Synthesis of biomass-derived activated carbons for liquid phase application

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Abstract

In this communication an overview of the studies developed in the Adsorption and Adsorbent Materials Group related with the preparation of biomass-derived activated carbon materials is presented, highlighting the results of the most important research line of the group in the carbon materials thematic, i.e., the assessment of the potentialities of these materials as adsorbents of various pharmaceutical compounds from aqueous solution.

Resumen

En esta comunicación se presenta una visión general de los estudios que se realizan en el Grupo de Adsorción y Materiales Adsorbentes de la Universidad de Lisboa en la temática de los materiales de carbón. Estos trabajos se basan en la preparación de carbones activos derivados de biomasa y el estudio de sus aplicaciones como adsorbentes de diversos compuestos farmacéuticos en disolución acuosa. Aquí se han resaltado los resultados más importantes de esta línea de investigación.

1. Introduction

The present Adsorption and Adsorbent Materials Group (AAM) of the Centre of Chemistry and Biochemistry of the Faculty of Sciences of Lisbon University is the heir of the Adsorption Group that for more than 30 years developed studies mainly centered on the adsorption from gas phase on several porous materials, namely zeolites and clay-derived solids. As a natural enlargement of interests, in the late 90´s the group started to develop a new research line focused on carbon materials. The first studies were focused on the preparation of cork-derived materials followed by the evaluation of their performance in gas phase processes. However, being aware of the importance of the use of activated carbons in advanced water treatment technologies to allow an efficient removal of recalcitrant pharmaceutical compounds, the group turned the attention to this problematic. In this context, in the last 15 years the research line related with carbon materials has been centered on assessing the potentialities of different biomass-derived activated carbons as adsorbents of various pharmaceutical compounds detected all over the world. In the following, a description of the most relevant results will be presented, highlighting the studies where unexpected results allowed a deeper insight into the mechanism of these processes, what was only possible due to the establishment of collaborations with different research areas. The applied character of the studies drew the attention of the industry, which gave us the opportunity to integrate a QREN project team headed by the world leading company in cork processing.

The collaborations with Portuguese (Inorganic Chemistry Group of Faculty of Sciences from University of Porto (FCUP), Catalysis Group of Lisbon Superior Engineering Institute (ISEL) and Chemistry Department of Faculty of Science and Technology, New University of Lisbon (FCT-UNL)) and foreign, mainly Spanish (ADPOR Group, Dpt. Chemical Processes for Energy and Environment, Instituto Nacional del Carbón, (INCAR)) research groups was also fundamental to test the prepared materials in applications other than adsorption, being the developed works listed in the final of this communication.

Lastly, it must be mentioned that since our research interests have been centered on the field of carbon materials, the developed studies gave rise to several projects of undergraduate students, as well as MSc and PhD theses and, as a natural consequence, allowed numerous panel and oral presentations in international conferences, namely in Carbon or GEC congresses.

2. Investigation of different precursors for the synthesis of activated carbons

The industrial production of activated carbons is generally based on coal, wood and coconut shell, the first being a non-renewable feedstock with a progressively decrease of quality (high ash content), and the last largely available biomasses, but with variable price. In this context, the search of other sustainable alternatives for activated carbons precursors is a research subject that, although extensively reported in the literature, remains as a hot topic in the field of carbon materials. In fact, the use of carbon-rich agro-industrial residues as raw materials for the production of activated carbons is a possible strategy to add value to biomasses that otherwise would be landfilled or used as fuel. This approach decreases wastes and enables the production of goods, therefore contributing to a more circular economy and more sustainable industrial processes.

Due to the importance of cork for the Portuguese economy, cork powder waste was the first biomass residue explored by the group for the production of activated carbons. The first results revealed the potentialities of this biomass to prepare carbons with molecular sieve properties [1, 2] and, as previously mentioned, were the starting point of a new research line focused on the preparation of activated carbons. Cork powder has been extensively tested to prepare activated carbons by different activation methodologies [1, 3-9], being the obtained materials tested as adsorbents in both gas and liquid phase processes. The work developed received the attention of the industry and national funding entities, and the AAM group integrated the team of a consortium headed by Corticeira Amorins, the world leading company of cork processing industry (QREN5532–WaterCork). The close cooperation with the cork industry allowed AAM group to explore the potentialities of a large set of cork processing by-products as precursors of activated carbons (Figure 1(a)), namely granules of expanded corkboard.

