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**Sustainable activated carbons prepared from a sucrose-
derived hydrochar: remarkable adsorbents for
pharmaceutical compounds**

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ABSTRACT

We present a two-step methodology for the preparation of highly activated carbons with tailored morphologies and micropore size distributions (MPSD) through the hydrothermal carbonization (HTC) of renewable biomass – sucrose – and further activation. Depending on the activation agent, activated carbons with spherical (K_2CO_3 or steam activation) or sponge-like morphologies (KOH activation) were obtained. The control of the activation variables allows tailoring the MPSD of the materials, with K_2CO_3 activation at 700 – 800 °C originating porous materials with molecular sieve properties and KOH activation giving porous carbon materials with wider MPSD.

The highly developed porous structures of the activated carbons give them remarkable adsorption capacities for the removal of pharmaceutical compounds of distinct therapeutical classes (i.e. ibuprofen, paracetamol, clofibric acid, caffeine and iopamidol). While the superactivated carbon obtained by KOH activation at 800 °C has very high adsorption capacities for all the pharmaceutical compounds assayed the material obtained by K_2CO_3 activation at 800 °C has similar adsorption capacity for all pharmaceuticals but iopamidol, the most voluminous compounds. The distinct performance of the porous carbons materials for the removal of the pharmaceutical compounds is mainly related to their MPSD.

The high performance of some of the synthesized carbons allied to the possibility of controlling the size of the particles in the HTC step allows envisaging their use as filter media but also coupled to other advanced water treatment technologies (e.g. membrane systems). Moreover, the above mentioned properties associated with the acidic surface chemistry of the developed activated carbons opens new possibilities for the synthesis of functional carbon-based materials.

1. Introduction

The development of medical care and the use of increasingly more effective active pharmaceutical ingredients are unquestionably responsible for the high lifestyle patterns in modern society. However, the large consumption of pharmaceuticals possess a great stress to the aquatic environment since these compounds are not totally removed/degraded by implemented water treatment technologies leading to toxic effects in aquatic organisms.^{1, 2} This reality led to a widespread consensus between scientists and governmental entities, which consider that this kind of contamination may require legislative intervention, with various pharmaceuticals appearing in a Watch List in the 2013/39/EU directive. The recalcitrant behavior of pharmaceutical compounds in conventional water treatment plants requires the use of more powerful treatment processes for assuring the maintenance of water quality. Adsorption by activated carbons arises as one of the best available technologies to face this threat,³ mainly due to its non-specific adsorption properties.

Hydrothermal carbonization (HTC) is a cost effective and eco-friendly process to obtain spherical hydrophilic materials from carbon rich precursors (including renewable carbohydrate-rich biomass); it uses water as solvent, mild temperatures and self-generated pressure with no CO₂ emission. Carbon materials obtained from HTC – hydrochars – have outstanding properties, related with their spherical morphology and high content of oxygenated surface groups, which can be used for the synthesis of functional carbon-based materials.

The potentialities of hydrothermal carbons, including their use as precursor for the preparation of porous and/or functional materials and for the synthesis of nanocomposites, were recently reviewed by Titirici *et al.*⁴ Therefore, in the last few years carbon materials obtained by HTC have been used in challenging areas for

modern society such as catalysis, energy storage, CO₂ sequestration or water purification.^{4, 5} However, in adsorption processes hydrochars have as major drawback their low porosity and surface area. Several activation routes have been assayed to increase their textural properties,⁶⁻¹⁰ although the most commonly used activation methodology employing KOH generally promotes the disruption of the spherical morphology of the resulting activated carbon materials. In a newly published work by our group it was proved that sucrose-derived hydrochars activated with K₂CO₃ are high performance materials for methane storage or biogas upgrade, mainly due to the combination of narrow micropore size distributions and microspherical morphology that leads to high packing density, only attained with K₂CO₃ activation.¹⁰

Considering the promising results from our previous publication, the first aim of the present work is to evaluate the effect of activating agent, impregnation methodology and activation temperature in the textural and morphological characteristics of hydrochar-derived activated carbons. The preparation procedure is a two-step route involving an initial hydrothermal treatment of sucrose followed by physical (steam) or chemical (KOH and K₂CO₃) activation. The second aim of this work is to evaluate the potentialities of these eco-friendly activated carbons for the adsorption of several pharmaceutical compounds from distinct therapeutical classes (i.e. ibuprofen, paracetamol, clofibric acid, caffeine and iopamidol). The highly developed microporous structure and tunable porosity of these sucrose-derived materials revealed to be crucial for their remarkable adsorption capacities for pharmaceutical compounds with very distinct chemical moieties and dimensions, when compared with activated carbons prepared from lignocellulosic materials by conventional activation processes, or even with commercial carbons used in conventional water treatment technologies.¹¹⁻¹⁹

2. Experimental Section

2.1 Chemical compounds

All chemicals were used as received: sucrose (Analar Normapur, > 90 %), potassium carbonate (Aldrich, 99 %), potassium hydroxide (Panreac, 85 %), ibuprofen (Sigma-Aldrich – Lot BCBC9914V), paracetamol (Merck – Lot S6137725 035, ≥ 99 %), caffeine (Normapur – Batch 08J300011, analytical grade), clofibrac acid (Alfa Aesar – Lot G1266B, 98 %) and iopamidol (synthesized by Hovione – Lot 163926HQ01324).

2.2 Activated carbons synthesis

The sucrose-derived activated carbons were prepared by two consecutive steps:¹⁰ hydrothermal carbonization of a sucrose solution followed by chemical or physical activation of the hydrochar.

The hydrochar was synthesized introducing 15 cm³ of a 1.5 mol dm⁻³ sucrose aqueous solution in a Teflon-line stainless steel autoclave. The HTC was made during 5 h at 190 °C in an oven (Medline Scientific Limited, model ON-02G) pre-heated to the desired temperature. The autoclave was cooled down to room temperature and the powder (hydrochar S) was further washed with distilled water and acetone, and dried (60 °C).

For steam activation, the hydrochar (1 g) was introduced in a quartz reactor placed in a vertical furnace (Thermolyne, model 21100). The steam was generated in a bubbler with distilled water at 90 °C and carried by a N₂ flow (8 cm³ s⁻¹). The material was activated at 800 °C during 1 h (10 °C min⁻¹); subsequently, the steam flow was turned off and the material was cooled to room temperature under N₂.

For chemical activation, 1 g of hydrochar was impregnated in solution with 4 g of K₂CO₃ or KOH, during 2 h and then dried; for K₂CO₃ physical impregnation was also

used. Activation was performed at temperatures between 600 and 900 °C in a horizontal furnace (Thermolyne, model 21100) for 1 h under N₂ flow of 5 cm³ s⁻¹ (10 °C min⁻¹). After cooling under N₂ flow, the materials were thoroughly washed with distilled water until pH 7, dried overnight at 100 °C and stored. The materials are labelled as: S (hydrochar) followed by the activating agent abbreviation (St, H or C for, respectively, steam, KOH and K₂CO₃) and the temperature (°C). Materials prepared by physical impregnation are labelled with a P (physical) after the activation temperature.

For comparison purposes commercial carbons used in water remediation processes were also tested (CP and VP materials supplied by Quimitejo, Portugal, and NS material supplied by Norit, Salmon & Cia, Portugal).

