Using activated carbon based technologies for the removal of emerging contaminants from water/wastewater – UQTA (LNEC) Projects

El uso de tecnologias basadas en carbón activo para la eliminación de contaminantes emergentes de aguas /aguas residuales – Proyectos UQTA (LNEC)

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Abstract

An overview is presented on the projects that are being carried out by Water Quality and Treatment Laboratory team of LNEC which use activated carbon based technologies for treating water or wastewater. Emphasis is given to the chemical enhancement of conventional wastewater treatment using "green" powdered activated carbon options, hybrid adsorption/ membrane processes or biologically active carbon (BAC) filtration which are considered promising options for upgrading the water/wastewater treatment plants for controlling emerging contaminants such as pharmaceuticals, pesticides and cyanotoxins.

Resumen

Este artículo presenta una visión general de los proyectos que se están llevando a cabo por nuestro equipo en el Laboratorio de Calidad y Tratamiento del Agua de LNEC que utilizan tecnologías basadas en carbón activado para el tratamiento de agua o aguas residuales. Se da énfasis a la mejora química del tratamiento convencional de aguas residuales utilizando soluciones "green" con carbón activos en polvo y a los procesos híbridos adsorción/membrana o filtración con carbón biológicamente activo (BAC), que se consideran opciones prometedoras para la mejora de las plantas de tratamiento de agua/ aguas residuales en el control de contaminantes emergentes, tales como productos farmacéuticos, pesticidas y cyanotoxinas.

1. The problem – emerging contaminants

Anthropogenic pressures and global climate change are putting increasing stress on Europe's freshwater resources, being responsible for sharp variations of raw water availability and quality, and for the degradation of water sources by emerging contaminants (ECs). Besides defying drinking water management, water scarcity and asymmetric space-time distribution is also driving many countries to seek non-conventional water sources. WWTPs play therefore a crucial role both in the safeguard of the drinking water sources and the production of an alternative water source, the treated wastewater which, depending on its use(s), may require an increased level of water treatment. Two of the greatest challenges for WWTPs in a near future are the monitoring and reduction of trace pollutants and the adaptation/development of existing/ new wastewater treatment technologies in order to minimize costs and optimize resource consumption [1-2].

Emerging contaminants include: personal care products and pharmaceuticals, increasingly used by the population and not fully retained by the wastewater treatment plants; pesticides from agriculture and cyanotoxins produced by toxic cyanobacterial (blue-green algal) blooms in surface waterbodies. In the last years, regulators and the general public have been expressing an increased concern regarding the presence of emerging contaminants in drinking water and treated wastewaters, since some of the compounds are implied in risk cancer increase, bacterial resistance to antibiotics and reproductive abnormalities in aquatic organisms, based on which a more restrictive legislation is expected in a near future.

For microcystin-LR (MC-LR), a potent hepatotoxin which is one of the most frequently detected cyanotoxin in toxic bloom events [3], WHO established a guideline value of 1.0 μg/L in drinking water [4], limit also adopted by the Portuguese legislation (DL 306/2007). Nevertheless, most of the other ECs, particularly pharmaceuticals, are not yet legislated due to the lack of ecotoxicity data (studies not yet performed or not conclusive) and analytical limitations. Besides the risk, these contaminants share a resistance, partial or total, to conventional treatments at the water treatment plants (WTPs) and urban wastewater treatment plants (WWTPs) since they are often water soluble, polar to semipolar, organic compounds, of intermediate to low molar mass, commonly present in very low concentrations (pg/L to μg/L range).

The control of ECs in WTPs and WWTPs is therefore a priority goal that requires the assessment of the risks involved, the improvement of the current barriers and, if necessary, the (W)WTP rehabilitation with advanced treatment technologies [2]. In this context, in Water Quality and Treatment Laboratory (UQTA) of LNEC several treatment studies pursuing eco-efficient barriers against microcontaminants are being conducted, namely the optimization of the current sedimentation steps in wastewater treatment and the development of advanced treatment essentially based on adsorption, hybrid adsorption/membrane processes and/or biodegradation. The studies are integrated in several European Projects which will be presented in the following sections. Although these projects contain several complementary actions, they will be purposely presented in the perspective of activated carbon interest.

