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

Hayet Mansouri[1,2], Rocio J. Carmona[2], Alicia Gomis-Berenguer[2], Souad Souissi-Najar[1], Abdelmottaleb Ouederni[1] and Conchi O. Ania[2]*

[1] 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

[2] Group of Adsorption and Environmental Remediation on Porous Solids (ADPOR), Instituto Nacional del Carbón, INCAR-CSIC, Apdo. 73, 33080 Oviedo, Spain

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.

Keywords: competitive adsorption; binary mixtures; pharmaceuticals; dynamic breakthrough experiments; real wastewater

*Corresponding author. Tel.: +34 985118846. E-mail address: conchi.ania@incar.csic.es (CO Ania)

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 [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.

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 Figure 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, 800ºC, 50% burn-off degree) and sample OC was obtained by chemical activation of the raw precursor using phosphoric acid (300 mL/min N_2, 450ºC, 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 displaye very different porous features. Activated carbon OPox was obtained by wet oxidation of OP in a saturated solution of ammonium persulfate in 4N sulfuric acid (1 gram 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 ºC overnight and stored in a desiccator. A particle size fraction between 0.212-0.710 mm was selected for all the adsorbents.

2.2 Batch equilibrium adsorption from single component solutions and binary mixtures

To study the adsorption kinetics, 100 ml of unbuffered solution of each compound (initial concentration 100 mg l^{-1}) were mixed with ca. 30 mg of activated carbon in dark glass flasks and continuously stirred (100 rpm) at 25 ºC in a thermostatic regulated water bath. The pH of IBU and AMX solutions without any adjustment was ca. 4.3. Aliquots were measured at different time intervals until equilibrium was attained. Solutions were filtered and the concentration was measured on a Shimadzu 2501 UV-Vis spectrophotometer at the corresponding wavelength of each compound (ca. 230 nm for IBU and 272 nm for AMX). The composition of the solutions was also analyzed by reverse-phase HPLC in an apparatus equipped with a photodiode array detector. The separation was conducted using a Spherisorb C-18 column with 5 μm particle size (4.0 mm x 125 mm) using water (0.1% phosphoric acid):MeOH (ratio equal to 85:15) as mobile phase in isocratic mode (flow rate of 0.7 mL min^{-1}, injection volume of 20μl). The concentration of each compound was calculated based on the relative peak areas, using standards of known concentrations for quantification. Equilibrium adsorption isotherms were also carried out from unbuffered solutions of initial concentration ranging from 5-100 mg l^{-1}. All adsorption assays were made in triplicate. The amount adsorbed was determined according to $Q_t = (C_0-C_t)V/m$, where Q_t is the amount (mg g^{-1}) adsorbed at time t, C_0 is the initial concentration (mg l^{-1}), C_t is the concentration at time t (mg l^{-1}), V is the volume (l) of the adsorbate solution and m is the mass (g) of dried carbon. Experiments were carried out on individual component solutions and mixtures of IBU and AMX of various molar concentrations.

2.3 Dynamic breakthrough curves

For the dynamic adsorption experiments (fixed-bed mode operation) the adsorbents were packed into a stainless steel column of 1 cm inner diameter and 5 cm length (ca. bed volume, BV=4 ml). Before the experiments, the columns were rinsed with deionized water for at least 60 min (or until the absorbance of the effluent from the column was zero). The volume was completed with glass balls in order to avoid dead volumes and preferential channels. The aqueous solutions containing the known concentrations of the pharmaceuticals were continuously fed to the column at a flow rate of 4 mL/min and the inlet concentration of the pollutants was set to 100 ppm. The effluent from the column was collected and monitored online by UV-Vis spectrophotometry and aliquots were also analyzed by HPLC as described. After saturation, the columns were rinsed in water. Experiments were carried out on individual component solutions (initial concentration of 100 ppm), and 1:1 binary mixtures of IBU and AMX. To evaluate the effect of the water matrix, a treated wastewater from a wastewater treatment plant was used, and the adequate amounts of IBU and AMX were spiked into it.

2.4 Characterization of the adsorbents

The porosity of the samples was characterized by measuring the N_2 and CO_2 adsorption isotherms at -196 and 0 ºC, respectively (ASAP 2010 and Tristar 3020, Micromeritics). Before the experiments, the samples were outgassed under vacuum (ca. 10^{-3} torr) at 120 °C overnight. The isotherms were used to calculate the specific surface area, S_{BET}, total pore volume, V_{total}, while the micropore volumes were analyzed using the Dubinin–Radushkevich formulism to the N_2 and CO_2 adsorption data ($W_{0,N2}$, $W_{0,CO2}$) [23]. The distribution of narrow micropore sizes was obtained from the Dubinin-Stoeckli theory [24] applied to the CO_2 adsorption isotherms. Elemental analysis was carried out in LECO CHNS-932 and LECO VTF-900 automatic analyzers. The surface chemistry was characterized by the determination of the pH at the point of zero charge (pH_{PZC}) using the mass-titration procedure, according to the experimental procedure described elsewhere [25]. Briefly about 0.25 g of carbon powders were dispersed in a suitable volume of distilled water and stirred at room temperature -solid/water ratios (w/v) of 1, 2, 4, 6, 8, 10, 12, 14 and 16 were measured-. Once equilibrium had been reached, the pH value was measured using a glass electrode. Fresh distilled water was then added in order to obtain the next solid/water fraction. The plateau in the plot of equilibrium pH versus solid/mass fraction corresponded to the pH_{PZC} value of the activated carbon. The samples were further characterized by thermogravimetric analysis in a Setaram Labsys instrument, using a nitrogen flow rate of 50 cm^3 min^{-1}, at a heating rate of 15 °C min^{-1}, up to a final temperature of 900 °C. For each experiment, about 25 mg of a carbon sample was used.

3. RESULTS AND DISCUSSION

It is known that certain penicillin-derived compounds (AMX being one of them) are unstable in aqueous solutions and might decompose under different pH conditions [18, 26]. Given the differences in the surface acidity/basicity of the nanoporous carbons used in this study (Table 2), we first evaluated the stability of IBU and AMX solutions at different pH between 2-10 by monitoring the evolution of the UV-Vis spectrum and concentration over time. Both compounds were stable at all studied pH for over a week, with no evident modifications in the concentrations or the species detected in solution upon time or after contact with the activated carbons in blank experiments (also confirmed by the HPLC analysis of the solution). Hence any likely changes in the concentration in solution arising from hydrolysis/breakdown reactions have been discarded.

