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# *Integration of advanced wastewater treatment and reclamation technologies for organic micropollutants removal and promote water reuse*

**Carlos Echevarría**

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# **Integration of advanced wastewater treatment and reclamation technologies for organic micropollutants removal and promote water reuse**

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Doctoral Programme on Chemical Engineering Processes.



**UNIVERSITAT POLITÈCNICA DE CATALUNYA  
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*No se aprecia el valor del agua hasta que se seca el pozo*



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## Abstract

Climate change and overpopulation are responsible for more frequent droughts, and the imbalance in the water resources management leads to a greater competition in the exploitation of freshwater sources. The introduction of alternative water resources such as reclaimed water seems to be one of the most sustainable option, compared with other alternatives such as seawater desalination or water transfer. Nevertheless, the wide implementation of water reuse is still far from its whole potential and faces with different local barriers related to public awareness and governance.

The presence of organic micropollutants (OMP) in the water cycle, specifically in the wastewater effluents intended to be reclaimed and reused, has generated concern in public authorities due to their uncertain effects in human health. Limited removal efficiencies are found for some OMP in conventional wastewater and reclamation schemes; in this sense, it is necessary to resort to alternative and advanced technologies to guarantee the cost-effective removal of these compounds.

Through three published articles (Chapter 3-5) this PhD thesis evaluates and compares from a technical and economic point of view different advanced municipal wastewater reclamation schemes to produce cost-effective reclaimed water to be reused, considering the removal of organic micro-pollutants, scalability, and the requirements of the end-users. The ultimate goal is to provide knowledge to overcome some of the identified barriers and contribute to a higher implementation of water reuse.



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## List of abbreviations





# Chapter 1



# 1. Chapter 1: Introduction

## 1.1 Water Reuse: a sustainable strategy to face water scarcity

The balance between water resources availability and demand has reached a critical level in many areas of the planet, mainly in the coastal semiarid regions (e.g. Mediterranean Basin, Southern Australia). Climate change and overpopulation are responsible for more frequent droughts, and the imbalance in the water resources management leads to a greater competition in the exploitation of freshwater sources (Fukasawa et al., 2020). This issue results in the overexploitation of groundwater or the degradation of surface water bodies, representing an environmental concern and increasing the operational expenditures (OPEX) in water utilities (Muio et al. 2020; Bagheri et al. 2019).

Water Reclamation (WR) refers to the process of converting pre-treated wastewater (from a secondary effluent) into water that meets quality requirements to be reused for other purposes. Figure 1 shows an adapted illustration from Asano et al. (1998), in which the water cycle and the role of water reuse can be visualized at a glance.

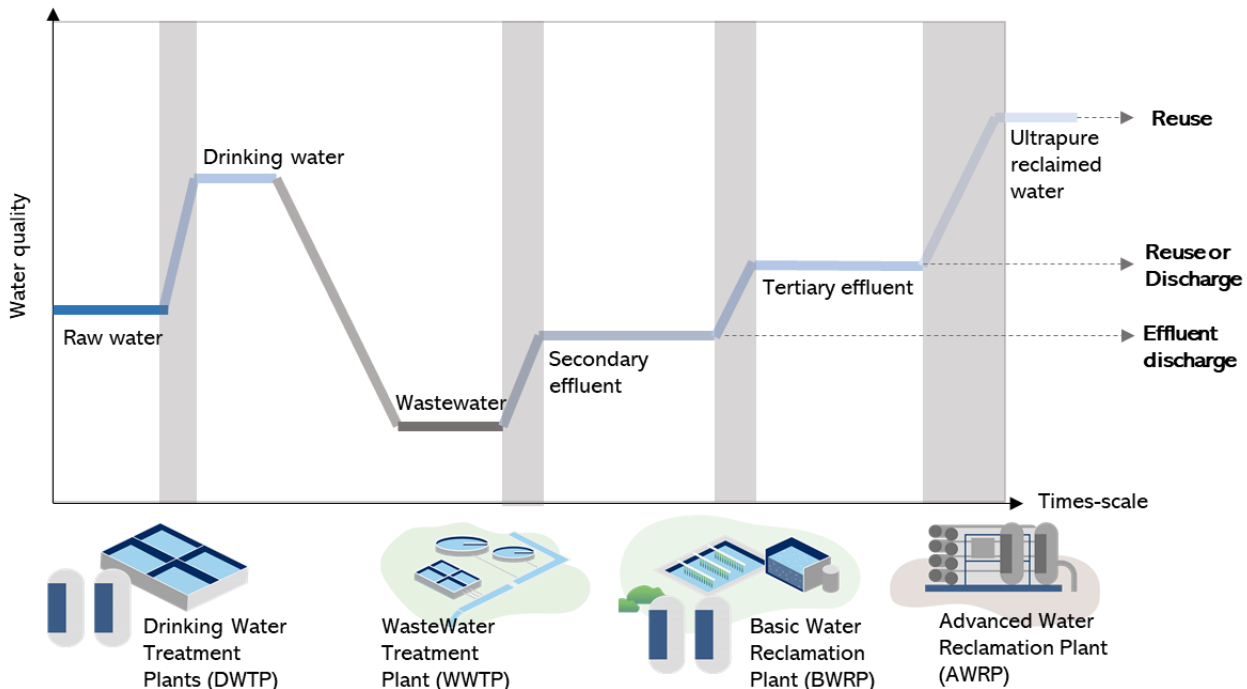


Figure 1 Water cycle and water reuse opportunities at a glance (adaptation from Asano et al. (1998))

As it can be seen, Drinking Water Treatment Plants (DWTP) are designed to raise raw water quality (e.g., surface and groundwater) to the standards established to be consumed by humans. After its flushing in households and

drainage, together with other wastewater sources (e.g., industrial, agricultural), the effluents are derived to Wastewater Treatment Plants (WWTP), designed to remove organic matter and nutrients prior its discharge into the environment. This water conditioning leads to the opportunity of giving a second life to the effluent by applying water reclamation technologies, which can produce a wide range of water qualities, suitable to cover different uses. From one hand, Basic Water Reclamation Plants (BWRP) allow the production of a tertiary effluent, in which suspended solids (SS) and turbidity are removed and a disinfection is done (*E. Coli* removal) (Spanish Royal Decree 1620/2007). Finally, Advanced Water Reclamation Plants (AWRP), as it will be demonstrated in this thesis, are prepared to remove the most persistent physico-chemical (e.g., hazardous metals, organic micropollutants (OMP) and dissolved salts) and microbiological (e.g. *viruses*, *clostridium spores*) compounds. In addition, these facilities also allow ultrapure reclaimed water (quaternary effluent) to be obtained, suitable to reuse in most restrictive applications, whose quality standards can be even higher than those of drinking water (Bourgin et al., 2017; Margot et al., 2013).

### 1.1.1 Reclaimed water uses

For an efficient management of the water resources, reclaimed water needs to be adapted in quality and quantity to the requirements defined by potential end-users, existing different applications that can be covered with this alternative resource. Table 1 summarizes the different reclaimed water uses identified, as well as the main target pollutants regulated:

*Table 1 Water reclamation and reuse applications (Kalavrouziotis et al., 2013; Lazarova et al. 2005; Spanish RD 1620/2007).*

Reclaimed Water Uses			Target Pollutants to be removed
Non-potable Reuse	Environmental uses	Landscape irrigation Fire prevention Wetland's maintenance River flow maintenance Aquifer recharge for non-potable uses	SS, Turbidity
Non-potable Reuse	Recreational uses	Golf courses irrigation Publica fountains and ponds	SS, Turbidity
Non-potable Reuse	Urban and domestic uses	Street's cleaning Parks and green areas irrigation Toilette flushing	SS, Turbidity

Reclaimed Water Uses			Target Pollutants to be removed
Non-potable Reuse	Agriculture irrigation	Crop's irrigation	SS, Turbidity Salinity Metals OMP
Non-potable Reuse	Industrial uses	Process water Boiler's feed Cooling Cleanings Reagent's preparation	SS, Turbidity Salinity Metals DOC
Potable Reuse	Indirect Potable Reuse (IPR) Direct Potable Reuse (DPR)		SS, Turbidity Salinity Metals OMP

**Planned non-potable reuse** encompasses those uses that do not imply the direct or indirect entrance of reclaimed water in the drinking water supply systems (Arden et al., 2021). The less restrictive uses from a water quality perspective are environmental uses (e.g., landscape irrigation, fire prevention, managed aquifer recharge (MAR)), recreational uses (e.g., golf courses irrigation, public fountains maintenance), or urban and domestic uses (e.g., street's cleaning, park and green areas irrigation and toilette flushing). These uses can be covered with BWR technologies, being SS, turbidity and *E.Coli* the target pollutants to be removed. Depending on the secondary effluent quality, in agricultural uses (crops irrigation) salinity removal can be also required. Additionally, the new European regulation (EU 2020/741) in water reuse requires for the most restrictive type of irrigation the removal of more specific microbiological indicators (e.g., *clostridium spores*); and the tendency seem to indicate that hazardous metals or OMP will need to be removed in the near future. Regarding industrial uses (e.g., process water, boiler's feed, cooling, cleanings, and reagent preparation), depending on the industrial sector, the quality requirements are restrictive in terms of conductivity, metals (e.g., Fe, Cu, Al) and dissolved organic matter (DOC). The regulated and recommended water quality parameters for the described uses are dependent on each administration. A revision of the main water reuse regulations is summarized in section 1.3.