The methodology developed during the project was protected by a National Patent [10], the work was published [11] and presented in the 2013 Carbon Conference. The scale-up of the methodology developed during the WaterCork project allowed the preparation of a large amount of cork-derived activated carbon, which was selected to be tested in the recently started LIFE Impetus project coordinated by researchers from LNEC (National Laboratory of Civil Engineering) Hydraulic and Environment Department. The project aims to evaluate several strategies to improve current barriers for controlling pharmaceutical compounds in urban wastewater treatment plants (LIFE14 ENV/PT/000739) where activated carbons may have a strategic importance.

Sisal fibres wastes, discarded by a rope industry (CORDEX), were also used as precursors of activated carbons (see Figure 1(b)) and further assayed as adsorbents of pharmaceutical compounds [12, 13], or as additives to TiO_2 in the photooxidation of phenol [14, 15].

The solid wastes generated during the processing of pine wood, and pine wood and coal blends in the pilot gasification facility of LNEG (National Laboratory of Energy and Geology) were chemically activated with K_2CO_3 [16, 17] obtaining porous carbons with apparent surface areas that reached 1500 $m^2\ g^{-1}$ when pine wood was the raw materials used to feed the gasification reactor (see Figure 1(c)).

More recently, a biodiesel production by-product – low particle size rapeseed recovered from warehouse air filtration system – was also assayed as precursor for the synthesis of reusable activated carbons (Figure 1(d)) for the adsorption of caffeine from aqueous solution [18].

Regarding less conventional methodologies, in the context of a FCT projects, the group has also developed mesoporous carbon materials through a template approach using porous clay heterostructures [19] and porous silica [20].

More recently, sugar-derived activated carbons (Figure 2) were obtained through a two-step procedure involving an initial hydrothermal carbonization for the synthesis of spherical hydrochars, which were further activated aiming the preparation of spherical activated carbons [21-23]. The results of this study illustrate the importance of the choice of the activating agent to tune the carbons properties, since the most commonly used agent, KOH, originated superactivated carbons, but at the expense of the spherical morphology and with very low preparation yields, while the K_2CO_3 mediated process maintained the spherical shape of the hydrochar along with a high developed microporous structure and preparation yields of ~ 50 % [21].

Chemical activation of different biomasses using essentially K_2CO_3 has been explored in the work developed in the AAM group, which allowed to gather a set of carbons with distinct textural, surface and morphological properties, which make them interesting materials for a wide range of possible applications, as it will be briefly described in the following sections.

3. Gas and Liquid phase applications

3.1.1 Gas phase

The first studies of the AAM group regarding the application of activated carbon materials were focused on their use in gas phase adsorption processes.

VOCs adsorption was studied with cork-derived activated carbons, in both powdered and granular forms [4, 8] and also with CMK-3, the carbon replica of ordered mesoporous silica SBA-15 [24].

Natural gas components adsorption was evaluated in one of the first works published by the group in carbon materials [3] and also more recently in a study with the superactivated sucrose-derived carbons [21]. This last work allowed to highlight the importance of the chemical activating agent to assure the enhancement of the carbons performance for a given task. In fact, the carbons obtained by K_2CO_3 activation of sucrose-derived hydrochars presented high performance for landfill gas or biogas upgrade (better than the best performing carbon in the literature) mainly due to their high packing densities and tailored micropore size distributions. On the opposite, the activated carbon obtained by KOH activation of the hydrochar presented a higher apparent surface area (» 2400 m^2g^{-1} vs 1500 m^2g^{-1}) at the expense of the spherical morphology, leading to a material with a very low packing density, and consequently lower adsorption capacity per volume than the K_2CO_3 derived sample. Additionally, the extensive textural characterization allowed to justify the high methane storage capacity in a volume basis of one of the K_2CO_3 derived samples, since the maximum of the micropore size distribution of this sample is centered in the predicted pore width for enhanced methane storage (0.8 nm).