3.1 Batch adsorption from single component solutions and binary mixtures

Fig. 2 shows the rate of IBU and AMX adsorption from single component solutions on the studied activated carbons. Similar kinetic profiles were obtained for both IBU and AMX regardless the nature of the carbon adsorbent, although the uptake at equilibrium conditions (long times) was very different for the studied carbons. The experimental data were fitted by a pseudo-second order kinetic model [27], with correlation coefficients (r^2) higher than 0.99 along with high determination coefficients (R^2) for all the carbons (Table 3). Data was also fitted to the pseudo-first order kinetic model, but the correlations (not shown) were very unfavorable. Quite fast adsorption kinetics were obtained for all three studied carbons with similar rate constants (Table 3) and equilibrium conditions attained after 24 hours and most of the uptake within the first 8 hours for all adsorbate/carbon systems. The rapid adsorption is attributed to the presence of a large network of a transport pores (mesopores) in the studied activated carbons, being the effect somewhat more visible for carbon OP due to its larger mesopore volume (Table 2). The fast kinetics also indicates that accessibility restrictions do not apply, which is in good agreement with the molecular dimensions of ibuprofen (ca. 1.03 × 0.52 × 0.43 nm) [8] and amoxicillin (ca. 1.24 x 0.56 x 0.46 nm, computed from ChemSketch software after 3D optimization for the lowest energy configuration) and the mean micropore size of the carbons evaluated from gas adsorption data (Fig. 3, inset) indicating that the microporosity is accessible to the adsorbed molecules. The higher initial adsorption rate of both compounds in carbon OP is attributed to the presence of narrower micropores, as seen in the analysis of the micropore size distribution evaluated from the CO_2 adsorption isotherms (Fig. 3, inset).

The values of the initial adsorption rate (h_0) of IBU and AMX varied according to the micropore volume of the carbons (Table 2), with lower values for the oxidized carbon (for both compounds) suggesting that a different adsorption mechanism applies for this material. Similar results showing the dependence of the surface chemistry of carbon adsorbents on the adsorption kinetics have been reported for other emerging contaminants such as caffeine and paracetamol [18, 30-32].

It is interestingly to note that despite the similarities in the textural features of all three studied carbons (Fig. 3 and Table 2), important differences are obtained on the uptake of both compounds. Indeed, the chosen activated carbons present quite similar porous features with surface areas between 900-1100 m^2/g and type I N_2 adsorption isotherms according to BDDT classification [23] indicating that these are essentially microporous carbons. Sample OP, prepared by physical activation also presented a well-developed mesoporosity. Differences in porosity became more evident by the analysis of the narrow microporosity inferred from the CO_2 adsorption isotherms. The micropore volumes detected by CO_2 were smaller than those of N_2 ($W_{0,N2} < W_{0,CO2}$) for all the carbons, indicating wide distribution of micropore sizes in all the samples. More interestingly, sample OP displayed a narrower micropore size distribution than the carbon obtained by chemical activation (Fig. 3, inset). This is most interesting, since OP carbon displays the highest micropore volume with a well developed mesoporous structure (Table 2); such combination would explain the large differences in the uptake of IBU and AMX among the carbons.

It should be noted that the adsorption capacities of IBU and AMX were drastically reduced upon surface functionalization of carbon OP, despite no significant changes were observed in the adsorption rate. To understand this we must take into account the modifications induced in the carbon upon the oxidation in terms of chemistry and porosity. First of all, oxidation of sample OP brought about a slight decrease of the porous features seen by N_2 probe (Table 2) accompanied by a slight increase in the population of narrow micropores determined by CO_2 adsorption at 0 ºC (Fig. 3). This is typically observed upon functionalization of carbons prepared from lignocellulosic precursors due to the destruction of some thin pore walls and/or blocking of the pore entrances by the O-groups [28]. However the effect is quite small for herein studied carbon, thus cannot account for the two-fold decrease in IBU and AMX retention (i.e., 57 and 46 % fall for AMX and IBU, respectively); the observed trend that can only be attributed to the modifications of the surface charge density of the carbon and the ionization state of the adsorbates (both weak electrolytes) upon oxidation.

In this regard, the elemental analysis and corresponding values of the pH_{PZC} of the studied carbons are shown in Table 2. As seen, pristine OP and OC carbons present rather large oxygen contents characteristic of materials prepared from lignocellulosic precursors [29,30] but quite different surface acidity. Sample OP has a basic character as expected considering the synthetic route, whereas the carbon prepared by activation using phosphoric acid shows a slightly acidic character. Based on the thermal profile of the carbon (Fig. S1 in the Electronic Supporting Information File, ESI) showing the absence of O-groups of acidic nature typically desorbing below 500ºC) and low content of P (detected by SEM-EDX) suggesting a negligible contribution of acidic P-groups on the carbon surface, we attribute the acidic pH of carbon OC to the residual acid used during the activation step that would remain inside the pore network of the carbon (even after extensive washing).

We have observed similar findings in activated carbons subjected to acid digestion at mild temperatures [33]. Additional evidences corroborating this observation were obtained by some other

complementary techniques (Fig. S2 in ESI). On the other hand, the oxidation gave rise to significant increase in the oxygen content accompanied by a fall in the surface pH, due to the incorporation of O-functionalities mainly of acidic character.

According to the dissociation constants of IBU and AMX (Table 2, Fig. 1) and the solution pH during adsorption (ca. 4 pH units), AMX exists in its neutral/zwitterionic form due to the dissociation/protonation of the carboxylic (ca. over 90 mol%) and amine moieties (ca. 99 mol%), respectively [31]. On the other hand, the surface of carbon OPox is negatively charged (pH_{PZC} < solution pH), all of this leading the occurrence of repulsive interactions that drastically reduce the amount adsorbed. This effect is less visible for IBU as it is a weaker electrolyte than AMX, thus the protonated (neutral) species are dominant in solution (anionic form accounts for about 10 mol%). Competitive adsorption of water molecules should also be considered as oxidation renders the carbon more hydrophilic. Similar trends have been reported for charged aromatic compounds, including pharmaceuticals [32,34,35]. Furthermore, the oxygen groups located on the edges of the graphitic planes of the carbon adsorbent act as electron-withdrawing groups of the p electron density of the aromatic rings, weakening the dispersive interactions between the p-electrons of the aromatic ring of IBU and AMX and those of the graphene planes of the carbon materials [32]. The negative (repulsive) interactions between the surface groups of OPox carbon and the moieties of IBU and AMX have a clear effect on the adsorption capacity of the carbons but do not seem to affect the adsorption rate.

The adsorption isotherms of IBU and AMX on the studied nanoporous carbons are depicted in Fig. 4. All of them belong to type L of Giles classification [36], showing a steep initial rise and a concave curvature at low equilibrium concentrations followed by a well-defined plateau (saturation limit). This is characteristic of a high affinity of the adsorbates for the solid phase (with no strong competition of the solvent and almost negligible interactions between the adsorbed molecules), hence adsorption proceeds by the formation of a monolayer in the range of concentrations used [36]. The experimental isotherms were fitted to classical Freundlich and Langmuir models; overall, best fittings (in terms of smaller non-linear chi-square test analysis χ^2, values) were obtained to the Langmuir equation, indicating its adequateness (better physical significance) over the Freundlich model to evaluate the maximum adsorption capacity.

