The potential and challenges of activated carbon technologies for controlling emerging contaminants in water treatment and reclamation

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Introduction

The presence of emerging contaminants (ECs) in drinking water and treated wastewaters is a recent raising concern in water and wastewater treatment plants (WTPs and WWTPs), as some compounds were already implied in risk cancer increase, bacterial resistance to antibiotics and reproductive abnormalities in aquatic organisms. While many ECs are directly introduced by anthropogenic actions, e.g pharmaceuticals and pesticides, others are natural responses to these actions, such as cyanotoxins produced by toxic blue-green algal blooms in surface waterbodies, both cases aggravated by climate change. Besides the environmental and chronic health risk at low concentrations in which they often occur, they have a partial or total recalcitrance towards conventional treatments at WTPs and WWTPs since many of these contaminants are water soluble, polar to semi polar, organic compounds of intermediate to low molar weight.

The control of ECs in WTPs and WWTPs is therefore a priority that requires the assessment of the risks involved, the improvement of the current barriers and, if necessary, their rehabilitation with advanced treatment technologies. Activated carbon-based technologies have been considered one of the best available solutions for they minimize the by-products formation, but their sustainability and cost-efficiency still calls for activated carbon development and process optimization. The main challenges for activated carbon full-scale application for ECs control are: 1) the selection of a cost-effective application (powdered or granular activated carbon - PAC or GAC); 2) the use of tailored, green and cost-effective carbons; 3) the minimisation of organic matter, biomass or coagulant competition/interference with adsorption; 4) to insure an effective contact time and mixing conditions in order to take advantage of the activated carbon full adsorption capacity; 5) to insure an effective retention of PAC particles; 6) to extend the lifetime of GAC filters.

To overcome these challenges and upgrade WTPs/WWTPs for ECs control our research group is working with several environmental applications of activated carbon based technologies, *per se* or coupled with biodegradation and membrane processes. The research involves lab-scale trials with synthetic and real waters, characterisation of competing organic matter (content and nature), modelling, pilot-scale development and demonstration in prototypes and at full-scale. This communication presents examples of applications and main achievements. Emphasis is given to: i) chemical enhancement of conventional wastewater treatment using "green" PAC; ii) hybrid PAC/ low-pressure membrane processes for advanced drinking water production and water reclamation aiming at water reuse; iii) biologically active carbon (BAC) filtration for drinking water treatment.

Experimental

i) A new carob-based activated carbon was developed and supplied, according to Mestre et al. [1], and tested with three target pharmaceutical compounds (PhCs): carbamazepine (CBZ), diclofenac (DCF) and sulfamethoxazole (SMX). PhCs adsorption isotherms and kinetics assays (10 mg/L PAC in kinetic tests and 5-20 mg/L in isotherms) were performed in mixed liquor (MxL) and clarified mixed liquor (clarified MxL) of two Portuguese WWTPs spiked with 100 µg/L of each PhC. It was intended to simulate PAC addition into conventional activated sludge (CAS) reactor vs. in a post-secondary step to elucidate the impact of biomass on PAC adsorption efficiency. Modelling was used to predict the removal efficiency of the PAC towards the three PhCs in pilot and full scales.

ii) Hybrid processes, integrating PAC adsorption with low-pressure membrane filtration such as microfiltration (MF), ultrafiltration (UF) or loose nanofiltration (NF) were tested at lab and pilot-scales with real (waste)waters. PAC/MF with ceramic membranes was demonstrated at pilot scale during 1.5 years in a Portuguese WTP. The process was tested with different waters targeting the removal of a wide range of contaminants, from aerobic endospores, as indicators of protozoan oo(cysts), to natural organic matter, microcystins, pesticides (10) and PhCs (22). PAC/UF was investigated at lab scale for removing five pharmaceutical and personal care products (PPCPs) from wastewater. Adsorption kinetics, standalone UF and PAC/UF experiments were performed focusing on PPCP adsorption as a function of their characteristics and organic matter competition. PAC/NF was tested at lab scale with wastewater aiming at water reuse. Four PhCs were targeted based on their adsorption behaviour (CBZ, DCF, SMX and atenolol) and on the compounds detected in a Spanish WWTP and in the respective receiving waterbody. Adsorption kinetics, isotherms and PAC/NF experiments were performed and the benefit of PAC recirculation from PAC/NF to an upstream process was also assessed.

