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Research article

Insights of competitive adsorption on activated carbon of binary caffeine and diclofenac solutions

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ABSTRACT

A commercial activated carbon (AC), obtained from peanut shells, was characterized and tested as adsorbent for the removal of the pharmaceutical products caffeine (CF) and diclofenac (DIC), which were used as model emerging contaminants. Nitrogen adsorption, XRD, SEM, FT-IR spectroscopy, and chemical analyses were typical of ACs, and Boehm titrations, calculations of surface sites distributions and zeta potential measurements indicated that reactions of deprotonable oxygenated groups at the AC surface lead to an isoelectric point of 3.2. A theoretical equation derived from the Langmuir isotherm is proposed to explain the adsorption percentage or adsorbed fraction (f_{ads}) as a function of the adsorbent dose (D, adsorbent "concentration"). Good fittings of the f_{ads} vs. D curves and the normal adsorption isotherms were obtained with the same Langmuir parameters. An important and practical application of this new equation is to permit a straightforward calculation of the solid dose needed to achieve a required adsorption percentage. With the aim of describing the adsorption processes of CF and DIC and their competition for surface sites under an ample range of concentrations, the adsorption of the emerging contaminants was investigated in single adsorbate experiments and with binary mixtures, and the competitive Langmuir model was applied. CF adsorption was high and independent of pH, whereas DIC adsorption was high between pH 4 and 6 and showed a continuous decrease from pH 6 to 10.5. The use of the competitive Langmuir isotherm for binary mixtures indicated that there was no *pure competition* between CF and DIC for surface sites. Instead, there was *influenced competition*, meaning that the presence of one substance at the surface modified the adsorption parameters of the other, either through lateral interaction forces or by changing the molecular orientation at the surface. In both cases, one substance favored the adsorption of the other, compared to pure competition.

1. Introduction

Studies regarding water quality are usually focused on nutrients, microbial pollutants, heavy metals, and priority pollutants. However, in the last years numerous emerging contaminants (ECs) that significantly affect water quality have been reported (Rodriguez-Narvaez et al., 2017; Benstoem et al., 2018; Delgado et al., 2019) and are growing concerns into the scientific community. This group of contaminants includes compounds such as pharmaceutical and personal care products, pesticides, flame retardants and hormones (Richardson and Ternes, 2018). Many substances of the ECs group are soluble in water and can be transported by water flows, becoming present in wastewater effluent, surface and groundwater, with high potential as a threat to organisms (Nikolaou, 2013). This is the case of pharmaceutical drugs, which are the main subject of this article. For example, in the case of painkillers and anti-inflammatory drugs, such as diclofenac, there is an important concern regarding their ecotoxicity and removal capacity by conventional wastewater treatment plants. This drug has been frequently detected in wastewater and surface water at concentrations up to 2 μg L^{-1} (Álvarez et al., 2015), and its chronic effects need to be analyzed. Another example is caffeine, a psychostimulant and analeptic that is highly consumed by the human population and expelled mainly in urine. It is often found in surface waters, and even at low concentrations caffeine can negatively affect the metabolism of fish, amphibians, and reptiles (Fraker and Smith, 2004; Brausch et al., 2012; Santos-Silva et al., 2018; Oliveira et al., 2019).

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