TÉCNICO LISBOA

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SUMMARY

SEMINAR

Controlling organic micropollutants in urban (waste)water treatment by activated carbon adsorption and membrane technology

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Acronyms and abbreviations

A254	UV absorbance at 254 nm
AC	activated carbon
AMX	amoxicillin (PhC)
AOC	assimilable organic carbon
AOP	advanced oxidation process
APAP	acetaminophen (PhC)
ARB	antibiotic-resistant bacteria
ARG	antibiotic resistance gene
AS	activated sludge
ATN	atenolol (PhC)
BAC	biologically active carbon
BEI	Beirolas (WWTP)
BET	Brunauer-Emmet-Teller
BOD_5	biochemical oxygen demand at 5 days
BTZ	bentazone (pesticide)
BZ	1-H-benzotriazole (anticorrosive)
BZF	bezafibrate (PhC)
C	carbon
CAF	caffeine (PhC)
CAPEX	capital expenditures
CBZ	carbamazepine (PhC)
CEB	chemically enhanced bakwash
CEC	contaminant of emerging concern
CFA	clofibric acid (PhC)
C/F/S	coagulation/flocculation/sedimentation
CHL	chlortoluron (pesticide)
COD	chemical oxygen demand
CP	chlorophene (biocide)
CTS	cortisone (PhC)
CYP	cyclophosphamide (PhC)
d_{50}	median diameter
D_{pH}	(octanol-water) distribution coeficiente at a given pH
DAF	dissolved air flotation
DCF	diclofenac (PhC)
DT	DEET (N,N-diethyl-3-methylbenzamide) (insect repellent)
DES	diethylstilbestrol (hormone)
DIU	diuron (pesticide)
DMT	dimethoate (pesticide)
DOC	dissolved organic carbon
DPR	direct potable reuse
DW	drinking water
DWT	drinking water treatment
DWTP	drinking water treatment plant
E1	estrone (hormone)
E2	17-β-estradiol (hormone)
EE2	17α-ethinylestradiol (hormone)
E3	estriol (hormone)
ECTS	European credit transfer and accumulation system
EDC	endocrine-disrupting compound
EfOM	effluent organic matter
EQS	environmental quality standard
EQSD	environmental quality standard directive
ERY	erythromycin (PhC)
EU	European Union
FLX	fluoxetine (PhC)
F/M	food to microorganisms ratio
FNW	Faro Noroeste (WWTP)
GAC	granular activated carbon
GTD	gestodene (hormone)
HAA	haloacetic acid
HSDM	homogeneous surface diffusion model
IBUP	ibuprofen (PhC)
IND	indomethacin (PhC)
IPR	indirect potable reuse
ISO	International Standardisation Organisation
IST/UL	Instituto Superior Técnico / Universidade de Lisboa (TÉCNICO LISBOA)
JRC	Joint Research Centre
k_{bio}	biodegradability coefficient

K_d	sorption onto biomass coefficient
K_{ow}	octanol-water partition coefficient
LIN	linuron (pesticide)
LINC	lincomycin (PhC)
lmh	L/(m².h)
MBBR	moving bed biofilm reactor
MBR	membrane bioreactor
MC-LF	microcystin-LF
MC-LR	microcystin-LR
$MC\text{-}LR_{eq}$	microcystin-LR equivalent (overall concentration of all MC variants)
MC-LY	microcystin-LY
MC-LW	microcystin-LW
MF	microfiltration
µF	micro filter
MIB	2-methylisoborneol
ML	3-methylindole (fragrance)
MM	molar mass
MS	milestone
MTPL	metoprolol (PhC)
MXL	mixed liquor
N	nitrogen
NF	nanofiltration
NH	nortriptyline.HCl (antidepressant)
NOM	natural organic matter
NPX	naproxen (PhC)
OPEX	operational expenditures
P	phosphorus
PAC	powdered activated carbon
PFAS	per- and poly-fluoroalkyl substance
PI	performance indicator
pH_{poc}	point of overall zero charge
PPNL	propranolol
PS	priority substance
PSA	polar surface area
PT	Portugal / Portuguese
PX	performance index
RAN	ranitidine (PhC)
RO	reverse osmosis
RR	resource recovery
SAT	soil-aquifer treatment
SDG	sustainable development goal
SDZ	sulfadizine (PhC)
SF	sand filtration
SMX	sulfamethoxazole (PhC)
SPD	sulfapyridine (PhC)
SUVA	specific UV absorbance, given by A254/DOC
SWOT	strengths, weaknesses, opportunities, and threats
T254	transmittance at 254 nm
TCp	treatment capacity
TCZ	tebuconazole (pesticide)
THM	trihalomethane
THMFP	trihalomethane formation potential
TSS	total suspended solids
TTE	testosterone (hormone)
UABS	upflow anaerobic sludge blanket
UF	ultrafiltration
UN	United Nations
UV	ultraviolet radiation
UWW	urban wastewater
UWWT	urban wastewater treatment
UWWTD	urban wastewater treatment directive
UWWTP	urban wastewater treatment plant, often referred simply as WWTP – wastewater treatment plant
VOC	volatile organic compound
WEI+	water exploitation index +
WFD	Water Framework Directive
WHO	World Health Organisation
WL	Watch List
WTP	water treatment plant
WWTP	wastewater treatment plant

1 Scope and contents

This document in the form of a monograph summarises the 50-minute seminar entitled **"Controlling organic micropollutants in urban (waste)water treatment by activated carbon adsorption and membrane technology"** prepared for submission to Habilitation ("Provas de Agregação") in Environmental Engineering at Instituto Superior Técnico, Lisbon University, according to point c), article 5 of the Decree-law 239/2007, of 19th June. The monograph presents the strategic vision and a summary of the advances and state of the art in which I have been developing my research activity while frames my contributions in the global vision of this area.

The seminar differs from a lesson due to the intended content and format. Regarding the content, it is intentionally more focused on my research activity in the last decade and on the associated invited oral communications than on the topic's state-of-the-art, which is covered in the curricular unit "Advanced management of urban water treatment", also submitted to Habilitation. With respect to the format, it is more expositive, and the students / audience will not be asked to participate (questions and answers) as they should during a 'normal' lesson. This seminar is suited as part of a "Seminars" curricular unit of a Doctoral or Master's programme on Environmental engineering, Environmental sciences, Chemical engineering, or other related areas.

Although it is not a lesson, coherently with the intended learning outcomes (knowledge and competences) of the curricular unit, the seminar pedagogically follows a problem-solving, data-based approach. Therefore, it starts by introducing a problem and then proposes a solution whose performance is assessed and benchmarked against alternative solutions based on lab, pilot, and full-scale data.

The problem addressed is a current key challenge to urban water systems, consisting of the "control of organic micropollutants in drinking water production, urban wastewater treatment and water reclamation for reuse, summarised in the title as "urban (waste)water treatment". The solution consists of using one or a combination of two best available technologies for this problem, i.e., adsorption onto powdered activated carbon and low-pressure membrane technology. These technologies were selected based on the following criteria: minimisation of the health and environmental risks associated with the potential formation of undesired byproducts, minimisation of energy use, and flexibility & resilience to cope with severe, climate change-driven variations in raw water composition.

2 The problem - organic micropollutants in water

Water is central to all human activities, to all components of the EU Green Deal and to several United Nations sustainable development goals (UN SDGs), starting with SDG 6 'Clean water and sanitation'. Furthermore, population growth & ageing (SDGs 3, 11) and economic growth (SDG 8) are increasing the water demand & contaminants' discharge, while climate change (SDG 13) is decreasing source water availability (droughts and time concentrated rainfall) and increasing water demand (for irrigation, cleaning), thus promoting water exploitation & scarcity, and decreasing source water quality (increased organics, salts, toxic cyanobacterial blooms). These are reasons why we need to 'Take urgent action to combat climate change and its impacts' (SDG 13), 'Build resilient infrastructure' (SDG 9), promote 'Sustainable cities and communities' (SDG 11), carbon neutrality, energy self-sufficiency, resource efficiency, and circular economy, e.g., water reuse [SDGs 6, 7 (energy), and 12 (responsible consumption)].

More than ever, effective, and efficient urban water systems are therefore crucial, and the drinking water treatment (DWT) and the urban wastewater treatment (UWWT) are, in addition to the pollution-source control, the key barriers for protecting the human health, the ecosystems and their services against contaminants of health-environmental concern. These include regulated contaminants, but barriers must be prepared for addressing also 'contaminants of emerging concern' (CECs).

As clearly proposed by Sauvé & Desrosiers (2014), "contaminants of emerging concern (CECs) are naturally occurring or manufactured contaminants present or suspected to be present in various environmental compartments and whose toxicity or persistence are likely to significantly alter the metabolism of a living being"; "should remain 'emerging' as long as there is a scarcity of information in the scientific literature or there are poorly documented issues about the associated potential problems they could cause"; "are expected to be chemicals that show some potential to pose risks to human health or the environment and which are not yet subjected to regulatory criteria or norms for the protection of human health or the environment"; "not all will actually prove to be evil and have some potential to cause tangible concerns"; "an already regulated presumed well-known contaminant could certainly regain "emerging" status as new scientific information becomes available and thus force regulatory agencies to re-evaluate their norms and guidelines"; "will remain a moving target as new chemical compounds are continuously being produced and science continuously improves its understanding of current and past contaminants".

CECs include synthetic chemicals, naturally produced metabolites and biological hazards. Among the latter, currently, antibiotic-resistant bacteria (ARB) and antibiotic resistance genes (ARGs), viruses and virions are of top concern. Naturally occurring CECs include natural hormones excreted to water (Ternes & Joss 2006) and cyanotoxins (hepato-, neuro-, and dermatotoxins) produced by toxic cyanobacterial blooms in surface waters. These blooms (in fresh and transitional waters) are generally triggered by phosphorus, temperature, and solar light conditions, and the most commonly occurring cyanotoxin is microcystin-LR (Menaia & Rosa 2006, Chorus & Welker 2021). MC-LR was therefore included in the Portuguese legislation relative to drinking water quality standards (Decree-law 306/2007, Decree-law 152/2017) following the World Health Organisation (WHO) guidelines (Chorus & Welker 2021, the 2nd edition of the WHO Guide published in 1999) and some Portuguese or EU research projects developed in Portugal, e.g., TOXIC and CIANOTOX projects (described in M.J. Rosa c. Vitae), among others.

Industrial chemicals, such as pharmaceutical compounds (PhCs) (human and veterinary drugs), synthetic hormones, cosmetics and personal care products, pesticides, flame-retardants, plasticizers, food additives, per- and poly-fluoroalkyl substances (PFAS), and nano- and microplastics, raise considerable toxicological concerns for the aquatic environment since they may be transported into waterbodies in some stage of their lifecycle (Mestre et al. 2022a). Actually, most of these chemicals have been already detected in surface and groundwater in pg/L to µg/L worldwide (Geissen et al. 2015), as illustrated for PhCs in Figure 1 (aus der Beek et al. 2016) and Figure 2 (Silva et al. 2021).

Figure 2 compares the concentrations of 13 PhCs found by others in urban wastewaters in Portugal and beyond with those found in BEI and FNW WWTPs' influents in 2016-2019, in LIFE Impetus project (described in M.J. Rosa c. vitae). Within this project we have statistically found the PhC occurrence seasonality is well-defined by the maximum air temperature, with a turning point of 20 °C in Lisbon and 22 °C in Faro. Some PhCs showed lower concentrations in colder (wet) months due to rainwater dilution, whereas others showed higher concentrations, reflecting an increased seasonal consumption and/or slower transformation due to lower air temperatures and/or shorter hydraulic retention times. Seasonal studies should therefore focus on temperature and rainfall rather than on calendar seasons, increasingly uncertain due to climate change (Silva et al. 2021).

Figure 1. Country survey on the number of pharmaceutical compounds detected in surface waters, groundwater, or tap/drinking water (from aus der Beek et al. 2016)

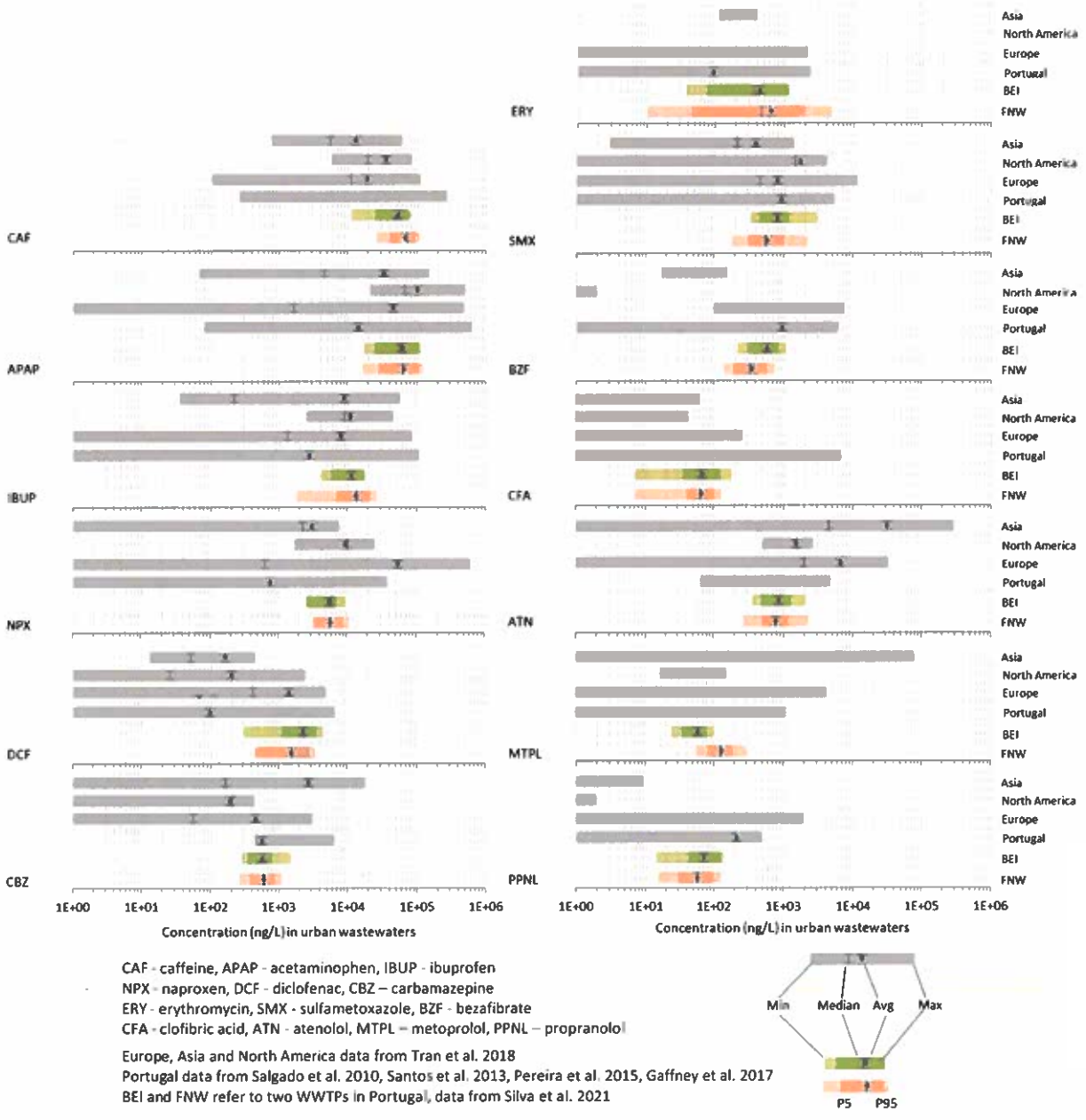


Figure 2. Examples of pharmaceuticals' concentration in urban wastewater (adapted from Silva et al. 2021)

On the other hand, a review of pesticides' monitoring studies of surface waters worldwide (Souza et al. 2020) showed a critical occurrence of atrazine and its metabolites, metalochlor, chlorpyrifos and tebuconazole, and high concentrations and frequency of diuron (0.03-22 770 ng/L) and of the insecticide dimethoate (0.57-61 200 ng/L).