The corresponding values of the maximum adsorption capacites are gathered in Table 4 and follow the sequence: OP>>OC>OPox, showing an increasing trend with the hydrophobic character of the carbons; additionally, the slope of the isotherm at low concentrations is steeper for carbon OP. Comparatively for carbon OC and OP with quite similar surface chemistry apparent surface areas, the uptake of IBU was almost twice higher in carbon OP than in OC. The same trend applies for AMX, although the effect is less pronounced. This behavior must be explained in terms of the different pore volumes. As seen in Fig. 3, the carbon prepared by physical activation does not only present a larger volume of micropores, but also displays a sharp narrow distribution centered at about 0.9 nm; at

converse the mean micropore size for carbon OC is ca. 1.2 nm. These pores commensurate the molecular dimensions of ibuprofen (Table 1), thus lead to higher uptake and stronger affinity with carbon OP (also corroborated by the higher value of the Langmuir constant, b compiled in Table 4). For the oxidized carbon sample, the adsorption capacity is lower despite the micropores distribution is sharper and appears shifted towards lower pore sizes; the reduced uptake in this case is explained by the contribution of electrostatic repulsive interactions, as mentioned above.

Additionally, the adsorption capacities obtained for all three studied carbons are higher or similar to those reported in the literature for carbon adsorbents [8,28,37-40]; moreover, IBU uptake is larger than that of AMX in all three studied carbons; the higher affinity of IBU towards the carbon phase is in agreement with its higher octanol/water partition coefficient and lower solubility in water (Table 1).

In binary mixtures, the uptake of IBU and AMX decreased for all the carbons compared to data from single component solutions due to the competitive adsorption of both components in the mixture. The fall in the amount adsorbed is larger for AMX than for IBU, indicating that main competitive effects are associated to the affinity of the individual compounds for the carbon adsorbent. This is more clearly seen in Fig. 5 showing the dependence of the competitive adsorption with the molar ratio of both components in the mixture for the different carbons. The perturbing effect of the second component in the binary mixtures is more significant for AMX, even when the concentration of IBU is below 50% in the mixture.

3.2 Adsorption in fixed bed

Breakthrough curves for AMX and IBU adsorption from single component solutions are shown in Fig. 6. Data has been normalized vs. the mass of the column so as to allow direct comparison of breakthrough times (other parameters such as column length, flow rate, initial concentration or temperature were kept constant). For all three studied carbons the curves present an S-shape profile characteristic of the adsorption of compounds with high affinity for the solid phase; this is in agreement with the trend obtained from batch equilibrium adsorption mentioned above and with data available in the literature reported for other pharmaceuticals [22, 37].

As a general rule, adsorption capacities measured from dynamic adsorption tests were lower than those found in batch experiments, as the external diffusion is favored under the strong stirring conditions in batch adsorption, whereas for fixed- bed experiments, the mass transfer resistance inside the micropores is usually higher (thus intra-particle diffusion controls the adsorption rate). On the other hand, breakthrough times (corresponding to $C_t/C_0 = 0.02$) and saturation times ($C_t/C_0 = 0.95$) of single component solutions followed a similar trend for all the carbons, as AMX breaks through the bed faster than IBU in all cases, as expected based on the lower affinity and higher molecular of AMX (thus diffusion into narrow micropores is not favored).

Experimental breakthrough curves for binary mixtures of AMX and IBU are also shown in Fig. 6. The curves become flatter for both compounds, although the effect is more evident for AMX. This suggests

a higher mass transfer resistance in the column provided by the competitive adsorption between both pharmaceuticals for the adsorption sites.

Breakthrough times are also smaller than those of the single component solutions, which seems reasonable considering that the overall concentration in the binary mixture is higher (concentrations of individual compounds are the same as in the monocomponent solutions). This effect is more pronounced for OP as it showed the largest adsorption capacity. Interestingly the breakthrough curves on carbons OP and OC showed a different pattern with a clear overshot for AMX concentration (ca. the partial concentration at the column exit exceeds the feed concentration for some period of time) for the adsorption from the mixture. Such roll-up effect is characteristic of systems where the most weakly adsorbed compound (AMX) is displaced by the strongly bonded adsorbate (IBU) along the length of the column [41], and indicates that AMX rate of adsorption is faster in the binary mixture. The roll-up effect was however not detected for the oxidized carbon. Based on data from single component solution (both kinetic and equilibrium from batch adsorption), different adsorption sites for IBU and AMX are not expected for these carbons.

To understand this effect we must consider several possibilities. Based on the analysis of the UV-Vis spectra (and HPLC peaks) of the mixtures we have discarded any IBU-AMX interaction (i.e., interaction of carboxylic moiety of IBU with hydroxyl, amine groups of AMX). Thus, the displacement of AMX has to be attributed to the competitiveness of both pollutants for the same adsorption sites. At the initial stage, both pharmaceuticals tend to be adsorbed on the active sites of the carbon and thus the uptake is controlled by diffusion. In a second stage, counter diffusion should take place in the pores due to competition of the molecules; this counter diffusion is expected to be very slow in pores approaching molecular size, with part of the molecules locked in the inner pores. This would explain the smoother/flatter patterns of the breakthrough curves in the binary mixtures. On the other hand, the low affinity and fast adsorption rate of AMX on the oxidized carbon would hinder and/or accelerate the displacement so that the roll-up is not observed.

3.3 Effect of Water Matrix

As a final step we have investigated the influence of the water matrix on the adsorption capacity of the carbons towards a binary mixture of IBU and AMX on treated water from a wastewater treatment plant located in our region (concentrations of individual compounds are the same as in the monocomponent solutions; i.e., 1:1 concentration ratio). The wastewater has an alkaline pH with a moderate ionic content (see composition in Table S2). Compared to the adsorption capacities obtained from synthetic solutions in distilled water, the uptake of IBU remained rather constant (slightly enhanced) whereas that of AMX was reduced, being the effect more pronounced for the oxidized carbon (Fig. 7). An enhanced performance of adsorption on activated carbons on real wastewaters has been reported for some other compounds [42]; this has been attributed to the changes in the solubility

as the wastewater presents higher salinity and alkalinity and to the modification of the surface charge and ionization state of the compounds leading to electrostatic interactions.

The fall in AMX uptake is more pronounced for the oxidized carbon, due to its higher density of negative surface charges, as at the basic pH of the treated water AMX is also negatively charged (amine groups are neutral but carboxyl moieties are deprotonated), hence electrostatic repulsions become important. For the same reason, the salinity of the treated water after the adsorption of IBU and AMX on carbon OPox decreased significantly, indicating that along with the aromatics the ions are also adsorbed on the negatively charged surface of this functionalized carbon at the pH of the real wastewater (see Table S2 and Fig. 1). The effect is minimized in OP and OC carbons that present a higher density of positive surface charges (Fig. S2).

CONCLUSIONS

We have carried out competitive dynamic and equilibrium adsorption studies on the removal of two pharmaceutical compounds (ibuprofen and amoxicillin) to evaluate the feasibility of nanoporous carbons to simultaneously remove these pollutants from water bodies.