On the other hand, **planned potable reuse** was defined by the *Potable Reuse Compendium* (EPA, 2017) as the intentional use of reclaimed water for drinking water supply, and includes:

**Direct Potable Reuse (DPR)**, which is defined as the direct and planned introduction of high-quality reclaimed water into a DWTP. This includes the treatment of reclaimed water in the AWRP.

**Indirect Potable Reuse (IPR)**, which is understood as the planned augmentation of a drinking water source (surface water or groundwater) with treated reclaimed water, which provides an environmental buffer prior to subsequent use.

Regarding both non-potable and potable reuse applications, the term **De facto reuse** is often used and is referred to the unplanned reuse of treated wastewater (EPA, 2017). After its discharge from the WWTP, the secondary effluent may reach a water supply intake (e.g., DWTP or by another user such as an irrigation community) but the water reuse scheme is not officially recognized.

Figure 2 shows a comparison of the energy consumptions associated to water and wastewater treatment regarding its source (Allen et al., 2017). The range in the energy consumption associated to surface water or groundwater treatment (0.40-0.80 kWh/m<sup>3</sup> and 0.35-0.95 kWh/m<sup>3</sup> respectively) is dependent on the status of the water body. Thus, in coastal water scarce regions such as the Mediterranean Coast, the energy consumption in water treatment can be maximized due to the presence of high turbidity in surface water bodies or nitrates and salinity contamination in groundwater. In this context, reclaimed water reuse for non-potable and potable applications (0.5-0.8 kWh/m<sup>3</sup> and 1.3-1.6 kWh/m<sup>3</sup> respectively) is gaining importance and is postulated as the most sustainable alternative to the use of freshwater sources, in front of seawater desalination (3.3-4.2 kWh/m<sup>3</sup>) or water importation (1.6-2.6 kWh/m<sup>3</sup>).

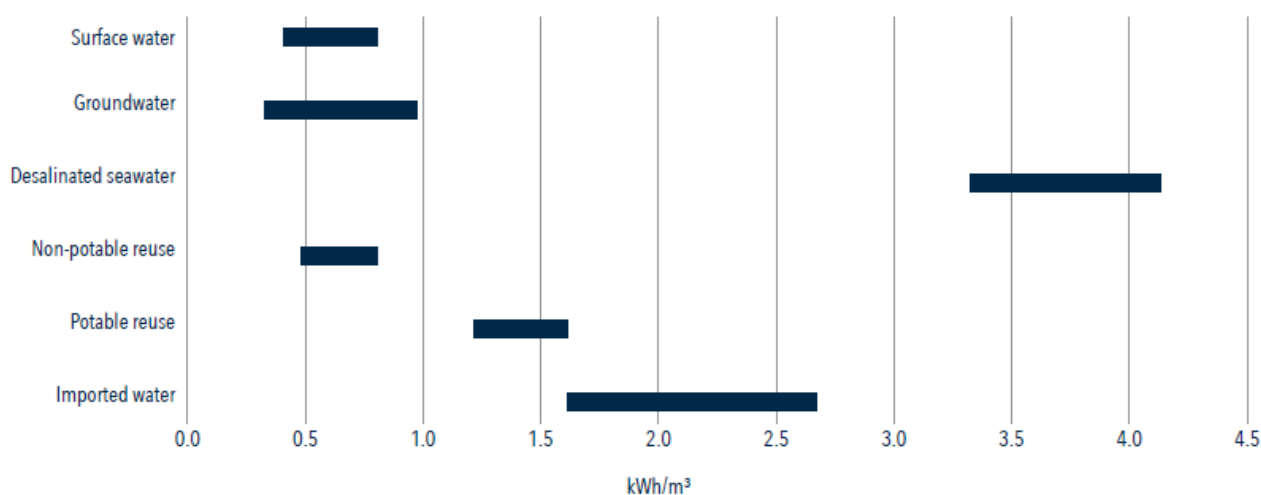


Figure 2 Energy consumption comparison regarding water source (Source: Allen et al., 2017)

### 1.1.2 Drivers and challenges in water reuse

During last three decades, according to the Global Water Intelligence (Allen et al., 2017), the water reuse market presented a Compound Annual Growth Rate (CAGR) of 8% in installed capacity. From an implementation

perspective, a total capacity of 140 Hm<sup>3</sup>/day is available at worldwide level, regarding 90 Hm<sup>3</sup>/day in seawater and brackish water desalination. Identified drivers that boosted this growth are: (i) the water scarcity situation and more extended and frequent droughts (especially in some areas of USA such as California), Australia, and Mediterranean Basin), (ii) the industrialization and urbanization 'boom' in China and (iii) the irruption of small but advanced markets (e.g., Singapore and Israel). Moreover, during the following years, global growth is expected to continue, with an additional capacity of 53 Hm<sup>3</sup>/day. The drivers are expected to be: (iv) a more extreme water scarcity situation associated to the effects of climate change, (v) a more restrictive regulatory framework, especially in industrial wastewater management, (vi) advances in technology and the lowering of costs, (vii) expansion of potable reuse (IPR and DRP) and (viii) emerging municipal-industrial partnerships.

Many successful water reuse projects can be found worldwide and some of them are summarized in Table 2. The USA account with large experience in water reuse, even for potable uses. According to EPA (2017), first IPR experiences were reported in Los Angeles (L.A) in 1962 through the Montebello Forebay project, followed in 1976 by the Orange County Water Factory 21, which in 2008 was upgraded to the Ground Water Replenishment System (GWRS). The case of Namibia (Windhoek) is of special interest since in 1968 it represented the first DPR reference in the world, aiding to guarantee the water supply to the capital city after years of droughts accentuated by a complete dependence on rainwater (Lazarova et al., 2013). It is worth to mention how Israel has managed efficiently water resources since 1977 through groundwater recharge in Dan Region and its extraction in the Negev Desert for agricultural irrigation (Shafdan Project). In Israel, 86% of treated wastewater is reused and agricultural irrigation accounts with the 96% of reclaimed water consumption (Goren et al., 2014). Singapore accounts with a clear strategy in water management, and the Public Utilities Board boosted the Four National Taps strategy, in which water reuse (NEWater) represents 40% of total water supply and it is expected to grow up to 55% before 2060 (Chew et al. 2011).

Nevertheless, the global implementation of this alternative water resource is far from its potential. The European Commission reported in 2021 that only 2.4% of the total treated wastewater in Europe was reclaimed and reused (964 Hm<sup>3</sup>/year) (European Commission, 2021), while the EU potential is much higher and is estimated in the order of 6000 Hm<sup>3</sup>/year (around six times higher than the current reused volume). Specifically, in Spain, the total water reclamation is estimated around 400 Hm<sup>3</sup>/year (AEAS, 2017; Allen et al., 2017), representing 12% of the total wastewater volume.

Different local transversal challenges or barriers towards water reuse implementation have been envisaged and are described in Figure 3. Depending on the level of maturity of water reuse implementation in a territory, these challenges refer to all non-potable uses or only focus on potable reuse (EPA, 2017).

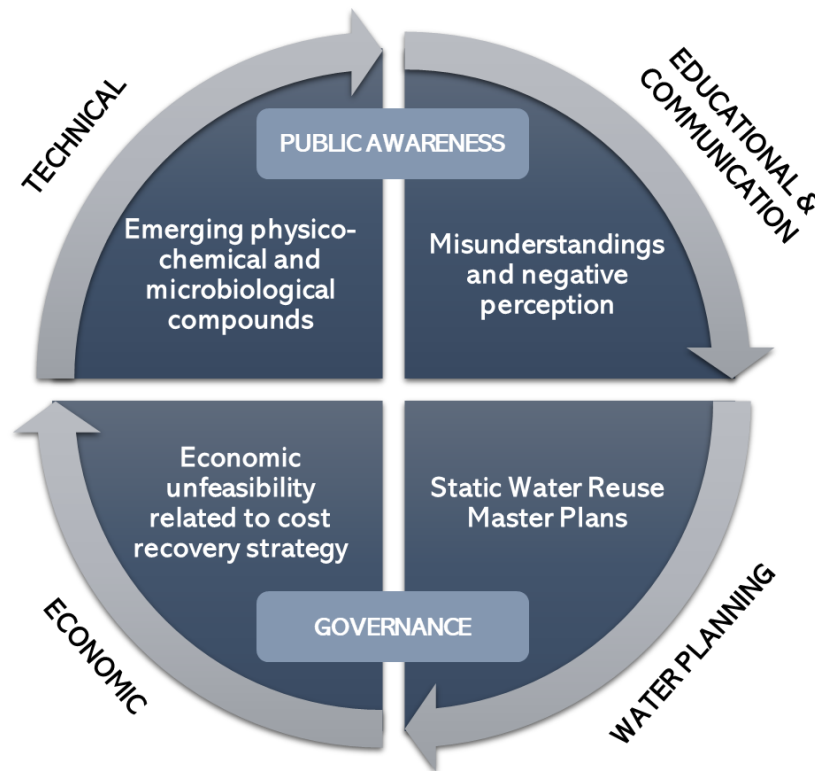


Figure 3 Water Reuse challenges

Reclaimed water source (treated wastewater effluents) has raised **public awareness** on related human health and environmental risks, usually generating misunderstandings and a negative public perception (Hartley et al. 2019). From a **technical** point of view, state-of-the-art water reclamation technologies have demonstrated robustness and efficiency for the removal of SS, turbidity, and basic disinfection (Rizzo et al., 2020). However, specific physico-chemical (e.g., OMP, hazardous metals) and microbiological (e.g., *viruses*, *clostridium spores*) parameters are generating an emerging concern in environmental and health authorities due to their uncertain removal rates in already operating BWRP (Gidstedt et al., 2022; Mansilla et al., 2021; Ruiz-Aguirre et al., 2017). From an **educational and communication** perspective, misunderstandings regarding the water cycle and the yuck factor associated to the idea of 'Toilet to Tap' concept can create a barrier in some regions and cultures. According to the *Public Consultation Analysis Report* developed by Deloitte in 2015 for the European Commission, the negative perception on the quality of reused water is an important barrier in water reuse