Domestic wastewater, hospital and industrial effluents, stormwater runoff, rural runoff, and manure media are the main sources of CECs entering the aquatic environment (Eggen et al. 2014, Luo et al. 2014). So far, urban WWTPs were essentially designed to remove total suspended solids (TSS) and reduce the chemical and the biochemical oxygen demands (COD and BOD_5, respectively) in the biological secondary treatment, and, when the receiving water requires so, also to remove nutrients (nitrogen and phosphorus) to avoid eutrophication or to disinfect to control water microbiological quality. CECs' control in such WWTPs starts with a good quality secondary effluent since biodegradation and sorption onto particulate matter and biomass are the two major elimination mechanisms (Ternes & Joss 2006, Siegrist & Joss 2012, Rosa et al. 2019). In turn, the non-biodegradable and polar CECs can easily escape the conventional secondary treatment (Ternes & Joss 2006, Siegrist & Joss 2012, Eggen et al. 2014, Luo et al. 2014, Rosa et al. 2019), being released into the water bodies, where they may accumulate in biota (Cravo et al. 2022). The same may happen with the CEC metabolites (e.g., PhCs produced and excreted by human and veterinary metabolism) that, although typically less studied (Pourchet et al. 2020), may be as toxic or more than their parent compounds (Golovko et al. 2021). The continuous discharge of CECs on ecosystems may affect their health, biodiversity and eventually the quality of raw water for human consumption, particularly where highly populated and industrialized urban areas have closed water cycles and/or the dilution factors of rivers or receiving waters are not enough to disregard the risk for aquatic environment, as in some cities in Central Europe (Eggen et al. 2014).

The EU water legislation evolution in the last two decades has been reflecting the CEC monitoring and mitigation needs, as illustrated in Figure 3, starting by monitoring and more recently addressing treatment. The Water Framework Directive (WFD) 2000/60/EC and subsequent directives and decisions established environmental quality standards (EQS) for 45 priority substances (specific herbicides, pesticides, insecticides, industrial chemicals, hydrocarbons, polyaromatic hydrocarbons, and heavy metals) and in 2013 (Directive 2013/39/EU) a new mechanism, the Watch List (WL), was introduced to support the identification of priority substances for regulation under WFD. A Watch List comprises CECs not yet regulated but that may pose significant risk due to their potential toxicological effects. Three Watch Lists have been published since 2015, comprising PhCs, hormones and pesticides/herbicides (Mestre et al. 2022a) and the Joint Research Centre (JRC) has already proposed seven substances or groups to be included in the 4th Watch List (Gomez Cortes et al. 2022). The same mechanism was recently adopted in drinking water, with the publication of the 1st watch list (C(2022) 142) entailing that the potential presence of two endocrine-disrupting substances (beta-estradiol and nonylphenol) will have to be monitored at relevant points throughout the whole water supply chain and indicating guidance values for each substance (CID 2022).

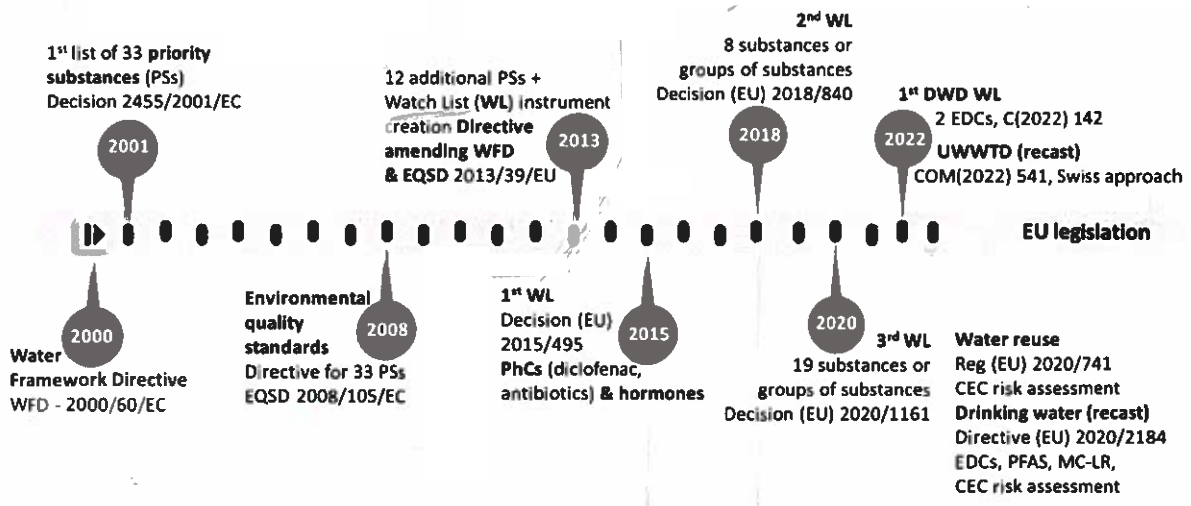


Figure 3. Evolution of water-related European legislation concerning CECs (adapted from Viegas et al. 2021b, Mestre et al. 2022a, and updated)

In drinking water and in water reuse (namely for the highest quality reclaimed water for agriculture irrigation), there are no fixed limits for CECs, but additional requirements may have to be adopted for pharmaceuticals and other CECs depending on the outcome of the monitoring according to the 1st DWD WL (C(2022) 142) or of the mandatory risk assessment (Directive (EU) 2020/2184 and Regulation (EU) 2020/741). The same happens in the national legislation, namely Decree-law 152/2017 (drinking water quality) and Decree-law 119/2019 (water reuse), the latter (as well as the Regulation (EU) 2020/741) fully aligned with the ISO standards on water reuse (ISO 16075 series – Guidelines for treated wastewater use for irrigation projects, ISO 16075 series (2015-2021) – Guidelines for treated wastewater use for irrigation projects, ISO 20426:2018 – Guidelines for health risk assessment and management for non-potable water reuse).

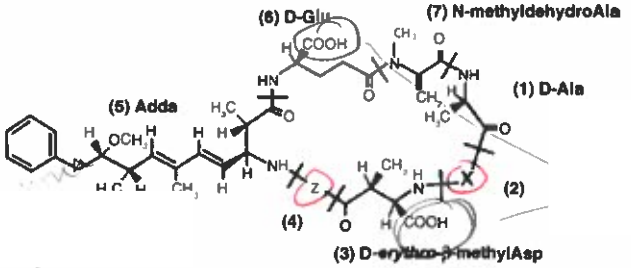
Regarding wastewater, the recently proposed revised text for the Urban Wastewater Treatment Directive (UWWTD recast, COM (2022)) adopts the Swiss approach, with whom the German Federal Centres for Trace Substances (KomS) in Baden-Württemberg, North Rhine-Westphalia, and Berlin (Central Europe) agree. This is, UWWTD (recast) introduces the obligation to apply additional treatment to urban wastewater (quaternary treatment) in order to eliminate the broadest possible spectrum of micropollutants, i.e., 80% removal (contrasting with the typical WFD approach of limit concentrations) of 6 CECs of a list of 12 in all UWWTPs treating ≥ 100000 p.e. by 31 December 2035 (at the latest) and, by 2040, in all facilities ≥ 10000 p.e. in areas where the concentration or accumulation of micropollutants poses a risk to human health or the environment according to the specified criteria (areas to be identified by the Member States). Furthermore, it introduces the extended producer (including importers) responsibility (EPR) to contribute to support the costs of the quaternary treatment, such financial contribution being established based on the quantities and toxicity of the products the producer (including importers) places on the market. In Germany, late 2019, more than 20 plants have been expanded with advanced treatment technologies and put into operation to provide 80% reduction of selected indicator substances, and further 27 facilities were planned or under construction (Metzer et al. 2019).

Once a CEC is regulated it becomes a micropollutant, as the new UWWTD refers to the 12 PhCs from which 6 must be selected for minimum 80% removal in UWWTP and the EU & PT drinking water standards refer to microcystin-LR and pesticides.

This seminar aims to raise the awareness and the technical and scientific preparedness of the audience/students to support transforming the latest regulation in DWT and UWWT into practical impact, namely by comprehensively explaining a solution for controlling organic micropollutants of different molar mass (MM), charge, hydrophobicity/hydrophilicity, biodegradability, and sorption onto biomass – the key properties for removal by the targeted solutions.

For DWTPs, the selected organic micropollutants are MC-LR (and other microcystin variants naturally occurring with MC-LR, Table 1, often overall expressed as MC-LR$_{eq}$) and pesticides, regulated contaminants, as well as representative PhCs, considered via the risk assessment.

Table 1. Microcystin variants properties (adapted from Campinas & Rosa 2006, Ribau Teixeira & Rosa 2005)

	MC-LR	MC-LY	MC-LW	MC-LF
				
Amino acids (X and Z)	Leucine, arginine	Leucine, tyrosine	Leucine, tryptophane	Leucine, phenylalanine
Molar mass (g/mol)	994	1001	1024	985
Net charge at pH 7	-1	-2	-2	-2
		increasing hydrophobicity →		

For UWWTPs, the selected organic micropollutants for advanced adsorption/membrane treatment are representative recalcitrant PhCs (i.e., of low biodegradability (k_{bio}) and sorption onto biomass (K_d), Figure 4), escaping the secondary (for C removal) or tertiary (for C, N and P removal) treatment, i.e., poorly removed or exhibiting variable and unreliable removal by secondary/tertiary treatment. Considering their distinct physical-chemical properties, namely charge at pH 7.4 and hydrophobic/hydrophilic character[1], our studies have been often conducted with carbamazepine (CBZ), diclofenac (DCF), and sulfamethoxazole (SMX) (Table 2), though not limited to (other examples in Table 3 and sections 6 and 7).

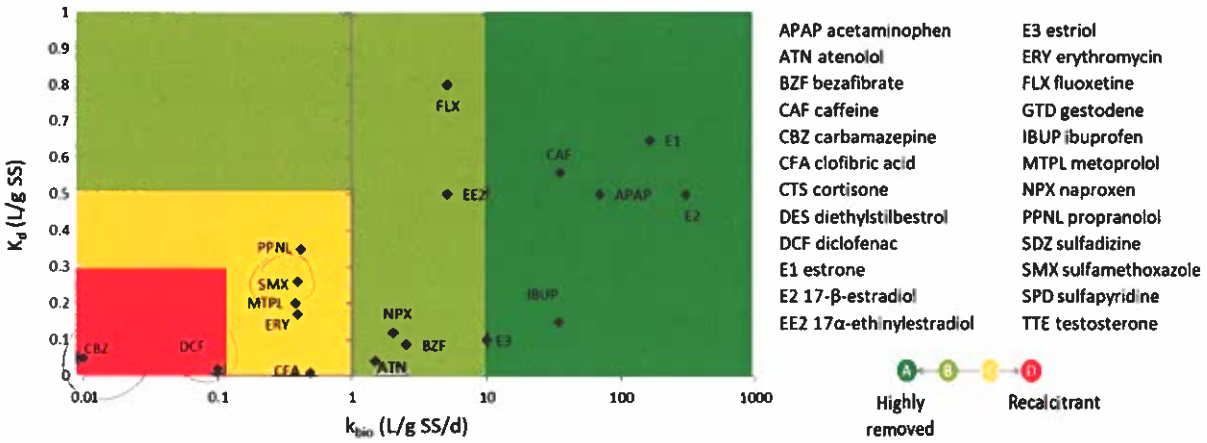
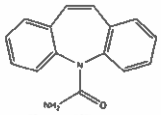
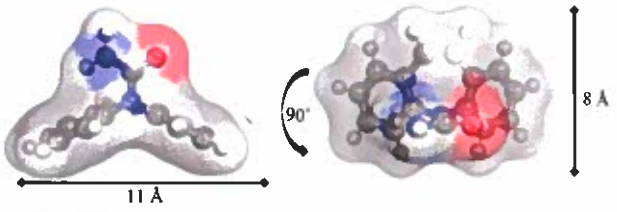
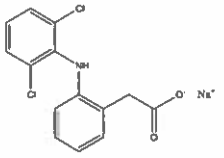
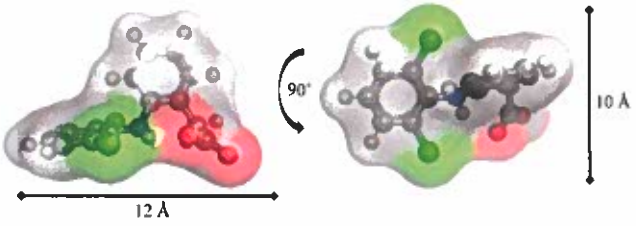
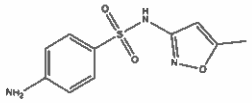
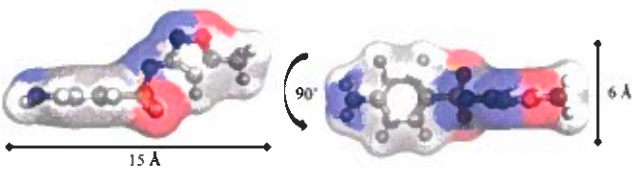