2.3 Characterization of the activated carbons

The textural properties of the activated carbons were characterized by N₂ adsorption isotherms obtained in an automatic equipment (Micromeritics ASAP 2010) at -196 °C and by CO₂ adsorption isotherms acquired in a conventional volumetric apparatus equipped with a MKS-Baratron (310BHS-1000) pressure transducer (0-133 kPa). Before the isotherms acquisition the solid materials (~ 50 mg) were outgassed overnight at 120 °C, under a vacuum better than 10⁻² Pa. The N₂ isotherms were used to estimate the apparent specific surface area, A_{BET} , applying the BET equation in the range $0.05 < p/p^0 < 0.15$,²⁰ and also the total pore volume, V_{total} , using the Gurvich rule,²¹ corresponding to the volume of N₂ adsorbed at $p/p^0 = 0.975$. The microporosity was assessed applying the Dubinin-Radushkevich (DR) equation to the N₂ and CO₂ adsorption data ($W_{0 \text{ N}_2}$ and $W_{0 \text{ CO}_2}$, respectively). The α_S method was also applied to the N₂ adsorption data, taking as reference the isotherm reported by Rodríguez-Reinoso et al..²² With this method the values of total, $V_{\alpha\text{total}}$, ultra (width less than 0.7 nm), $V_{\alpha\text{ultra}}$,

and supermicropore (width between 0.7 and 2 nm), V_{osuper} , volumes were obtained.²⁰ The mesoporous volume, V_{meso} , corresponds to the difference between V_{total} and V_{ototal} . The micropore size distributions were obtained from CO₂ adsorption isotherms according to the method described by Pinto et al..²³

The surface chemistry of the materials was characterized by the determination of the pH at the point of zero charge (pH_{PZC}), following the reversed mass titration procedure.^{15, 24} Briefly, a slurry of 10% was prepared by mixing the activated carbon with ultra-pure water in a glass bottle, bubbled and sealed under N₂ (to eliminate CO₂). The pH of the slurry was measured (Symphony SP70P pH meter) after shaking for at least 24 h at room temperature. In order to obtain the pH values for lower solid weight fractions, this procedure was repeated for slurries of 8, 6, 4, 2 and 1% obtained by successive dilution of the initial 10% slurry. The pH_{PZC} value corresponds to the plateau of the curve of equilibrium pH *versus* solid weight fraction. The analysis of the elemental composition was performed on an Elemental Analyser (EA 1108 CHN-O Fisions Instruments) at “Laboratório de Análises”, IST, Lisboa (Portugal). Finally, the morphological characterization of the hydrochar (S) and the activated carbons was made by scanning electron microscopy (SEM, JEOL, mod. 7001F) using an accelerating voltage of 25 kV.

2.4 Liquid phase adsorption

The sucrose-derived activated carbons and three commercial materials were tested as adsorbents of pharmaceutical active compounds (PhACs) through three sequential types of assays: screening, kinetic and equilibrium. As target molecules five PhACs were selected: ibuprofen, paracetamol, caffeine, clofibric acid and iopamidol. The pharmaceutical compound solutions were prepared with ultra-pure water obtained from

Milli-Q purification systems, and no pH adjustments were made. With the exception of clofibric acid and caffeine solutions, which have a pH value of ~ 3 and ~ 7 , respectively, all the other solutions presented pH values around 5.

In typical experiment, a known amount of activated carbon and PhAC solution were mixed in a glass flask that was introduced in a water bath at 30 °C (Grant GD100 controller), stirred at 700 rpm (multipoint agitation plate Variomag Poly) being the sample collected after the desired contact time (see details in the following). After filtration, the remaining amount of PhAC was determined by UV-vis spectrophotometry (Genesys 10S) at the wavelength corresponding to the maximum of absorbance: 221 nm (ibuprofen), 243 nm (paracetamol), 228 nm (clofibric acid), 272 nm (caffeine), and 242 nm (iopamidol). PhAC uptake was calculated according to the following equation:

$$q_t = \frac{(C_0 - C_t)}{W} V \quad \text{Eq. (1)}$$

where q_t is the amount (mg g^{-1}) of PhAC adsorbed at time t , C_0 is the PhAC initial concentration (mg dm^{-3}), C_t is the PhAC concentration at time t (mg dm^{-3}), V is the volume (dm^3) of the adsorbate solution and W is the weight (g) of dried carbon.

The screening, kinetic and equilibrium assays were made according to the experimental conditions summarized in Table 1. All the kinetic and equilibrium adsorption assays were made in triplicate. The results from the preliminary screening assays allowed to evaluate the removal efficiencies ($\text{Removal efficiency} = [(C_0 - C_{24\text{h}})/C_0] \times 100$, where C_0 and $C_{24\text{h}}$ are the initial concentration of PhAC and that determined after 24h in contact with activated carbon, respectively). The kinetic data were analysed considering the pseudo-first and pseudo-second order kinetic models,²⁵ while the equilibrium adsorption data were analysed considering linear forms of the Langmuir²⁶ and Freundlich²⁷ isotherm models presented in Table S1 of Supporting Information.

Table 1. Experimental conditions used in the screening, kinetic and equilibrium assays. The activated carbons tested and pharmaceutical active compounds (PhACs) used as target molecules for each assay are also presented.

Assay	Activated carbons	PhAC	Conditions
Screening	SH800		
	SH700	Ibuprofen	$m_{AC} = 6 \text{ mg}$
	SC800	Paracetamol	$V_{PhAC} = 9 \text{ and } 30 \text{ cm}^3$
	SC800P	Caffeine	$[PhAC] = 180 \text{ mg dm}^{-3}$
	CP	Clofibric acid	$t_{contact} = 24 \text{ h}$
	VP	Iopamidol	
	NS		
Kinetic	SH800	Paracetamol	$m_{AC} = 6 \text{ mg}$
	SC800	Iopamidol	$V_{PhAC} = 30 \text{ cm}^3$
	NS		$[PhAC] = 180 \text{ mg dm}^{-3}$ $t_{contact} = 1 \text{ min to } 48 \text{ h}$
Equilibrium	SH800	Paracetamol	$m_{AC} = 6 \text{ mg}$
	SC800	Iopamidol	$V_{PhAC} = 9 \text{ and } 30 \text{ cm}^3$
	NS		$[PhAC] = 45\text{-}300 \text{ mg dm}^{-3}$ $t_{contact} = 24 \text{ h}$

3. Results and discussion

3.1 Activated carbons properties

The morphological analysis performed by SEM (Figure 1) reveals that the sucrose-derived hydrochar S is constituted by spheres with diameters around 3 μm . The solids activated with steam (SSt800) and K_2CO_3 (SC800 and SC800P) at 800 $^\circ\text{C}$ retain the spherical morphology and smooth surface of the pristine hydrochar, while K_2CO_3 activation at 900 $^\circ\text{C}$ (SC900) originates microspheres with a rough (exfoliated) surface. On the contrary, the use of KOH as activating agent (materials SH600, SH700 and SH800) promoted the disruption of the spherical morphology regardless the activation temperature used. In fact, in the range of activation temperatures studied (600 – 800 $^\circ\text{C}$), KOH-activated materials have always a sponge-like morphology (Figure S1 of

Supporting Information) and the lower the activation temperature the smaller the amount of cavities present in the smooth surface.