acceptance for 85% of respondents, while any of the respondents provided any evidence to demonstrate that reclaimed water could generate issues or damages in the environment or human health.

**Conventional local water reuse planning** and applied **governance models** are usually based on static documents, generated through a preliminary assessment where territorial pressures are detected, end-users' groups are visualized, and reclaimed wastewater volumes are determined to cover certain uses (Kandiah et al. 2019). Nevertheless, the rapid social and economic changes may disturb the established master plans, which are usually set for the following 5 or 10 years. Also related to this issue, **local economic feasibility** represents an important constraint in water reuse projects implementation (Pardo et al. 2021). Capital expenditures (CAPEX) and operational expenditures (OPEX) of switching from a freshwater source to an alternative water resource can be misunderstood by the relevant local and territorial actors as well as the sizing of water reuse projects capacity. Usually, it is related to a lack of communication or understanding of the end-users needs and a static planning. This ends-up in the impossibility of costs recovery and the financial failure of these projects (Silva Pinto et al. 2021). The fragmentation of administrations and water responsibilities in a territory (e.g., Water agencies and regulators) also represent a barrier to many water reuse projects.

In this line, **innovation must bring suitable solutions to unblock current barriers**. Novel **advanced water reclamation technologies** need to be demonstrated to guarantee the cost-effective removal of those concerning compounds (e.g., OMP), as well as provide solutions in terms of brine management or valorization (Ogunbiyi et al. 2021). It is necessary to propose educational and communication initiatives and address innovative governance models to achieve the economic feasibility of water reuse projects.

Table 2 List of some of the main worldwide emblematic references in water reuse (EPA, 2017; Allen et al., 2017; Lazarova et al., 2013).

Country	Site	WRP / Project	Status	Capacity	Treatment Train	Uses
Australia	Melbourne	Western Treatment Plant	Operational	109,000 m <sup>3</sup> /day	Wetland (lagoon)	Agricultural
Australia	Melbourne	Eastern Treatment Plant	Operational	330,000 m <sup>3</sup> /day	O <sub>3</sub> +BAC+O <sub>3</sub>	Urban
Australia	Queensland	West Corridor Recycled Water Scheme	Decommissioned	66,000 m <sup>3</sup> /day	MF+ RO+UV/H <sub>2</sub> O <sub>2</sub>	IPR
Australia	Perth	Beenyup Groundwater Replenishment Trial	Decommissioned	4,500 m <sup>3</sup> /day	UF+RO+UV	IPR
Israel	Dan Region	Shafdan WRP	Operational	360,000 m <sup>3</sup> /day	Cl <sub>2</sub>	Agricultural
Israel	Haifa Region	Haifa WRP	Operational	120,000 m <sup>3</sup> /day	SF+UV/Cl <sub>2</sub>	Agricultural, Industrial
Namibia	Windhoek	Goreangab WRP	Operational	21,000 m <sup>3</sup> /day	GAC+O <sub>3</sub> +BAC+UF	DPR IPR
Spain	Barcelona	El Baix Llobregat WRP	Operational	320.000 m <sup>3</sup> /day	BWRP+UF+RO	Urban Industrial Agricultural Environmental
Spain	Sabadell	Riu Sec WRP	Operational	33,000 m <sup>3</sup> /day	MBR +UV/Cl <sub>2</sub>	Urban Environmental
Spain	Alicante	Rincón de León WRP	Operational	75,000 m <sup>3</sup> /day	SF+UF+RO	Urban Agricultural
Singapore	Singapore	Changi BEWG-UESH NEWater plant	Operational	228,000 m <sup>3</sup> /day	MF+RO+UV	Industrial IPR
Singapore	Singapore	Kranji NEWater plant	Operational	82,000 m <sup>3</sup> /day	MF+RO+UV	Industrial IPR

Country	Site	WRP / Project	Status	Capacity	Treatment Train	Uses
Singapore	Singapore	Tuas NEWater plant	Operational	800,000 m <sup>3</sup> /day	MBR+RO+UV	Industrial IPR
USA	Montebello Forebay (CA, USA)	Montebello Forebay	Operational	200,200 m <sup>3</sup> /day	SF+Cl <sub>2</sub>	IPR
USA	Orange County (CA, USA)	Water Factory 21	Suspended by Orange County GWRS	66,750 m <sup>3</sup> /day	MF+ RO+UV/H <sub>2</sub> O <sub>2</sub>	IPR
USA	West Basin Municipal Water District (CA, USA)	Edward C. Little Water Recycling Facility	Operational	152,000 m <sup>3</sup> /day	PC+MF+RO+UV/H <sub>2</sub> O <sub>2</sub>	Urban Industrial IPR
USA	Orange County (CA, USA)	Groundwater Replenishment System (GWRS)	Operational	380,000 m <sup>3</sup> /day	MF+ RO+UV/H <sub>2</sub> O <sub>2</sub>	IPR Industrial
USA	Los Angeles (CA, USA)	San José Creek WRP	Operational	398,560 m <sup>3</sup> /day	SF+UV/Cl <sub>2</sub>	Environmental
USA	Big Spring (TX, USA)	Colorado River Municipal Water District (CRMWD) Raw Water Production Facility	Operational	9,500 m <sup>3</sup> /day	MF+ RO+UV/H <sub>2</sub> O <sub>2</sub>	DPR IPR
USA	Wichita Falls (TX, USA)	River Road WWTP (IPR) and Cyrpres WTP (DPR) projects	Decommissioned	28,500 m <sup>3</sup> /day	MF+ RO+UV/H <sub>2</sub> O <sub>2</sub>	DPR IPR
USA	El Paso (TX, USA)	Advanced Water Purification Facility	Undergoing regulatory approval	45,500 m <sup>3</sup> /day	MF+ RO + UV/H <sub>2</sub> O <sub>2</sub> + GAC+ Cl <sub>2</sub>	DPR

<i>Country</i>	<i>Site</i>	<i>WRP / Project</i>	<i>Status</i>	<i>Capacity</i>	<i>Treatment Train</i>	<i>Uses</i>
USA	Scottsdale (AZ, USA)	Scottsdale Water Campus	Operational	91,000 m <sup>3</sup> /da	SF+MF+RO+UV	IPR

## 1.2 Organic Micropollutants: an emerging concern

During last decades, developments on analytical techniques, mainly through the Liquid Chromatography (LC) coupled with Mass Spectrometry (MS), has allowed to detect organic compounds from anthropogenic origin in WWTP effluents, which presence was unknown due to their relatively low concentrations ( $\mu\text{g/L}$  –  $\text{ng/L}$ ) (Wilkinson et al., 2017; Thomaidi et al., 2017). These compounds are generally known as OMP, contaminants of emerging concern (CEC) or trace organic contaminants (TrOCs), and their effects on environment and human health are uncertain (Ekblad et al. 2021). Specifically, **represent a certain concern for public authorities when municipal wastewater is aimed to be reclaimed and reused** for restrictive uses such as potable reuse or agricultural irrigation (Khan and Anderson, 2018; Rock et al., 2018; Smith et al., 2018; Gavrilesco et al., 2015).

The term of OMP is associated to a large and diverse collection of **thousands of chemical compounds** including biogenic hormones, pharmaceuticals, personal care products, pesticides, flame-retardants, detergents, veterinary drugs, industrial chemicals and their metabolites and by-products. Table 3 shows some of the most representative OMP's grouped by categories (Guillossou et al. 2019; Alvarino et al. 2018; Reif et al. 2008).