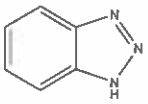
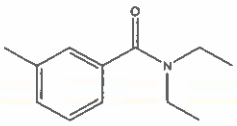
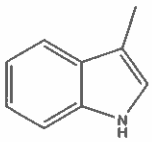
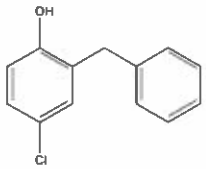
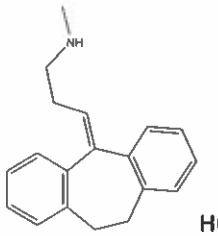
Figure 4. K_d vs k_{bio} for selected organic micropollutants and CECs (from Rosa et al. 2019)

Table 2. Carbamazepine, diclofenac, and sulfamethoxazole key properties for removal by adsorption and adsorption/membrane filtration (from Mestre et al. 2022b, Viegas et al. 2022)

PhC molecular structure & therapeutic class	Physical-chemical properties	Optimised geometries and dimensions
Carbamazepine/CBZ  Anti-epileptic & psychiatric drug	MM = 236.3 g/mol Log K_{ow} = 2.67 Log $D_{7.4}$ = 2.28 pK_a = 13.9 Neutral & hydrophobic	
Diclofenac/DCF  Non-steroidal analgesic & anti-inflammatory drug	MM = 318.1 g/mol Log K_{ow} = 4.06 Log $D_{7.4}$ = 1.37 pK_a = 4.0 Anionic & relatively hydrophobic	
Sulfamethoxazole/SMX  Antibiotic	MW = 253.3 g/mol Log K_{ow} = 0.89 Log $D_{7.4}$ = -0.56 pK_{a1} = 1.7; pK_{a2} = 5.6 Anionic & hydrophilic	

[1] expressed by Log K_{ow} (the logarithm of the n-octanol/water partition coefficient) or Log D_{pH} (the logarithm of the distribution coefficient, which corrects the Log K_{ow} for the pKa of each compound by quantifying the amount of both the ionized and non-ionized forms of the PhCs in octanol and water at the pH values under study; Viegas et al. 2022), the higher the more hydrophobic.

Table 3. Other selected organic micropollutants and their key properties for removal by activated carbon adsorption and membrane filtration (from Rodriguez et al. 2016)

PPCP	Structure	Molecular formula	MM, g/mol	V_{molar}, cm^3 (1)	Log K_{ow}	Charge at pH 7	Log D at pH 7-7.5	Category
1-H-Benzotriazole (BZ)		$C_6H_5N_3$	119.1	88.3	1.44	neutral	1.42-1.39	Anticorrosive
DEET (DT)		$C_{12}H_{17}NO$	191.3	194.0	2.18	neutral	2.18	Insect repellent
3-Methylindole (ML)		C_9H_9N	131.3	118.1	2.60	neutral	2.60	Fragrance
Chlorophene (CP)		$C_{13}H_{11}ClO$	218.7	179.2	4.18	neutral	4.18	Biocide
Nortriptyline.HCl (NH)		$C_{19}H_{21}NO \cdot HCl$	299.8	242.9	4.51	positive	1.40-1.80	Antidepressant

(1) calculated by ChemSketch

3 Available technologies for controlling organic micropollutants

As introduced earlier, conventional UWWTPs essentially target TSS, COD, and BODs reduction via physical unit operations and biological processes, as well as nitrogen and phosphorus reduction or disinfection (*E. coli* inactivation) when needed, respectively, to avoid eutrophication or protect bathing waters/aquaculture. In turn, as described in Rosa et al. (2009), conventional DWTPs include (i) preoxidation, for controlling biological growth, taste & odour compounds, ferrous & manganese ions, (ii) coagulation/flocculation/sedimentation and rapid sand filtration for removing turbidity and reducing the natural organic matter (NOM), particularly the more hydrophobic fraction (expressed by SUVA > 4-5 L/(mgC m), where SUVA represents the specific UV absorbance), the major precursor of organochlorinated byproducts, and (iii) final chlorination for water disinfection and for providing a disinfectant residual in the water distribution system (to prevent biological regrowth). Consequently, the conventional treatment plants were not designed as full barriers against organic micropollutants. The strategy to control them must therefore start by assessing and improving the performance of the existing barriers and then upgrade them with advanced treatment, as needed.

Operational, low-investment measures for improving current UWWTPs include providing conditions for the build-up of the slowly growing nitrifying bacteria, which can excrete enzymes and, by co-metabolism, may break down some low degradable molecules (Clara et al. 2005, Ternes & Joss 2006). These conditions include sludge retention times of, at least, 10-15 days (Clara et al. 2005) or F/M (food to microrganisms) ratios below 0.08 d^{-1} (Rosa et al. 2019), which were associated with N-removal > 80% and alkalinity reduction > 40% (due to nitrification) (Rosa et al. 2019).

Improvement measures in conventional DWTP include adjusting preoxidation and C/F/S operating conditions for promoting NOM removal by enhanced coagulation and implementing C/F/S assisted with powdered activated carbon (PAC) addition. For instance, an enhanced control of microcystins (cyanobacteria and other cyanotoxins) may be achieved using low ozone doses in preoxidation (to avoid cell disruption prior to C/F/S and maximise intracellular MC-LR_{eq} removal), adequate PAC and coagulant doses, dissolved air flotation (DAF) instead of sedimentation, smooth start-up/shut-down of sand filtration cycles, and multilayer filtration (Hall et al. 2005, Raspati et al. 2015, Ribau Teixeira et al. 2020, Rosa et al. 2009, Smeets et al. 2015).

DWTP and UWWTP upgrade relies on implementing advanced treatment (quaternary treatment according to the proposed recasted UWWTD). Established advanced (waste)water treatment options for enhanced control of organic micropollutants and CECs (Baresel et al. 2017, Campinas et al. 2017, Campinas et al. 2022, Chorus & Welker 2021, Egen et al. 2014, Hall et al. 2005, Hillenbrand et al. 2016, Luo et al. 2014, Mestre et al. 2022a,b, Metzer et al. 2019, Mulder et al. 2015, Pesqueira et al. 2020, Rizzo et al. 2019, Rizzo et al. 2020, Rosa et al. 2009, Rosa et al. 2019, Smeets et al. 2015, Ternes & Joss 2006, UMWELT.NRW 2019, Viegas et al. 2021b, Zietzschmann et al. 2014, Zietzschmann 2020) include:

- ozonation and advanced oxidation processes (AOPs, e.g., O_3/H_2O_2, UV/ H_2O_2, Fenton);
- adsorption-based systems, including PAC, granular activated carbon (GAC) filtration or biologically active GAC filters (BAC);
- membrane filtration, i.e., microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO);
- adsorption/membrane hybrid processes, e.g., PAC/MF, PAC/UF, PAC/NF.

The technology applicability depends on its separation mechanisms vs the target contaminants' properties (e.g., charge, hydrophobicity/hydrophilicity, solubility, volatility, chemical resistance, biodegradability, sedimentability/floatability, colloidal character, release of intracellular metabolites), as illustrated in Table 4 for macro and microcontaminants (Rosa et al. 2009).

Each option has its pros and cons, as extensively compared in literature (e.g., in Luo et al. 2014, Pesqueira et al. 2020, Rizzo et al. 2019, Rizzo et al. 2020). Regarding adsorption-based treatment, during the last decade, several projects addressed its introduction in an increasing number of WWTPs in German-speaking countries, mainly because of Swiss and German governmental requirements or encouragement to accomplish CEC abatement from urban wastewater. As reviewed in Mestre et al. (2022), results on the different technologies implemented have been published in reference journals, but the practical knowledge on the activated carbons' selection for pilot-, large-, and full-scale implementation can only be consulted in project reports and other documents written mostly in German. An exception is the Zietzschmann's (2020) book chapter, providing valuable information on the adsorptive removal of organic microcontaminants from wastewater, covering practical

aspects of PAC and GAC processes and operation fundamentals, tools for their performance prediction and general considerations for an informed selection of an activated carbon product.

This seminar focuses on **PAC adsorption** and on **PAC/low-pressure membrane** technology. These are two best available technologies, flexible and resilient to severe, climate change-driven variations in raw water composition. Moreover, these technologies rely on physical separation, which allows minimising the health and environmental risks associated with the potential formation of undesired byproducts. Low-pressure driven membranes are preferentially addressed to minimise the energy use and carbon footprint.

GAC/BAC filtration is a more adequate solution when a permanent barrier is needed, rather than a seasonal/sporadic (for episodes) control as suited for PAC but will not be addressed due to time restrictions.

Table 4. Effectiveness of alternative and advanced processes for macro and microcontaminant control (from Rosa et al. 2009, Smeets et al. 2015)

Contaminant	C/F+DAF	UV	GAC	BAC	MF	UF	PAC/ UF	NF [a]	RO
Protozoa (cysts, oocysts)	+/-	+	+/-		+	+	+	+	+
Bacteria (vegetative forms)	-/+	+	-		+	+	+	+	+
Bacteria (endospores)	-/+	-	-		+	+	+	+	+
Helmint eggs	+/-	-	+/-		+	+	+	+	+
Cyanobacteria	+	- [b]	+/-		+	+	+	+	+
Enteroviruses	-	-	+/-		+/-	+	+	+	+
NOM_SUVA < 3 L/(mgC.m) [c]	-/+	+/-	-/+		+	-	-	+/-	+
NOM_SUVA > 4 L/(mgC.m) [c]	+/-		+/-		+/-	-/+	+/-	+	+
Assimilable organic carbon (AOC)	-	+/-	-/+	+	-	-	-/+	+/-	+
Trihalomethanes (THMs)	-		+		-	-	+	+/-	+
Haloacetic acids (HAAs)	-		+		-	-	+	+/-	+
Bromate	-		+/-	+/-	-	-	-/+	+	+
Bromide	-				-	-	-	+/-	+
Chlorate	-				-	-	-	+	+
Chloride	-				-	-	-	+/-	+
Nitrate	-				-	-	-	+	+
Sodium	-				-	-	-	+/-	+
Sulphate	-				-	-	-	+	+
Microcystins	+ or -/+ [d]		+ or +/- [e]		-	-	+ or +/- [e]	+	+
Taste & odour compounds (MIB, geosmin)	-/+		+		-	-	+	+	+
Volatile organic compounds (VOCs)	+ [f]		+		-	-	+/-	-/+	+
EDCs and pharmaceuticals (hydrophobic and chemically resistant)	-/+		+		-	-	+	+	+
Pesticides (including chemically resistant)	-/+		+ or +/- [e]		-	-	+	+	+

- \- Not adequate
- -/+ Limited effectiveness
- +/- Partial control if adequate operation conditions are guaranteed
- \+ Effective provided adequate operation conditions are guaranteed
- No information available

[a] Considering 200 Da molecular cut-off

[b] UV should not be used to control cyanobacteria, since it leads to cell rupture and cyanotoxin release

[c] values < 3 L/(mgC. m) indicate mainly hydrophilic NOM, values > 4 L/(mgC.m) indicate mainly hydrophobic NOM and especially aromatic compounds

[d] Effective removal of intracellular toxins; no significant removal of dissolved toxins

[e] Depends on chemical characteristics of the target compound

[f] There are volatilisation conditions in C/F/DAF

4 Activated carbon adsorption

In water treatment, **adsorption** is the physical (or chemical) mechanism by which dissolved molecules (adsorbates or solutes) are captured on a solid interface (adsorbent). **Activated carbon** (AC) is the most used adsorbent in DWT and UWWT due to its **nanoporous structure**, responsible for an outstanding **surface area**, typically from hundreds to 2000 m^2/g (Mestre et al. 2022a,b).

Most carbon-rich materials may be used as raw materials for activated carbon production, but a large-scale production requires large amounts of precursors with reproducible features, controlled ash content, and cost. Commercially available products are mainly produced from coal, wood, or coconut shell; water treatment applications represent around one third of the market share and are expected to remain the largest throughout 2020-2027, being the current driver for market growth (Figure 5, Mestre et al. 2022a).

Figure 5. Global activated carbon market share by raw material & type (data adapted from Inkwood Research 2019) and application (data adapted from Fortune Business Insights 2019) (from Mestre et al. 2022a)

The precursors are first carbonized, and the chars are then physically or chemically activated (using high temperatures under controlled atmosphere, e.g., steam activation) to increase the porous network (of macro-, meso-, and micropores, Figure 6) yielding a high surface area. Given their relevance for PhC adsorption, the micropores' classification is further breakdown into supermicropores (0.7-2 nm wide) and ultramicropores (< 0.7 nm width). Manufacturers commonly report the iodine number and BET (Brunauer-Emmet-Teller) area values as indicators of the apparent surface area of a given activated carbon, with both parameters usually presenting close values despite their distinct units (mg/g and m^2/g, respectively) (Zietzschmann et al. 2014, Mestre et al. 2022a).

