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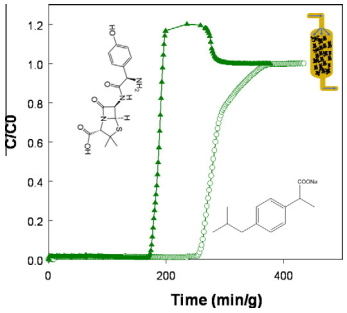
Competitive adsorption of ibuprofen and amoxicillin mixtures from aqueous solution on activated carbons

Hayet Mansouri [a,b], Rocio J. Carmona [b], Alicia Gomis-Berenguer [b], Souad Souissi-Najar [a], Abdelmottaleb Ouederni [a], Conchi O. Ania [b,*]

[a] Laboratory of Engineering Process and Industrial System (LR GPSI), National School of Engineers of Gabes (ENIG), University of Gabes (UG), Omar Ibn Elkhattab Street, 6029 Gabes, Tunisia
[b] Group of Adsorption and Environmental Remediation on Porous Solids (ADPOR), Instituto Nacional del Carbón, INCAR-CSIC, Apdo. 73, 33080 Oviedo, Spain

GRAPHICAL ABSTRACT



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ABSTRACT

This work investigates the competitive adsorption under dynamic and equilibrium conditions of ibuprofen (IBU) and amoxicillin (AMX), two widely consumed pharmaceuticals, on nanoporous carbons of different characteristics. Batch adsorption experiments of pure components in water and their binary mixtures were carried out to measure both adsorption equilibrium and kinetics, and dynamic tests were performed to validate the simultaneous removal of the mixtures in breakthrough experiments. The equilibrium adsorption capacities evaluated from pure component solutions were higher than those measured in dynamic conditions, and were found to depend on the porous features of the adsorbent and the nature of the specific/dispersive interactions that are controlled by the solution pH, density of surface change on the carbon and ionization of the pollutant. A marked roll-up effect was observed for AMX retention on the hydrophobic carbons, not seen for the functionalized adsorbent likely due to the lower affinity of amoxicillin towards the carbon adsorbent. Dynamic adsorption of binary mixtures from wastewater of high salinity and alkalinity showed a slight increase in IBU uptake and a reduced adsorption of AMX, demonstrating the feasibility of the simultaneous removal of both compounds from complex water matrices.

1. Introduction

For the last few decades, concern and awareness of potential problems related to water pollution due to the occurrence of emerging contaminants are of growing interest among society

* Corresponding author.
E-mail address: conchi.ania@incar.csic.es (C.O. Ania).

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[1,2]. These compounds are chemicals that originate from industrial, agricultural and human activities, very often as consumer products and by-products used every day. Many of these compounds are hardly biodegradable, for which much is yet unknown on their fate and potential impact on human health [3,4] and environment [5,6], as well as on current water treatment technologies [2,7]. Besides, most of them are not yet included in routine monitoring programs worldwide, although there is a widespread consensus that it is urgent to undertake actions as different levels [8].

Pharmaceuticals represent an overgrowing fraction of trace emerging contaminants in urban aquatic environments due to their worldwide consumption. Although concentrations are usually much lower that the therapeutic doses, they are continually introduced in the environment; so the levels remain quite constant, raising considerable toxicological concerns to human health and aquatic ecosystems, particularly when present as components of complex mixtures [7,9].

Most of them are only poorly removed and/or degraded by conventional biological treatment, for which their removal by wastewater treatment plants is a major subject of concern [10–14]. Hence the actual challenge in wastewater treatment is to upgrade existing treatment plants with more efficient end-of-pipe technologies to face the emerging micropollutants. In previous studies we have reported the limitations of activated sludge treatment technologies in removing several pharmaceuticals and their metabolites from sewage waters, pointing out the need for improving current treatment technologies [15]. The studies also highlighted the effectiveness of adsorption technology based on activated carbons as post-treatment process to face water pollution due to organic micropollutants [8,14]. On the other hand, most studies on the removal of pharmaceuticals on activated carbons report adsorption capacities from single component solutions [16–18], while studies on the removal of mixtures are scarce [19–22].