2. Activated carbon for improving conventional

Figure 1. LNECs lamellar sedimentation prototype which will be adapted for pilot trials in two WWTPs (LIFE Impetus).

Figura 1. Prototipo lamelar de sedimentación que será adaptado para ensayos piloto en duas plantas de depuración de aguas (LIFE Impetus).

Figure 2. PAC/MF prototype designed by LNEC and installed in Alcantarilha WTP (LIFE Hymemb).

Figura 2. Prototipo PAC/MF instalado en la planta de tratamiento de agua de Alcantarilha (LIFE Hymemb).

wastewater treatment - LIFE Impetus

LIFE Impetus "Improving current barriers for controlling pharmaceutical compounds in urban wastewater treatment plants" started in January 2016 and will be developed during 3.5 years. It is coordinated by LNEC and has the participation of two wastewater management entities - Águas do Algarve, S.A. and EPAL, SA., one company – EHS Environment and Regional Development Consulting, Lda., and three universities – Algarve University and Science and Pharmacy Faculties of Lisbon University (FCUL and FFUL).

The project aims at demonstrating feasible improvement measures to enhance the removal of pharmaceuticals (PhCs) removal in urban WWTPs with conventional activated sludge (CAS) treatment, the most common biological process in urban WWTPs. The project was developed in the logic of resource efficiency, developing cost-effective solutions based on the existing infrastructures (many of them recently built), as new investments are probably limited in the near future due to economic constraints.

LIFE Impetus involves a 3-year field test in two Portuguese CAS-WWTPs in water stressed regions (Lisbon and Algarve) for demonstrating improved operation strategies and the chemical enhancement of existing barriers for PhC control. Concerning this last one, different clarification strategies will be demonstrated, at pilot scale, including the use of absorbents and coagulants for improving the clarification process, comparing commercial and newly developed materials using natural wastes and plants.

In an early phase, the project includes the preparation and characterization of new adsorbents prepared from local vegetal wastes, cork and carob, and their lab testing to assess the adsorption kinetics and capacity for a short list of target PhCs in synthetic waters. The activated carbons will be prepared and characterized at FCUL, where the screening and the lab-scale assays will also be carried out. Adsorbent(s) with adequate performance will be further tested by LNEC team at lab-scale for the target PhC removal from real wastewaters and used in demonstration trials at pilot-scale.

Pilot scale tests will be conducted with 3 sedimentation prototypes which will be constructed or adapted (Figure 1) and installed in Beirolas WWTP (Lisbon) and Faro Noroeste WWTP (Faro-Algarve): one rapid mixer/ lamellar sedimentation prototype for the primary clarification step in Beirolas WWTP, and two conventional sedimentation prototypes for the secondary clarification steps in both WWTPs. Pilot trials will be performed during 18 months in several operating conditions allowing to demonstrate the impact of coagulant and activated carbon addition in the quality of the wastewater resulting from primary and secondary clarification.

3. Activated carbon for hybrid adsorption/ membrane processes – LIFE Hymemb and LIFE aWARE

LIFE Hymemb Project (2014-2016) "Tailoring hybrid membrane process for sustainable drinking water production" is coordinated by LNEC and has the partnership of the water company, Águas do Algarve S.A. The project involves a 2-year field test of a powdered activated carbon/ceramic microfiltration (PAC/MF) prototype (Figure 2), designed by UQTA team, in Alcantarilha WTP, to demonstrate the process effectiveness, reliability and efficiency, and ensure a meaningful benchmarking between the advanced and the conventional water treatment processes.

Figure 3 shows the target contaminants of this project as well as the concept of the hybrid PAC/MF process, which integrates the advantages of both low pressure membrane processes and PAC adsorption, and minimizes some of their disadvantages. Low-pressure membranes are not able, unless by adsorption onto the membrane, to retain microcontaminants (e.g. pharmaceuticals, cyanotoxins), but are a safe barrier against (oo)cysts and bacteria and allow a total removal of particles (< 0.1 NTU), including PAC of smaller size (< 10 µm) than usual and thus with faster adsorption kinetics. On the other hand, PAC is able to improve the removal of microcontaminants while enabling to control the irreversible membrane fouling [5].