Table 3 Types of organic micro-pollutants (OMP)

Organic micropollutants		
Categories	Main sub-categories	Representative OMP's
<i>Pharmaceuticals</i>	Anti-depressants	Fluoxetine Citalopram
	Anti-inflammatories	Ibuprofen Naproxen Diclofenac
	Anti-epileptic	Carbamazepine
	Antibiotics	Erythromycin Azythromycin Sulphametoxazole Trimethoprim
	Beta-blockers	Atenolol Metoprolol
	<i>Personal Care Products (PCPs)</i>	Polycyclic musk fragrances
Sunscreen agents		Benzophenols
Preservatives		Methylparaben

<i>Organic micropollutants</i>		
<i>Categories</i>	<i>Main sub-categories</i>	<i>Representative OMP's</i>
<i>Endocrine Disrupting Compounds (EDCs)</i>	Hormones	Estrone (E1) 17- $\beta$ -estradiol (E2) 17 $\alpha$ -ethinylestradiol (EE2) Bisphenol A Nonylphenol
	Phthalates (used in manufactured plastics)	
	Polychlorinated biphenyls (PCBs) (used in electrical equipments)	
	Alkylphenols (detergents)	
	Dioxins (related from incinerators)	
	Plasticizers	
<i>Disinfectants, anti-septics and other biocides</i>	Alcohols	Triclosan
	Phenols	
	Iodine	
	Chlorine	
<i>Pesticides</i>		Diuron
		Simazine
		Isoproturon
<i>Brominated flame retardants</i>		Polybrominated diphenyl ethers (PBDEs)
		Hexabromocyclododecanes (HBCDs)
		Tetrabromobisphenol-A (TBBP-A)

### 1.2.1 Occurrence of OMP in the water cycle

Their presence in WWTPs or in the environment is directly related to the sewage discharge from households (or urban wastewater (UWW)), hospital wastewater (HWW) or agricultural and industrial wastewater. Table 4 collects the occurrence of the main groups of organic micro-pollutants regarding the discharge point. As shown in Figure 6, UWW and HWW are generally collected by sewage collectors and, from there, conducted to the assigned urban wastewater treatment plant (WWTP). In industries, however, wastewater can be derived, depending on its nature, composition, and regulations, to an industrial wastewater treatment plant (iWWTP). Then, once treated, or pre-treated, this effluent is discharged to the natural body or derived to the nearest urban WWTP or marine outfall. These treatment facilities (both urban and industrial wastewater treatment plants), as it will be explained with more detail, are not specifically designed to remove organic micro-pollutants (many of them recalcitrant in conventional biological processes), which, in consequence, easily reach the environment or are transferred to reclaimed water.

*Table 4 Occurrence of OMP in the urban, agriculture and industrial water cycle*

<b>SOURCE</b>		<b>Organic micro-pollutants</b>
1	Urban areas (households)	<ul style="list-style-type: none"> <li>• Pharmaceuticals</li> <li>• PCPs</li> <li>• Hormones</li> <li>• Alkylphenols</li> <li>• Illegal drugs</li> </ul>
2	Hospitals	<ul style="list-style-type: none"> <li>• Pharmaceuticals</li> <li>• Disinfectants, antiseptics, biocides</li> </ul>
3	Industries	<ul style="list-style-type: none"> <li>• Solvents</li> <li>• Alkylphenols</li> <li>• PCB</li> <li>• Plasticizers</li> <li>• Pharmaceuticals</li> <li>• Pesticides</li> <li>• (*) Depends on the industrial activity</li> </ul>
4	Agriculture and Farming	<ul style="list-style-type: none"> <li>• Pesticides, Herbicides, Plaguicides</li> <li>• Pharmaceuticals (veterinary drugs)</li> </ul>

Another source for organic micro-pollutants to enter in the water cycle are agriculture activities (mainly due to the excessive use of pesticides and herbicides), being a source of diffuse pollution in groundwater and in consequence a risk for environment and human health when water supply of drinking water treatment plants depends on wells.

Finally, when treated wastewater is reclaimed and reused, the presence of OMP can represent an uncertain risk on human health when IPR and DPR schemes are proposed. In agriculture, irrigation also could represent a risk when soil and crops may absorb these compounds. On the other hand, in industrial (unless in food and beverage sector) or urban uses, organic micro-pollutants do not represent a risk neither in environment nor in human health. Nevertheless, represent a risk in terms of its concentration in the water cycle since these compounds are reincorporated repeatedly in WWTPs and in the environment.

OMP concentrations in urban WWTP have been largely investigated. The reported average concentrations of OMP in urban WWTP influents in different coastal regions in Spain are shown in Figure 4. Regarding the location of the plant, the presence of different OMP varies (residential area, industrial area and/or presence of agricultural activities...etc.). Reported studies show that, in urban wastewaters (UWWs), higher frequency and concentrations (>5000 ng/L) were found for pharmaceuticals and secondly for PCP, alkylphenols and pesticides (Cabeza et al. 2012; Teijon et al. 2010). Finally, hormones were detected in very low concentrations (<10 ng/L).

It is worth to mention that most frequent compounds mainly are pharmaceuticals without prescription or PCP, which consumption is uncontrolled.

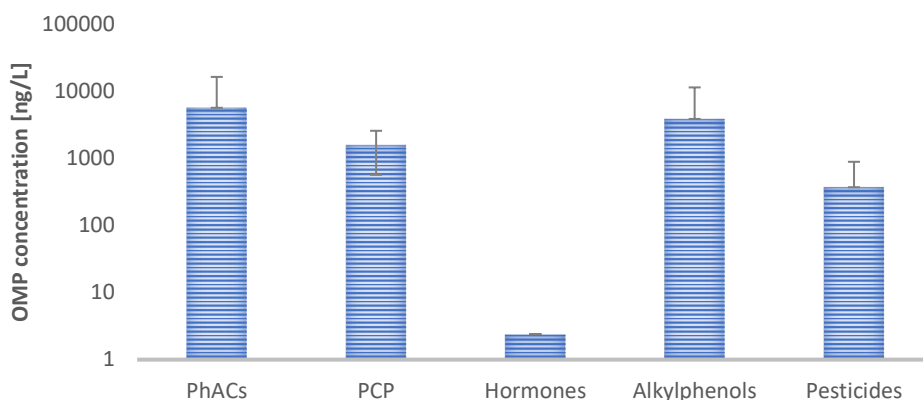


Figure 4 Occurrence of OMP in urban WWTP influents (Cabeza et al. 2012; Teijon et al. 2010)

As it can be seen in Figure 5, there is a great variability in the removal efficiencies of the different compounds in biological based urban WWTPs. Ibuprofen, Octylphenol, Acetaminophen, Estradiol or Triclosan present average removal rates higher than 80%; while for other compounds such as Diclofenac, Diazepam, Carbamazepine or Atrazine are below 40%. Removal mechanisms involved are explained and discussed in more detail further on.

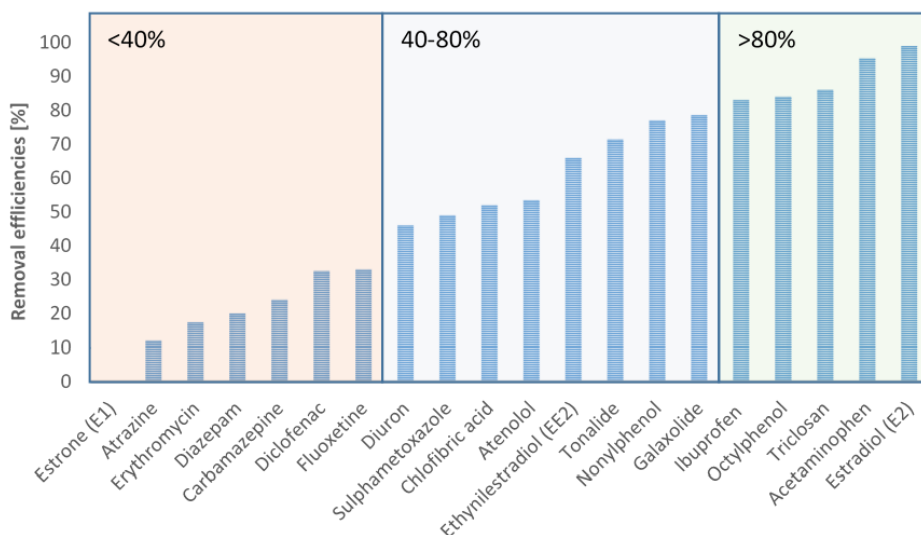


Figure 5 Removal efficiencies in conventional biological based WWTP (Gros et al., 2017; Luo et al., 2014)