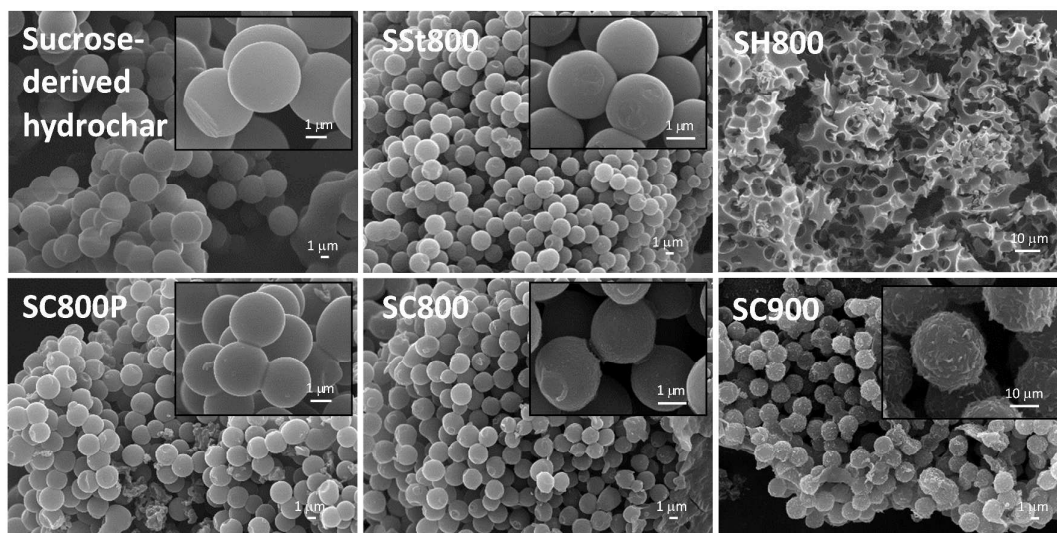


Figure 1. SEM images of sucrose-derived hydrochar and activated carbons. The inserts correspond to higher amplifications to better illustrate the surface of the materials.

The N_2 isotherms of the materials activated at 800 °C (Figure 2) reveal that different activation agents and procedures originated porous materials with well developed microporosity (type I isotherms). KOH activation leads to the material with the most developed microporous structure, but at the expense of spherical morphology (Figure 1). The activation with K_2CO_3 originated microspheres with significantly lower adsorption capacities, and the spherical material obtained by steam activation has the less developed microporous network. The effect of the impregnation methodology in the activation with K_2CO_3 is illustrated by materials SC800 (solution) and SC800P (physically), with the wet impregnation allowing a higher development of the microporous structure, as expected. From all the isotherms presented in Figure 2, that of carbon SH800 has a rounder off knee which is characteristic of the widening of the micropore size distribution due to the formation of larger micropores (supermicropores).

The textural parameters of the activated carbons (Table 2) reveal that although the KOH activation lead to higher porosity development ($A_{\text{BET}} \sim 2500 \text{ m}^2 \text{ g}^{-1}$), the use of K_2CO_3 , allowed a better compromise between the porosity development ($A_{\text{BET}} \sim 1400 \text{ m}^2 \text{ g}^{-1}$) and the yield of the activation process (45% vs 13% for materials SC800 and SH800, respectively). The impregnation methodology also influenced the textural parameters - impregnation in solution originates solids with 32 to 41 % higher micropore volume than those obtained by physical impregnation - but the yields of the two procedures are very similar.

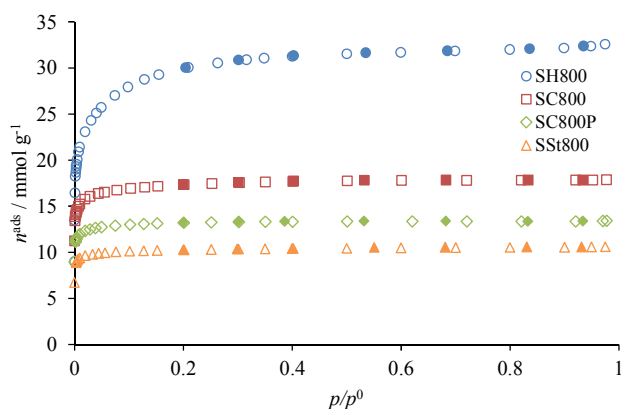


Figure 2. N_2 adsorption-desorption isotherms at $-196 \text{ }^\circ\text{C}$ of the sucrose-derived carbons activated with KOH (SH800), K_2CO_3 (SC800 and SC800P) and steam (SSt800) at $800 \text{ }^\circ\text{C}$, closed symbols are desorption points.

The analysis of the microporosity assessed from α_s method and DR equation applied to N_2 and CO_2 adsorption data reveal that the materials have distinct microporous structures. Materials activated with KOH at 700 and $800 \text{ }^\circ\text{C}$ have higher micropore volumes assessed by N_2 data ($W_{\text{DR N}_2}$) and higher volumes of larger micropores ($V_{\alpha \text{ super}}$), while all the materials activated at the same temperatures but with K_2CO_3 have higher volumes assessed by CO_2 data ($W_{\text{DR CO}_2}$), in agreement with higher volumes of narrow micropores assessed by N_2 data ($V_{\alpha \text{ ultra}}$), Table 2. Concerning the activation with K_2CO_3 it is interesting to notice that the activation at $900 \text{ }^\circ\text{C}$, which originated

microspheres with rougher surface, lead to a porous material with higher predominance of supermicropores ($V_{\alpha \text{ super}}$) and also with a mesopore volume that corresponds to 14 % of the total pore volume, while all the other K_2CO_3 -activated materials obtained at lower temperatures are exclusively microporous solids. It is worth noting that the preparation yield of this material (SC900) is only slightly lower than those of the materials prepared at lower temperatures.

Table 2. Textural properties of the activated carbons, preparation yield (η), maintenance or not of the hydrochar spherical shape, and pH_{PZC} value.

Materials	η (%)	Spherical shape	A_{BET} ($m^2 g^{-1}$)	V_{total}^a ($cm^3 g^{-1}$)	V_{meso}^b ($cm^3 g^{-1}$)	α_s Method			DR Equation		pH_{PZC}
						$V_{\alpha \text{ total}}$ ($cm^3 g^{-1}$)	$V_{\alpha \text{ ultra}}$ ($cm^3 g^{-1}$)	$V_{\alpha \text{ super}}$ ($cm^3 g^{-1}$)	$W_{DR N_2}$ ($cm^3 g^{-1}$)	$W_{DR CO_2}$ ($cm^3 g^{-1}$)	
Steam											
SS1800	38	Yes	814	0.37	0.01	0.36	0.25	0.11	0.36	0.45	8.6
KOH											
SH600	25	No	1169	0.57	0.07	0.50	0.17	0.33	0.49	0.50	-
SH700	24	No	1987	0.91	0.05	0.86	0.16	0.71	0.79	0.71	-
SH800 ^c	13	No	2431	1.14	0.06	1.08	0.00	1.08	0.90	0.71	4.0
K_2CO_3											
SC700	55	Yes	987	0.44	0.00	0.44	0.33	0.11	0.43	0.57	-
SC700P ^c	51	Yes	694	0.31	0.00	0.31	0.23	0.08	0.31	0.41	-
SC800 ^c	45	Yes	1375	0.63	0.01	0.62	0.35	0.27	0.58	0.65	4.3
SC800P	48	Yes	1053	0.47	0.00	0.47	0.30	0.17	0.46	0.52	4.9
SC900	40	Yes	1200	0.59	0.08	0.51	0.21	0.30	0.50	0.50	-
Commercial											
CP	-	No	907	0.43	0.03	0.40	0.16	0.24	0.40	0.27	10.3
VP	-	No	758	0.43	0.13	0.30	0.15	0.15	0.32	0.29	9.8
NS	-	No	1065	0.70	0.30	0.40	0.02	0.38	0.39	0.27	8.4

^a evaluated at $p/p^0 = 0.975$ in the N_2 adsorption isotherms at $-196^\circ C$.