Adsorption to activated carbon is therefore the key-step of adsorption/membrane processes for the removal of low molar mass (< 300 Da) and intermediate molar

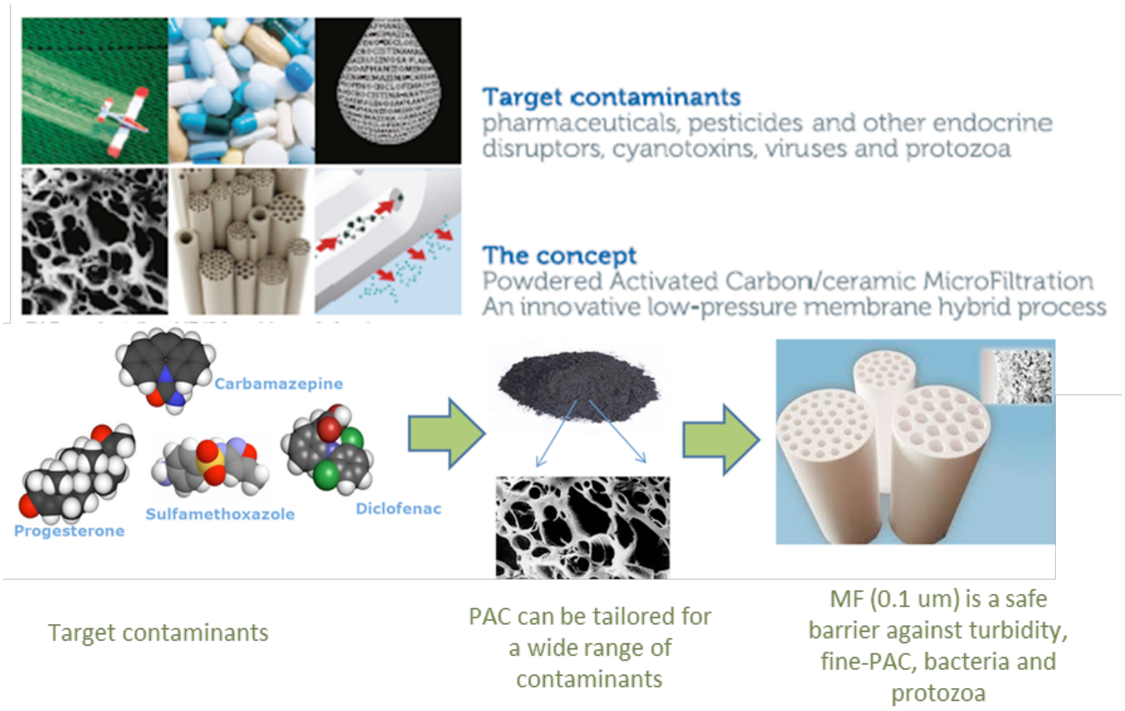

Figure 3. The target contaminants and the concept of LIFE Hymemb project.

Figura 3. Los contaminantes objetivo y lo concepto de proyecto LIFE Hymemb.

mass contaminants (300-1000 Da), and also for viruses, and should allow the adaptation to space-time specificities, presenting solutions for a wide range of applications. For such purpose, one of the innovation pillars of this project is the "tailoring", i.e. the adjustment of PAC type and dosing to specific contaminants and the high flexibility of membrane process. Therefore, pretreatment is easily adjustable to water quality (PAC and/or coagulant addition and pH adjustment), low-pressure membranes may work with or without PAC addition, in dead-end operation, minimizing the operating costs, or in cross-flow when/if necessary (semi dead-end operation).

The selection of the powdered activated carbons adequate to control the project's target contaminants through PAC conventional addition and the hybrid PAC/MF process followed a 3-step methodology developed in UQTA/LNEC [6]: i) selection of a short-list of ECs representative of the target contaminants;