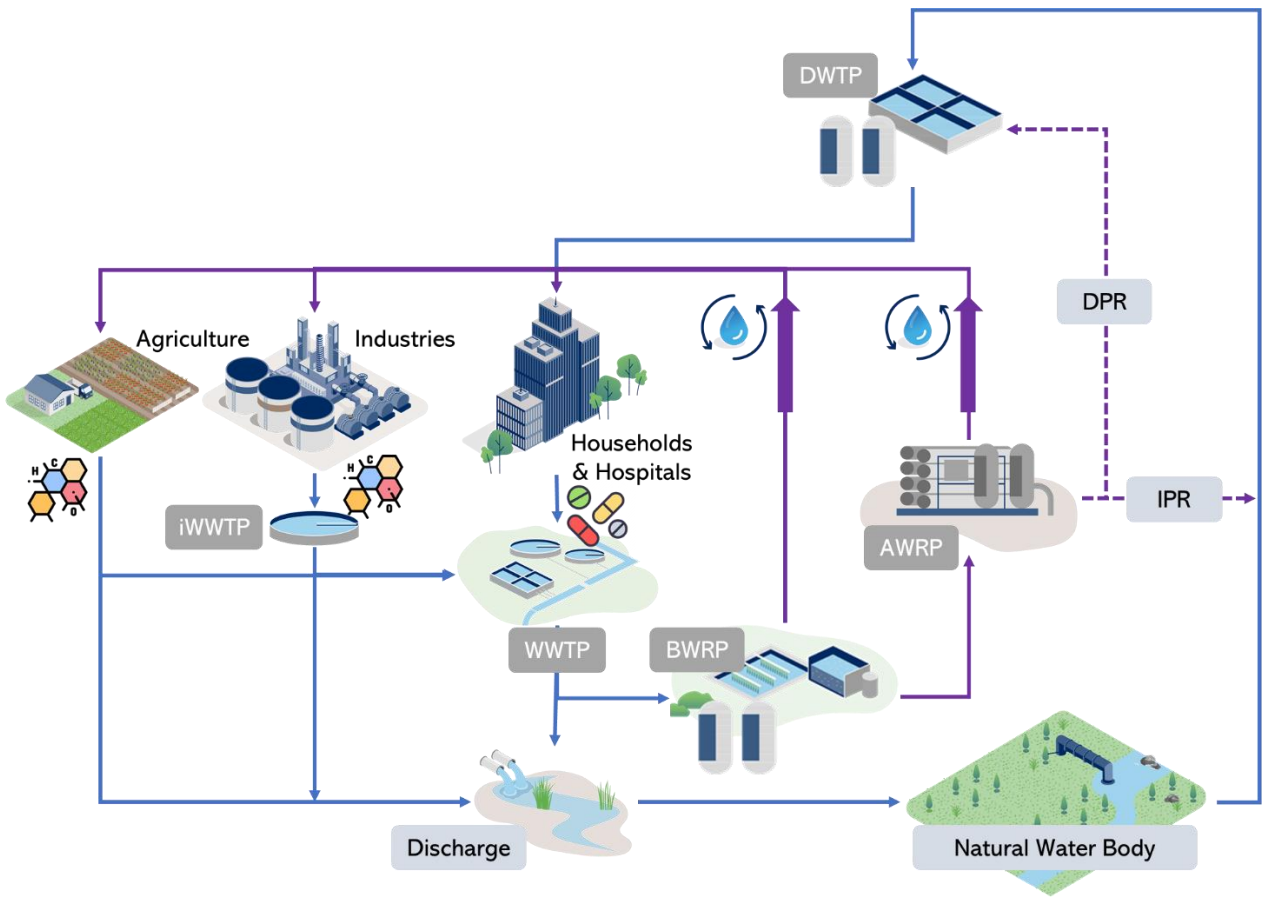


Figure 6 Occurrence of OMP in the water cycle

## 1.2.2 Fate of OMP in conventional wastewater treatment and reclamation schemes

Urban and industrial WWTPs are the main source of emission of OMP to enter the environment or represent a risk in human health when reclaimed water is reused. Nowadays, most of urban WWTPs are based on conventional biological treatment, which have achieved convincing results on the removal of organic matter and nutrients through the combination of anaerobic, anoxic and aerobic systems. Nevertheless, these conventional treatments were not specifically designed to achieve high removal efficiencies of OMP. Although in Conventional Activated Sludge systems (CAS) part of the most volatile organic compounds is stripped along the aeration stages in the bioreactors and the most hydrophobic get sorbed to the biosolid particles. Removal efficiencies for many recalcitrant organic compounds are relatively low or null ((Ávila and García, 2015; Carballa et al., 2005; Gros et al., 2017; Luo et al., 2014; Sipma et al., 2010). This heterogeneity in removal efficiencies was also reported in conventional water reclamation plants (WRP), generally based on physicochemical and separation processes (coagulation-flocculation and lamellar sedimentation/sand filtration/ microfiltration) (Teijon et al. 2010). Despite coagulation-flocculation is a useful strategy to remove certain compounds (those with high sorption properties) does not cover all OMP. Therefore, in order to achieve high global removal rates, it is necessary to resort to advanced wastewater treatment and reclamation technologies.

### 1.2.2.1 Removal mechanisms

Suárez et al. (2010) defined three main OMP removal mechanisms in conventional (biological process based) WWTPs according to the following processes: biological transformation, sorption and volatilization.

#### *Biological transformation*

This transformation is related to the chemical reactions caused by the presence of microorganisms present in the water bodies. Complete mineralization of the OMP is possible in biological processes, nevertheless for most of them normally the transformation is partial (leading to by-products or metabolites) or negligible (for those completely recalcitrant).

During the bio-transformation process the main mechanism are the metabolic reaction, in which the OMP is used as source of primary carbon or nutrients by the microorganisms, and co-metabolism, which is based on the transformation of the no growth-limiting compound (in this case, the OMP) in the presence of a primary substrate (which induces the corresponding enzymes for the biotransformation) ( Alvarino et al., 2018; Suárez et al., 2010).

By determining the kinetics of the biological reaction ( $k_{\text{biol}}$ ), it is possible to estimate in a qualitative way the biodegradability of a certain compound. In general, as simplification of such complex reactions, it is assumed a first order reaction mechanism. Joss et al (2006) determined the pseudo first-order degradation kinetics ( $k_{\text{biol}}$ ) for a large number of compounds and Suárez et al. (2008), according to the degradation constant values, differentiated OMPs in three main categories.

- **Hardly biodegradable** ( $k_{\text{biol}} < 0.1$  l/g SS/day). Representative compounds: Sulphametzazole, Carbamazepine and Diazepam.
- **Moderate biodegradable** ( $0.1 < k_{\text{biol}} < 10$  l/g SS/day). Representative compounds: Citalopram
- **Highly biodegradable** ( $k_{\text{biol}} > 10$  l/g SS/day). Representative compounds: Ibuprofen, Fluoxetine, Hormones E1 and E2.

### *Sorption*

This mechanism is defined as the capability of a certain compound to be transferred to a solid phase due to the affinity between the substance and the sorbent. It is dependent on the lipophilic character and chemical structure of the compound (presence of amino or carboxyl groups, etc.) and on the physical-chemical characteristics (organic compound fraction, ion exchange capacity or particle size). The distribution coefficient ( $K_d$ ) coefficient defines the sorption potential, which refers to the fraction of OMPs sorbed into the sludge (solid) and which takes into account two main mechanisms (Alvarino et al., 2018; Verlicchi et al., 2015):

**Sorption onto living structures (e.g., biomass):** Molecules present in a given fluid enter into another bulk phase (e.g., living biomass present in most of the treatment reactors). It is related to the hydrophobic interactions between the aliphatic and aromatic groups of a compound with the lipophilic cell membrane of the microorganisms present in the sludge. The octanol-water partition coefficient ( $K_{ow}$ ) is an indication of the substance hydrophobicity. Omil et al. (2010) mentions that compounds can be classified by:

- **Low sorption potential:**  $\log K_{ow} < 2.5$
- **Medium sorption potential:**  $2.5 < \log K_{ow} < 4.0$
- **High sorption potential:**  $\log K_{ow} > 4.0$

**Sorption onto non-living solid phases:** Physical adherence or binding of ions and molecules onto the surface of solid phase. It refers to the electrostatic interactions of positively charged groups of chemicals with the negatively charged surfaces of the sludge (e.g., dead biomass) or other solid particles present in the wastewater (Suárez et al. 2008). To describe this sorption process, a distribution ratio between both phases ( $D$ ) is being used in the state of the art. Distribution ratio values ( $D$ ) depends on properties of the aqueous solutions as the pH, and in the physicochemical properties of the sorbent as the acid-

base dissociation constant ( $K_a$ ) and  $K_{ow}$ . It indicates the trend of a certain OMP to get adsorbed on the sludge/adsorbent surface (Verlicchi et al., 2015). Generally, negatively charged compounds (anionic species of acidic compounds) do not adsorb whereas cationic species of other OMPs do due to Van der Waals interactions (Suarez et al., 2010)

### *Volatilization processes*

Volatility is the tendency of a certain compound to be transferred from the liquid phase to the gaseous phase (air). The fraction of compound volatilized depends on the Henry coefficient as well as process conditions such as the airflow in contact with the water (Alvarino et al., 2018).

Nevertheless, losses due to stripping are completely negligible for pharmaceuticals and estrogens according to the air flows used in CAS systems and the low values of the Henry coefficient of these compounds ( $<10^{-6} \mu\text{g}\cdot\text{m}^{-3} \text{ air} / \mu\text{g}\cdot\text{m}^{-3} \text{ wastewater}$ ). (Suárez et al. 2008). Only musk fragrances with higher Henry coefficients ( $10^{-1}$ - $10^{-2}$ ) can be volatilized in conventional wastewater treatment plants.

## **1.3 Advanced Water Reclamation Technologies**

Advanced wastewater reclamation technologies must allow the removal of recalcitrant compounds required for the most sensitive reclaimed water uses. These technologies can be grouped in two main blocks regarding their main removal mechanism: separation and transformation processes as collected in Table 5.

