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ENGINEERED ACTIVATED CARBONS FOR IMPROVED RECALCITRANT PHARMACEUTICALS REMOVAL DURING URBAN WASTEWATER TREATMENT: LIFE IMPETUS PROJECT

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Introduction

The improvement of pharmaceutical compounds (PhCs) removal during wastewater treatment is the smartest option to avoid their release into the environment, since conventional treatments fail to control several PhCs that end up in recipient water bodies. LIFE Impetus project (LIFE14 ENV/PT/000739) aims to tackle this problem by developing and testing novel powdered activated carbons (PACs) for improved control of PhCs in urban wastewater treatment plants (WWTPs) with conventional activated sludge (CAS) treatment.

PAC adsorption is one of the best available technologies for PhC control, yet its cost-efficiency and sustainability calls for environmental-friendly PACs and process design in a circular economy framework. Novel PACs were prepared using locally available biomass – pine nut production residues – and were benchmarked against commercially available products for the adsorption of a short-list of representative PhCs spiked in synthetic inorganic matrix (single-solute conditions) and in real wastewater (competitive conditions) from a WWTP. The target PhCs were selected considering their worldwide occurrence and persistence in CAS-WWTP effluents, results validated in the two LIFE Impetus case study plants, and diversity in adsorption key-properties: sulfamethoxazole/SMX (anionic, hydrophilic), diclofenac/DCF (anionic, relatively hydrophobic) and carbamazepine/CBZ (neutral, hydrophobic).

Materials and Methods

The lab-made PACs were produced by the steam activation of the carbonized pine nut shell (PNS) and pine cone (PC) residues. The carbonization was performed during 1 h at 400 ºC under N_2 flow (5 cm^3/s). Before the activation, the PNS-char and PC-char were crushed and sieved to collect the fraction with particle dimension < 0.148 mm. For the activation, 1 g of char was treated during 1 h at 800-900 ºC in a N_2 flow (3-5 cm^3/s) with water vapour provided by a bath at 70 ºC[1,2]. The PAC materials were labelled according to the precursor and burn-off degree, *e.g.* PNS77 corresponds to the sample prepared from pine nut shell whose burn-off during steam activation was 77 %. The lab-made and the commercial PAC materials were characterised by SEM, N_2 adsorption isotherms at -196 ºC, elemental analysis, ash content, pH at the point of zero charge (pH_{PZC}) and apparent density.

Preliminary tests of adsorption kinetics were performed in spiked bioreactor mixed liquor and in

secondary effluent water samples from a CAS-WWTP (competitive adsorption conditions), with lab-made and commercial PACs (10 mg/dm^3), to assess the removal of the three target PhCs (100 µg/dm^3, SMX, DCF and CBZ) with 1 h and 21 h contact time. For comparison purposes, the single-solute adsorption of each PhC (2.5 mg/dm^3) onto each PAC (15 mg/dm^3) was also assayed in synthetic inorganic matrix, and the removals after 1 h and 6 h contact time were determined. PhC adsorption isotherms were also carried out with lab-made and selected commercial PACs, in secondary effluent and mixed liquor. The test waters were characterised for 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 colour). PhCs were quantified by HPLC-DAD as detailed in Viegas et al.[3] or by molecular absorption spectrophotometry, in the case of single-solute adsorption assays.

Results and Discussion

The PNS proved to be the most promising precursor for the synthesis of high performing PACs. PNS-derived PACs attained BET areas higher than 1400 m^2/g gathering a hierarchical pore network composed of supermicropores and mesopores with widths up to 40 nm. The PNS-PACs present slightly more basic pH_{PZC} values than the commercial counterparts (9.6-10.1 vs 7.4-8.0) and have similar elemental composition, ash and moisture content, as well as adequate apparent density values (370 – 500 kg/m^3).

The performance of two commercial (Pulsorb WP220 and Norit W35) and two lab-made (PNS69 and PNS77) PACs for the removal of the target PhCs spiked in synthetic inorganic matrix and in secondary effluent is presented in **Figure 1** (top and middle). Norit W35 and PNS77 were also tested with mixed liquor to access the biomass particle effect on PhC adsorption, **Figure 1** (bottom). Regardless of the system and contact time, the removal efficiency trend is CBZ > DCF > SMX, in line with the increase of the PhC hydrophilic character. SMX is the PhC whose adsorption is more hindered by the presence of other PhCs and/or effluent organic matter and biomass. Moreover, the mixed liquor biomass further reduces the PhC adsorption at least for longer contact times.