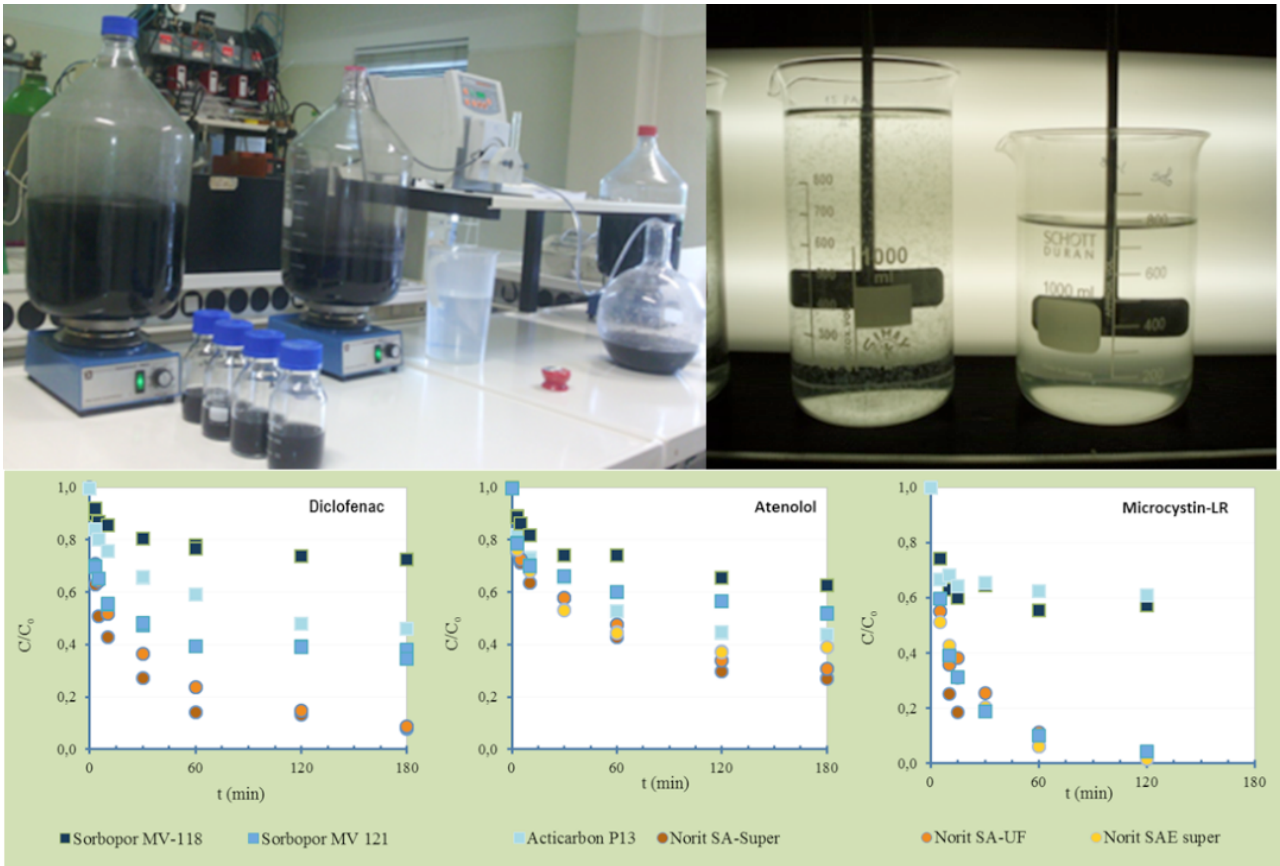

Figure 4. Laboratory tests for selecting PACs and optimizing PAC dosing.

Figura 4. Ensayos de laboratorio para selección de los PAC y la optimización de la dosificación.

ii) pre-selection of commercial PACs with the adequate chemical and textural properties for each application (classification/elimination process based on average particle size, surface charge and pore volume distribution); iii) performance of adsorption kinetics (Figure 4) with the selected PACs and a short-list of ECs in model waters and in natural waters from Alcantarilha WTP.

The preselected PACs were characterized, including their elemental analysis, porosimetry and point of zero charge (pH_{pzc}). Adsorption kinetic assays were performed with the short-list of ECs (5 pharmaceuticals, 1 pesticide and 4 microcystins, natural organic matter). Four PACs were tested for PAC conventional addition and five for PAC/MF application. This methodology allowed selecting one PAC for each application – PAC conventional addition and PAC/MF – which are being tested/demonstrated at pilot scale for EC removal.