^b difference between V_{total} and $V_{\alpha \text{ total}}$.

^c Data from ref.¹⁰

Further characterization of the carbons' microporous structure by micropore size distributions (MPSDs) assessed from CO_2 data (Figure 3) reveals that regardless the

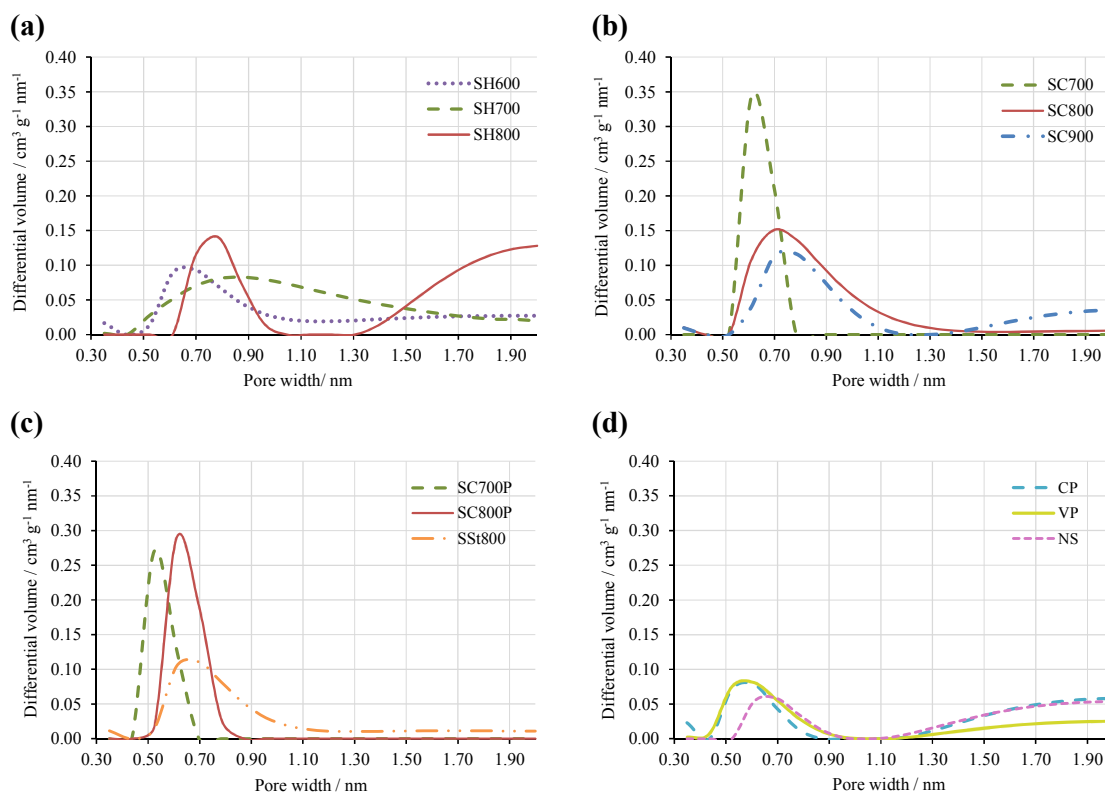


Figure 3. Micropore size distributions obtained by fitting the CO₂ adsorption isotherms at 0 °C to the method described by Pinto *et al.*²³ (a) Sucrose-derived carbons activated with KOH; (b) Sucrose-derived activated carbons impregnated in solution with K₂CO₃; (c) Sucrose-derived activated carbons physically impregnated with K₂CO₃ and sucrose-derived carbon activated with steam; and (d) commercial materials.

chemical activation agent (Figure 3(a) and (b)) the increase of the activation temperature leads to the broadening of the micropore size distribution, changing from a monomodal to a bimodal distribution. Materials SC700P, SC800P and SC700 (Figure 3(b) and (c)) present very narrow micropore size distributions, centred at 0.52 nm for SC700P and at 0.61 nm for the other two materials, pointing out that the lower the porosity development (see Table 2) the smaller the micropore widths of the material. Comparing the MPSDs of the sucrose-derived carbons with those of the carbons commercialized for water treatment it is clearly seen that the majority of the lab-made materials present much higher volumes of narrow micropores which, in the particular

case of materials SH700 and SH800, are associated also to high volumes of larger micropores. In fact, the superactivated carbon SH800 combines a high volumes of micropores between 0.6 and 1.0 nm and with widths > 1.3 nm, being the volume of the latter more than two times higher than those of commercial materials CP or NS (Figure 3 (a) and (d)).

Summarizing, using K_2CO_3 as activating agent, in optimized conditions, the methodology followed allowed the preparation of microspherical activated carbons with high micropore volumes and very narrow micropore size distributions centred at widths < 0.7 nm, thus showing molecular sieve properties. On the other hand, the activation of the sucrose-derived hydrochar with KOH leads to materials with very high microporous volumes, being the textural parameters and the preparation yields in accordance with those reported in literature studies concerning activated carbons obtained by KOH activation of hydrochars prepared from carbohydrates or biomass, in similar experimental conditions.⁶⁻⁸ The loss of the hydrochar spherical morphology after KOH-activation, herein observed regardless the temperature used, was also reported in the literature.^{8, 28} It is commonly accepted that the activation with KOH and K_2CO_3 will incorporate metallic potassium in the carbon structure during activation, and its removal during the washing step will be responsible for unblocking the micropore network. So, the fact that KOH and K_2CO_3 activation lead to the synthesis of, respectively, carbons with sponge-like morphology and spherical activated carbons was earlier interpreted as an indicative that the activation with these chemicals follows distinct mechanisms.¹⁰ In fact, KOH activation mechanism involves reactions that start at ~ 400 °C leading to the formation of several gases that, in addition to the presence of K compounds, can also contribute to the activation of the precursor.²⁹⁻³¹ On the other hand K_2CO_3 , which is also formed during KOH activation mechanism, decomposes only at 700-800 °C²⁹⁻³¹ leading

to a less extensive consumption of the carbon matrix and consequently allowing to maintain the spherical morphology of the hydrochar after activation.

It is interesting to notice that the spherical morphology of the K_2CO_3 -activated materials lead to much higher densities (tap and packing) when compared to the KOH-activated carbon SH800. This property is crucial when the application of these materials in storage vessels of separation processes is envisaged, since an activated carbon with high packing density will allow the use of smaller storage containers or separation towers.