The carbon PNS77 outperforms the commercial counterparts for the removal of the target PhCs in spiked secondary effluent, attaining one and a half times the SMX removal by the best performing commercial PAC (30 % vs 19 %).

Conclusions

A pine nut shell derived PAC obtained by steam activation (PNS77) proved to be the best performing material for the less-adsorbing PhC tested (SMX) or as good as the best commercial PAC for the other PhCs targeted, presenting the highest adsorption capacity in real wastewaters. Further, by modelling the lab results it is shown that 80 % removal of the target PhCs would be achieved dosing ~ 15 mg/dm^3 PNS77 to the CAS bioreactor or ~ 10 mg/dm^3 to the secondary effluent (in a post-treatment step).

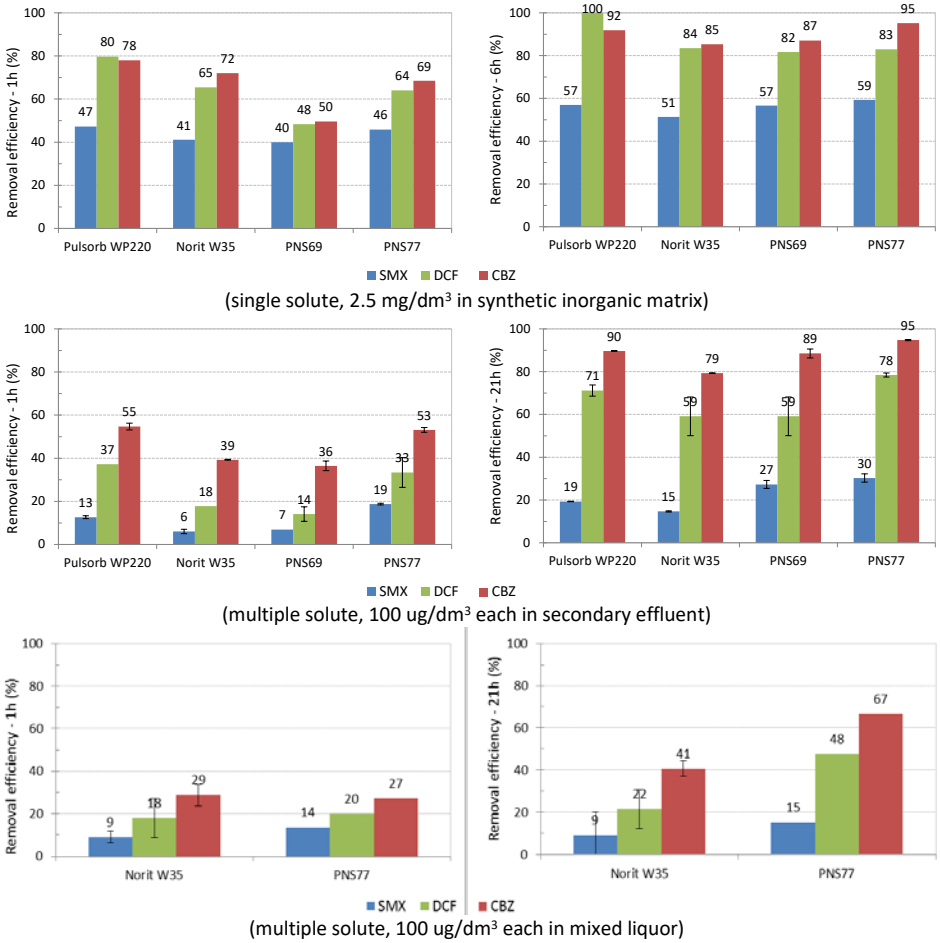

Figure 1. Removal efficiencies of the four tested PACs for the target PhCs (top) in synthetic inorganic matrix spiked with 2.5 mg/dm^3 of each PhC in single-solute conditions and (middle) in secondary effluent spiked with 100 µg/dm^3 of each PhC in multi-solute conditions and of Norit W35 and PNS77 (bottom) in mixed liquor spiked with 100 µg/dm^3 of each PhC in multi-solute conditions

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