Modelling and predicting the potential application of new waste-derived activated carbons for controlling pharmaceutical compounds in conventional wastewater treatment

Rui M.C. Viegas*, Elsa Mesquita*, Margarida Campinas*, Ana S. Mestre**, Ana P. Carvalho**, Maria João Rosa*

* Water Quality and Treatment Laboratory, Urban Water Unit, Hydraulics and Environment Department, LNEC – National Civil Engineering Laboratory, Lisbon, Portugal; ** Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa, Portugal

Introduction
Sustainable water services demand a circular economy-driven operation of wastewater treatment plants (WWTPs), enabling water reuse and using renewable materials. LIFE Impetus project (2016-2019) aims at demonstrating feasible improvement measures to control pharmaceutical compounds (PhCs) in urban WWTPs with conventional activated sludge treatment (CAS), using resource efficient processes and low capex solutions, i.e. chemical enhancement with new waste-based powdered activated carbons (PACs). This paper addresses the potential application of new waste-derived PACs for PhC removal in CAS-WWTPs during the secondary treatment, using bench-scale tests to assist PAC adsorption demonstration at pilot and full scales. PAC direct application to CAS reactor lacks in practice to fully understand its advantages (high contact times and PAC concentration due to sludge recirculation) and limitations (PAC blocking by the biomass in the mixed liquor). The results of PhC adsorption in mixed liquor and secondary effluent are used to model and simulate PAC addition into CAS reactor vs. in a post-secondary step, and to elucidate the impact of mixed liquor on PAC adsorption efficiency.

Materials and Methods
A new carob-based PAC was prepared by steam activation (Mestre et al. 2014) of the solid recovered from the carob pulp acid effluent washed until neutral pH. PAC textural and surface chemistry properties and morphology were assessed. PhCs were selected for their occurrence in the case study WWTPs and diversity in properties: diclofenac/DCF (anionic relatively hydrophobic), carbamazepine/CBZ (neutral hydrophobic) and sulfamethoxazole/SMX (anionic hydrophilic). Adsorption isotherms (5-20 mg/L PAC) and kinetics (10 mg/L PAC) assays of these PhCs spiked (100 µg/L) in mixed liquor and in clarificic mixed liquor were conducted. The water
inorganic and organic matrices were characterised (including dissolved organic matter (DOM) fractionation) and the PhCs were quantified by HPLC-DAD. The adsorption results were modelled with the Freundlich isotherm equation and the Homogeneous Surface Diffusion Model (HSDM) (Campinas et al. 2013).

Results and Conclusions
The carob-derived PAC is a 50/50 micro-mesoporous material with alkaline character (pH\text{PZC} 8.0), with a mixture of fibers and nonspecific shape particles. The WWTP mixed liquor DOM is predominantly hydrophobic, thus of high adsorption competing nature. The results showed that the adsorption capacity follows the trend CBZ > DCF > SMX whereas the adsorption rate trend is CBZ ≈ DCF > SMX. Further, the particulate matter (mixed liquor vs. clarified mixed liquor data) slightly reduces the PAC capacity towards the hydrophobic CBZ (19%) and DCF (9%) and does not affect its capacity towards SMX (hydrophilic) nor the adsorption rates.

The results allowed calibrating the Freundlich model and the HSDM and predicting the PAC removal efficiency towards the PhCs in their naturally occurring concentrations. The projections show that to achieve the same removal of the target PhCs only slightly higher PAC concentrations are required if the PAC is dosed in the bioreactor, e.g. 21 mg/L are required to achieve 80% removal of diclofenac vs. 16 mg/L if the PAC is dosed in a post-secondary step. These results are assisting the operation of the pilot prototypes installed at the project WWTPs, aiming at minimizing its dosing at full scale.

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References