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Activated carbons prepared from industrial pre-treated cork: Sustainable adsorbents for pharmaceutical compounds removal ☆

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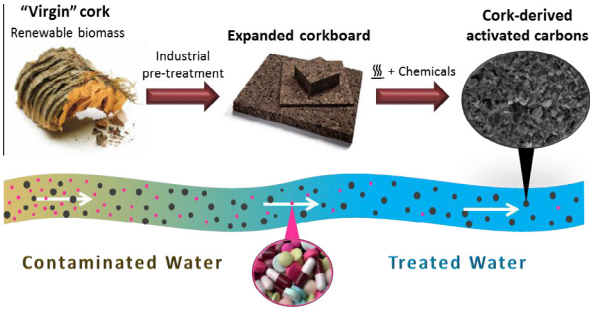
HIGHLIGHTS

- Industrial expanded corkboard was used as activated carbons precursor.
- Carbons with BET area up to 950 $m^2 g^{-1}$ and distinct surface chemistry were obtained.
- Lab-made carbons have adequate properties for pharmaceuticals compounds removal.
- Steam activated sample attains 40–90% removal for the six pharmaceuticals.
- KOH derived carbon has high capacity (174.4 mg g^{-1}) and affinity for ibuprofen.

GRAPHICAL ABSTRACT



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ABSTRACT

Industrial pre-treated cork – granules of expanded corkboard, prepared from renewable biomass – was used for the first time as precursor for the preparation of eco-friendly activated carbons by chemical (K_2CO_3 and KOH) and physical (steam) activation. Samples with different textural (microporosity/micro + mesoporosity) and surface chemistry (acidic/basic) were obtained. In the best compromise between porosity development/preparation yield, apparent surface areas $\geqslant$900 $m^2 g^{-1}$ were attained. Selected samples were assayed as adsorbents for the removal of pharmaceutical compounds (ibuprofen, paracetamol, acetylsalicylic acid, clofibric acid, caffeine and iopamidol). Kinetic results show that the steam activated carbon removes all the pharmaceutical compounds under study with removal efficiencies between 40% and 90%. Ibuprofen equilibrium adsorption isotherms showed that sample chemically activated with KOH at 800 °C presents higher adsorption capacity (174.4 mg g^{-1}) and affinity for this target molecule than the steam activated and commercial samples. The overall results reveal that the lab-made carbons have adequate properties for pharmaceutical compounds removal, the results comparing favourably to those obtained with samples commercialized for water treatment purposes.

☆ The production process of activated carbons prepared from cork transformation products here presented is documented in the Portuguese patent application number 106637.

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1. Introduction

Cork is a renewable ecological material, consisting of the outer bark of the cork oak tree, known botanically as *Quercus suber* L. Cork harvest and subsequent transformation is one of the most important and sustainable industries in the Portuguese and Mediterranean region economies. The traditional use of cork has been highly focused on stoppers for wine bottling, although cork industry produces a series of other materials that span from agglomerates to composites applied in a series of end products, e.g. thermal and acoustic insulation corkboards, flooring panels, etc. The manufacturing of these cork-derived materials produces a set of by-products that have a limited value, as is the case of cork powder, granules of expanded corkboard, among many others. For example, annually around 50 000 ton of cork powder are created worldwide, what corresponds, on average, to 25–30% of the processed cork [1–3].

Cork has already been evaluated as precursor for the preparation of activated carbons [4–9]. However, for the best of our knowledge this is the first study reporting the use of industrial expanded corkboard granules – a cork industry by-product – as activated carbon precursor.

Granules of expanded corkboard are mostly prepared from cork not suitable for cork stoppers production (*i.e.* "falca", virgin cork, higher density cork or too small pieces of cork) which is treated under pressure with steam at mild temperatures (around 350 °C). Compared to the residues commonly used as activated carbon precursors, the granules of expanded corkboard have the advantage of being already partially carbonized.

The prepared carbon samples were further evaluated for the removal of several pharmaceutical compounds from aqueous phase. In the last decades pharmaceutical active compounds (PhACs) have been detected all around the world in sewage, wastewater and even drinking water [10–12]. Although these organic compounds are not included in routine monitoring programs, some of them have been added to the Candidates Contaminant List for prioritizing their regulation in the near future due to their occurrence, potential health effects, and ecotoxicity [13]. In this study, several pharmaceutical compounds from distinct therapeutical classes were selected as target molecules: analgesics (ibuprofen, paracetamol and acetylsalicylic acid); a lipid regulator (clofibric acid); a stimulant (caffeine); and an iodinated contrast medium (iopamidol).