These compounds were largely adsorbed on the chosen nanoporous carbons, validating the selection of the adsorbents to evaluate the competitive adsorption by means of breakthrough experiments. Batch adsorption studies also demonstrated that both pollutants present similar adsorption sites and kinetics, despite the differences observed in the adsorption capacities. These followed the expected trend based on the porous features of the adsorbent and the appearance of specific and/or dispersive interactions that are controlled by the solution pH, density of surface change on the carbon and ionization of the pollutant. Comparatively, IBU is more strongly adsorbed than AMX (higher uptakes) regardless the nature of the adsorbent, although the effect is more pronounced for the hydrophobic carbons.

As a general rule, the equilibrium adsorption capacities evaluated from pure component solutions on batch adsorption were higher than those measured in dynamic conditions. For the competitive adsorption on binary mixtures, a marked roll-up effect was observed for amoxicillin retention on the hydrophobic carbons, not seen for the functionalized adsorbent likely due to the lower affinity of AMX towards the carbon adsorbent.

We have also explored the effect of the water matrix on the uptake of 1:1 binary mixtures by performing dynamic adsorption tests on treated wastewater of high salinity and alkalinity. Under these conditions, two different behaviors were observed; the uptake of IBU is enhanced by the adsorption of ionic species existing in the wastewater, whereas the opposed trend applied for AMX with a large fall in the amount adsorbed. Nevertheless, the effect is minimized on carbons of hydrophobic nature, demonstrating the feasibility of the simultaneous removal of both compounds from complex water matrices when carbon adsorbents of optimized physicochemical features are chosen.

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Supplementary material

Supplementary data associated with this article can be found in the online version.

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TABLES CAPTIONS

Table 1. Physicochemical properties of ibuprofen and amoxicillin.

Table 2. Main textural parameters of the investigated materials obtained from gas adsorption data (N_2 at -196 ºC and CO_2 at 0 ºC), elemental analysis (wt.%, DAF basis) and pH of the point of zero charge.

Table 3. Pseudo-second order ibuprofen adsorption parameters for the studied carbon samples: $q_{e,calc}$ is the uptake at equilibrium, k_2 is the pseudo-second order rate constant; R^2 is the coefficient of determination h_0 is the initial adsorption rate and $t_{½}$ is the half-life time.

Table 4. Fitting parameters of the equilibrium adsortpion isotherms to the Langmuir and Freundlich models and chi-square test analysis, χ^2.

FIGURES CAPTIONS

Fig. 1. Molecular structure and speciation diagram of IBU (red dashed line) and AMX (black solid line) in aqueous solution.

Fig. 2. Adsorption kinetic curves of amoxicillin (left) and ibuprofen (right) from single component solutions on the studied nanoporous carbons.

Fig. 3. (left) Nitrogen and (right) carbon dioxide adsorption/desorption isotherms at -196 and 0 ºC, respectively, of the selected nanoporous carbons (close symbols represent adsorption; empty symbols represent desorption). Inset: narrow micropore size distribution evaluated from the carbon dioxide adsorption data using the DS method.

Fig. 4. Equilibrium adsorption isotherms of amoxicillin (left) and ibuprofen (right) from single component solutions on the studied nanoporous carbons. Symbols represent experimental data and lines are the fitting to the Langmuir equation.

Fig. 5. Effect of the composition of the AMX:IBU binary mixtures (in terms of AMX molar fraction) on the uptake of each individual compound. Top (carbon OC), center (carbon OPox), down (carbon OP).

Fig. 6. Experimental breakthrough curves for the adsorption of AMX and IBU from a 1:1 binary mixture (mix). Data corresponding to the adsorption of each individual compound from single component solutions (single) is also included for comparison.

Fig. 7. Effect of water matrix on the adsorption capacities of IBU and AMX from a 1:1 binary mixture in terms of the amount adsorbed from the treated wastewater referred to the uptake from synthetic solutions using distilled water. The line is a guide for the eye accounting for the relative adsorption from synthetic solutions.

Table 1. Physicochemical properties of ibuprofen and amoxicillin.

	IBUPROFEN	AMOXICILLIN
Molecular formulae	$C_{13}H_{17}O_2Na$	$C_{16}H_{19}N_3O_5S.3H_2O$
CAS number	31121-93-4	26787-78-0
Molecular weight	228.26 g mol^{-1}	387.4 g mol^{-1}
Log Kow	3.5-3.97 [A,B]	0.87 [B]
pKa	4.91 [B]	2.4, 7.4, 9.6 [C]
Water solubility (25ºC)	0.1 g L^{-1} [B]	1-3 g L^{-1} [D]
Molecular size (nm)	1.03 (l) × 0.52 (w) × 0.43 (t) [B]	1.24 x 0.56 x 0.46

[A] NIST DATABASE, www. www.nist.gov

[B] reference [8]

[C] reference [31]

[D] http://www.drugbank.ca/drugs/db01060 (drug Bank)

Table 2. Main textural parameters of the investigated materials obtained from gas adsorption data (N_2 at -196 ºC and CO_2 at 0 ºC), elemental analysis (wt.%, DAF basis) and pH of the point of zero charge.

	S_{BET} m^2/g, STP	V_{TOTAL} cm^3g, STP	Vmicro cm^3g, STP	Vmeso cm^3g, STP	Wo micro (DR, N_2) cm^3g, STP	Wo micro (DR, CO_2) cm^3g, STP
OP	1055	0.733	0.368	0.335	0.54	0.25
OC	1106	0.560	0.385	0.122	0.39	0.20
OPox	903	0.634	0.203	0.164	0.32	0.26
	C	**H**	**N**	**O**	**S**	**pH_{PZC}**
OC	78.8	2.1	0.2	18.8	0.04	5.6
OP	86.2	0.5	0.5	12.7	0.01	9.5
OPox	75.4	0.7	0.2	23.6	0.04	3.4

Table 3. Pseudo-second order ibuprofen adsorption parameters for the studied carbon samples: $q_{e,calc}$ is the uptake at equilibrium, k_2 is the pseudo-second order rate constant; R^2 is the coefficient of determination h_0 is the initial adsorption rate and $t_{½}$ is the half-life time.

	$q_{e,calc}$ (mmol g^{-1})	k_2 x 10^6 (g mmol^{-1} h^{-1})	R^2	h_0 (mmol g^{-1} h^{-1})	$t_{½}$ (h)
IBUPROFEN					
OC	0.78	1.53	0.99	5.2	13
OP	1.30	1.27	0.89	10.1	15
OPox	0.61	1.75	0.89	3.5	18
	$q_{e,calc}$ (mmol g^{-1})	k_2 x 10^6 (g mmol^{-1} h^{-1})	R^2	h_0 (mmol g^{-1} h^{-1})	$t_{½}$ (h)
AMOXICILLIN					
OC	0.38	0.59	0.88	1.4	30
OP	0.28	1.65	0.95	1.3	19
OPox	0.16	1.14	0.74	0.5	36

$R^2 = 1 - \left[\frac{\sum (q_e - q_c)^2}{\sum (q_e - q_m)^2} \right]$ where q_e is the experimental uptake, qc is the equilibrium uptake calculated from the model and q_m is the average experimental uptake.