*Table 5. Advanced treatment technologies and removal mechanisms involved.*

<i>Removal mechanism</i>		<i>Advanced treatment technologies</i>
<i>Separation</i>	Sorption	GAC (Granular Activated Carbon) filter PAC (Powdered Activated Carbon) dosage Other sorbents (e.g., Carbon Nanostructured Materials, Zeolite)
	Membrane filtration	NF/RO
<i>Transformation</i>	Oxidation Processes	AOP (Advanced Oxidation Processes)
	Advanced Biotransformation	MBR, SBR, MBBR. Combined with adsorbents in order to remove those organic compounds non-biodegradable (hybrid systems)

<i>Removal mechanism</i>	<i>Advanced treatment technologies</i>
<i>Hybrid systems</i> (Adsorption – filtration – Biodegradation - Oxidation)	PAC – CAS/MBR/SBR/MBBR PAC – Sand filtration PAC -UF/NF

### 1.3.1 Separation processes

OMP can be effectively **separated** from wastewater matrix by several mechanisms, including **sorption** or **membrane filtration**. In this section, the main fundamentals, advantages and limitations of both separation processes are described:

#### 1.3.1.1 Sorption processes

**Sorption processes** in water treatment technologies refer to the use of adsorbent materials to uptake pollutants. Activated carbon is the most widely used sorbent in both drinking and wastewater treatments. This sorbent significantly reduces dissolved organic carbon (DOC) and selected micro-pollutants by binding them into the sorption sites in the activated carbon structure through physical forces of the van der Waals type and hydrogen bonding. Pore diameters can be classified as: (i) Primary micropores (>0.8 nm), (ii) secondary micropores (0.8 - 2 nm), (iii) mesopores (2-50 nm) and (iv) macropores (>50 nm) (Rattier et al., 2012).

In addition to the surface area and porosity, the surface chemistry also plays an important role in the sorptive properties of activated carbon. It depends on the heteroatom content of the surface, which are brought during the activation and provide charged groups with stronger valence forces. Thus, it can be summarized that the efficiency of activated carbon will mainly rely in three parameters: i) accessible surface area where physical sorption takes place, ii) heteroatom content, and iii) sorbed pollutants properties (size, charge, hydrophobicity) (Sher et al., 2021). Sorption efficiencies also rely on the competition with other organic compounds encountered, therefore, those organic compounds with a higher log  $K_{ow}$  are expected to be better removed by activated carbon).

After a certain operational time (which will be mainly bounded to the influent water quality and to operational conditions such as filtration velocity or contact time), the activated carbon is saturated with sorbed organic matter and other pollutants. To restore its properties, the activated carbon must be regenerated. This operation is done by removing it from the installation and heating it up to 1000°C in industrial ovens. Regeneration process is the main drawback of this technology since operational expenditures associated to transport and energy

consumption need to be considered, as well as a loose of part of the bed volume during the thermal regeneration, which needs to be replaced.

The two common configurations of activated carbon are: i) Granular Activated Carbon (GAC) (particles are granular and generally conform filters) and ii) Powdered Activated Carbon (PAC) (particles are in powder form and are dosed and blended with the water influent). The activated carbon configuration characteristics are summarized in Table 6.

*Table 6 Activated Carbon configurations and characteristics*

Sorbent	Granular Activated Carbon (GAC)	Powdered Activated Carbon (PAC)
Particle size	≥1 mm	1 μm
Infrastructure associated	<ul style="list-style-type: none"> <li>• Pressure vessels</li> <li>• Fluidized beds</li> <li>• Gravity filters (non-pressurized)</li> </ul>	<ul style="list-style-type: none"> <li>• Contact tank</li> <li>• Continuous dosing</li> </ul>
Advantages	<ul style="list-style-type: none"> <li>• Can be applied as post-treatment and does not require further solid-liquid separation steps</li> </ul>	<ul style="list-style-type: none"> <li>• Higher adsorption surface than GAC and thus higher removal efficiencies.</li> </ul>
Disadvantages	<ul style="list-style-type: none"> <li>• Regeneration is required</li> </ul>	<ul style="list-style-type: none"> <li>• It is necessary a further solid-liquid separation step.</li> <li>• Needs to be managed as a consumable and cannot be regenerated.</li> <li>• It is necessary to replace the saturated and purged PAC.</li> </ul>

Some authors have evaluated novel materials with claims on nanostructured properties that may act as high efficiency sorbents (Moradi et al., 2021). Some of them, in base to a polymeric structure, could be regenerated chemically on-site and then overcome the limitation of GAC that only could be thermally regenerated off-site (Larasati et al., 2021). As an example, Lewatit® AF 5 a microporous carbonaceous sorbent in bed form, derived from a synthetic polymer with a high surface area of 1300 m<sup>2</sup>/g, has been designed for downstream process separation and purification (Reczek et al., 2020). Another example is the Carbon Nanostructured Material (CNM) from Blücher (SARATECH®) validated at industrial pilot-scale in the present thesis framework (Chapter 5).

In both cases (conventional activated carbon or novel high efficiency sorbents), since sorption processes are based on the separation of pollutants from the water matrix but not in their removal, OMP are not eliminated

from water but fixed into a solid phase. Then, in GAC filters, during thermal regeneration OMP are degraded; nevertheless, in PAC systems OMP get attached to the PAC, which need to be separated from the liquid stream and purged.

### 1.3.1.2 Membrane filtration

Membrane processes are usually applied when high quality of water is needed (drinking water treatment or water reclamation and reuse). Membranes can be defined as **separation** processes where a feed stream (containing pollutants and micro-pollutants to be removed), is divided into a clean water stream (permeate) and a concentrated stream (concentrate or brine) (Yangali Quintanilla, 2010; Verliefe 2008). According to the driving force that leads the separation process, several membrane processes can be distinguished (Table 7):

*Table 7 Membrane separation processes applied in water treatment processes (adapted from Oztekin et al. (2016))*

Driver	Technologies	Pore size [nm]	MWCO [g/mol]	Application	Filtration fluxes [L/m <sup>2</sup> ·h]	Energy consumption [kWh/m <sup>3</sup> ]
Pressure gradient	Microfiltration (MF)	>100	10 <sup>5</sup> -10 <sup>6</sup>	Particles removal	>100	0.05-0.1
	Ultrafiltration (UF)	5-100	10 <sup>3</sup> -10 <sup>5</sup>	Particles, macromole- cules, bacteria and virus removal	20-100	0.1-0.2
	Nanofiltration (NF)	0.5-5	200-1000	Multivalent salts and small organic molecules removal	10-30	0.5-2
	Reverse Os- mosis (RO)	0.1-1	200-300 <sup>a</sup>	Monovalent salts and small organic molecules removal	10-30	1-5
Potential gradient	Electrodialy- sis Reversal (EDR)	0.1-1	200-300	Monovalent salts and small organic molecules removal	30-40 <sup>b</sup>	1.5 -2.6 <sup>b</sup>
Thermal gradient	Membrane distillation (MD)	>100 <sup>c</sup>	-	Monovalent salts and small organic molecules removal	5-10	100-200
Concentra- tion gradient	Forward os- mosis (FO)	0.1-1	200-300	Monovalent salts and small organic molecules removal	5-10	3-4

<sup>a</sup> Verliefe (2008)

<sup>b</sup> Tanaka (2015); 1-1.2 kWh/m<sup>3</sup> to remove 1 kg of salt.

<sup>c</sup> Khayet (2011); Hydrophobic membranes

<sup>d</sup> Graeme (2015); McGovern and Lienhard V (2014)

Pressure driven membrane operations can be divided into four overlapping categories of increasing selectivity: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). In RO, it is generally accepted that the solution-diffusion mechanism is responsible for solute and solvent flux through the membrane. The size exclusion mechanism is the one contemplated to explain solute transport through UF membranes, and in the case of NF membranes, both solution-diffusion and size exclusion are involved together with other mechanisms such as electrostatic interactions. However, membrane composition combined with solvent and solute characteristics can influence rejection via electrostatic double layer interactions or other hindrances. In fact, when a solution containing ions is brought in contact with membranes possessing a fixed surface charge, the passage of ions possessing the same charge as the membrane (co-ion) can be inhibited. This condition is termed Donnan Exclusion (Macedonio and Drioli, 2008).

Accumulation of solids, scaling, organic and biological fouling are the main drawbacks in membrane processes; maximized in pressure driven processes due to the formation of the cake layer and concentration polarization. Nevertheless, the application of pressure in the feed stream allows to reach higher filtration fluxes regarding thermal or concentration driven processes, which results in a key advantage since it is directly related to the membrane area necessary and therefore to the investment associated to their implementation. In addition, the complex architecture, materials and configurations of membrane distillation and forward osmosis, combined with its higher capital and operational expenses (OPEX and CAPEX) (related to their newer development) are still additional disadvantages to their full-scale implementation.