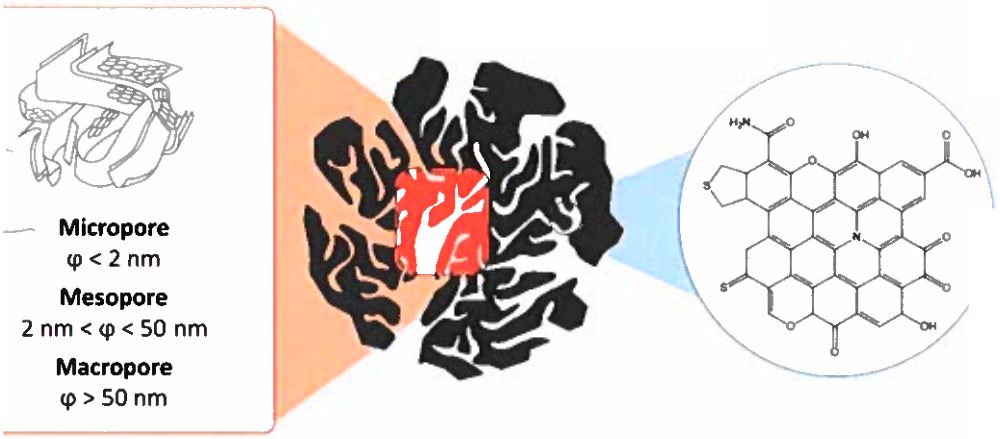
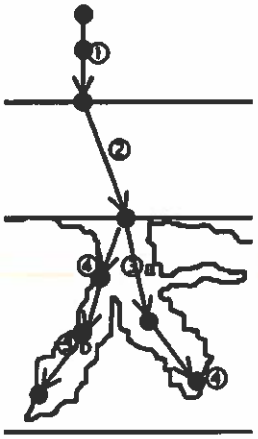


Figure 6. Representation of nanoporous structure and surface chemistry groups on activated carbon (from Mestre et al. 2022a)

Activated carbons are industrially applied as powdered activated carbons (**PACs**, average particle size < 100 µm) or as granular activated carbon (**GAC**) filters (average particle size > 100 µm and median d_{50} > 1 mm) (Figure 5),

the lower the particle size, the lower the adsorption path and therefore the faster the adsorption kinetics to the active sites for a similar porous structure (Figure 7). Super fine PACs (**sPAC**) with enhanced kinetics are emerging for applications not requiring particle settleability, i.e., for PAC/membrane applications (section 6). After exhaustion, PACs are usually discharged in landfill or incinerated, while GACs can be reactivated (or regenerated) and reused.



1. CEC bulk diffusion/convection to stagnant boundary layer surrounding the AC particle

2. CEC external mass transfer across the boundary layer (external mass transfer)

3. CEC porous diffusion (in water filled pores) or ***surface diffusion*** (series of hops with adsorption-desorption along the pore surface) or both (intraparticle diffusion).

4. CEC adsorption, physical or chemical attachment onto the surface of the adsorbent surface site

Figure 7. Activated carbon adsorption representation (adapted from Viegas et al. 2014)

Activated carbon **adsorption capacity** (adsorbate/adsorbent mass ratio, often determined through Freundlich or Langmuir isotherms) and **kinetics** (HSDM vs Boyd's model, Viegas et al. 2014) depend on (external and intraparticle) diffusion & mass transfer and affinity (Campinas et al. 2013), i.e., adsorbent-adsorbate hydrophobic & electrostatic **interactions**. These are determined by the AC textural properties (the closer the active-site pore size to the solute's size the better; Zietzschmann 2020) and surface chemistry (e.g., hydrophobicity and net surface charge, expressed by pH_{pzc} – examples in Figure 8), as well as by the solutes' properties (e.g., size, hydrophobicity, net charge, examples in Table 2, Table 3) and the water background organics and inorganics.

Water **background organics** determine the **competitive adsorption** by (i) direct competition for the adsorption sites (the closer the NOM/EfOM (effluent organic matter) size and hydrophobicity to the target solute the stronger the competition; Campinas et al. 2013) or (ii) pore blockage and are often characterised by DOC content and character (e.g., Rodriguez et al. 2016). This is the reason why, in practical applications, one uses the DOC-normalised PAC dose (mg PAC/mg DOC). **Background inorganic** matrix may be easily characterised by two bulk parameters (i) the water pH, determining the AC and solute's **ionisation/net charge**, and (ii) the electrical conductivity (expressing the ionic strength), determining the electrostatic repulsions' **shielding effect** and so the solute's hydrodynamic size (Campinas & Rosa 2006).

BET surface area (m^2/g)	1112
Ash content (%)	8.17
Moisture (%)	2
Apparent density (g/cm^3)	0.16
Geometric mean diameter (μm)	6
Primary micropore (<7 Å) volume (cm^3/g)	0.343
Secondary micropore (7-20 Å) volume (cm^3/g)	0.194
Mesopore (20-500 Å) volume (cm^3/g)	0.357
Micropore surface area (m^2/g)	733
Mesopore surface area (m^2/g)	379

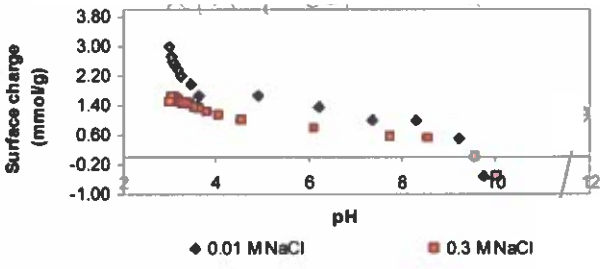
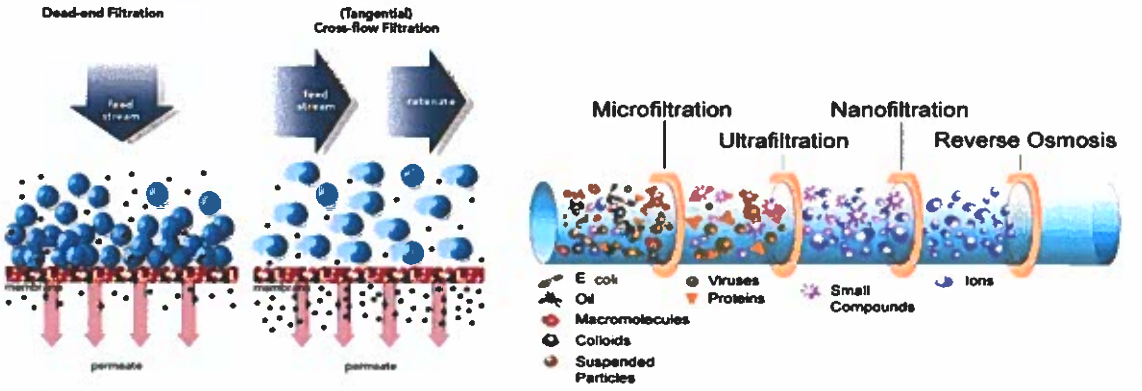


Figure 8. Key characteristics (textural, left; surface charge, right) of an activated carbon illustrated for a high performing (mesoporous & microporous, alkaline, i.e., pH_{pzc} ~ 9.5) commercial PAC for CEC control (PAC Norit SA-UF) (adapted from Campinas & Rosa 2006)

The development of high-performing, environmental-friendly (biomass-derived, steam activated) PACs from local biomasses is very important for the sake of the technology's sustainability (Mestre et al. 2022b, Viegas et al. 2020b), as well as of fine sPAC and magnetic PACs allowing their recovery and regeneration (as ongoing within EMPOWER+ project).

5 Membrane filtration

In membrane filtration for water treatment, an applied pressure forces water to pass through a semi-permeable membrane, which retains the solutes larger than the membrane pores, the narrower the pores, the higher the pressure, as illustrated in Figure 9 for **MF, UF, NF, and RO** (and also for sand filters, for comparison).



SAND FILTERS	MICROFILTRATION	ULTRAFILTRATION	NANOFILTRATION	REVERSE OSMOSIS
10 µm	0.1-2 µm	0.01-0.1 µm	1-10 nm	
	> 500.000 Da	1.000 – 500.000 Da	100-1.000 Da	< 100 Da
	0.1 - 1 bar	0.5 - 5 bar	5-40 bar	20-100 bar

Figure 9. Membrane filtration in water treatment – MF, UF, NF and RO

Membrane filtration covers a broad spectrum of options in terms of membrane pore/selectivity/applied pressure, but also in terms of (i) membrane materials and modules, (ii) filtration mode, dead-end or crossflow, in/out or out/in, pressurized or immersed, and (iii) number of stages (Figure 10) (Pinho & Rosa 1995). Common **applications** include (i) 1-stage cross-flow polymeric spiral-wound RO membranes for seawater desalination, (ii) polymeric spiral-wound NF membranes for DWT, i.e., groundwater softening and NOM and CEC removal from surface water, (iii) pressurized in/out polymeric hollow-fibre UF membranes for DWT and water reclamation, (iv) immersed out/in polymeric hollow-fiber or flat sheet UF membranes for membrane bioreactors (MBRs) for UWWT/water reclamation, and (v) the emerging ceramic in/out dead-end tubular MF membranes for surface water treatment. All membranes (from MF to RO) are full physical barriers against particles (TSS and turbidity) and bacteria; UF membranes are also effective against viruses and macromolecules; NF membranes further remove small organics (usually > 300 Da), divalent salts, and partially monovalent salts, which are highly removed by RO. This is, all membranes are adequate for water (physical) disinfection, but the low-pressure MF and UF are not able to remove the organic micropollutants targeted.

As ceramic membranes have evolved, so far, higher initial capital costs than polymeric membranes, they represented only 2-3% of the membrane market in 2015 and 12% of the membrane materials used until 2016 for drinking water treatment by membrane processes with backwashing. However, ceramic MF application is expected to grow over the next years due to their many advantages over polymeric membranes and also due to their significant cost decrease (Wise et al. 2020). Ceramic membranes have higher chemical, thermal and mechanical stability, making them easily backwashed and allowing more aggressive physical and chemical cleaning that can extend their lifetime. Ceramic membranes are also better candidates for hybrid adsorption/membrane processes than polymeric membranes as they can be significantly resistant to deterioration by biofilm growth and to surface abrasion by coarse particles circulation, two concerns mostly related with PAC long-term use (Campinas et al. 2021c). My research team has been investigating PAC/ceramic MF and/or PAC/ceramic UF at pilot scale for drinking water production and water reclamation in several R&I projects (e.g., FP7 TRUST and LIFE Hymemb).

Membrane performance (fluxes, selectivity, water recovery and fouling rate over time) greatly depends on the intake water quality and on the membrane operation conditions and cleaning, which control the membrane

(reversible and irreversible, bio- and chemical) fouling, scaling, and ageing, ultimately determining the membrane productivity, lifespan and the energy costs (Figure 11). A new indicator was developed for performance assessment and optimisation, the **treatment capacity** (TCp), i.e., the design flowrate normalized to membrane area and intake pressure. TCp ($m^3/(m^2.d.bar)$) is the effective volume of permeate produced by unit time, membrane area and intake feed pressure, deducting the permeate volume used for backwashing and chemically enhanced bakwashing (CEB), and considering the productive time (filtration time) and the time a unit is off-line for cleaning procedures (backwashing and CEB). TCp integrates all key aspects of process productivity and therefore constitutes a useful indicator to balance flux, energy consumption, backwash frequency and chemical cleaning frequency (Campinas et al. 2021c).

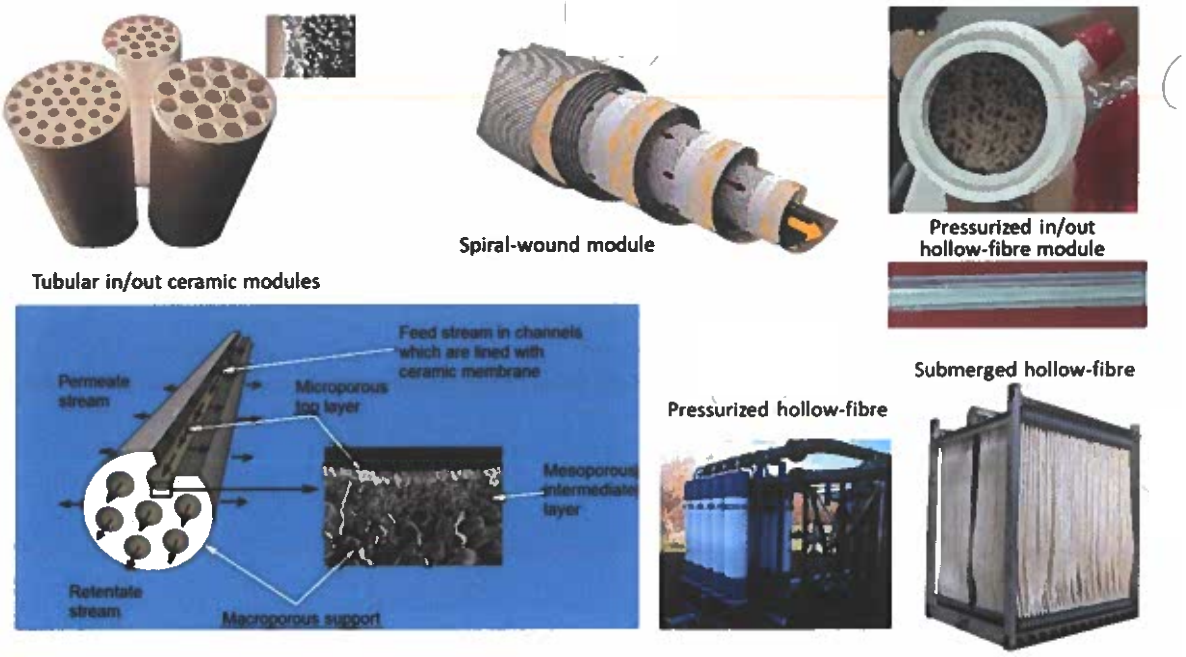


Figure 10. Membranes and modules

The intake water **background organics** play a key role on membrane fouling, usually requiring coagulation pre-treatment for NOM control (Ribau Teixeira & Rosa 2006, Campinas et al. 2021c), whereas the water **inorganics** (pH, ions) affect the membrane scaling (inorganic precipitation) but also the flux and selectivity of NF membranes due to charge (pH) and shielding (ions) effects (higher pH corresponding to higher electrostatic repulsions, narrower pores, lower flux and higher solute retention; deleterious effects partially balanced by the ions' shielding effect) (Ribau Teixeira et al. 2005).