3.1.2 Liquid phase

As it was mentioned the assessment of the carbons as adsorbents of pharmaceutical compounds is nowadays the most important research line of the group, concerning the carbon materials thematic. The relevance of this type of studies is recognized by the scientific community and government entities, since trace level contamination of water bodies with pharmaceutical compounds were detected in the last decades of the XX century [25-27]. Nowadays, monitoring studies all over the world confirm this reality, as the result of the high consumption of prescription and non-prescription medicines combined with the inefficiency of the implemented wastewater treatment technologies to assure an effective barrier to this particular class of compounds. Pharmaceutical compounds are considered emerging contaminants, and to this date the European Parliament has included diclofenac (anti-inflammatory & analgesic), 17a-ethynilestradiol and 17β-estradiol (both contraceptive hormones), in the first watch list of Directive 2013/39/EU, which will allow to gather more monitoring data, thus facilitating the determination of appropriate measures to address the risk posed by these substances.

Since activated carbons adsorption has been considered one of the best available technologies for the removal of pharmaceutical compounds, the research of the AAM group in this thematic has been focused on the adsorption of several pharmaceutical active compounds commonly detected in river water, sea water and some also in drinking water. So far

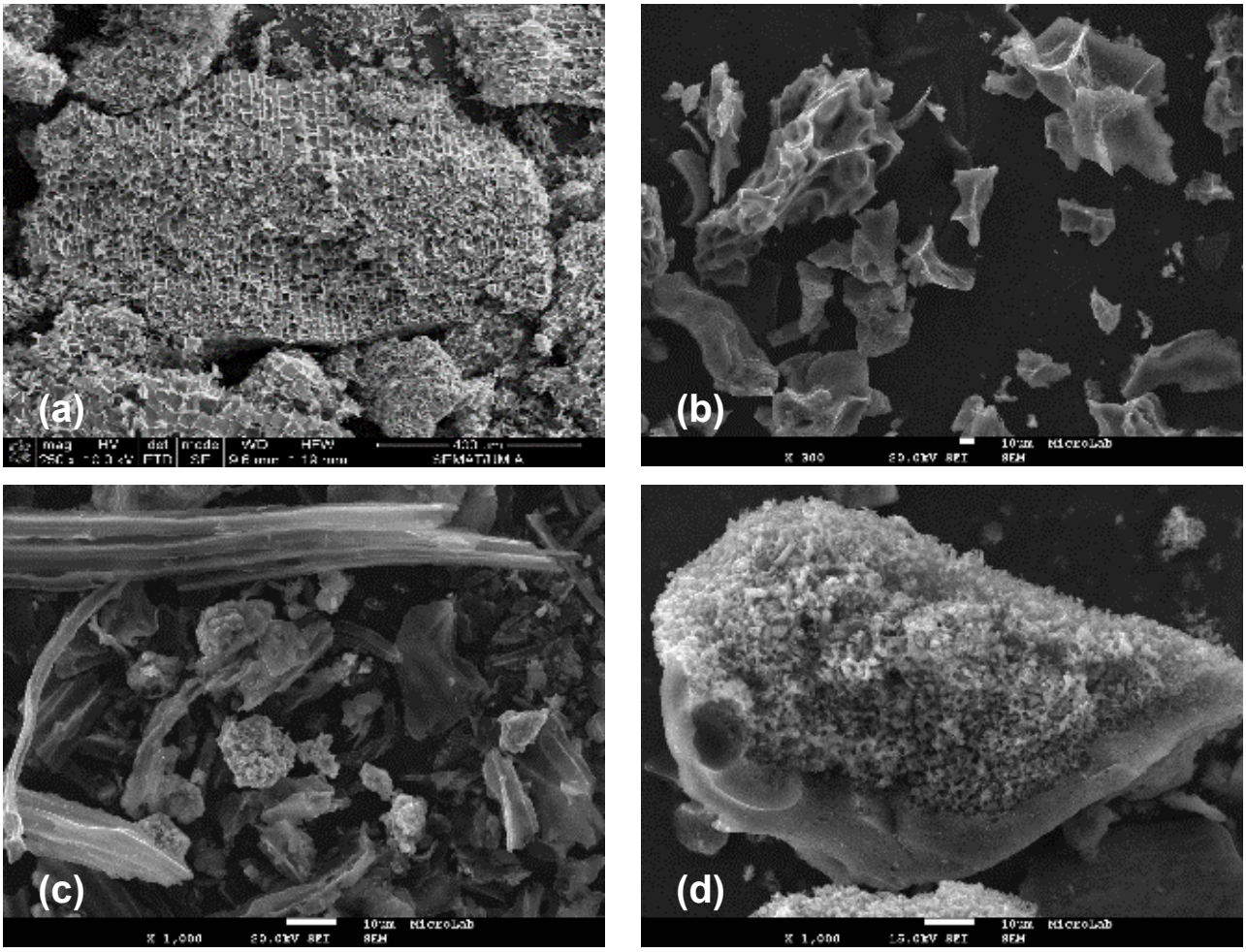


Figure 1. SEM imagens of activated carbons obtained from distinct raw materials: (a) cork - steam activation; (b) sisal - copper loaded and K_2CO_3 activated; (c) fly ash from pine gasification process - K_2CO_3 activated; and (d) rapeseed - K_2CO_3 activated.

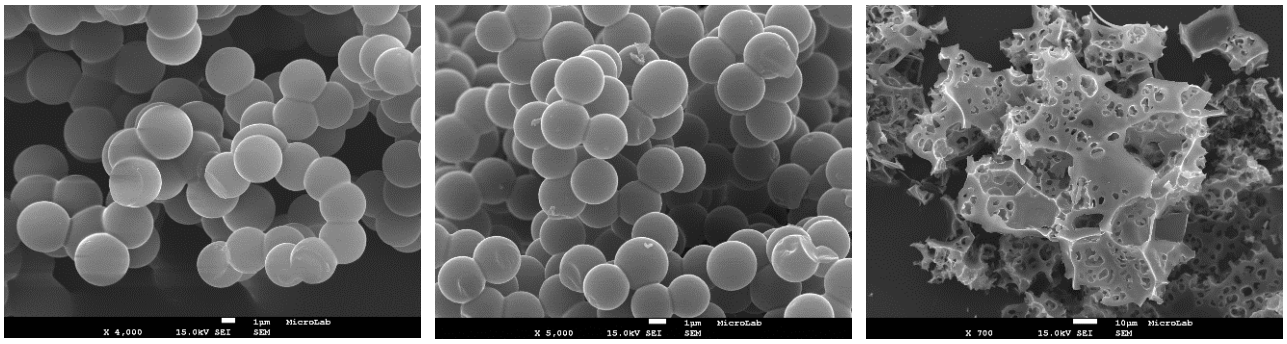


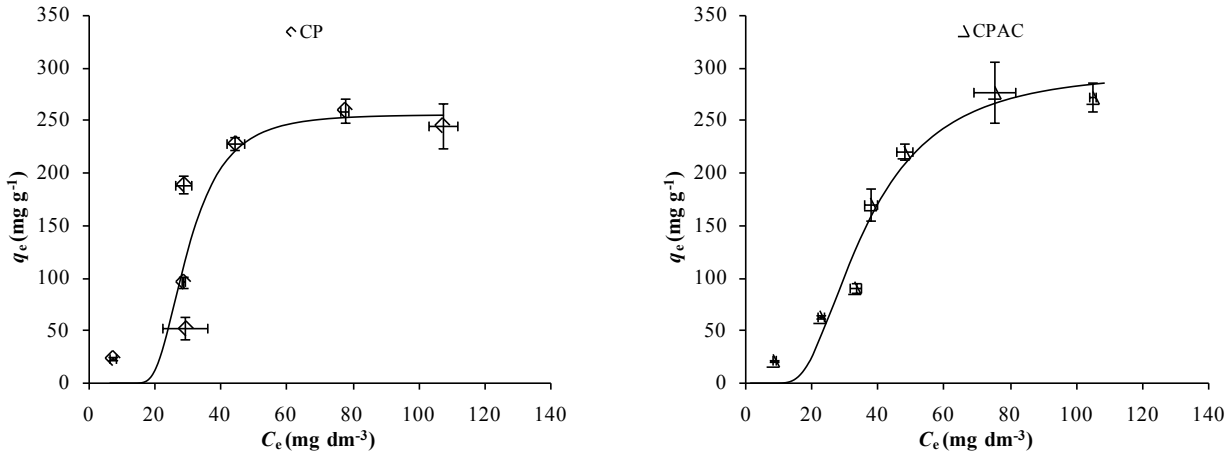
Figure 2. SEM images of (a) sucrose-derived hydrochar, (b) activated carbon obtained by physical impregnation of the hydrochar with K_2CO_3, and (c) activated carbon obtained by KOH activation of the hydrochar (solution impregnation).

