Activated carbons from pine nut production residues for pharmaceutical compounds removal from urban wastewaters in the framework of LIFE IMPETUS project

Ana S. Mestre[a]*, Rui M. C. Viegas[b], Elsa Mesquita[b], M. Campinas[b], Maria João Rosa[b], Ana P. Carvalho[a]

[a] *Centro de Química e Bioquímica and Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal*
[b] *Water Quality and Treatment Laboratory, Urban Water Unit, Hydraulics and Environment Department, National Civil Engineering Laboratory (LNEC), Av. Brasil 101, 1700-066 Lisboa, Portugal*
*Corresponding author: asmestre@fc.ul.pt

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Introduction

LIFE Impetus project (LIFE14 ENV/PT/000739) aims at demonstrating feasible measures for improving the control of pharmaceutical compounds (PhCs) in urban wastewater treatment plants (WWTPs) with conventional activated sludge (CAS) treatment. Namely, strategies based on chemically enhanced barriers, with adsorbent and/or coagulant addition, are underway.

Nuts production generates high amounts of lignocellulosic residues that are known to be good activated carbon biomass precursors, namely due to their high carbon content and hardness. Aiming to contribute to a sustainable and circular economy, sub-products of Portuguese pine nut production – *i.e.* pine nut shell and pine cone – were evaluated as precursors for the synthesis of activated carbon (AC) materials by steam activation. The novel adsorbent materials are being successfully tested, along with commercial counterparts, for the improvement of WWTPs barriers against PhCs in order to search for cost-effective and resource efficient solutions based on existing infrastructures. The tests are being performed with secondary effluents spiked with representative PhCs, thus allowing to evaluate the performance of the novel and commercial carbon adsorbents in competition scenario (*i.e.* inorganic background, organic matter competition and multi-pharmaceuticals).

Experimental

The lab-made ACs were produced by a two-step method starting with carbonization of two biomasses, pine nut shell (PNS) and pine cone (PC), followed by the physical activation with steam [1,2]. The AC materials were labelled according with the precursor and burn-off degree as follows:

PNS77 corresponds to the sample prepared from pine nut shell whose burn-off during steam activation was 77 %.

Characterization of the lab-made and commercial AC materials is being performed by SEM, N_2 and CO_2 adsorption isotherms at, respectively, -196 and 0 ºC, elemental analysis, ash content, determination of the pH at the point of zero charge (pH_{PZC}) and apparent density, FTIR and DRX.

Preliminary kinetic adsorption tests were performed with lab-made and commercial ACs to assess the PhCs and effluent organic matter removals with 1h and 21h contact time. PhCs adsorption isotherms and kinetics assays are being carried out with lab-made and selected commercial ACs (10 mg/dm^3 PAC in kinetic tests, and 5-20 mg/dm^3 in isotherms), in secondary effluent. Three target PhCs (100 μg/dm^3) were spiked in the test waters, diclofenac/DCF (anionic relatively hydrophobic), carbamazepine/CBZ (neutral hydrophobic) and sulfamethoxazole/SMX (anionic hydrophilic). These PhCs were selected as representative of the PhCs (24) addressed in LIFE Impetus project, given the diversity of their properties, as charge and hydrophilicity/hydrophobicity, and for their occurrence in the WWTPs studied in the project. The test waters were characterized in terms of pH, electrical conductivity and organic matter, the latter through dissolved organic carbon (DOC) content, UV absorbance at 254 nm (representing organic compounds with aromatic rings and double C-C bonds) and absorbance at 436 nm (representing color). PhCs were quantified by HPLC-DAD using the method detailed in Viegas et al. [3].

Results and discussion

Both pine nut production residues - PNS and PC - allowed obtaining ACs with BET area values higher than 1000 m^2/g for steam activation burn-off degrees higher than 50 %. The N_2 isotherms of lab-made carbons with burn-off > 50 % and commercial samples are of type I(b)+IV(a) characteristic of micro-mesoporous materials, while materials PNS48 and PC44 have type I(a) isotherms indicating their microporous nature [4]. The hysteresis loops of type H4 observed for all but samples PNS48 and PC44 corroborate the micro-mesoporous features of the majority of lab-made and commercial materials [4].

The textural parameters reveal a linear dependence of the total and mesopore volumes with the steady increase of burn-off during steam activation of PNS-char. When activating PC-char this is also true, but the volumes attained are much lower. In fact, comparing samples PNS77 and PC80, with similar burn-off degrees, it is possible to conclude that PNS allows higher porosity development in micro-mesopore range with the micropore volume being mainly composed by supermicropores. Material PNS77 has similar volumes of supermicropores and mesopores while in material PC80 the mesopore volume is only half of the micropore volume, and 27 % of the micropore volume corresponds to narrower micropores.

To evaluate the effect of activated carbons' pore network composition on their performance for PhC removal in secondary effluent from a WWTP, materials PNS77 and PNS69 where benchmarked against two samples – Norit W35 and Pulsorb WP220 – commercially available for water treatment

purposes. Both commercial materials are steam activated, and carbon Norit W35 from Cabot-Norit is prepared from vegetable raw materials while Pulsorb WP220 from Calgon is a virgin coal-based material. The selection of the two lab-made materials followed the rationale: (i) micropore network mainly composed by supermicropores and mesopore volume > 0.20 cm^3/g; (ii) apparent density > 300 kg/m^3, since it influences ACs settleability during removal by coagulation, flocculation and sedimentation processes in WWTPs; and (iii) assuring global preparation yield between 5 and 10 %. As mentioned the volume of mesopores is a critical parameter when envisaging ACs application in water treatment to assure adsorption kinetics in competition environments compatible with hydraulic residence time of the treatment processes in the available WWTPs infrastructures. Moreover, the pore size distribution has to be considered, and, like commercial ACs, both selected lab-made ACs have mesopores up to 30 nm. The two commercial samples were selected considering the first above-mentioned criteria along with the request of presenting basic character and competitive price for delivery in Portugal, among other requisites.

Preliminary adsorption kinetic assays were performed with the two commercial and the two PNS-derived ACs (10 mg/dm^3), for 1 h and 21 h, representing typical AC contact times in the secondary clarifier and in the bioreactor of a WWTP, with the three target PhCs spiked (100 μg/dm^3) to the secondary effluent. The results show that the lab-made material PNS77 is the best performing as it presents the higher capacity of the tested ACs, both for the three target PhCs and for the competing organic matter, as expected considering the characterization results. The removal efficiencies of this sample for shorter contact times compare favorably with those of the best performing commercial AC – Pulsorb WP220.

In competition scenario, and regardless the contact time or the ACs used, SMX is consistently less removed than CBZ or DCF most probably due to its hydrophilic character, while the higher removal for CBZ is most probably related with its neutral net charge and higher hydrophobic character. Kinetic and equilibrium data as well as the characterization of the micropore size distribution and surface chemistry of the adsorbents will be used to support a deeper analysis of the adsorption process namely relating with the properties of the three PhCs and their interactions with the complex water matrix.

Conclusions

Pine nut production residues - PNS and PC - proved to be promising precursors for the synthesis of ACs by steam activation since micro-mesoporous materials with BET areas higher than 1000 m^2/g and high apparent density were obtained. Preliminary assays showed that the material PNS77 outperformed two commercial ACs for wastewater treatment in the removal of three PhCs and organic matter from secondary effluent in competition scenario. Ongoing studies regarding liquid phase assays and materials characterization will allow gathering experimental data to support a deeper analysis of the complex adsorption process.

References
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