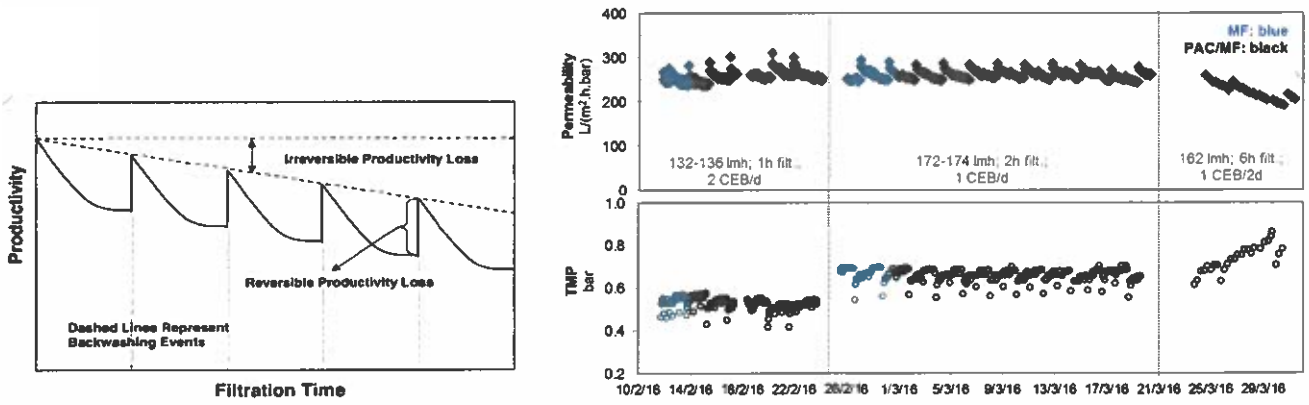


Figure 11. Membrane productivity over time/filtration cycles - conceptual scheme (left) and PAC/MF pilot results (right) (from Campinas et al. 2021c)

6 Hybrid activated carbon adsorption/membrane processes

The **hybrid adsorption/membrane** process aims at taking the best of each technology while overcoming their limitations. **PAC** (type, concentration, and dosing conditions, e.g., continuous or pulse addition) can be easily adjusted to the organic micropollutants (or other CECs) targeted and a finer PAC, with faster kinetics and higher efficiency may be used with no risk of PAC release into the treated water. In turn, a **low-pressure** (low energy) **membrane** may be used to fully retain the fine PAC particles (unlike PAC conventional addition; Campinas et al. 2021a), whereas PAC may help controlling the membrane fouling by NOM (Campinas & Rosa 2010a) (Figure 12).

This combination ('hybridisation') yields a flexible, compact, and modular solution consisting of a safe and reliable barrier for disinfection and organic CEC control, able to cope with severe water quality changes driven by climate change. MF, UF and loose-NF membranes may be used, with or without coagulation, depending on the upstream treatment – **PAC/(C)/MF** (Campinas et al. 2021b,c; Viegas et al. 2020a, 2021a), **PAC/UF** (Campinas & Rosa 2010a,b,c,d; Rodriguez et al. 2016) or **PAC/NF** (Viegas et al. 2018). Despite its potential, when we published our first results on the hybrid adsorption/membrane process for the removal of cyanotoxins from drinking water, back in 2010, only one published study was known on PAC/UF for such application (Campinas & Rosa 2010b). In addition, and as introduced in section 5, **ceramic membranes** are particularly suited for hybrid adsorption/ membrane processes due to their lower abrasion by PAC and subsequent longer lifetime (2-5 times the lifetime of polymeric membanes), their low energy consumption (< 0.1 kWh/m^3) and high water recovery rate (> 95%) both in DWT (Campinas et al. 2021c) and in water reclamation (Viegas et al. 2020a). Again, in 2012, when our studies with pressurized hybrid low-pressure ceramic membrane processes started[2], most research on PAC/MF was mainly dedicated to conventional polymeric membranes and submerged configuration. Moreover, many studies focused on membrane fouling and traditional water quality parameters conducted at lab scale, sometimes with synthetic waters. Pilot studies of pressurized PAC/coagulation/ceramic MF envisaging organic microcontaminants, NOM and microorganisms' removal under real scenarios, with real waters and quality variations were, and still are, scarce.

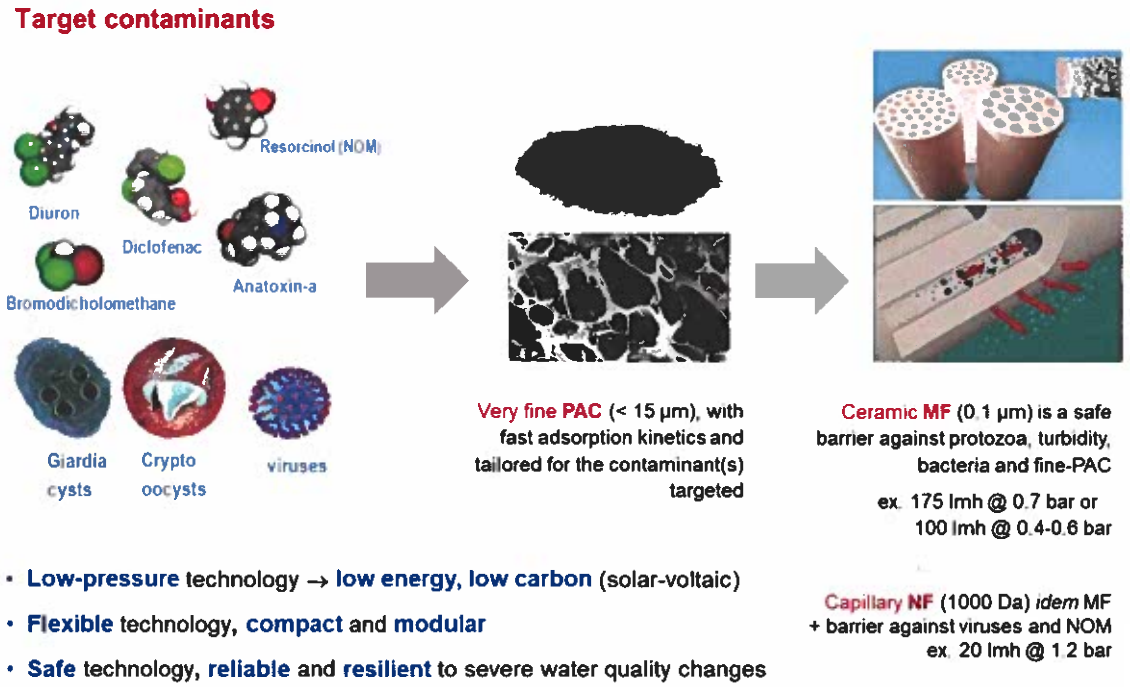


Figure 12. Hybrid adsorption/membrane process

[2] We started investigating ceramic MF and PAC/MF for water reclamation in 2012 (FP7 TRUST, 2011-2014), the same year we submitted for funding LIFE Hymemb for benchmarking PAC/ceramic MF against PAC conventional addition in drinking water production (executed in 2014-2016, awarded as a best LIFE ENV project 2016-2017).

7 Applications in drinking water treatment

Whereas the former sections (1 to 6) included a short critical state-of-the-art, this and the next section (7 and 8), relative to the applications, are focused on the last decade's results of my research team, thus presenting our main contributions in the global vision of this area. The applications studied are illustrated in Figure 13 and aimed at answering the following questions: "to what extent & why?", "where, how & at what cost?" PAC conventional application (PAC / C/F/S) and the innovative PAC/MF (or PAC/UF) can control organic micropollutants and CECs in surface water treatment for drinking water production. Our strategy was to start by optimising the current barriers (option 1), then to find the best (tailored) solution to upgrade the treatment, if needed, by investigating the several alternative points where to apply the advanced treatment solution proposed (PAC/MF or UF, options 2-5). Such strategy involved studies at lab, but also at pilot and full-scale (Figure 14), which allowed developing cost analysis, and were carried out within PhD (Campinas & Rosa 2006, 2010a,b), Post-Doc (Campinas et al. 2013), and demonstration projects (LIFE Hymemb; Campinas et al. 2017, 2021a,b,c, Viegas et al. 2021a).

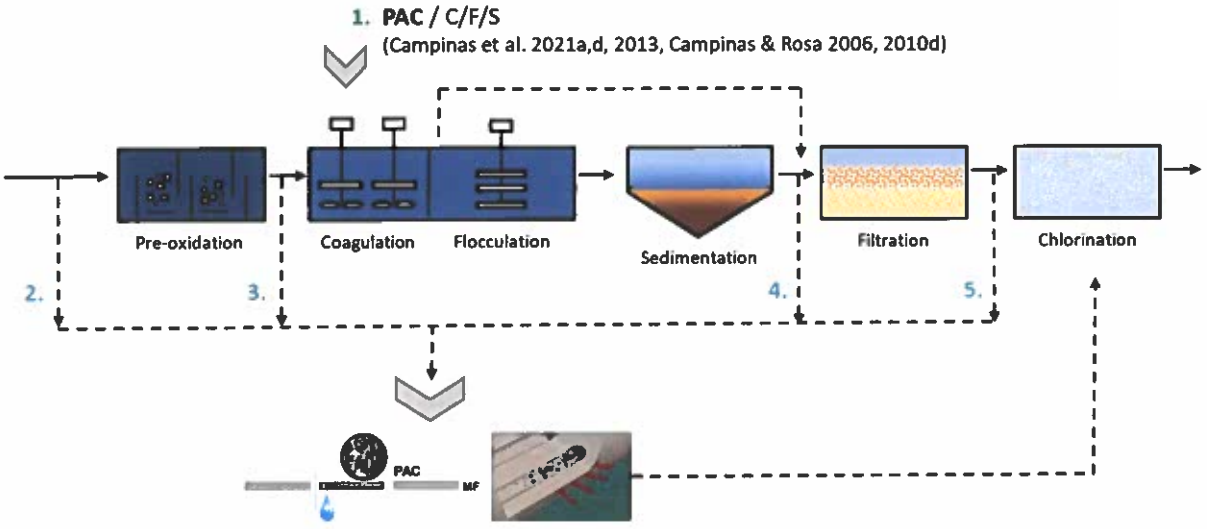


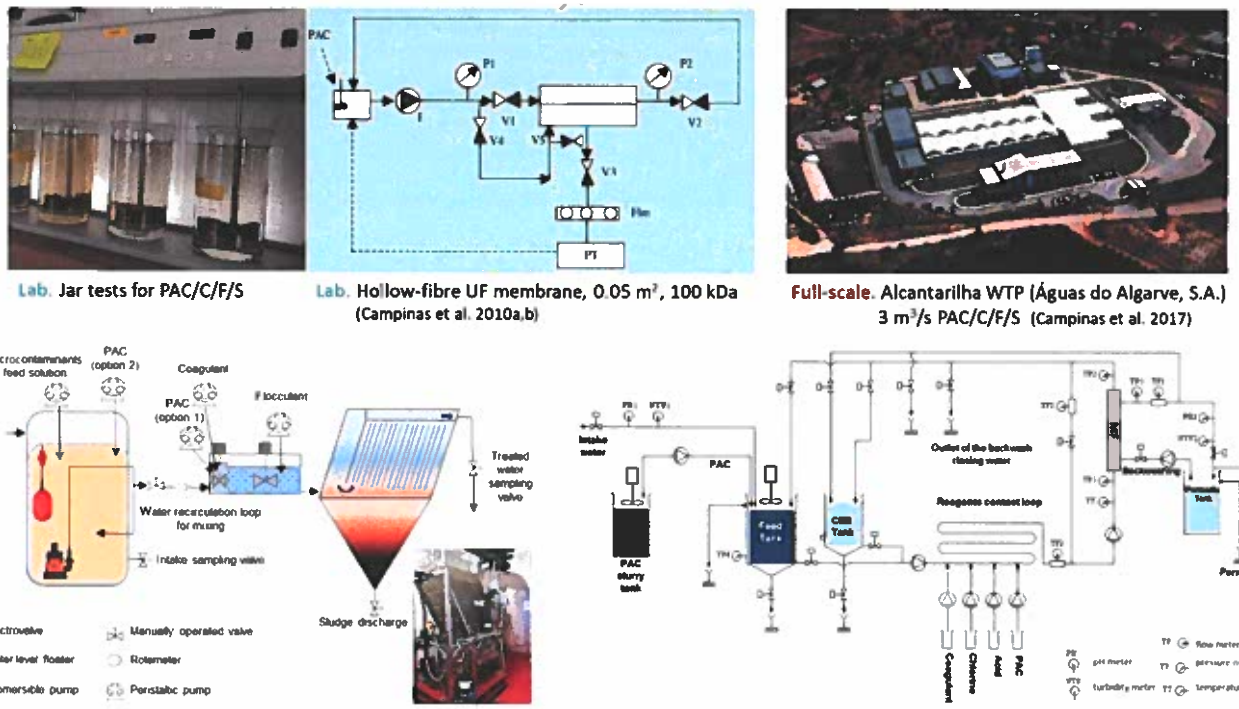
Figure 13. PAC application for controlling organic micropollutants in DWT
(the conventional sequence represents Alcantarilha WTP)

Regarding the **"to what extent & why"**, our results allowed understanding and modelling the adsorption process. In brief:

- All options (1 to 5) achieve good removal of the pesticides, PhCs & hormones, and MC-LR_{eq} targeted (Campinas & Rosa 2006, 2010b, Campinas et al. 2017, 2021a,b).
- Charge, hydrophobicity (Log K_{ow}, Log D), and aromaticity are the adsorbate's key factors for adsorption (Figure 15), with a turning point for Log K_{ow} 2.2, above which the compounds are very amenable to adsorption (Figure 16, Campinas et al. 2021a), as found earlier in a UWWT study (Rodriguez et al. 2016). Positively charged functional groups, low surface polar area (PSA) and/or high aromaticity acted as adsorption enhancers of low-hydrophobicity compounds (Log K_{ow} < 2.2) (Figure 17). Coherently with other studies, a better removal of the positively charged compounds was observed, the difference depending on the PAC net charge, i.e., better with the negatively charged PAC (Campinas et al. 2021a). Log D vs charge plot (Figure 15, Campinas et al. 2021a) may be used to select the indicator CECs (surrogates) – an exhaustive monitoring is technically and economically unfeasible.
- Water background organics increase the PAC dose for balancing background NOM competition, which is stronger for the compounds less-amenable to adsorption (Campinas et al. 2021a,b) and for similar-size NOM, e.g., tannic acid and MC-LR (Campinas et al. 2013). Background inorganics affect the extent and

mecanisms of NOM-target adsorption (via shielding mechanisms) and may have a positive effect on PAC adsorption depending on the PAC overall charge (Campinas & Rosa 2006, Campinas et al. 2013).