The factors influencing the permeate quality and membrane performance during direct pressure-driven membrane filtration are the membrane type and material, pore size, pre-treatment of feed water and fouling control methods (Hube et al., 2020). Fouling is a major challenge due to the relatively higher amounts of organic matter and particulates when treating wastewater. It can lead to an increase of operation cost due to higher feed pressures and a decrease of membrane lifetime due to more frequent physical/chemical cleanings. Therefore, proper membrane fouling control strategies are necessary to improve direct pressure-driven membrane filtration performance (Anis et al., 2019).

Asymmetric membranes such as nanofiltration (NF) or reverse osmosis (RO) represent a highly efficient technology in terms of removal of organic and inorganic compounds. As stated by Bellona et al. (2004), the



rejection of solutes in membranes is driven by the combination of feed water and membrane properties, as well as operational conditions applied. Solute-solute, solute-liquid and membrane-solute are the main mechanisms governing solute rejections and interactions, which usually determine the mechanisms limiting the removal processes (Teodosiu et al., 2011).

Van der Bruggen et al. (1999) reported the first data on retention ratios for different asymmetric membranes (NF/RO) of different organic compounds as function of molecular weight (MW). Results obtained showed very high removal efficiencies (>90%) for those compounds with MW higher than 0.2kDa (which corresponds approximately to the molecular weight cut off (MWCO) of RO and NF tested membranes). Furthermore, as also stated by Kimura et al. (2003), in NF/RO, MWCO results more useful than 'salt passage' to evaluate OMP removal capacities.

In water reclamation, NF/RO typically requires substantial pre-treatment to reduce the fouling and clogging potential of secondary effluent (Kazner, 2011). MF or UF are commonly recommended pre-treatments for RO since they provide total removal of suspended solids (SS) that could clog the spiral wound configuration of NF/RO as well as significantly reduce turbidity and the microbiological load (Judd, 2006). Additionally, it is usual (when quality requirements allow it) to blend the UF permeate with the RO permeate in order to reduce operational costs (Gu et al., 2019).

Moreover, the concentrated rejection or brine stream generated in RO systems represents one of the main drawbacks for its implementation, together with the associated high treatment cost. Typically, resulting intensive in energy and chemicals consumption. Rejection streams with high salinity and high OMP concentration usually cannot be recirculated to Wastewater Reclamation Plant (WWRP) headworks due to an inhibition of the biological activity. Thus, in inland areas, where discharge to the sea is not an option, the brine management represents a significant technical, economic and environmental issue.

Following the same idea of sorption processes, OMPs are not removed but separated; therefore, pollutants get concentrated in brines (concentrated stream), which must be managed appropriately.

### **1.3.2 OMP chemical and biochemical transformation processes**

As an alternative to separation, it is possible to chemically or biologically transform OMP by in general chemical or biochemical oxidation processes. The review of the state of art indicates that the chemical or biochemical reduction routes have been scarcely explored. In this section, the main fundamentals in transformation processes are depicted:

### 1.3.2.1 Advanced Oxidation processes (AOP)

Advanced Oxidation Processes (AOPs) are based on the in-situ generation of oxidants (ozone and hydroxyl radicals), which applied to treated effluents enable to oxidize (break up) these compounds. This chemical transformation (as in biotransformation) can be completed (leading to mineralization) or be partial, which generates by-products or metabolites. AOP can be divided into two blocks: homogeneous and heterogeneous as depicted in Figure 7.

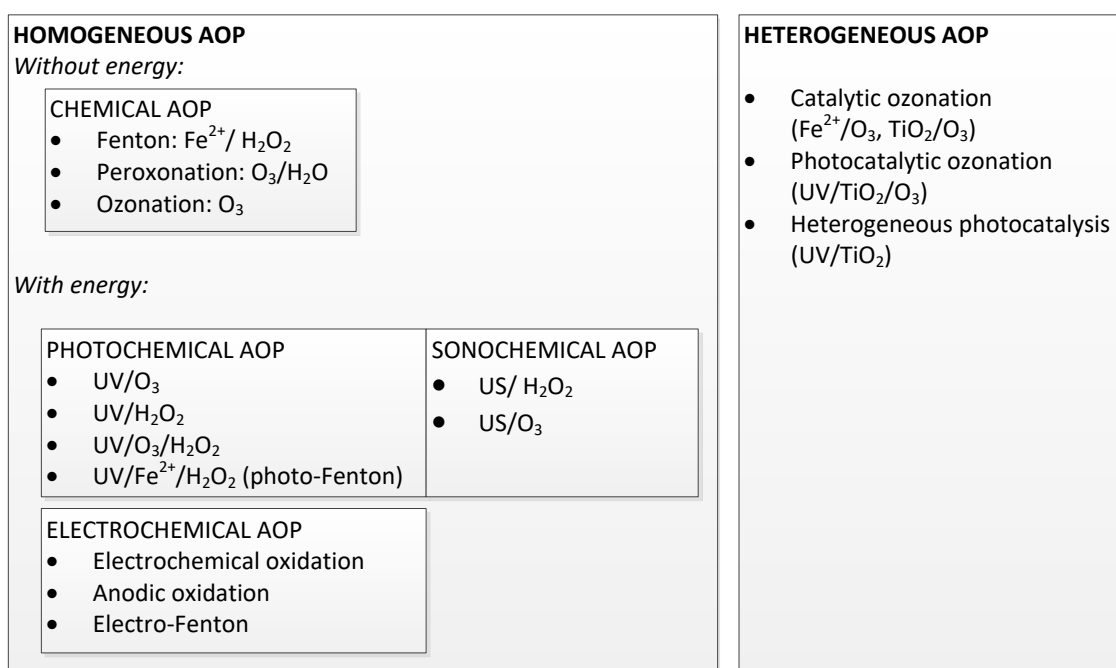


Figure 7 Advanced Oxidation Processes scheme adapted from (Vaiano et al. 2017)

Homogeneous AOP can also be subdivided regarding the use or not of energy. From one hand, without energy, are based on the addition of chemical oxidants to react within the organic matter present in the water matrix. Fenton process ( $\text{Fe}^{2+} / \text{H}_2\text{O}_2$ ), peroxidation ( $\text{H}_2\text{O}_2$ ) and ozonation ( $\text{O}_3(\text{g})$ ) are the main processes applied (Vaiano et al., 2017). Particularly, ozone can be considered a selective agent; nevertheless, its spontaneous decomposition into hydroxyl radicals can act unselectively in the degradation of OMP (Gorito et al., 2021). When energy consumption is applied, these hydroxyl radicals generation can be accelerated. Examples can be the use of ultraviolet (UV) lamps (photochemical AOP), ultrasound (sonochemical AOP) or electrical (electrochemical AOP). The combination of  $\text{O}_3(\text{g})$  and UV can also be considered as will be described in Chapter 3.

Heterogeneous AOP require the addition of catalysts (metal oxides or organometallic catalysts) in order to provoke the chemical transformation reactions. Their main advantage regarding homogeneous AOP is the recovery or easier separation of the catalysts from the treated effluent.

As mentioned, the partial oxidation of a wastewater effluent can lead to the generation of intermediate by-products (or metabolites). Some authors indicate that ecotoxicological effects in wastewater effluents after ozonation have been inconclusive since analytical methods does not allow to detect all metabolites formed (Mulder et al. 2015). On the other hand, Zimmermann et al. (2011) reported the formation of undesirable toxic by-products such as nitrosamines (NDMA), bromate or formaldehyde after ozonation. On the other hand, AOP may increase biodegradability of oxidized compounds (Knopp et al. 2016). In this line, some authors advise the inclusion of a post-treatment to ozonation based on a biological sand filtration, or activated carbon filtration in order to remove part of the remaining metabolites (Knopp et al., 2016; Melin et al., 2000).

### 1.3.2.2 *Advanced Biological Processes*

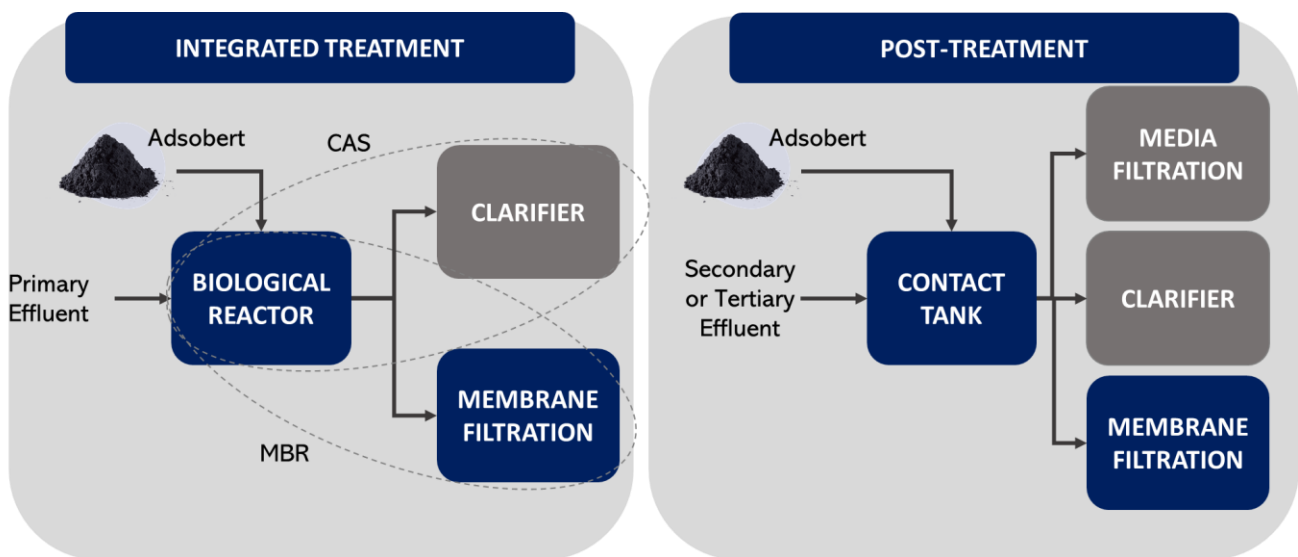
The **solid retention time** (SRT) and mixed liquor suspended solids (MLSS) have been indicated as operational parameters with a clear dependence with OMP biodegradation and removal rate (Reif et al. 2008; Asif et al., 2020). Specifically, Suárez et al. (2012) detected an increase of 11% on the removal of hormone EE2 (17 $\alpha$ -ethinylestradiol) when SRT was set above 20 days. This behavior was also reported for other lipophilic compounds such as other estrogens or musk fragrances (Alvarino et al., 2017; Alvarino et al., 2016).