PAC/MF prototype is working at Alcantarilha WTP since July 2015. The membrane module (KleanSep, Orelis) contains three tubular ceramic membranes with a total area of 0.75 m^2 and a pore diameter of 0.1μm. One of the main objectives of the project is to identify PAC/MF optimal pre-treatment and optimize the PAC/MF operating conditions under different feed water qualities. Up to this moment very promising results have been obtained in terms of treated water fluxes and quality.

LIFE aWARE (2013-2016) "Innovative hybrid MBR-(PAC-NF) systems to promote Water Reuse" is being developed in El Prat WWTP (Barcelona, Spain), combining the technology of membrane bioreactors (MBR) with the hybrid adsorption/membrane process of PAC/nanofiltration (PAC/NF). The project is coordinated by CETAqua (Barcelona), and the UQTA team was responsible for: i) selecting the adequate PAC for controlling ECs and ii) evaluating, at lab scale, of different PAC/NF configurations to be implemented at a pilot scale in El Prat WWTP.

PAC selection followed the methodology developed by UQTA/LNEC and already presented in this section. For the short-list of ECs, the starting point was the contaminants previously detected in campaigns in El Prat WWTP and Llobregat river [7] and afterwards a classification according to the properties that are important for PAC adsorption, namely size, charge and hydrophobicity. Four classes were identified and a compound representative of each class was chosen.

Two activated carbons were preselected for performing the adsorption kinetics until equilibrium of the target pharmaceuticals and, through the analysis of the PAC capacity and removal rate, one activated carbon was chosen to perform the lab PAC/NF trials. For the evaluation of the adsorption capacity complementary adsorption isotherms of the 4 target PhCs in mineral matrix were performed, as well as kinetics and isotherms with micro screened secondary effluent of El Prat WWTP. Adsorption isotherms were modeled with the Freundlich model, for single solutes, or with the Fritz & Schlünder model in competition scenario [8], and the adsorption kinetics were modeled with the Homogeneous Surface Diffusion Model – HSDM [9]. Combining the calibrated models of competitive adsorption isotherms and kinetics batch numeric simulations of the PhC removal vs PAC dose and contact time were performed for predicting removals for different PAC concentrations and contact times.

The PAC/NF configuration tests were performed in a laboratorial unity dimensioned and built by UQTA team. Two configurations were tested: i) one with a single PAC dose at the beginning of the filtration cycle (pulse dosing) and ii) other with continuous PAC dosing (step dosing). The membrane (X-FLOW HFW 1000 da Pentair) has a molecular weight cut-off of 1000 Da, which is high for nanofiltration, allowing to remove dissolved organic compounds of intermediate-high molecular weight (e.g. natural organic matter), but working at a relatively low pressure (around 1 bar) with relatively high fluxes (20- 25 $L/m^2.h$). The tests included NF trials (no PAC addition) and PAC/NF trials (single and step PAC dosing) with the evaluation of the removal of the four pharmaceuticals supplemented to the micro screened secondary effluent of El Prat WWTP. No pressure increase was observed with PAC addition and the higher removals (between 68-98%) were observed for a pulse dosing of 100 mg/L PAC [10].

4. Biological actived carbon (BAC) filtration

Due to MC-LR chemical stability and the strong competition with natural organic matter (NOM) (μg MC-LR/L vs mg NOM/L) for adsorbents and oxidants, conventional drinking water treatment may not guarantee the absence of MC-LR in the distributed water [4]. Adsorption-based processes, as hybrid adsorption/ low-pressure processes [5] or biological activated carbon (BAC) filtration [11] are promising