studied target compounds were ibuprofen [6, 9, 11, 12, 22, 28], paracetamol [7, 11, 12, 16, 17, 22, 29] and acetylsalicylic acid [11], clofibric acid [5, 11, 22, 28, 30], caffeine [17, 22, 31] and iopamidol [11, 13, 22].

The performance of activated carbons is strongly dependent on the interactions adsorbent-adsorbate, but also on adsorbate-liquid media and adsorbent-liquid media, so the effect of several experimental parameters, such as solution pH, temperature, co-solvent addition and water hardness has also been explored. Some of the most relevant conclusions of the works developed by the AAM group in this thematic are described in the following.

Clofibric acid: is one of the most persistent drug residues detected in the aquatic environment worldwide, and besides being the metabolite and active principle of blood lipid regulators, it also represents the class of acidic pharmaceuticals. The studies evaluating clofibric acid adsorption onto activated carbons revealed that the increase of solution pH always lead to the decrease of the activated carbons performance as a consequence of the deprotonation. The resulting anionic specie has higher solubility/higher solvation energy [5, 30] preventing the interaction of the specie with the carbon surface. As reproduced in Figure 3, the adsorption isotherms of this compound at pH 3 (pH < pK_a) onto cork-based and commercial sample present an uncommon sigmoidal shape revealing the existence of a cooperative process.

Regarding water hardness, our recently published results show that the complexation of the deprotonated specie with calcium ($CaClof^+$ and $CaClof_2$) favors



igure 3. Clofibric acid adsorption isotherms on cork-based (CPAC) and commercial (CP) activated carbons at 30 ºC and solution pH 3.6 (distilled water solution with 10 % methanol (V/V)). Symbols correspond to the experimental data, whereas lines represent the fitting to the Dubinin-Astakhov equation. Error bars are included. Adapted from [5] with permission from Elsevier.

its adsorption onto activated carbons, partially overcoming the decreased adsorption observed at higher pH values [30]. Since this complexation can also occur for other acidic pharmaceuticals, the insights of this work afforded an explanation to results previously reported in the literature for other molecules, and is of crucial importance in the design of improved water treatment processes.

Iopamidol: is an iodinated contrast media more resistant to the biological degradation than other compounds of its class, possibly as a consequence of its branched side chains. This recalcitrant behavior, allied with the high dosages used in clinical exams, leads to its detection in wastewater treatment plants effluent and also in potable water. To study the adsorption of this voluminous pharmaceutical, both lab-made and commercial activated carbons were selected in order to assay materials with distinct pore structures. The results revealed a complex adsorption process characterized by two-step isotherms (Figure 4) that were rationalized considering the textural characterization data along with conductivity measurements and computational calculations. After demonstrating that iopamidol can be adsorbed as a monomer or in the form of aggregates, the uncommon isotherms configuration were interpreted as a consequence of a particular micropore distribution [32], i.e., when the sample does not have micropores with widths between 1.2 and 2.0 nm [13].

Paracetamol: is an over-the-counter medicine whose adsorption onto activated carbons has been extensively explored in the literature [33] and also by the AAM group [7, 11, 12, 16, 17, 22, 29, 34]. The study focused on the temperature dependence of the adsorption of paracetamol onto several activated carbons with distinct pore size networks, revealed all the possible dependences: positive, negative or no influence of the temperature. To understand the data obtained the adsorbed species were back-extracted and identified by ^{1}H NMR spectroscopy, proving that during the adsorption process, paracetamol oligomers are formed. The unexpected increase of adsorption capacity with the temperature was interpreted considering that when carbons do not present a continuous micropore size distribution, the energy associated with the adsorption process is enough to change the paracetamol dimer configuration, from the low energy geometry to a planar form. This evolution results in an accentuated decrease of the critical dimension which enables the access of paracetamol species to the narrow micropores of the activated carbons.