Table 4. Fitting parameters of the equilibrium adsortpion isotherms to the Langmuir and Freundlich models and chi-square test analysis, χ^2.

	Langmuir Equation			**Freundlich Equation**		
	q_m (mmol g^{-1})	b (L mmol^{-1})	χ^{2}*	$1/n$	K_F (mmol$^{1-1/n}$(L)$^{1/n}$ g^{-1})	χ^{2}*
			IBUPROFEN			
OC	0.78	74	0.1	0.29	0.31	7.8
OP	1.37	294	3	0.14	0.95	25
OPox	0.70	46	2.1	0.20	0.36	0.6
			AMOXICILLIN			
OC	0.41	147	1.1	0.23	0.22	1.1
OP	0.56	174	3.6	0.18	0.32	124
OPox	0.33	194	0.9	0.19	0.19	12

* $\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}}$ where q_e is the experimental equilibrium uptake and $q_{e,m}$ is the equilibrium uptake calculated from the model.

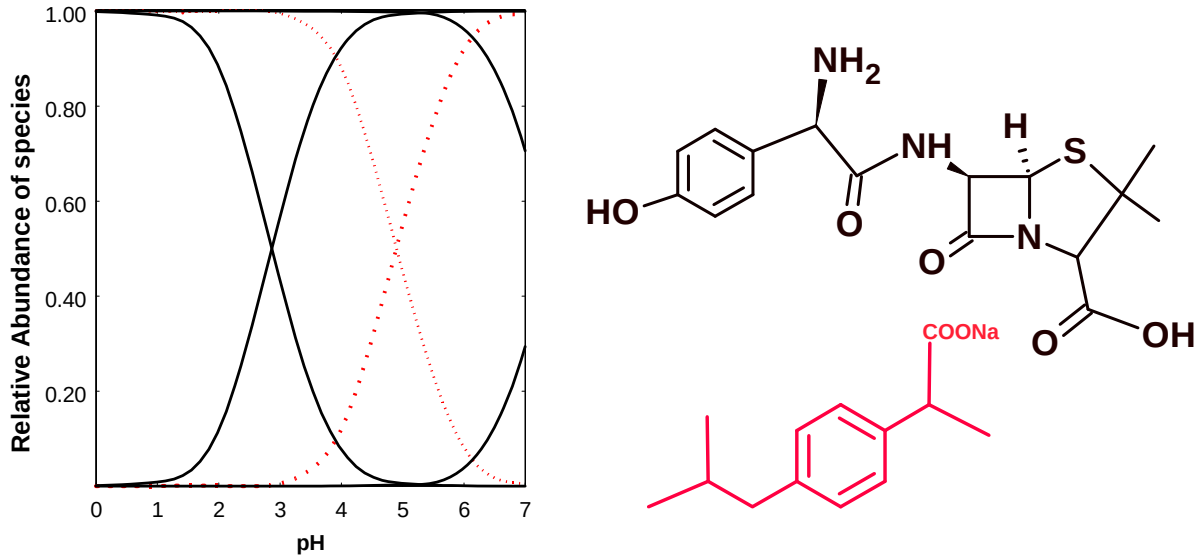
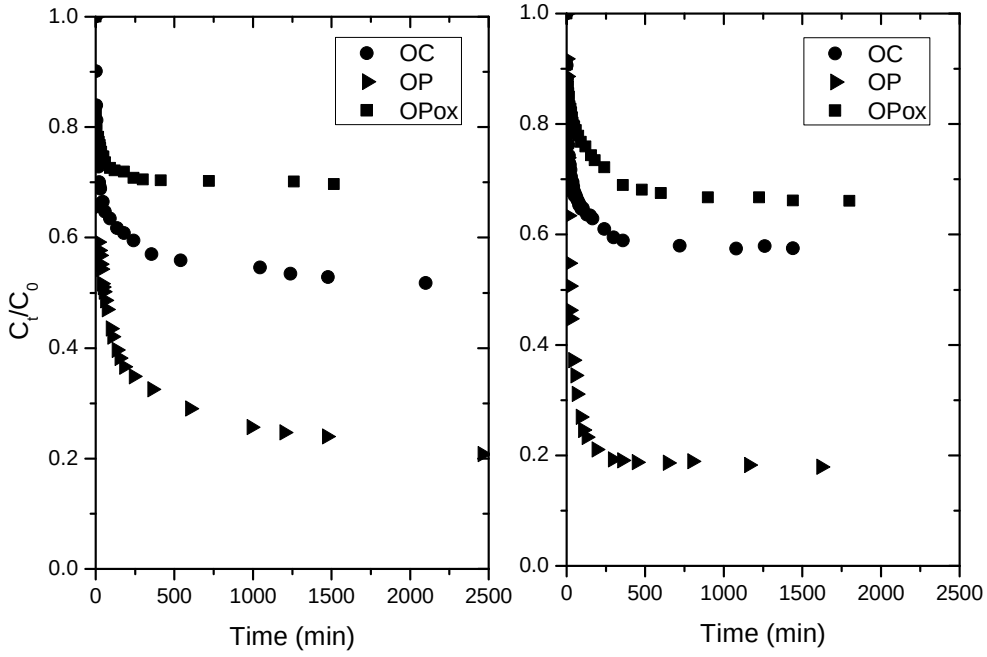


Figure 1.



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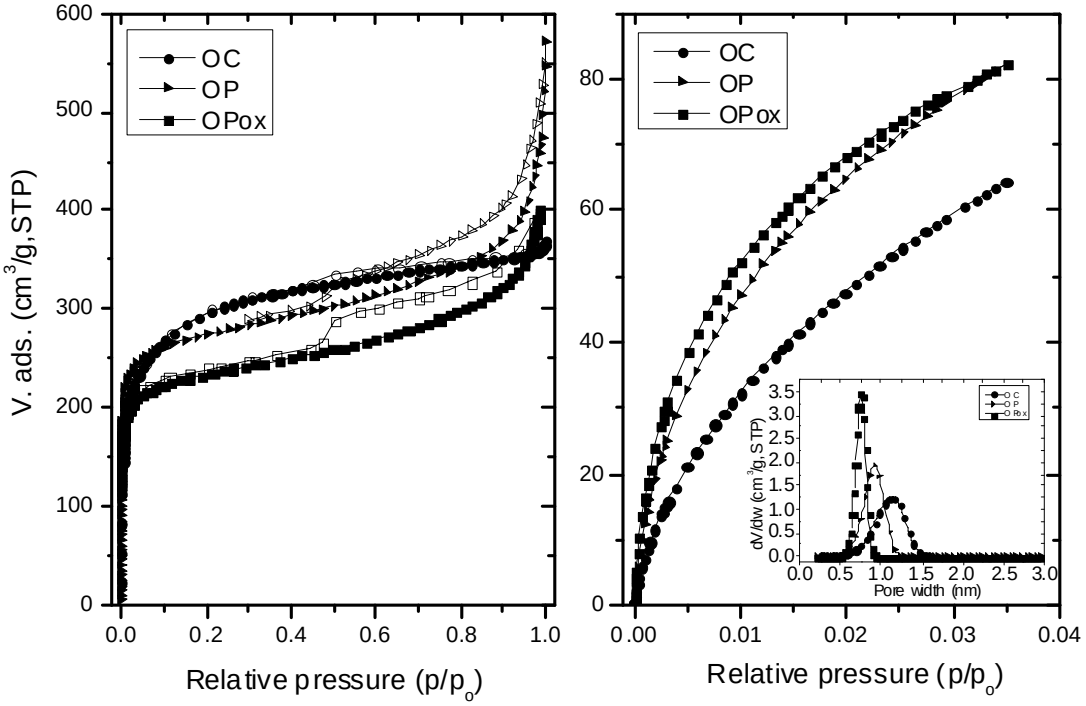