In what concerns the surface chemistry, the pH_{PZC} values (Table 2) of the materials activated at 800 °C reveal that steam activation produces a material with basic surface chemistry (pH_{PZC} 8.6), while chemical activation produces acidic carbons (pH_{PZC} 4.0 and 4.9) but less acidic than the hydrochar (pH_{PZC} 2.1). The elemental analysis data indicate that material SH800 is the one presenting the lower percentage of carbon (74.5 wt.%), material activated with steam, SSt800, has the highest carbon percentage (87.1 wt.%) and K_2CO_3 -activated material SC800 has 81.2 wt.% of carbon. Amounts of other heteroatoms were similar for these three materials and in below 0.5% for nitrogen and 2% for hydrogen and sulfur. The elemental compositions of the sucrose-derived activated carbon materials are in the usual range of values obtained for activated carbon materials prepared from hydrochars, other precursors and also commercial materials.^{7,}

12, 17, 32

The commercial activated carbons used for comparison purposes are micro and mesoporous materials, with exception of material CP that is only microporous (Table 2). While carbon NS has mainly supermicropores, the other commercial materials present both ultra and supermicropores. The pH_{PZC} values of the commercial carbons range between 8.4 and 10.3 being indicative of materials with basic surface chemistry.

3.2 Liquid phase adsorption

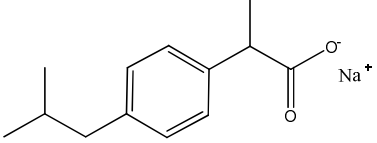
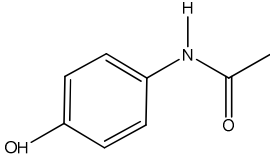
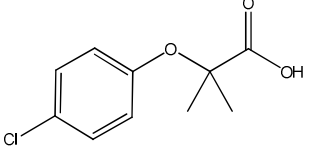
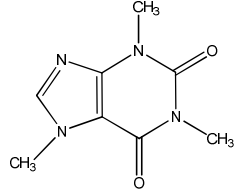
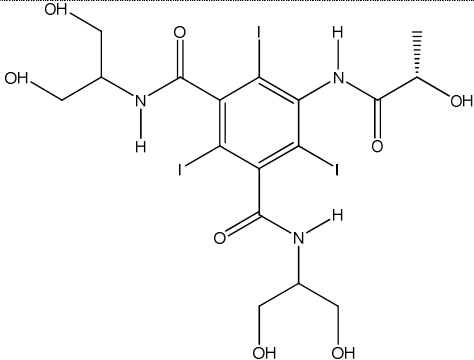
Although the highly microporous carbons obtained by activation of hydrochars have been tested mainly in energy storage applications,^{4, 7, 9, 10, 28, 33, 34} their well-developed micropore network, surface chemistry and morphology turn them very interesting materials also for liquid phase applications. In this study, the sucrose-derived activated carbons were, to the best of our knowledge, tested for the first time as adsorbents for the removal of several pharmaceutical compounds in liquid phase: ibuprofen and paracetamol (analgesics), clofibrac acid (metabolite of lipid regulators), caffeine (stimulant) and iopamidol (iodinated contrast medium). The molecular structure, solubility, pK_a , $\log K_{ow}$ and dimensions of the mentioned pharmaceuticals are summarized in Table 3.

The data gathered reveal that the target pharmaceutical compounds of this study have different hydrophilic-hydrophobic character (water solubility and $\log K_{ow}$ values); on the other hand, some are present in solution as aggregates. In fact, literature data reveal that in the experimental conditions used in the present work (pH \sim 5) paracetamol is present in solution as a dimer,³⁵ while iopamidol may be in the form of a monomer, dimer or trimer¹⁸ which leads to species with very distinct dimensions in solution.¹⁸

With exception of ibuprofen that was used in the form of sodium salt, for all the other pharmaceuticals, the log-log octanol-water partition coefficient (K_{ow}) and water solubility (S_w) are linear related (see Figure S2 of Supporting Information), which is in accordance with larger sets of data concerning organic compounds.^{36, 37} According to the hydrophilic-hydrophobic characteristics, and excluding ibuprofen that is an anion,

the PhACs can be ordered from the most hydrophilic to the most hydrophobic as iopamidol, caffeine, paracetamol and clofibric acid.

Table 3. Molecular structure, solubility in water (S_w), pK_a , $\log K_{ow}$ and dimensions of the pharmaceutical compounds under study. The critical dimension of each specie is highlighted in bold.

Pharmaceutical compound	Molecular structure and other relevant properties
Ibuprofen (Ibu)	 <p>$\log K_{ow} = 4.0$³⁸ $S_w = 100\,000\text{ mg dm}^{-3}$</p> <p>1.32 (length) \times 0.72 (width) \times 0.77 (thickness) in nm¹⁷</p>
Paracetamol (Para)	 <p>$\log K_{ow} = 0.46$³⁹ $S_w = 17\,390\text{ mg dm}^{-3}$⁴⁰ $pK_a = 9.7$⁴¹</p> <p>Monomer – 1.19 (length) \times 0.75 (width) \times 0.46 (thickness) in nm¹¹ Dimer – 1.58 (length) \times 1.19 (width) \times 0.66 (thickness) in nm¹¹</p>
Clofibric acid (Claf)	 <p>$\log K_{ow} = 2.57$³⁸ $S_w = 755\text{ mg dm}^{-3}$¹⁷ $pK_a = 2.9$</p> <p>1.22 (length) \times 0.70 (width) \times 0.72 (thickness) in nm⁴²</p>
Caffeine (Caf)	 <p>$\log K_{ow} = -0.5$³⁹ $S_w = 30\,000\text{ mg dm}^{-3}$¹³</p> <p>1.06 (length) \times 0.85 (width) \times 0.45 (thickness) in nm¹⁹</p>
Iopamidol (Iop)	 <p>$\log K_{ow} = -2.42$³⁸ $S_w > 200\,000\text{ mg dm}^{-3}$⁴³ $pK_a = 10.7$</p> <p>Monomer – 1.5 (length) \times 1.5 (width) \times 0.6 (thickness) in nm¹⁸ Dimer – 1.5 (length) \times 1.5 (width) \times 1.2 (thickness) in nm¹⁸ Trimer – 1.5 (length) \times 1.5 (width) \times 1.8 (thickness) in nm¹⁸</p>

3.2.1 Screening studies of PhACs removal

The performance of selected lab-made materials and activated carbons commercialized for water treatment technologies for the removal of pharmaceutical compounds was made throughout the evaluation of removal efficiencies. For illustration purposes the removal efficiencies achieved by the tested activated carbons for clofibric acid are displayed in Figure 4. The lab-made carbons prepared by chemical activation of the hydrochar outperform the commercial materials, attaining removal efficiencies near 100 % (bars above the orange horizontal line that marks the removal efficiency attained with the best commercial carbon – material NS). Figure S3 of Supporting Information resumes the removal efficiencies attained for all the systems and it is interesting to notice that, in general, each particular carbon attain similar removals for paracetamol, clofibric acid and caffeine. Ibuprofen and iopamidol were the compounds for which more distinct removal efficiencies were attained. Ibuprofen is systematically less removed than all the other small PhACs which is certainly related with its ionic character associated to a high solubility in water. In what concerns iopamidol, the most voluminous compound, with exception of lab-made materials SH800 and SH700, all the other activated carbons present removal efficiencies much lower (< 50 %) than those obtained for the other molecular PhACs (> 50 %).