- PAC (10 mg/L in Campinas & Rosa 2010b; 6-24 mg/L in Campinas et al. 2021c) does not impair the membrane flux, rather it helps controlling the irreversible membrane fouling, minimising the chemical cleaning frequency. It enhances NOM retention by UF/MF, including of algogenic organic matter (AOM) (Campinas & Rosa 2010a), though not significantly for the highly hydrophilic compounds, whose membrane foulant bahaviour may increase driven by water divalent salts (Campinas & Rosa 2010a).
- Modelling is a powerful tool to understand and predict PAC adsorption, assisting in the design & operation of real systems (Campinas et al. 2013, Viegas et al. 2014).



Lab. Jar tests for PAC/C/F/S

Lab. Hollow-fibre UF membrane, 0.05 m², 100 kDa (Campinas et al. 2010a,b)

Full-scale. Alcantarilha WTP (Águas do Algarve, S.A.) 3 m³/s PAC/C/F/S (Campinas et al. 2017)

Pilot. PAC/C/F/S at Alcantarilha WTP (Campinas et al. 2021a)

Pilot. PAC / (C)/MF, ceramic 0.75 m², 0.1 µm, dead-end, 80-330 L/(m².h) constant flux at Alcantarilha WTP (Campinas et al. 2021c)

Figure 14. Lab, pilot and full-scale tests of PAC application in DWT

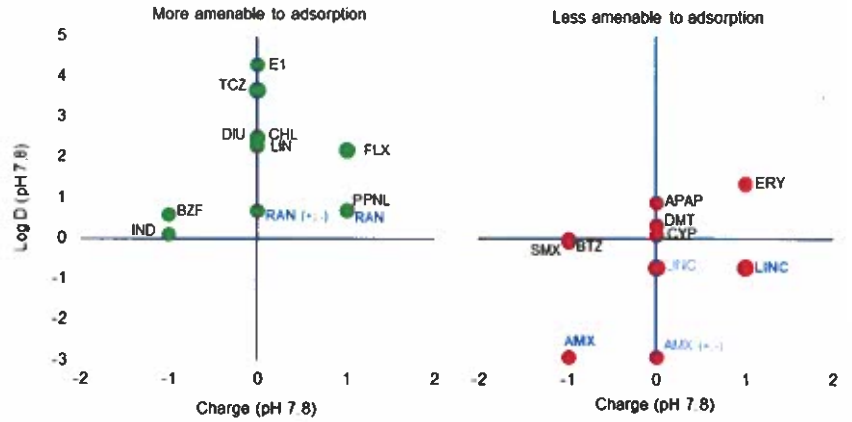


Figure 15. Log D vs charge for selected PhCs and pesticides (from Campinas et al. 2021a)
(very amenable to adsorption (green), relatively amenable (yellow), less amenable (red). Compounds in blue indicate they have a distribution of species between two charges at the working pH, the dominant charge emphasized in bold letter. For neutral compounds, (+,-) highlights they have positive and negative functional groups, despite the overall neutral charge

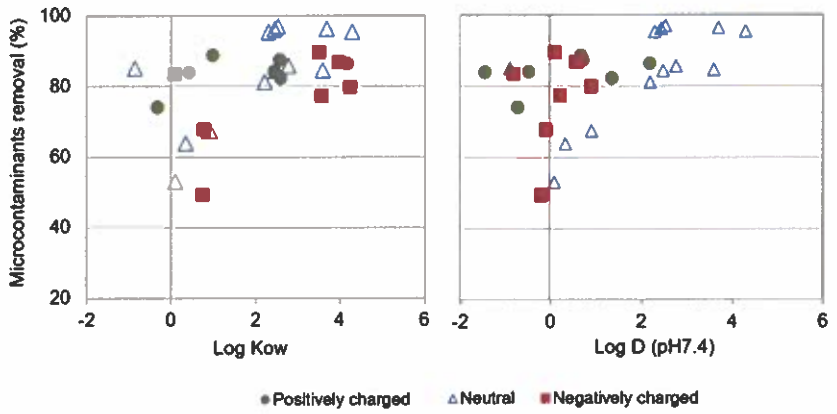


Figure 16. Microcontaminants' removal vs hydrophobicity measured by Log K_{ow} (left) or Log $D_{7.4}$ (right) (from Campinas et al. 2021a)

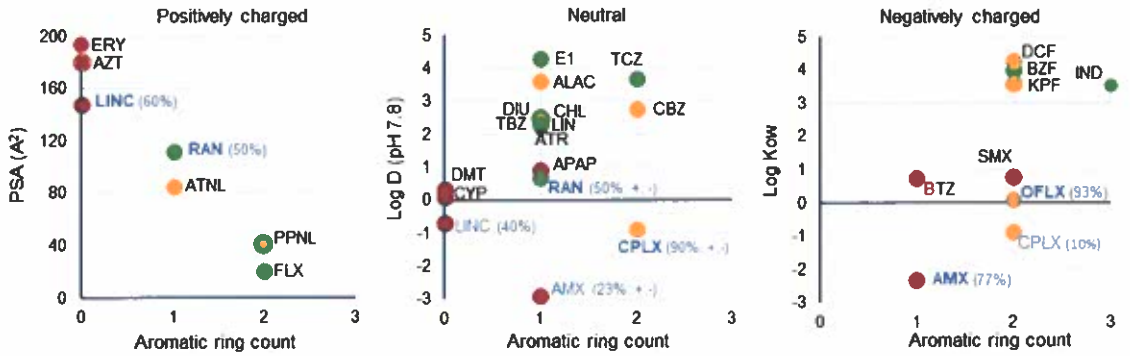


Figure 17. Charge, PSA, aromatic ring count, Log $D_{7.8}$ and Log K_{ow} role on microcontaminants' adsorption (left) positively charged compounds' PSA vs aromatic ring count, (centre) neutral compounds' Log D vs aromatic ring count, (right) negatively charged compounds' Log K_{ow} vs aromatic ring count (compounds very amenable to removal in green, relatively amenable in yellow and less amenable in red) (from Campinas et al. 2021a)

Regarding the **"where, how & at what cost"**, the main results are:

- **All options** (1 to 5) allow an effective control of the target micropollutants and CECs as long as an adequate PAC type & dose is applied. The differences are more related with (i) the risk of PAC particles escaping the treatment (in PAC / C/F/S the dose appears to be limited to 10 mg/L) and (ii) the energy consumption and the cost, for the upgrading solution or overall (Campinas et al. 2021c).
- **Option 1. PAC /C/F/S** (Campinas et al. 2021a) – removals of 65-79 % for total-pharmaceuticals (19) and 73-83 % for total-pesticides (9) were achieved with 3-9 mg/L of a mesoporous negatively charged PAC or with 20-24 mg/L of a microporous positively charged PAC. For hydrophilic low NOM waters, PAC textural properties and PAC surface chemistry were both important for adsorption. Half to one third of PAC dose would be enough as long as a PAC with adequate pore size distribution is used, this means using a PAC with high secondary microporous volume but also with high volume of mesopores to avoid microcontaminants' size exclusion and minimise PAC pore blocking phenomenon by NOM. Similar PAC savings are possible providing an extra 1-h PAC contact time to the very short time observed in the regular operation of the WTP where the PAC/CFS pilot was installed (around 15 min), with benefits particularly for the compounds of higher molar mass and/or less amenable to adsorption. A high vulnerability of clarification effectiveness to PAC dosing was observed with the low-turbidity waters tested, with a higher risk of negative impact for PAC doses above 10 mg/L towards residual turbidity due to PAC fines (with particulate microcontaminants), residual aluminium and aerobic endospores, the latter used as surrogates of biological forms resistant to chemical disinfection, as *Cryptosporidium* oocysts and *Giardia* cysts. This result may compromise the microcontaminants' removal reliability unless a downstream filtration safely retains the PAC fines.
- **Options 2-5. PAC/MF** (Campinas et al. 2021b) – PAC/(Alum)/MF (conditions below) achieved 75% to complete removal of total microcontaminants (pesticides, pharmaceutical compounds, or microcystins) with 4-18 mg/L of a mesoporous PAC and 2 h contact time (Figure 18), with a reliable particle separation

(turbidity < 0.03 NTU) and low aluminium residuals. Microcontaminants showed different amenabilities to PAC adsorption, depending on their charge, hydrophobicity (Log K_{ow}), polar surface area and aromatic rings count. Compounds less amenable to adsorption showed higher vulnerability to NOM competition (higher A254 waters), greatly benefiting from DOC-normalized PAC dose increase. PAC/Alum/MF also attained 29-47% NOM median removal as DOC, decreasing THMFP by 26%. PAC complemented NOM removal by coagulation (+15% to +19%, percentual points), though with no substantial improvement towards THMFP and membrane fouling. Furthermore, PAC/Alum/MF was a full barrier against aerobic endospores, and PAC dosing was crucial for ≥ 1.1-log reduction in bacteriophages.

Options 2-5. PAC/MF with 15 µm particle PAC, pH_{pzc} 10-11, 1126 m^2/g BET area and 0.83 cm^3/g total pore volume with 53% of mesopores (2-50 nm diameter); pressurized module, with 3 tubular MF (0.1 µm) ceramic (ZrO_2/TiO_2) membranes (0.75 m^2), operated in a continuous dead-end mode with constant permeate flowrate in the 80-330 L/(m^2.h) range (Campinas et al. 2021c) – PAC addition (6-24 mg/L) did not promote membrane fouling and, for all conditions tested, TCp kept constant or slightly increased with PAC dosing. Membrane fouling observed during the 1.5-year demonstration period was essentially reversible, since no significant change in clean membrane permeability was observed. As expected, a higher treatment capacity was obtained with filtered water (9.6 $m^3/(m^2.d.bar)$, option 5), followed by ozonated/pre-coagulated water (5.6 $m^3/(m^2.d.bar)$, option 4), with similar results for raw water and ozonated water with recirculated filter-backwash waters (4.7-4.9 $m^3/(m^2.d.bar)$, options 2 & 3). The non-clarified waters tested (options 2 & 3) required pretreatment with in-line alum coagulation to minimize membrane fouling (PAC/C/MF). Water recovery was 97-99%. PAC/MF energy consumption was 0.045-0.053 kWh/m^3 (options 5-3, 0.02 kWh/m^3 for PAC dosing), inversely varying with TCp. The cost analysis showed MF total production costs (CAPEX and OPEX) of 0.07 €/m^3 and 0.04 €/m^3 for treating 100 000 m^3/d raw and filtered waters, respectively; PAC dosing increases costs in 0.03 €/m^3 for both waters. Figure 19 shows PAC/MF total costs' breakdown.

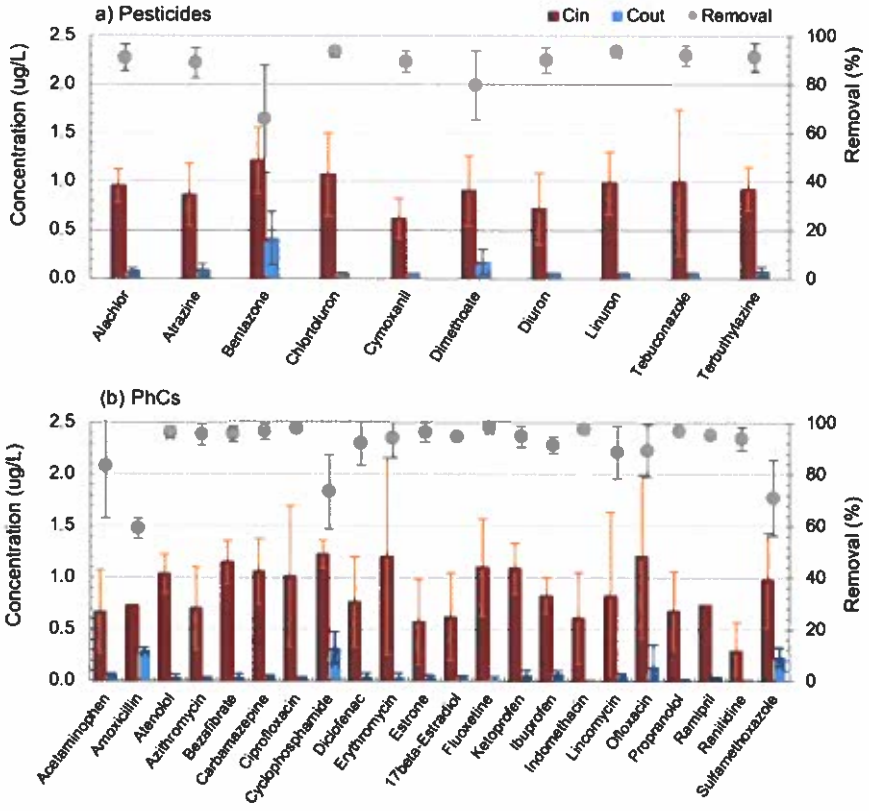


Figure 18. Average intake (brown bars) and permeate (blue bars) concentrations and removals (circles) of pesticides (a) and pharmaceuticals (b) after PAC/(Alum)/MF (average values of all spiking trials; error bars represent standard deviations between trials) (from Campinas et al. 2021b)

- **Options 2-5. PAC/MF** idem (Viegas et al. 2021a) showed the way PAC is dosed matters – two pilot trials were conducted to compare continuous 10-12 mg/L PAC inline dosing with 8-10 mg/L dosing to a 2 h-contact tank. Two low turbidity/low natural organic matter (NOM < 2 mgC/L) surface waters spiked with 7.2-10.3 µg/L total-pesticides were tested. Removal differences between the two PAC dosing options depended on pesticides' amenability to adsorption and NOM characteristics (A254) (Figure 20). Waters with low A254-absorbing NOM and only pesticides amenable to adsorption showed very high removals (all pesticides ≥ 93%) and no significant differences between the two PAC dosing options. Waters containing higher A254-absorbing NOM and high loads of pesticides less amenable to adsorption (dimethoate, bentazone) required higher inline PAC dose. Those or more severe conditions may require PAC doses higher than tested to comply with the Drinking Water Directive limits for pesticides. Cost analysis showed PAC inline dosing is more cost-effective than PAC dosing to the contact tank when identical PAC dose is sufficient or when the doses are low, even if 50% higher for inline dosing, and the plant is small.
- **Option 5. PAC/UF** with mesoporous & microporous positively charged (alkaline) fine PAC and hydrophilic hollow-fibre UF membrane, 100 kDa cut-off, in/out cross-flow filtration (Campinas & Rosa 2010a,b) – In the absence of background NOM, PAC/UF with 10 mg/L PAC and up to 20 µg/L MC-LR_{eq} feed concentration achieved 93-98% MC-LR_{eq} removal and a cycle-averaged permeate concentration below the WHO drinking water guideline-value for microcystin-LR variant. NOM type and concentration and MC initial concentration determined the PAC dose to be used. While 10 mg/L PAC effectively controlled ca. 5 µg/L MC-LR_{eq} in a model water with 2.5 mg/L NOM or with *M. aeruginosa* culture (cells and algogenic organic matter), 15 mg/L PAC were unable to achieve the WHO quality with a water containing higher concentrations of NOM (5 mg/L) and microcystins (ca. 20 µg/L MC-LR_{eq}) (Campinas & Rosa 2010c, 2011). UF is a safe barrier against cyanobacteria, ensuring an absolute removal of *M. aeruginosa* single cells, the smallest cyanobacterial cells and hence the most difficult to remove. An increased cell lysis was observed with cell ageing, although it did not necessarily degrade permeate quality, as in parallel to cell damage an enhancement of microcystin rejection by the UF hydrophilic membrane was observed with cell ageing, most probably due to AOM-driven microcystin adsorption on the membrane, connected to the greater content of the older cultures in segregated AOM (mucopolysaccharides) and/or protein lysed AOM (Campinas & Rosa 2010c, 2011).