The conventional water treatment technologies (*i.e.* biological treatment) fail to totally remove pharmaceutical compounds from wastewaters, mainly due to the combination of high and continuous loading rates with the low biodegradability of these molecules [13]. The evaluation of more powerful water treatment methodologies, namely the use of activated carbons known as nonspecific adsorbents, is a matter of major importance. In fact, adsorption onto activated carbons has been considered one of the best available technologies for the removal of trace contaminants, including pharmaceutical compounds, having has major drawback the poor economic feasibility. In this context, activated carbons prepared from residues may be a promising option to the activated carbons already in the market since, as it was already demonstrated by some of us, residue-based adsorbents present high adsorption capacities for ibuprofen [6,13–15], paracetamol [14,16,17] or clofibric acid [18].

The aim of the present work was to evaluate an unexplored by-product of the cork industry – granules of expanded corkboard – for the production of activated carbons using distinct activation methodologies, and to test selected samples as adsorbents for the removal of six pharmaceutical compounds from aqueous phase. For comparison purposes activated carbons commercialized for water treatment applications were also assayed.

2. Materials and methods

2.1. Adsorbents preparation

The activated carbons were prepared by physical and chemical activation using as precursor a by-product of cork industry – granules of expanded corkboard (obtained from Amorim Isolamentos, Vendas Novas, Portugal) – from now on denominated pre-treated cork. The industrial production of this material involves a hydrothermal treatment at around 350 °C during 20 min, and it was used as received. The pre-treated cork presents (in wt.%) 11.6% of extractables (8.2% with dichloromethane, 2.3% with ethanol, and 1.1% with water), 0.92% of suberin, 53.4% of lignin and 34.1% of others that include polysaccharides (characterization procedures described in Supplementary data).

For the physical activation with steam, the pre-treated cork (particle size between 2.0 and 2.8 mm) was introduced in a quartz reactor placed in a vertical furnace (Thermolyne, model 21100). The steam was generated in a bubbler half full with distilled water at 90 °C and carried to the sample by a N_2 flow (8 $cm^3\ s^{-1}$). The sample was heated (10 °C min^{-1}) until the activation temperature (800 °C) and kept for 1 h, after what the steam flow was turned off and the sample was cooled to ambient temperature. Before characterization and application in the liquid phase assays the steam activated carbon sample was milled and sieved being collected the fraction with particle size lower than 0.297 mm. This experimental procedure was established after an extensive optimization process where the influence of, for example, distinct cork materials, particle sizes, time and activation temperatures on the textural properties were evaluated.

For the chemical activation, the pre-treated cork (particle size between 0.5 and 1.0 mm) was impregnated in solution with the activating agent in a weight proportion cork:activating agent of 1:1 and 1:2, during 2 h for KOH (Panreac, 85%), and 24 h for K_2CO_3 (Aldrich, 99%), at room temperature. After drying, the mixtures were activated at 700 and 800 °C in a horizontal furnace (Thermolyne, model 21100) during 1 h under N_2 flow of 5 $cm^3\ s^{-1}$ (heating rate of 10 °C min^{-1}). After cooling under N_2 flow, the samples were thoroughly washed, with distilled water until pH 7 to assure the complete removal of all the reaction products, being then dried overnight at 100 °C and stored.

The samples were labelled according to the convention: activating agent and temperature (°C). The activating agent will be designated by S for steam, and by H or C for KOH or K_2CO_3, respectively. The activated carbons prepared with a weight ratio 1:2 were labelled with the ratio between brackets at the end (ex. C700(1:2)). For comparison purposes commercial carbons used in water remediation processes (carbons CP and VP from Quimitejo, and carbons NS and N2 from Norit) were also assayed.

2.2. Nanotextural and chemical characterization

The samples were characterized by N_2 and CO_2 adsorption at −196 and 0 °C, respectively. The N_2 adsorption isotherms were obtained in an automatic apparatus Micromeritics ASAP 2010 while the CO_2 adsorption experiments were made in a conventional volumetric apparatus equipped with an MKS-Baratron (310BHS-1000) pressure transducer (0–133 kPa). In any case, before the isotherms measurement, the samples (∼50 mg) were outgassed overnight at 120 °C under vacuum better than 10^{-2} Pa.