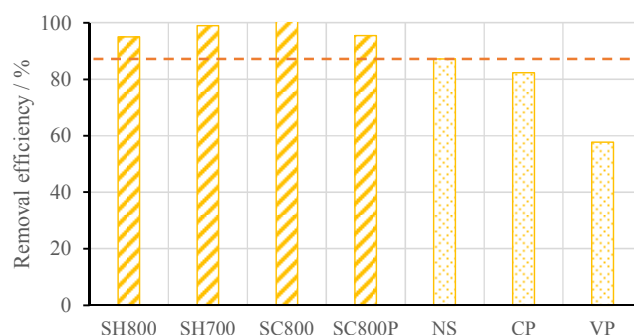


Figure 4. Removal efficiency of the mentioned activated carbons for clofibric acid (6 mg carbon/9 cm³ solution with 180 mg dm⁻³, 24 h contact time). The orange horizontal line marks the removal efficiency attained with the best commercial carbon (NS).

Figure 5 presents the removal efficiency variation of each carbon against the best commercial material assayed for each pharmaceutical compound, i.e. material NS. It is clearly seen that the lab-made carbons SH800 and SH700, prepared by KOH activation of the hydrochar, attain removal efficiencies at least 10 percentage points higher than material NS, and in the case of the most voluminous molecule – iopamidol – the removal efficiency of these carbons is almost the double of that obtained with carbon NS. The very high removal efficiencies of materials SH800 and SH700 for this particular PhAC is certainly related with their micropore size distributions, since the high amounts of larger micropores allow the adsorption of all the iopamidol species (monomers, dimers and trimers).

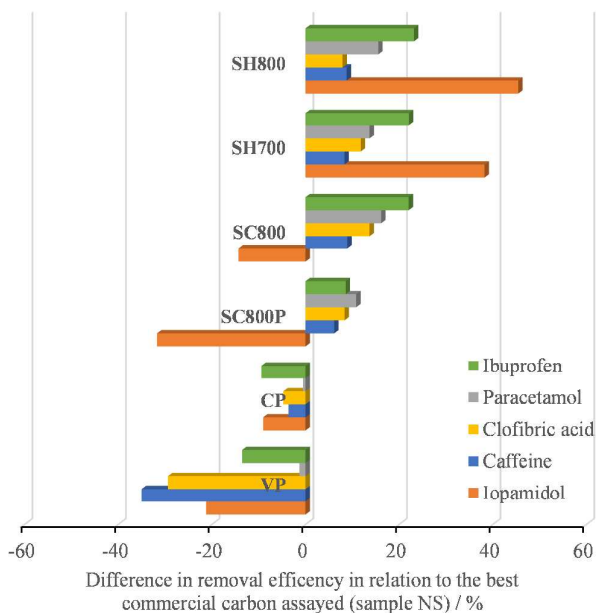


Figure 5. Removal efficiency variation of each carbon against and the best commercial material assayed (NS) for the mentioned pharmaceutical compounds (6 mg carbon/9 cm³ of PhAC solution with 180 mg dm⁻³, 24 h of contact time).

The lab-made carbons SC800 and SC800P also present very high removal efficiencies for the small PhACs (in the case of material SC800 comparable to those of materials activated with KOH) but are less effective for the removal of iopamidol, certainly due to

their narrower micropore size distributions centered at widths ~ 0.7 nm (Figures 3 (b) and (c)). On the opposite of what happens for KOH-activated materials, the micropore network of carbon SC800P only allows the adsorption of the iopamidol monomer, and material SC800, although presenting a wider micropore size distribution, may adsorb monomers and dimers but does not present pores that can accommodate the iopamidol trimer (i.e. micropores with widths > 1.5 nm).

The first screening results reveal the potentialities of the hydrochar-derived activated carbons for the removal of pharmaceutical compounds of distinct therapeutical classes and with different chemical properties. In general the characteristics of the carbons' micropore network correlate well with the removal efficiencies attained for the several PhACs, considering their critical dimensions.

In order to get more insights into the adsorptive properties of the lab-made materials two pharmaceutical compounds were selected: paracetamol that is an over-the-counter medicine, and iopamidol, a contrast media and the bulkiest compound evaluated.

The screening assays using higher amounts of paracetamol or iopamidol for the same dose of adsorbent, Figure S4 of Supporting Information, corroborate the trends observed in Figure 5 and highlight the superior adsorption performance of the majority of the chemically activated lab-made carbons for both pharmaceuticals.

3.2.2 Paracetamol and iopamidol kinetic adsorption studies

In order to have a deeper evaluation of the adsorptive properties of the sucrose-derived activated carbons and considering the preliminary results obtained in the screening assays, kinetic and equilibrium adsorption studies were made for the chemically activated materials SH800 and SC800 and also for the best performing commercial carbon (NS).

The kinetic curves for both pharmaceuticals are presented in Figure 6, showing that, in all the cases the paracetamol adsorption equilibrium is reached in about 1 h of contact time, and that lab-made materials have similar kinetic profiles but attained higher removals than the commercial material. Concerning iopamidol, very distinct kinetic profiles are observed for the tested carbons.

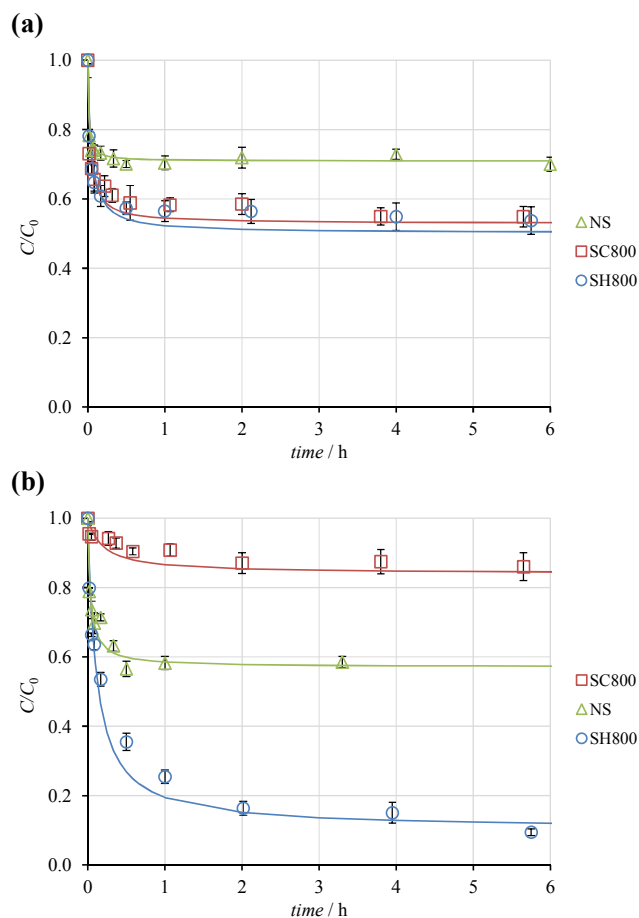


Figure 6. Kinetic results of paracetamol (a) and iopamidol (b) adsorption onto the mentioned carbons at 30 °C. Symbols correspond to the experimental data, whereas lines represent the fitting to the pseudo-second-order kinetic equation (6 mg carbon/30 cm³ of PhAC solution with 180 mg dm⁻³). Error bars are included.