3.2 3. Other applications

Carbon materials developed in the AAM group have

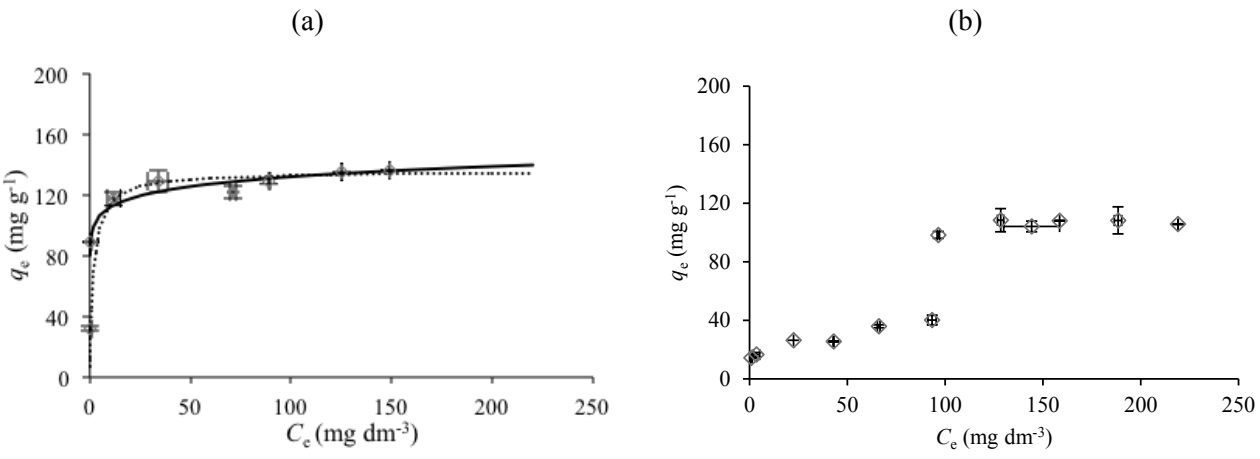


Figure 4. Iopamidol adsorption isotherms on (a) commercial carbon CP, and (b) on sisal-derived carbon S3. Symbols correspond to the experimental data, and in the case of sample CP dotted lines represent Langmuir equation fit and the solid lines the Freundlich equation fit. Adapted from [13] with permission from Elsevier.

been tested as catalysts and catalyst supports in collaboration with several research groups:

- Carbons prepared by template methodology were used as matrixes to anchor copper(II) bis(oxazoline) oxidovanadium (IV) acetylacetonate complexes, being the catalysts tested in asymmetric benzoylation of hydrobenzoin [35], and in the epoxidation of geraniol [36] reactions, respectively. In other studies, copper(II) aza-bis(oxazoline) and Mn(III) *salen* complexes were also immobilized on carbons replicas to prepare catalysts for the reaction of cyclopropanation of styrene [37] and epoxidation of *cis*-cyclooctene [38].
- Commercial and CMK-3 samples were used to prepared bifunctional carbon-supported platinum catalysts for hydroisomerization of *n*-alkanes, namely, *n*- decane [39].
- As-synthesised and copper doped sisal-derived carbons were tested in the photooxidation of phenol, either used alone or mixed with TiO_2 [14, 15].
- Sucrose-derived activated carbons prepared by KOH and K_2CO_3 activation of an hydrochar were recently tested for oxygen reduction reaction [23].

The potentialities of the commercial and lab-made carbons prepared by the AAM group as enrichment phases for sample preparation in analytical chemistry have been also explored, in order to quantify:

- drugs of abuse (morphine and codeine) [40]
- triazinic pesticides (atrazine, simazine and terbutylazine) [41]
- pharmaceutical compounds (ibuprofen and clofibric acid) [42]

The study focused on pharmaceuticals was made using cork-derived carbons using synthetic water, real water samples obtained from a wastewater treatment facility in the region of Lisbon and a biological sample (i.e. urine).

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