iii) Long term (3-months) lab scale tests were performed with F400 GAC column filters with and without biological activity to evaluate the removal of cyanotoxins (microcystin-LR) and natural organic matter (tannic acid) from water and to assess the effect of established biofilm/microbiota in the overall treatment process [2].

A modelling approach was developed integrating adsorption kinetics and isotherm models. Adsorption isotherm data is modelled with the Freundlich and Fritz & Schlunder models and the HSDM is used for fitting adsorption kinetics data. In the former, modified Freundlich constants, derived from K_F and 1/n obtained in single-solute adsorption isotherms, are determined. For HSDM, the k_f and D_s constants are determined. Upon calibration, the integrated modelling resulting from the combination of the 2 models [3,4] has the predictive ability needed to forecast the contaminant removal as a function of PAC doses and contact time. Furthermore, the parameters Ds, K_F and 1/n can further be used to describe and understand the competitive adsorption [3].

Results and discussion

i) Chemical enhancement of conventional wastewater treatment using "green" PAC options: comparing the adsorption in clarified mixed liquor and in mixed liquor, only minor interference of the biomass was observed in PAC adsorption rate and capacity towards the PhCs, with average differences lower than 10% (Figure 1), which is probably counterbalanced by the high contact times possible in bioreactors (10-24h vs. 1h) and PAC higher concentration due to sludge recirculation. Furthermore, the lab results will allow calibrating the HSDM and predicting the removal efficiency of the PAC towards the three PhCs in pilot and full scales, Further adsorption assays are being carried out with different waste-based PACs and the best feasible option will be tested at pilot scale.

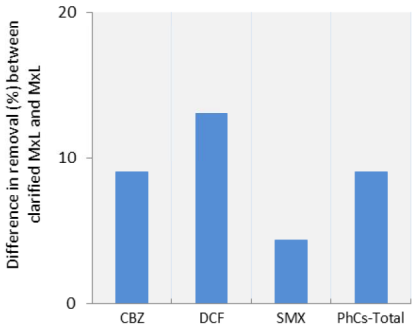

Figure 1. Biomass interference with target PhCs adsorption given by removal differences in mixed liquor and clarified mixed liquor.

ii) Hybrid adsorption/low pressure membrane processes for advanced drinking water production and water reclamation aiming at water reuse: During PAC/MF demonstration in a Portuguese WTP overall high removal of dissolved microcontaminants was observed (up to 98%), with 83% to ≥ 98% total-PhCs, 78%-98% total-pesticides and > 85% microcystin-LR using 2-18 mg/L PAC [5]. A commercial fine and mesoporous PAC was used (< 15 µm), granting high adsorption kinetics while the ceramic membrane assured a high disinfection and PAC efficient retention. This process allowed EC removals 20% higher than conventional treatment technology, using similar PAC doses, with much lower turbidity and aluminium residuals, smaller residual particulate organic matter and endospores and without PAC fines in the treated water. Also, in tests

carried out with different fluxes and PAC doses, no negative impact of PAC addition on membrane fouling was observed, one of the most sensitive points of PAC/membrane technologies [6].

In a PAC/UF lab study with five PPCPs was concluded that adsorption kinetics depended on PPCP hydrophobicity and charge (mostly hydrophobicity for neutral PPCPs) whereas the adsorption capacity was in agreement with PPCP hydrophobicity for all microcontaminants and conditions studied [7]. For all conditions and microcontaminants, PPCP uptake exhibited a sigmoid curve with log Kow, with a turning point at 2.2–2.6. For real applications, meso- and highly microporous PACs are recommended, and the dose should target the PPCPs with log Kow < 2.6.