The experimental data were fitted to the pseudo-first⁴⁴ and pseudo-second²⁵ order kinetic models, and presented a best fitting to the pseudo-second order kinetic model for both compounds being the correspondent kinetic parameters quoted in Table 4. For

paracetamol the initial adsorption rate (h) is of the same order of magnitude for all the carbons, while in the case of iopamidol distinct orders of magnitude are observed, and the materials can be ordered as NS > SH800 >> SC800.

The higher initial iopamidol adsorption rate of NS is related with its high volume of mesopores that allows a fast diffusion of this voluminous compound, in accordance with literature data.¹⁸ However, considering that the removal efficiency of iopamidol range from 16.0 % to 89.6 %, a more accurate evaluation of the overall kinetic process should be made through the global adsorption rate (k_2). These values reveal a much faster adsorption rate for the lab-made materials, and particularly for carbon SH800.

Table 4. Pseudo-second order PhACs adsorption parameters for the studied carbon materials at 30°C: k_2 is the pseudo-second order rate constant; h is the initial adsorption rate; $t_{1/2}$ is the half-life time; $q_{e,calc}$ and $C_{e,calc}$ are, respectively, the PhAC uptake and that remaining in solution at equilibrium both calculated by the pseudo-second order kinetic model.

Material	k_2 (g mg ⁻¹ h ⁻¹)	R^2	h (mg g ⁻¹ h ⁻¹)	$t_{1/2}$ (h)	$q_{e,calc}$ (mg g ⁻¹)	$C_{e,calc}$ (mg dm ⁻³)	RE (%)
<i>Paracetamol</i>							
SH800	0.050	0.999	10000	0.045	448.4	90.3	49.8
SC800	0.070	0.999	12500	0.034	423.7	95.3	47.1
NS	0.292	0.997	20000	0.013	261.8	127.6	29.1
<i>Iopamidol</i>							
SH800	0.011	0.999	7143	0.113	806.5	18.7	89.6
SC800	0.036	0.990	735	0.196	143.9	151.2	16.0
NS	0.075	0.999	11111	0.035	386.1	102.8	42.9

The initial and global adsorption rates (h and k_2 , respectively) of paracetamol by the lab-made materials SC800 and SH800 are very similar although these materials present very distinct volume of micropores. Their similar adsorption rates can be tentatively related with their micropore size distributions since both carbons have very high

amounts of micropores with widths higher than the critical dimensions of the paracetamol dimer (0.66 nm) compared with the commercial carbon NS, which allows a faster diffusion towards adsorption sites.

Although the mesopore volume controls the rate of the initial iopamidol adsorption process, the removal efficiency (*RE*) is linearly related with $V_{\alpha \text{ super}} + V_{\text{meso}}$ (determination coefficient of 0.987, see Figure S5 of Supporting Information). This finding is in accordance with the results obtained in a previous study using other commercial and lab-made materials,¹⁸ where it was proved the paramount importance of the micropore size distributions of the adsorbents for the adsorption of iopamidol that may be present in the form of monomers (0.6 nm), dimers (1.2 nm), trimers or bigger aggregates (1.5 nm). Thus, while the micropore size distributions of the best performing carbon – SH800 – and the commercial material NS allow to conclude that all iopamidol species can be adsorbed, the distribution of material SC800 indicates that only the monomer and dimer forms can access the adsorption sites. However, from conductivity data of aqueous iopamidol solutions¹⁸ we can assume that in the range of concentrations used, and particularly for the concentration of iopamidol remaining in solution at equilibrium when SC800 was used (i. e. 151.2 mg dm⁻³) iopamidol will be present as a trimer or bigger aggregate, so justifying the lowest removal efficiency attained with SC800 and the better performance of the carbon SH800 that has by far the highest amount of pores with widths > 1.5 nm. The incipient mesopore network in material SH800 is compensated by a very high volume of larger micropores ($V_{\alpha \text{ super}}$). The micropore distribution of the commercial material and its well-developed mesopore structure allows the adsorption of all the iopamidol species; however the total volume of pores available is still much lower than that of carbon SH800.

3.2.3 Paracetamol and iopamidol equilibrium adsorption studies

The equilibrium adsorption isotherms are displayed in Figure 7. In all the systems the curves are characterized by a steep initial rise that approaches a plateau attributed to the formation of a complete monolayer and belong to the L-type.^{45, 46} The experimental data were fitted to the linear forms of the Langmuir²⁶ and Freundlich²⁷ equations quoted in Table S1, being the fitting parameters, the determination coefficients and chi-square test analysis values presented in Table 5.

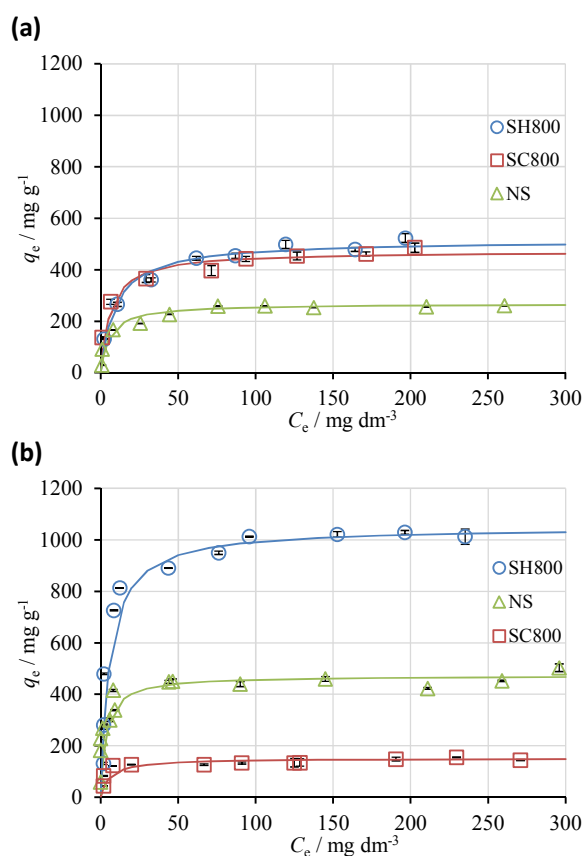


Figure 7. Paracetamol (a) and iopamidol (b) adsorption isotherms on the studied carbons at 30 °C. Symbols correspond to the experimental data, whereas lines represent the fitting to the Langmuir equation. Error bars are included.

In the case of paracetamol (Figure 7(a)) both lab-made materials have very similar curves and outperform the commercial activated carbon reaching almost the double of

the adsorption capacity in the plateau. From the isotherms obtained for iopamidol (Figure 7(b)) the lab-made carbon SH800 stands out with a remarkably high adsorption capacity, while the carbon SC800 has the lowest adsorption capacity.

The values of determination coefficient (R^2) and of the non-linear chi-square analysis (χ^2) indicate a better adjustment of the experimental data to the Langmuir model. The adsorption capacities (q_m) calculated from the model are in accordance with the analysis of the isotherms above made for all the systems. The values of the Langmuir constant (K_L) are similar in all the cases indicating the identical affinity of the two pharmaceutical compounds for the carbons assayed.

Table 5. Fitting parameters to the Langmuir and Freundlich models and chi-square test analysis, χ^2 . Langmuir parameters: q_m - monolayer adsorption capacity, K_L - Langmuir constant. Freundlich parameters: n_F - Freundlich exponent, K_F - Freundlich constant.

