Calisto and Esteves, 2009; Loos et al., 2009; Bahlmann et al., 2012). However, information on their removal from water is quite scarce. Although there are some published works on the adsorption of CBZ (Jung et al., 2013; Piel et al., 2013; Altmann et al., 2014) and SMX (Caliskan and Gokturk, 2010; Yao et al., 2012; Jung et al., 2013; Piel et al., 2013; Altmann et al., 2014) from water, very few studies approach the adsorption of VEN (Rúa-Gómez et al., 2012) and OXZ (Kosjek et al., 2012) and no data were found concerning PIR, CTRZ and PAR.

2. Experimental section

2.1. Adsorbents

Two powdered carbons were used as adsorbents for the pharmaceuticals under study: a commercially available activated carbon (PBFG4, provided by ChemViron Carbon) and a non-activated carbon produced by pyrolysis (under N_2 atmosphere, at 800 °C for 150 min) of primary paper mill sludge (PS800-150). Detailed information concerning the production and characterization of

PS800-150 can be found in previous work (Calisto et al., 2014). A summary of the main chemical and textural properties of these carbons is displayed in Tables S1 and S2 of the Supporting Information (SI).

2.2. Pharmaceuticals

The adsorption experiments were carried out with seven pharmaceuticals: CBZ (Sigma Aldrich, 99%); OXZ (TCI, >98%); SMX (TCI, >98%); PIR (Sigma Aldrich, 99%); CTRZ (TCI, >98%); VEN (TCI, >98%); PAR (TCI, >98%). Physico-chemical parameters relevant to this work are summarized in Table 1.

2.3. Micellar electrokinetic chromatography (MEKC) analyses

The quantification of the pharmaceuticals in the aqueous phase was carried out by MEKC analyses using a Beckman P/ACE MDQ (Fullerton, CA, USA) instrument, equipped with a UV–Vis detection system. A dynamically coated silica capillary was used as described in previous work (Calisto et al., 2011a). Briefly, a bare silica capillary of 40 cm (30 cm to the detection window) was coated with a cationic polymer (hexadimethrine bromide) followed by sodium dodecyl sulfate (SDS). The electrophoretic separation was performed at 25 °C, in direct polarity mode at 25 kV, for time intervals ranging from 2.5 to 4.5 min (depending on the pharmaceutical under analysis). Ethylvanilin was used as internal standard, spiked in all samples and standard solutions at a final concentration of 3.34 mg L⁻¹. Detection was monitored at 200 nm for SMX, PIR, CTRZ, VEN and PAR, at 214 nm for CBZ and at 230 nm for OXZ, according to their absorption spectra. The separation buffer consisted of 15 mM of sodium tetraborate and 30 mM of SDS for CBZ, OXZ, SMX and PIR and of 15 mM of sodium tetraborate and 20 mM of SDS for CTRZ, VEN and PAR. Separation buffer was renewed every six runs. Capillary washing between runs consisted on 1 min of ultra-pure water and 1.5 min of separation buffer at 20 psi. All the analyses were performed in triplicate. Calibration was carried out for each pharmaceutical using standard solutions of 0.25, 0.50, 1.00, 2.00, 3.00, 4.00 and 5.00 mg L⁻¹.

2.4. Adsorption batch experiments

Batch experiments were carried out in order to study the adsorption of the seven pharmaceuticals onto PBFG4 e PS800-150. For this purpose, single solutions of each pharmaceutical with an initial concentration of 5 mg L⁻¹ were prepared in ultra-pure water, obtained from a Milli-Q Millipore system (Milli-Q plus 185). These solutions were placed in 15 or 50 mL polypropylene tubes together with the corresponding adsorbent and shaken in an overhead shaker (Heidolph, Reax 2) at 80 rpm under controlled temperature (25.0 ± 0.1 °C). All the adsorption experiments were done in triplicate. In parallel with each experiment, a control (pharmaceutical solution without the adsorbent) and a blank (adsorbent in water without the presence of the pharmaceuticals) were run in order to test adsorption onto polypropylene tubes or thermo-degradation and matrix effects during MEKC analysis, respectively. After shaking, the polypropylene tubes content was filtered through 0.22 µm PVDF filters (Millipore) and immediately analyzed by MEKC as described in Section 2.3.

2.4.1. Adsorption kinetics

Prior to the adsorption equilibrium tests, the time needed for attaining the equilibrium between each pharmaceutical and the two carbons was determined. For that purpose, a 5 mg L⁻¹ solution of each pharmaceutical was shaken together with PS800-150 or PBFG4 during different time intervals (5, 15, 30, 60, 240 and

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