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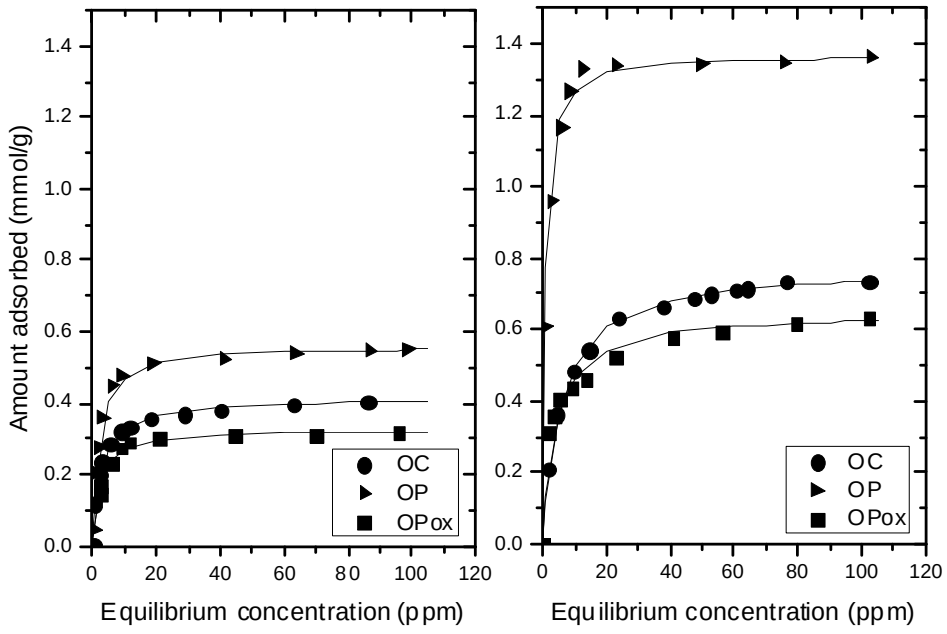

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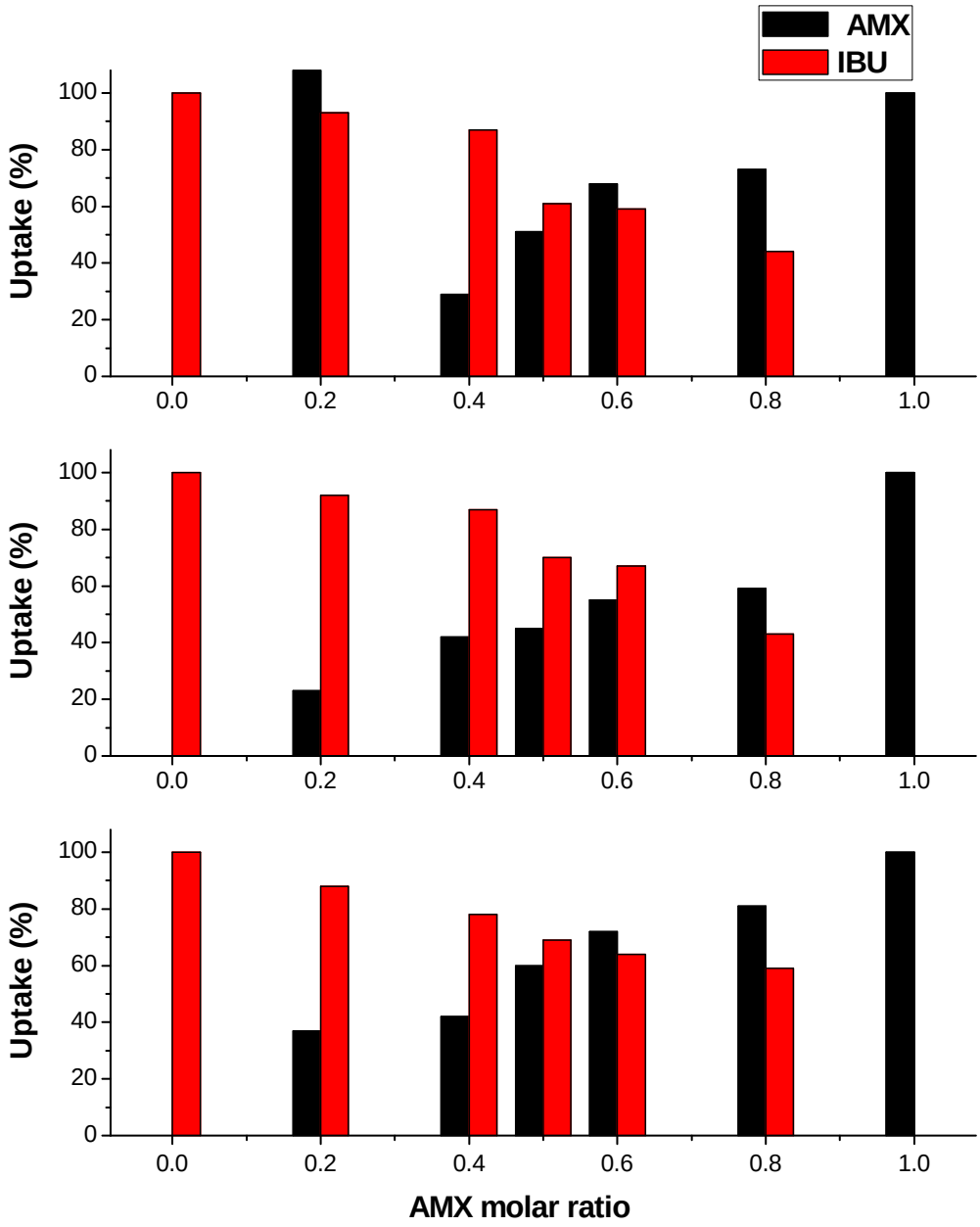

Figure 5.