Thus the main objectives of this work are to study the competitive adsorption of pharmaceutical compounds on nanoporous carbon adsorbents of varied characteristics, and to compare the removal efficiencies from equilibrium and dynamic adsorption tests on single component solutions and mixtures. Ibuprofen (IBU) and amoxicillin (AMX) were selected as representative of highly consumed pharmaceuticals (widely used human and veterinary applications) currently detected on all sorts of water.

Table 1
Physicochemical properties of ibuprofen and amoxicillin.

	Ibuprofen	Amoxicillin
Molecular formulae	$C_{13}H_{17}O_2Na$	$C_{16}H_{19}N_3O_5S{\cdot}3H_2O$
CAS number	31,121-93-4	26,787-78-0
Molecular weight	228.26 g mol^{-1}	387.4 g mol^{-1}
Log K_{ow}	3.5–3.97[a,b]	0.87[b]
pK_a	4.91[b]	2.4, 7.4, 9.6[c]
Water solubility (25 °C)	0.1 g L^{-1}[b]	1–3 g^{-1}[d]
Molecular size (nm)	1.03 (l) × 0.52 (w) × 0.43 (t)[b]	1.24 × 0.56 × 0.46

[a] NIST DATABASE, www.nist.gov.
[b] Ref. [8].
[c] Ref. [31].
[d] http://www.drugbank.ca/drugs/db01060 (drug Bank).

2. Experimental

2.1. Materials

Ibuprofen and amoxicillin sodium salts were purchased from Sigma–Aldrich (reagent purity) and used without further purification. Unless otherwise stated, all solutions were prepared with ultra-pure water obtained from Milli-Q water purification Systems without pH adjustment. For clarity, the structural formula and selected physicochemical properties of the studied pharmaceuticals are shown in Table 1 and Fig. 1. Two activated carbons prepared from activation of a lignocellulosic precursor (olive stones) were chosen for this study. Sample OP was synthesized by physical activation of the carbonized precursor using CO_2 (10 mL/min, 800 °C, 50% burn-off degree) and sample OC was obtained by chemical activation of the raw precursor using phosphoric acid (300 mL/min N_2, 450 °C, 150 min, ratio precursor:H_3PO_4 of 1:3). Based on the different conditions of the physical and chemical activation procedures, the prepared materials are expected to display very different porous features. Activated carbon OPox was obtained by wet oxidation of OP in a saturated solution of ammonium persulfate in 4 N sulfuric acid (1 g carbon:10 cm^3 oxidizing solution, stirring overnight). The sample was extensively washed in a Soxhlet apparatus to remove any water-soluble species and the excess of oxidizing agent. Before usage, all the samples were washed in distilled hot water, dried at 60 °C overnight and stored in a desiccator. A particle size fraction between 0.212 and 0.710 mm was selected for all the adsorbents.

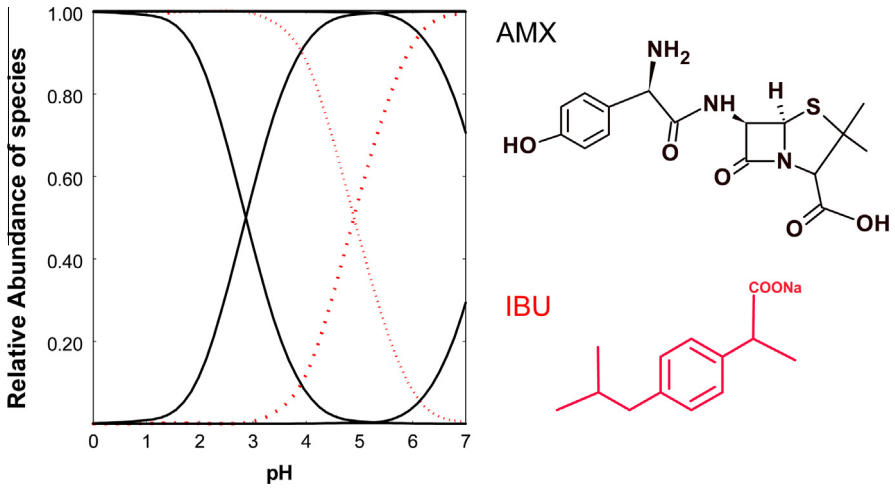

Fig. 1. Molecular structure and speciation diagram of IBU (red dashed line) and AMX (black solid line) in aqueous solution. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)