In PAC/NF studies with 4 PhCs results showed a significant (100 times) reduction in PAC adsorption capacity in secondary effluent when compared to its adsorption from a mineral matrix, specially impacting the hydrophobic compounds. It was concluded that there was a strong competition of the effluent organic matter and in particular of their hydrophobic acids fraction, which represented 46% of the dissolved organic carbon content. The PAC/NF results showed high removals of the target PhCs (68% total) with higher removals of the cationic hydrophilic atenolol (89%) [8]. Pilot-scale spent PACs, after 30-120 min contact time, were further assayed to assess the benefits of its recycling in the process, namely to the membrane bioreactor (MBR) upstream. The adsorption kinetic assays showed a further adsorption capacity of the PAC, as suggested by the textural characterisation of the spent PACs performed, which showed an average available volume of 61%, corresponding to 54% of micropores and 72% of mesopores.

iii) BAC filtration for drinking water treatment: Biological activity established in BAC filters minimized organic matter (tannic acid - TA) removal efficiency losses with time, since BAC filters with 3-4 months (11000 Bed Volumes) have performances identical to new activated carbon filters (with 7-8 days of operation) (Figure 2, left side). Filters continuously feed with high MC-LR levels (40-50 µg/L) seemed to reach a stationary MC-LR breakthrough of 10-20% that was kept at least for 3 months, due to biological activity (Figure 2, right side) [1].

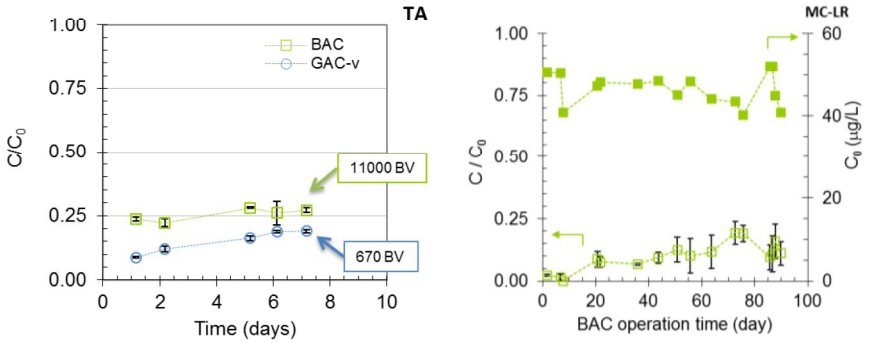

Figure 2 Comparison of tannic acid (TA) breakthrough in BAC and virgin GAC (GAC-v) filters (left side). Stationary breakthrough of microcistin-LR (MC-LR) in BAC filters (right side).

Conclusions

Activated carbon-based technologies have proven a huge potential for controlling ECs in water treatment and water reclamation. Nevertheless, their sustainability and cost-efficiency still calls for activated carbon development and process optimization. Since ECs show highly diversified physicochemical properties it is important to develop methodologies for selecting representative contaminants, to fully characterise the inorganic and organic matrices of the waters, as to understand and anticipate competing factors, namely through modelling, and, thus, tailor the technology for each application, water and target contaminants-specific. Meso- and highly microporous PACs have shown to more effectively control ECs and minimise competing effects. When dosed in conventional WTPs and WWTPs PAC with higher density, thus coarser, should be used and PAC recirculation in the process should be envisaged. Conversely, in hybrid low-pressure membrane processes, PAC is fully retained and thus finer PAC can be used, thus promoting faster kinetics. Granular activated carbon, besides being an excellent adsorbent material, has proven to be a good support media for the attachment and growth of microorganisms and biofilm development, thus promoting the regeneration of the activated carbon.

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