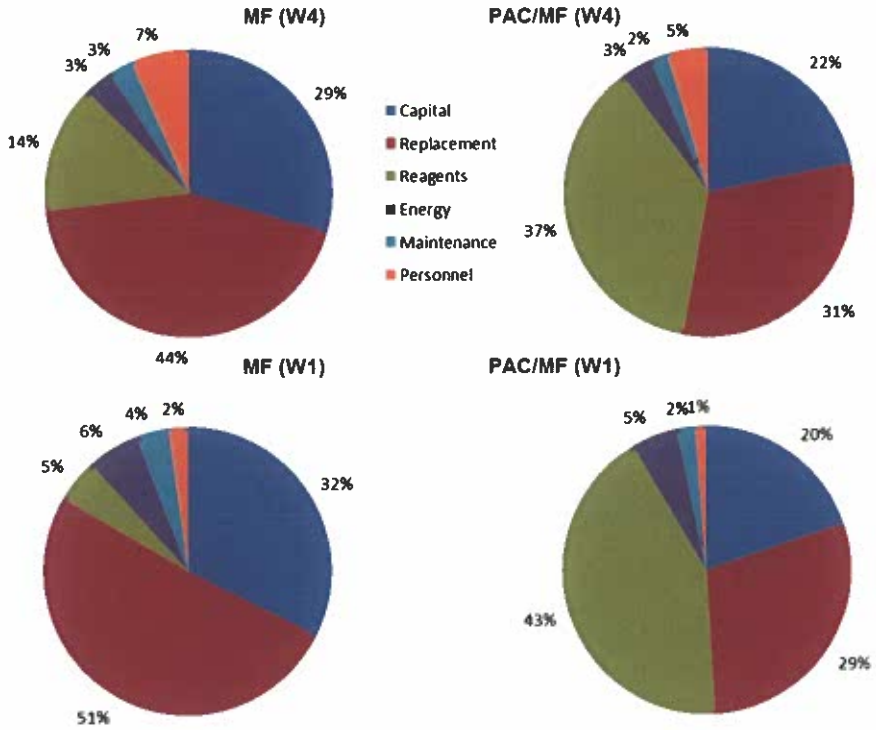


Figure 19. Cost structure of ceramic MF (left) and PAC/MF (right) for option 2 (W4) and option 5 (W1) (from Campinas et al. 2021c)

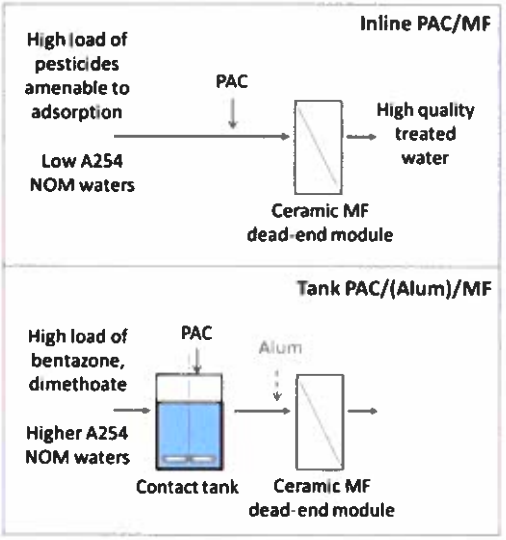


Figure 20. Inline vs tank PAC dosing in PAC/MF for pesticides and NOM removal in DWT (from Viegas et al. 2021a)

8 Applications in urban wastewater treatment and water reclamation

As in section 7, this section is focused on the last decade's results of my research team. The applications studied are illustrated in Figure 21 and aimed at answering the same questions: "to what extent & why?", "where, how & at what cost?" PAC different set-ups, PAC dosing directly into activated sludge reactor (PAC-AS) and PAC dosing downstream the biological treatment in a hybrid adsorption/membrane process (PAC/MF, or PAC/UF, or PAC/loose NF), can control organic micropollutants and CECs in urban wastewater treatment/resource recovery or water reclamation. Our strategy is to start by optimising the current barriers (option 1), then to find the best (tailored) solution to upgrade the treatment if needed by investigating several alternatives (options 2-5), and finally to look ahead to more demanding needs likely to occur in the (near) future, namely the direct potable reuse (DPR). Such strategy involved studies at lab, but also at pilot and full-scale (Figure 22), which allowed developing cost analysis, and were conducted within PhD (Rodriguez et al. 2016), Post-Doc (Viegas et al. 2018), and R&I projects – LIFE Impetus (Rosa et al. 2019, Campinas et al. 2022, Mestre et al. 2022), FP7 TRUST (Viegas et al. 2020a), LIFE aWARE (Viegas et al. 2018), and H2020 B-WaterSmart (Galego et al. 2022). We also investigate the development of new PACs, framed within a circular economy approach.

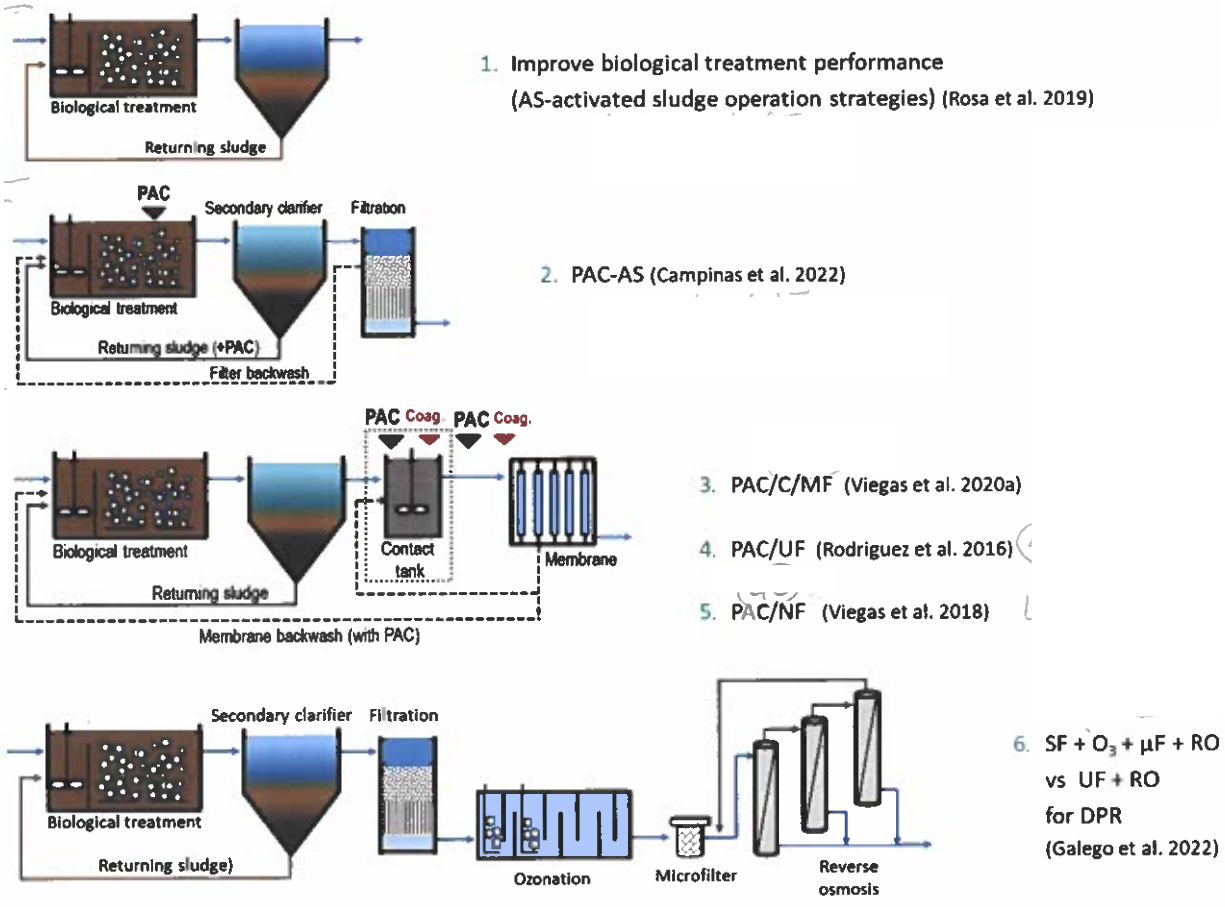
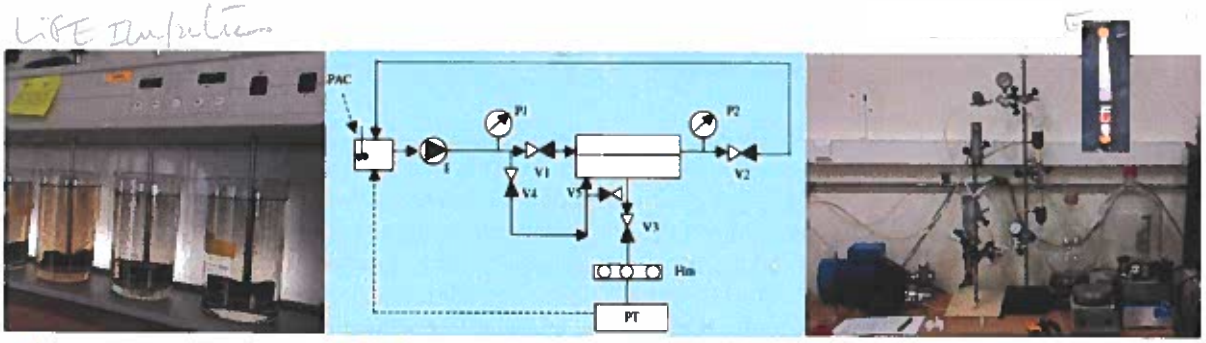


Figure 21. PAC application for controlling organic micropollutants in UWWT/water reclamation

Regarding **"to what extent & why"** and **"where, how & at what cost"**, briefly, our results showed:

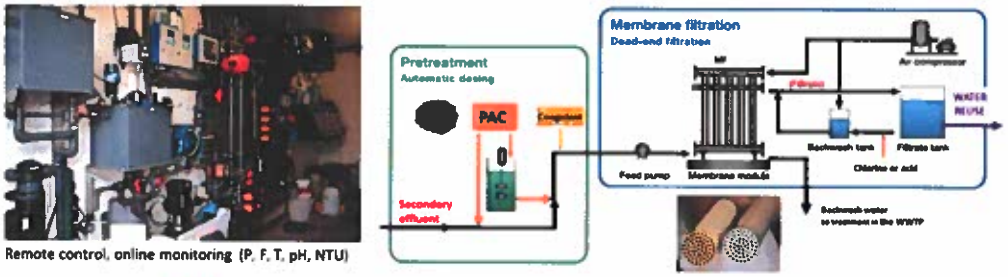
- **All options**, including option 1, achieve some or good removal of the organic micropollutants targeted. So, if possible, it is worth starting by implementing option 1 (no/low investment) and then upgrade as needed.