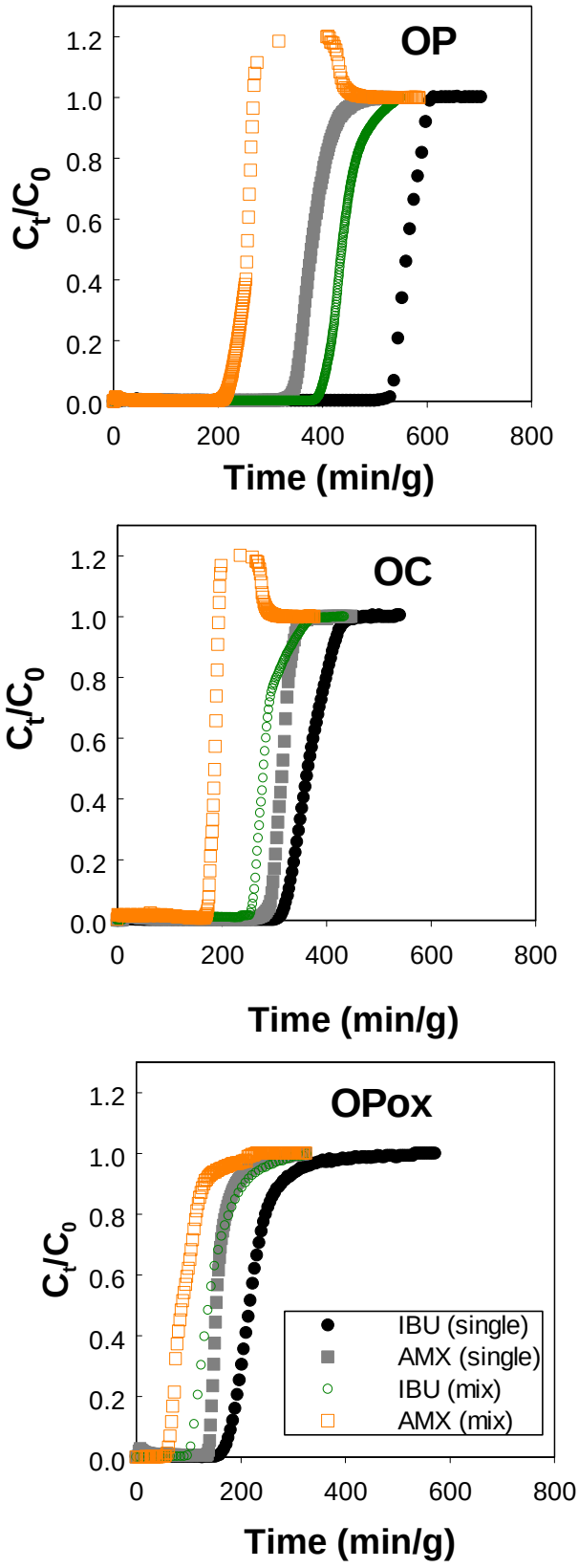
OP
OC
OPox
C_t/C_0
Time (min/g)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
200
400
600
800
IBU (single)
AMX (single)
IBU (mix)
AMX (mix)

Figure 6.

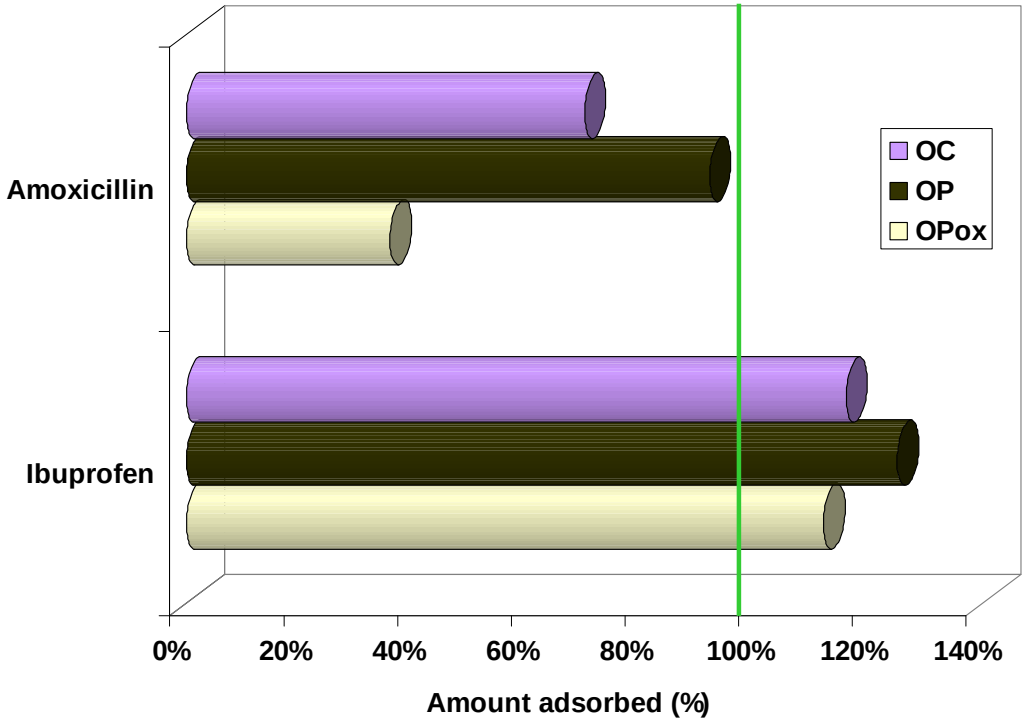
Amoxicillin
Ibuprofen
OC
OP
OPox
0%
20%
40%
60%
80%
100%
120%
140%
Amount adsorbed (%)

Figure 7.

Supplementary Information

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

Hayet Mansouri[1,2], Rocio J. Carmona[2], Alicia Gomis-Berenguer[2], Souad Souissi-Najar[2], Abdelmottaleb Ouederni[1], Conchi O. Ania[2]*

[1] 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

[2] Adsorption and Environmental Remediation on Porous Solids (ADPOR), Instituto Nacional del Carbón, INCAR-CSIC, Apdo. 73, 33080 Oviedo, Spain

*Corresponding author: conchi.ania@incar.csic.es (CO Ania)

Potentiometric Titration. Potentiometric titration measurements were performed with an automatic titrator (Metrohm). The instrument was set at the mode where the equilibrium pH is collected. Subsamples of the initial materials (~ 0.050 g) were added to $NaNO_3$ (0.01 M, 25 mL) and placed in a container maintained at 25 ^oC overnight for equilibrium. During the titration the suspension was continuously saturated with N_2 to eliminate the influence of atmospheric CO_2. The suspension was stirred throughout the measurements. Volumetric standard NaOH (0.1 M) was used as the titrant starting from the initial pH of the materials suspension up to pH 11. The experimental data was transformed into a proton binding curves, Q, representing the total amount of protonated sites.[S1, S2]

[S1] J. Jagiello, *Langmuir* **1994**, *10*, 2778.