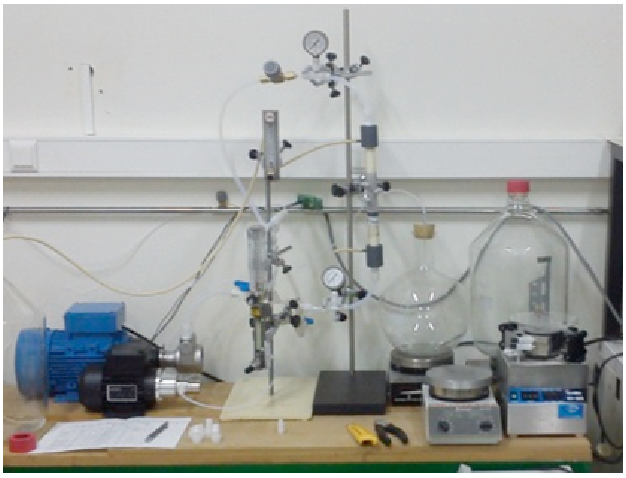

Figure 5. Laboratory unit of PAC/NF
Figura 5. Unidad PAC/NF de laboratorio

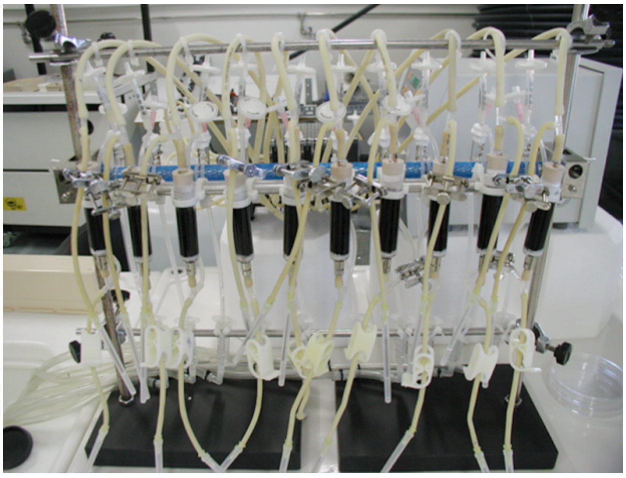

Figure 6. BAC filters assembly.
Figura 6. Ensamblaje de filtros BAC

options for upgrading the water treatment plants. BAC filters are typically robust systems, simple to assemble and with low energy requirements, representing an interesting alternative technology for controlling NOM MC-LR [12] and other microcontaminantss [13].

Granular activated carbon (GAC), besides being an excellent adsorbent material, is a good support media for the attachment and growth of microorganisms and biofilm development. Activated carbon biofilters take advantage of the accumulation of substrates in the GAC particle surface and of the roughness the carbon granules which protects microbial cells from the fluid shear stress. Microorganisms established therein can biodegrade the adsorbed compounds. The synergy of the adsorption, desorption, biodegradation and filtration processes determines the effectiveness of these systems. Biodegradation also promotes continuous bioregeneration of activated carbon and consequently increases filter lifetime. Furthermore, it allows removing assimilable and biodegradable organic carbon and thus controlling the undesirable development of biofilms in the water supply networks [14]. The efficacy of BAC filters depends on the quality of water to be treated (*eg.*, concentration and type of NOM, pH, temperature, ionic strength), the operating conditions (*eg.*, contact time, filtration flow rate and filter back washing frequency), on GAC characteristics (textural properties and surface chemistry), and on the composition and density of the microbial community installed. When operated under optimum conditions, BAC filters can be effective in the removal of biodegradable contaminants such as the cyanotoxins.

A bench-scale study on MC-LR removal by BAC filters was performed at UQTA, focusing the effects of i) organic matter of different absorbability and biodegradability and ii) the filter empty bed contact time (EBCT) on filter performance (Figure 6). This study was carried out with colonised F400 (Chemviron) columns fed with synthetic water that mimicked surface raw water after ozonation and, therefore, able to sustain biological activity in BAC filters (DOC 5 mg C/L as tannic acid, sodium acetate and benzaldehyde, pH 7.2, electrical conductivity 280 µS/cm).The main results were the following [14]:

- The establishment of biological activity is inevitable in activated carbon filters, provided biodegradable organic matter is present in feed water.
- The biological activity in BAC filters extended the filter lifetime - BAC removal efficiency of tannic acid after 4 months of operation was identical to the removal observed by virgin GAC filter with only one week of operation, in identical conditions.
- Adsorption and biodegradation processes contribute to microcystin-LR removal by BAC filters.
- BAC microbiota is able to biodegrade microcystin-LR in the presence of other carbon and energy sources.
- Lower EBCT values (10 min) favor the biological activity in BAC filters better than higher EBCTs (15 or 20 min) - higher EBCTs provided higher intake rates of dissolved oxygen and nutrients, which favored the uptake/removal rates of dissolved oxygen and tannic acid.

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