Lab. Jar tests for PAC/C/F/S

Lab. Hollow-fibre UF membrane, 0.05 m², 100 kDa (Campinas et al. 2010a,b)

Lab. Capillary NF, 0.075 m², 1000 Da (Viegas et al. 2018)



Remote control, online monitoring (P, F, T, pH, NTU)

Pilot. PAC / (C)/MF, ceramic 0.8 m², 0.1 µm, dead-end constant flux at BEI WWTP (Viegas et al. 2020a)

Full-scale WWTP
Beirolas (Águas Tejo Atlântico, S.A.)
50000 m³/d, AS system A2O
(Rosa et al. 2019)

Full-scale WWTP
Faro NW (Águas do Algarve, S.A.)
5000 m³/d, AS system oxidation ditch

PAC dosing
@ oxidation ditch

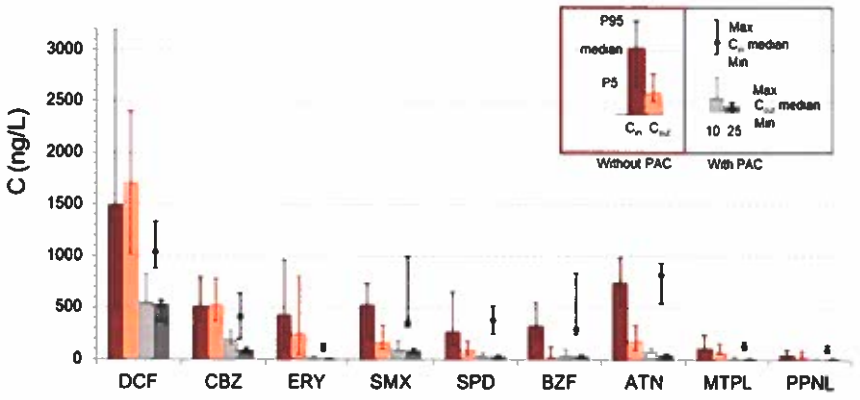
Figure 22. Lab, pilot and full-scale tests of PAC application in UWWT

- **Option 1. AS - activated sludge performance improvement** (Rosa et al. 2019) – the control of a representative range of PhCs (24) was studied in two activated sludge UWWTPs with nitrification/ denitrification (oxidation ditch in FNW, anaerobic/anoxic/aerobic system in BEI), involving 55 sampling campaigns during 2.5 years. The results show similar removals in both plants and, as earlier found, some of the most abundant PhCs at the WWTP inlet were highly removed during treatment (caffeine, acetaminophen, ibuprofen and naproxen), others presented intermediate and variable removals (the antibiotics erythromycin, sulfamethoxazole, sulfapyridine, and sulfadiazine; the beta-blockers metoprolol and propranolol) and some compounds were recalcitrant to treatment, as the antiepileptic/ anticonvulsant carbamazepine and the anti-inflammatory diclofenac. The PhC removals in both plants highly correlated with the PhCs' biodegradation constants (k_{bio}), with a turning point at 1 L/(g SS.d), above which the median removals were above 86% in BEI and above 74% in FNW. A 4-class (from A - easily removed to D - recalcitrant) biodegradation/sorption framework is proposed for interpreting and predicting PhC control in urban AS WWTPs (Figure 4), as well as for selecting the indicator CECs (surrogates, as proposed in UWWTD recast). A statistical analysis indicated significantly higher removals in BEI associated with F/M values below 0.08 d^{-1}, and in FNW associated with N-removals > 80% and alkalinity reductions > 40% (indirect effect of nitrification) and were associated with an effluent transmittance (T254) of 67% (coherent with Zietzschmann et al. (2014) and Zietzschmann (2020), who have found A254 to be a reasonable/good surrogate parameter). Though expressed by different proxys, these results are consistent with an enhanced

elimination of some low biodegradable PhCs when conditions for the build-up of the slowly growing nitrifying bacteria (which can excrete enzymes and, by co-metabolism, break down some low degradable molecules) are provided, as found by Clara et al. (2005) for sludge retention times of, at least, 10-15 days. Promoting nitrification is therefore an operational low-investment measure for improving current UWWTPs towards PhC elimination.

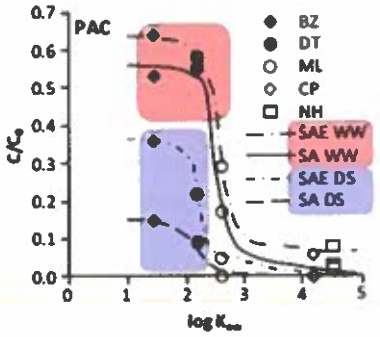
- **Option 2. PAC-AS** (Campinas et al. 2022) – PAC dosing to a conventional AS reactor is a low-investment option for controlling PhCs in UWWT, but its advantages and limitations in real operating environments are not fully assessed. A 3-week PAC-AS full-scale test was conducted in an oxidation ditch plant to assess PAC impact on effluent quality (PhCs, DOC and other parameters), energy consumption, sludge production and direct costs. DOC-normalized PAC doses of 0.7-2.6 mgPAC/mgDOC significantly reduced recalcitrant PhC discharged (e.g., by 63-84 % for carbamazepine and 63-70% for diclofenac), the higher dose yielding a more reliable effluent quality (Figure 23). Effluent quality for total phosphorus, colour, organic matter and transmittance was also enhanced and no interference with nitrification, oxidation-reduction potential or dissolved oxygen in the oxidation ditch was observed, resulting in no energy consumption increase. PAC had no impact on effluent turbidity and mixed liquor (MXL) suspended solids settleability, showing a positive effect on dewatered sludge dry weight and ultimately a 7-9% increase on final sludge production. After stopping PAC dosing, PAC remaining in the recirculated sludge presented adsorption capacity for some PhCs until it was completely out of system. Estimated direct costs (CAPEX + OPEX) for PAC addition to AS-reactor [0.064-0.055 €/m^3 for 50 000-500 000 m^3/d, for 20 mg/L PAC dosed 12 months/year] are almost plant-size independent and compare favourably with literature data for PAC and GAC post-treatment (Rizzo et al. 2019, Baresel et al. 2017) and similarly with post-ozonation (Abegglen & Siegrist 2012, Baresel et al. 2017, Hillenbrand et al. 2016, Mulder et al. 2015).
- **PAC adsorption UWWT vs DWT** – UWWT results are very consistent with the analogous ones found for DWT, though requiring more demanding conditions (higher PAC doses, lower membrane productivity) to balance the more concentrated water composition, so the removal mechanisms are essentially the same in both types of water. Charge, hydrophobicity, and aromaticity are again the adsorbate's key factors for PAC adsorption, as well as the water background organics and inorganics, the former with a stronger competing effect on the compounds less amenable to adsorption and the latter via the same shielding effect, as thouroughly analysed in option 4 investigation (conducted at lab-scale).
- **Option 4. PAC/UF** (Rodriguez et al. 2016) – for the compounds in Table 3, hydrophobicity is the adsorption key property for neutral adsorbates, with a turning point at Log K_{ow} 2.2-2.6, above which the compounds are very amenable to adsorption, i.e., present low residual normalised concentrations (Figure 24). The uptake of the positively charged nortriptyline by the positively charged, meso- and microporous PACs exceeded the expected from Log D due to its high aromaticity and the background ions, which partially shielded PAC-nortriptyline electrostatic repulsions. Adsorption capacity depended on the solute's hydrophobicity, whereas the kinetics further depended on its charge. Hydrophobic EfOM was preferentially adsorbed and a stronger competitor, particularly for microcontaminants with Log K_{ow} < 2.6. The highly microporous PAC better adsorbed these target compounds and the hydrophobic EfOM, and it attenuated the EfOM competition. So, in real applications, PACs with higher volume of secondary micropores or small mesopores (SA vs. SAE) might be a strategy for attenuating EfOM competition. For all waters, PAC had no effect on UF-flux, and it significantly improved the microcontaminants' and EfOM removal by PAC/UF over standalone PAC and UF; PAC/UF was more effective and efficient than PAC/sedimentation; PAC dose should target the contaminants with Log K_{ow} < 2.6, the weaker adsorbates, as found by others (e.g., Zietzschmann 2020).
- **Option 3. PAC/C/MF** (Viegas et al. 2020a) – pilot assays (100 L/(m^{2}h), 10 mg Fe/L) were conducted with sand-filtered secondary effluent spiked with 4 chemically diverse PhCs (ibuprofen, carbamazepine, sulfamethoxazole, and atenolol; Table 2, Figure 15, Figure 17) and 15 mg/L PAC dosed in-line or to a 15-min contactor. The results showed no PAC-driven membrane fouling and +15 to +18% added removal with PAC contactor, reaching significant removals of CBZ and ATN (59-60%), SMX (50%), colour (48%), A254 (35%) and DOC (28%). Earlier long-term demo tests with the same pilot proved PAC/Fe/ceramicMF to consistently produce highly clarified (monthly median < 0.1 NTU) and bacteria-free water, regardless the severe variations in its intake (Viegas et al. 2015). A detailed cost analysis points to total production costs of 0.21 €/m^3 for 50 000 m^3/day and 20 years membrane lifespan, mainly associated with equipment/ membranes replacement, capital and reagents, the energy having the smallest share (for a specific flux of 261 L/(m^2.h.bar) and an energy consumption of 0.026 kWh/m^3).

- **Option 5. PAC/NF** (Viegas et al. 2020a) – bench-scale results with a loose-NF membrane (capillary NF, 1000 Da cut-off) showed high removal efficiencies of 4 target PhCs (ATN, CBZ, DCF, SMX; 100 µg/L each spiked in secondary sand-filtered effluent) and the PAC continuous dosing to be more efficient than the pulse dosing, 50 mg/L PAC achieving a total-PhC removal of 68% (ranging from 58% to 89%), 58% DOC removal and 90% colour removal. NF fluxes of 20 L/(m^2.h) were achieved with 1.2 bar transmembrane pressure, 1 m/s crossflow velocity, with no pressure increase up to 100 mg/L PAC. The results were successfully used in the design and operation of the PAC/NF pilot for the technology demonstration in El Prat WWTP (Barcelona). Compared to UF/RO (50/50), PAC/NF at pilot scale yielded comparable EfOM and PhC removals, PAC costs similar to UF/RO reagent costs, 40% less energy. Furthermore, PAC/NF concentrate recirculation to MBR showed synergic effects (not possible for UF/RO concentrate) with economic (lower cost) and operational advantages – PAC in the MBR improved the removal of refractory microcontaminants (diuron and carbamazepine) and metals (Cu, Ni, Zn, Pb) (Martin et al. 2016).
- **PAC adsorption modelling** (integrating adsorption kinetics and isotherms) has the predictive ability to forecast the contaminant removal as a function of PAC dose, contact time and adsorbate concentration (Figure 25, Rosa et al. 2019); it is therefore a powerful tool to support the design & operation of real systems.
- **Options 3-5.** As in DWT, these options with MF, UF or NF membranes ensure a reliable water **disinfection** up to class A of reclaimed water (the highest water quality in Reg (EU) 741/2020, DL 119/2019), which is adequate for unrestricted water reuse, an extra feature which should be considered while comparing alternative options for PhC control. The pressure increase from MF to UF and NF [e.g., from 261 L/(m^2.h.bar) and 0.40 bar for ceramic MF (Viegas et al. 2020a) to 20 L/(m^2.h) at 1.2 bar for NF (Viegas et al. 2018)] corresponds to an **energy-intensity** increase.
- **Option 6. direct potable reuse** – building on an earlier experience on batch production (Galego et al. 2022), tests with a 24/7 automated pilot are starting to demonstrate the safety of potable water production by post-ozonation and or 3-stage reverse osmosis, after sand-filtration or UF, and to develop the protocol to produce reclaimed water for artisanal beer production.



Parameter	No PAC	PAC-AS trial 1 (10 mg/L)		PAC-AS trial 2 (25 mg/L)	
	Median effluent conc. or value	Median effluent conc. or value	Reduction (%)	Median effluent conc. or value	Reduction (%)
DOC (mg C/L)	12.5	8.7	31	8.7	30
A254 (cm^{-1})	0.21	0.14	35	0.12	44
SUVA (L/(mg.m))	1.7	1.6	6	1.3	20
COD-Total (mg O_2/L)	42	35	17	30	29
COD-soluble (mg O_2/L)	70	29	59	26	63
A436 (cm^{-1})	0.019	0.011	42	0.009	53

Figure 23. Example of PAC-AS performance in PhC (left) and EfOM (right) control (adapted from Campinas et al. 2022)



	WW	DS
pH	7.4 ± 0.4	7.1 ± 0.2
DOC, mg CL^{-1}	3.0 ± 0.6	–
Electrical conductivity, µS cm^{-1}	1432 ± 116	1523 ± 67
Alkalinity, mg $CaCO_3$ L^{-1}	117	117
Hardness, mg $CaCO_3$ L^{-1}	370	370
$UV_{254\ nm}$, m^{-1}	11.61 ± 0.27	–
$A_{436\ nm}$, m^{-1}	1.004 ± 0.035	–
SUVA, L m^{-1} $mg^{-1}C$	3.8 ± 0.4	–
EfOM composition, %		
Strongly hydrophobic	71.2	–
Moderately hydrophobic	14.0	–
Charged hydrophilic	10.5	–
Neutral hydrophilic	4.3	–

Figure 24. Log K_{ow} role on organic microcontaminants' control by PAC (SA and SAE) adsorption and the effect of water background organics (wastewater - WW and deionised water with equivalent inorganic matrix - DS) (compounds in Table 3) (adapted from Rodriguez et al. 2016)

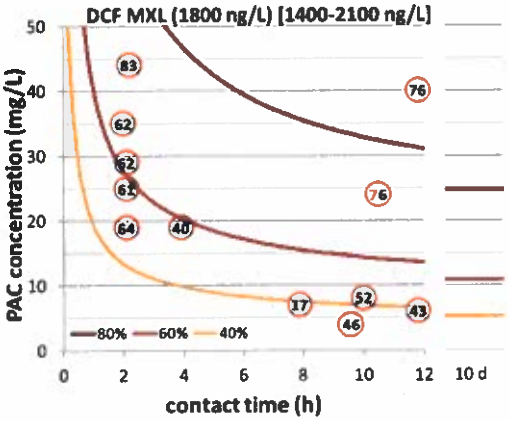


Figure 25. Model predicted PAC adsorption removals (solid lines for 80%, 60%, 40%) of diclofenac from FNW WWTP as a function of PAC dose and contact time compared to field results from pilot-scale trials (circles) (from Rosa et al. 2019) (the 10-day prediction corresponds to the PAC full capacity use due to PAC recirculation; the values inscribed in the circles are the removals obtained in the pilot trials)

9 Closing remarks

Population growth and ageing, as well as water scarcity driven by climate change call for an enhanced control of organic micropollutants and contaminants of emerging concern in the urban water cycle, as progressively entailed in the EU and Portuguese legal framework on drinking water, urban wastewater treatment and water reuse. In this context, there is a crucial need for multibarrier solutions, grounded on current barriers' improvement, prioritising low-energy, physical barriers (to minimize byproducts, resources' use, and carbon footprint) and producing fit-for-purpose water(s).

Activated carbon-based and hybrid PAC/membrane processes have proven a huge potential for controlling CECs in water treatment and water reclamation, but there is room for improving their sustainability and cost-efficiency with PAC development and process optimisation. For instance, new high-performing environmental-friendly (biomass-derived, steam activated) PACs from local biomasses (circular economy approach), as well as of more efficient finer sPAC and magnetic PACs allowing their recovery and regeneration are very important. Each application is water & target contaminant-specific and requires methodologies for selecting representative contaminants, the characterisation of the inorganic and organic matrices of the waters, and to understand and anticipate/overcome competing factors, namely through modelling. Pilot demonstration and mathematical modelling are therefore success factors for process design and operation.

Strategic planning, objective-driven (e.g., organic CEC control, ARB&ARGs control, disinfection for water reuse) and performance-based decisions are required to successfully address the moving targets the CECs constitute. Skilled and competent human resources make all the difference and the curricular unit "Advanced management of urban water treatment" (submitted to Habilitation) aims at making a contribution to such capacity building.

Acknowledgments

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