[S2] J. Jagiello, T.J. Bandosz, J.A. Schwarz, *Carbon* **1994**, *32*, 1026.

Table S1. Number of total acidic groups determined by potentiometric titration and surface pH of the studied carbons.

Sample	Total acidic groups (mmol g^{-1})	pH
OC	1.00/ 0.42 (*)	3.8
OP	0.35	8.0
OPox	0.82	3.4

(*) The first value accounts for the overall acidic groups quantified in the complete pH range between 3-10 pH units; the second value correspond to total amount in the range of 4-10 pH units, without the contribution of the sharp peak associated to the release of the remaining acid trapped in the pores.

Table S2. Physicochemical properties of the treated wastewater before and after adsorption of equimolar mixtures of IBU and AMX on the studied carbons.

	Initial	After adsorption of equimolar IBU:AMX mixture		
		OP	**OC**	**OPox**
pH	7.5	7.3	6.5	5.9
Conductivity (microS/cm)	1310	1105	1025	750
Total Carbon /Inorganic Carbon (mg C/L)	40 / 34	33 / 25	36 / 26	16 / 14
Na^+ (mg/L)	136	105	99	36
K^+ (mg/L)	85	71	70	22
Ca^{2+}(mg/L)	37	29	32	19
HCO_3^{2-} (mg/L)	455	420	405	310
Cl- (mg/L)	39	25	28	16
SO_4^{2-} (mg/L)	800	750	745	650
NO_3^- (mg/L)	3.6	3.5	2.8	1.1

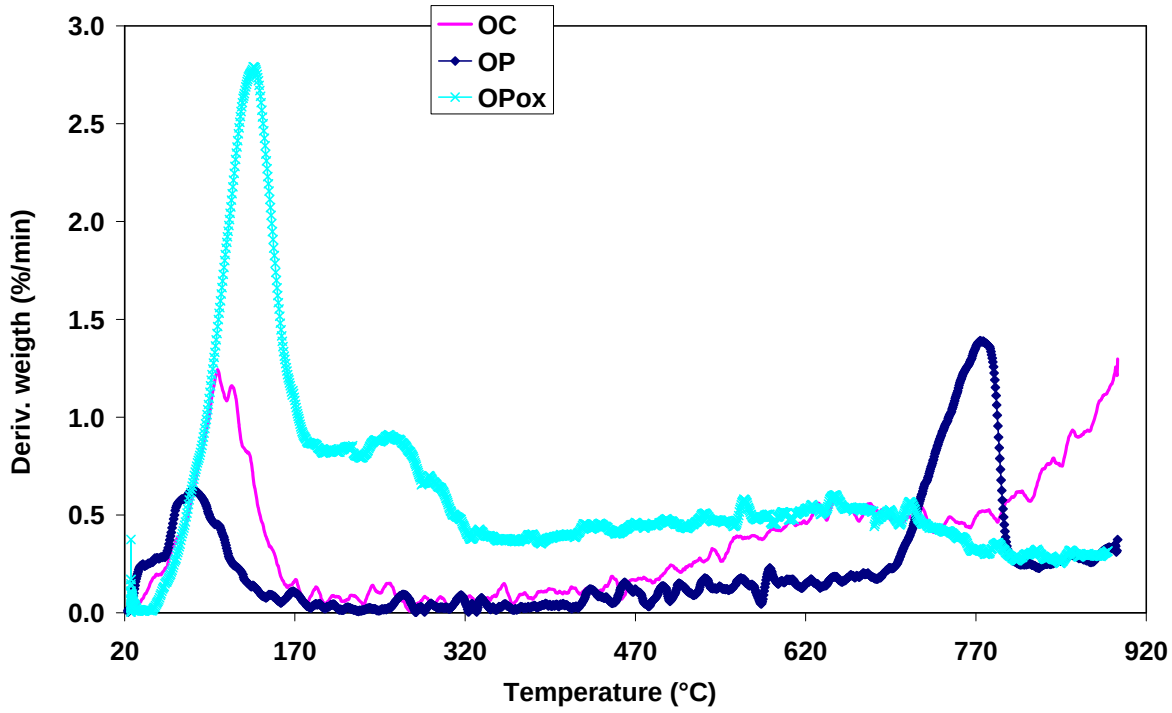

Figure S1. Thermogravimetric profiles of the nanoporous carbons studied obtained in inert atmosphere.

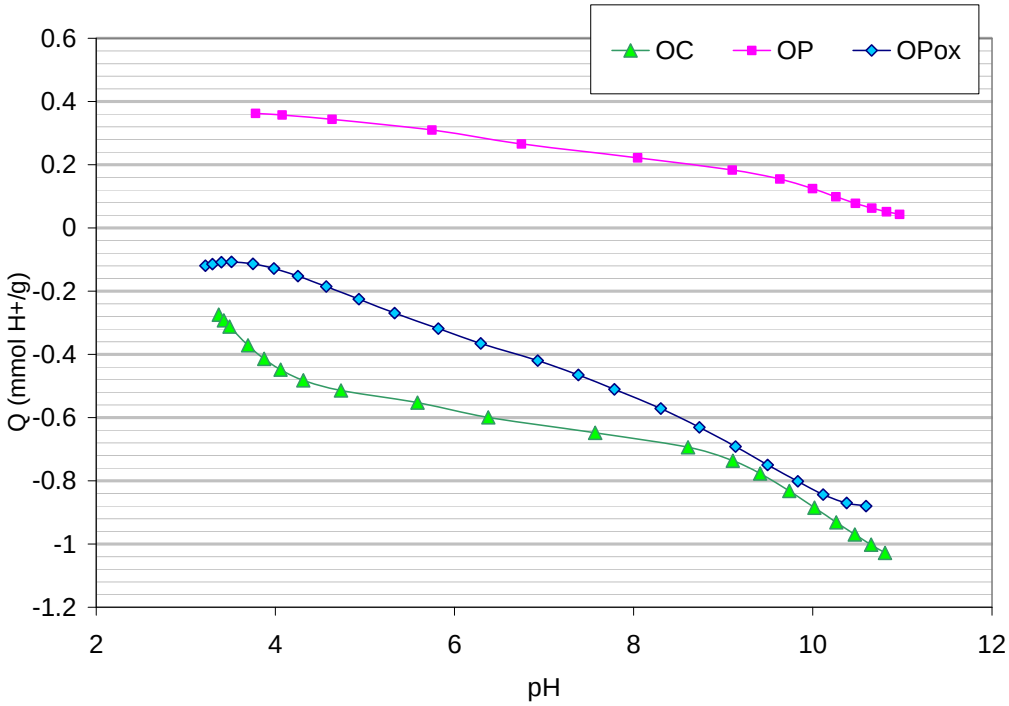

Figure S2. Proton binding of the studied nanoporous carbons.