	Langmuir Equation					Freundlich Equation			
	q_m (mg g ⁻¹)	q_m^{\S} (mmol g ⁻¹)	K_L (dm ³ mg ⁻¹)	R^2	χ^{2*}	$1/n$	K_F (mg ^{1-1/n} (dm ³) ^{1/n} g ⁻¹)	R^2	χ^{2*}
<i>Paracetamol</i>									
SH800	513.5	3.397	0.105	0.997	7.0	0.308	115.1	0.960	24.3
SC800	471.8	3.121	0.157	0.997	12.7	0.227	155.4	0.952	15.2
NS	267.7	1.771	0.180	0.997	5.3	0.350	56.4	0.862	47.0
<i>Iopamidol</i>									
SH800	1049.6	1.351	0.173	0.999	33.3	0.285	261.5	0.706	360.1
SC800	150.9	0.194	0.174	0.996	19.5	0.163	64.1	0.711	19.7
NS	472.4	0.608	0.284	0.992	30.2	0.097	282.7	0.755	33.9

[§] calculated considering the molecular weight of a paracetamol or iopamidol monomer.

* $\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}}$ where q_e is the experimental equilibrium uptake and $q_{e,m}$ is the equilibrium uptake calculated from the model.⁴⁷

The values of monolayer adsorption capacities are usually presented in mg of adsorbate per gram of adsorbent, however when species with very distinct molecular weights are

involved, as is the case of paracetamol and iopamidol, the comparison of the adsorption capacities must be made in mmol of adsorbate per gram of adsorbent. In fact, although carbon SH800 presents a very high adsorption capacity for iopamidol when expressed in mg g^{-1} , when the values are expressed in mmol g^{-1} it is clearly seen that the number of paracetamol structural units adsorbed onto carbon SH800 is more than the double of that of iopamidol (i.e. 3.4 *versus* 1.4 mmol g^{-1} , respectively). This is the expected behavior since smaller species allow the optimization of the porous volume occupied. The lower amount of iopamidol moles adsorbed compared with paracetamol is also in line with its higher solubility (see Table 3). For carbon SC800 the opposite trend is observed, $q_m(\text{Para}) \approx 16 \times q_m(\text{Iop})$ in mmol g^{-1} , what is understood considering the absence of micropores to adsorb the iopamidol bigger aggregates, but the presence of high amounts of micropores with apertures between 0.5 and 1.3 nm which allow the diffusion and adsorption of the paracetamol monomer or dimer.

The values gathered in Table 6 show that the sucrose-derived activated carbons assayed in this study for the adsorption of paracetamol and iopamidol outperform those of commercial and waste-derived activated carbons tested in similar experimental conditions, highlighting the potentialities of these sustainable materials to be used in water treatment technologies to remove organic compounds.

If the adsorption capacity is the only parameter taken into account to select an adsorbent for decontamination purposes, material SH800 would be elected. However, the preparation yield of this material is much lower than that of material SC800 which, in the case of paracetamol, has a similar performance. Thus the use of mixtures of these two materials, preferably with higher percentage of carbon SC800, could be an option to assure high removal efficiencies of organic compounds of different molecular weight. Moreover, carbon SC800 has a microspherical morphology which gives it much higher

tap and packing densities than those of material SH800,¹⁰ being this a crucial property for the storage and handling of these powdered materials. On the other hand, concerning water purification purposes the study developed by Ellerie *et al.*⁴⁸ highlights the importance of particle size of activated carbons used as adsorptive coating materials for microfiltration, since activated carbons constituted by submicron-sized and micron-sized particles (as is the case of K₂CO₃-activated hydrochars obtained in this study) can potentially serve as effective secondary membranes, preventing foulants such as organic matter from reaching the microfiltration or ultrafiltration membrane, without greatly restricting the flow.

Table 6. Maximum adsorption capacity values of several activated carbons for paracetamol and iopamidol in similar experimental conditions (i.e. temperature, range of concentration of PhAC, agitation speed). The maximum adsorption capacity for each PhAC is highlighted in bold

Adsorbent	Adsorption capacity		Ref.
	(mg g ⁻¹)	(mmol g ⁻¹) [§]	
<i>Paracetamol</i>			
Commercial activated carbon	255	1.687	
Cork-derived activated carbon	200	1.323	49
Peach stone-derived activated carbon	204	1.350	
Plastic-derived activated carbon	113	0.748	
Pine fly ash-derived activated carbons	189 – 244	1.250 – 1.614	11
Commercial activated carbon	170	1.125	
Pine char-derived activated carbons	270 and 434	1.786 and 2.871	19
Sucrose-derived activated carbons	472 and 514	3.123 and 3.401	Present
Commercial activated carbon	267	1.766	work
<i>Iopamidol</i>			
Commercial activated carbons	136 and 147	0.175 and 0.189	18
Sisal-derived activated carbons	105 and 112	0.135 and 0.144	
Sucrose-derived activated carbons	151 and 1050	0.194 and 1.351	Present
Commercial activated carbon	472	0.607	work

[§] calculated considering the molecular weight of a paracetamol or iopamidol monomer.

4. Conclusions

The two-step methodology involving the HTC of renewable biomass (i.e. sucrose) and further chemical activation allowed to obtain activated carbons with remarkably high adsorption capacities for pharmaceutical compounds, when compared with commercial materials or other lignocellulosic-derived activated carbons.

The sucrose-derived activated carbons obtained are microporous solids with distinct morphologies and micropore size distributions. KOH activation leads to superactivated carbons (up to $2400 \text{ m}^2 \text{ g}^{-1}$) presenting wide micropore size distributions and sponge-like morphologies. Carbons prepared with K_2CO_3 as activating agent retain the spherical shape of the hydrochar, attain apparent surface areas around $\sim 1400 \text{ m}^2 \text{ g}^{-1}$ and present narrow micropore size distributions centered in the ultramicropore region.

The high adsorption capacities of the KOH activated materials for all the pharmaceutical compounds assayed is related with their high amounts of larger micropores. The materials obtained by K_2CO_3 activation have similar capacity for the adsorption of the small pharmaceuticals but lower removal efficiency for the most voluminous compound – iopamidol – due to the absence of micropores to accommodate the iopamidol trimer.

K_2CO_3 activation of hydrochars is a promising methodology to prepare micrometer-sized activated carbons that can present great advantages to be used as filter media alone or coupled to membrane systems in water purification technologies. In this sense, the present work constitutes an important contribution towards the searching for the best available materials to water treatment processes in order to face the problematic of water streams' contamination with pharmaceutical compounds, which is receiving increasing attention of both scientific and governmental entities.

Acknowledgements

This work was supported by Fundação para a Ciência e a Tecnologia through grants nº PEst-OE/QUI/UI0612/2013 (CQB) and PEst-C/EQB/LA0006/2013 and FCOMP-01-0124-FEDER-037285 (REQUIMTE); the authors also acknowledge Operation NORTE-07-0124-FEDER-000067 – NANOCHEMISTRY. ASM, MAA and MG thank FCT for, respectively, Post-doctoral grant SFRH/BPD/86693/2012, PhD grant SFRH/BD/71673/2010 and PhD grant SFRH/BD/69909/2010. The authors thank Quimitejo for providing carbons CP and VP, Salmon & Cia for the supply of carbon NS, and Hovione for the supply of iopamidol.

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Graphical Abstract

From sugar to water free of medicines: biomass-derived carbons allow high adsorption capacities for the removal of pharmaceuticals from water.