Membrane bioreactor (MBR) systems are based on the substitution of the secondary clarifiers by filtration membranes in order to obtain a higher water quality (free of SS) and reduce footprint (Martí-Calatayud et al., 2020). With the aim to operate at a higher MLSS concentration and ease the sludge filterability, the SRT in MBR are higher than in CAS (Alvarino et al., 2018). Different MBR configurations have been developed by the main market players, including the use of submerged MF/UF membranes in the biological reactor also known as immersed MBR (iMBR), while other providers recommend the use of a 'sidestream' configuration (sMBR), in which the modules are externally located, and the sludge is pumped and recirculated through them (Judd, 2008). The use of a 'sidestream' MBR was also considered as will be described in Chapter 3.

### 1.3.3 **Hybrid processes**

Hybrid systems seek for synergies between technologies to maximize the removal efficiency of OMP as well as to reduce, when possible, specific energy and chemical reagents consumption, and other consumables. Figure 8 shows two options considered in this thesis (Chapter 3 and Chapter 4). On the other hand, integrated treatments are based on the use of sorbents combined with the WWTP biological processes, generating

synergistic benefits for OMP removal (through biotransformation and sorption processes) and in the operational performance of the system. One example is the addition of powdered activated carbon (PAC) in MBR. Several authors demonstrated the improvements in PAC-MBR in terms of sludge filterability and fouling reduction, being able to improve twice critical fluxes. Remy et al., (2010) reported that PAC addition represents an operational cost of 0.08 €/m<sup>3</sup>, increasing significantly the OPEX of the system. However, this increase should be compensated by taking advantage from the operational benefits expected in terms of higher flux, lower specific energy demand (more production and lower transmembrane pressure (TMP) ranges) and, finally, lower chemicals consumption (by enlarging the operation period between chemical cleanings).



*Figure 8. Description of potential hybrid processes.*

On the other hand, another possibility is to apply hybrid systems as post-treatments, by combining sorbent dosing and membrane filtration to separate or recover the sorbent. Meier and Melin (2005) reported several advantages of PAC-UF combination, such as: (i) the pre-cleaning effect of activated carbon through the adsorption of organic foulants when applied before the membrane; (ii) PAC acting as a filter layer and apparently having a scouring effect that protects the membrane and (iii) the adjustment of water quality through the regulation of PAC doses. Additionally, high OMP removal efficiencies might be achieved (Sheng et al., 2016). In PAC-UF systems, the rejected and partially saturated PAC might be recirculated to WRP headworks in order to act as biological support for microorganisms as well as a potential sorbent for OMP (Alvarino et al., 2017).

## 1.4 Legal framework

### 1.4.1 Water reuse

In this section, different representative water reuse regulations at worldwide level are depicted, including three regulations in the USA (section 1.4.1.1), the Spanish regulation (RD 1620/2007; section 1.4.1.2) and the new European Regulation (EU 2020/741; section 1.4.1.3) that establishes minimum water quality requirements for reclaimed water when intended for agricultural irrigation.

#### 1.4.1.1 United States of America (USA) water reuse regulation

As it has been discussed in section 1.1.2, USA accounts with large experience in terms of water reuse regulation and implementation. It does not account with a general legal framework and the quality requirements are defined by territorial regulation or recommended by guidelines specifically in each State (Table 8).

*Table 8 Review of the number of rules, regulation or guidelines addressing each water reuse category in the United States of America. This table has been from the EPA Guidelines in Water Reuse (2012).*

Category of reuse		Description	Number of States or Territories with Rules, Regulations, or Guidelines addressing reuse category
Urban Reuse	Unrestricted	The use of reclaimed water for nonpotable applications in municipal settings where public access is not restricted.	32
	Restricted	The use of reclaimed water for non-potable applications in municipal settings where public access is controlled or restricted by physical or institutional barriers, such as fencing, advisory signage, or temporal access restriction.	40
Agricultural Reuse	Food crops	The use of reclaimed water to irrigate food crops that are intended for human consumption.	27
	Processed food crops and non-food crops	The use of reclaimed water to irrigate crops that are either processed before human consumption or not consumed by humans.	43
Impoundments	Unrestricted	The use of reclaimed water in an impoundment in which no limitations are imposed on body-contact water recreation activities (some states categorize snow-making in this category).	13
	Restricted	The use of reclaimed water in an impoundment where body contact is restricted (some states included fishing and boating in this category)	17
Environmental Reuse		The use of reclaimed water to create, enhance, sustain or augment water bodies, including wetlands, aquatic habitats or stream flow.	17

Category of reuse		Description	Number of States or Territories with Rules, Regulations, or Guidelines addressing reuse category
Industrial Reuse		The use of reclaimed water in industrial applications and facilities, power production, and extraction of fossil fuels.	31
Groundwater recharge – non-potable reuse		The use of reclaimed water to recharge aquifers that are not used as a potable water source.	16
Potable Reuse	Indirect Potable Reuse (IPR)	Augmentation of a drinking water source (surface or groundwater) with reclaimed water followed by an environmental buffer that precedes normal drinking water treatment	9
	Direct Potable Reuse (DPR)	The introduction of reclaimed water (with or without retention in an engineered storage buffer) directly into a water treatment plant either collocated or remote from the advanced wastewater treatment system	0

From one hand, the State of California accounts since 2001 with the Title 22 regulation (Table 9), which defines different water types obtained through a technological solution. The reclaimed water uses are dependent on each water type.

Table 9. Description of the Title 22 regulation. This table has been obtained from the EPA Guidelines in Water Reuse (2012).

Water Type	Parameter	Quality criteria (Maximum Value)	Uses
Disinfected Tertiary (oxidation-filtration-disinfection)	Total Coliforms	2.2 MPN/100 mL	<ul style="list-style-type: none"> <li>Urban unrestricted</li> <li>Agricultural food-crops</li> <li>Impoundments unrestricted</li> <li>Industrial</li> </ul>
	Turbidity (Media filtration)	2 NTU	
	Turbidity (Membrane filtration)	0.2 NTU	
Disinfected Secondary 2.2	Total Coliform	2.2 MPN/100 mL	<ul style="list-style-type: none"> <li>Impoundments restricted</li> </ul>
Disinfected Secondary 23	Total Coliform	23 MPN/100 mL	<ul style="list-style-type: none"> <li>Urban restricted</li> </ul>
Un-disinfected Secondary	N/A	N/A	<ul style="list-style-type: none"> <li>Agricultural – nonfood crops and processed food</li> </ul>

As another example, the regulation of the State of Texas is summarized in Table 10.

Table 10 Description of the regulation of the State of Texas. This table has been obtained from the EPA Guidelines in Water Reuse (2012).

Parameters	Type I	Type II
BOD5	5 mg/L	20 mg/L
Turbidity	3 NTU	N/A
E.Coli	20 CFU/100 mL	200 CFU/100 mL
Uses	<ul style="list-style-type: none"> <li>Urban unrestricted</li> <li>Agricultural food crops</li> </ul>	<ul style="list-style-type: none"> <li>Urban restricted</li> </ul>

Parameters	Type I	Type II
	<ul style="list-style-type: none"> <li>• Impoundments unrestricted</li> <li>• Indirect Potable Reuse</li> </ul>	<ul style="list-style-type: none"> <li>• Agricultural – nonfood crops and processed food crops</li> </ul>

Finally, the regulation of the State of Florida is summarized in Table 11.

*Table 11 Description of the regulation of the State of Florida. This table has been obtained from the EPA Guidelines in Water Reuse (2012).*

Reclaimed water uses	BOD <sub>5</sub> [mg/L]	TSS [mg/L]	Turbidity [NTU]	E.Coli [CFU/100 mL]	Pathogens	Nitrogen
Urban unrestricted	20	<5	2-2-5 (Case by case)	<25	Giardia and Cryptosporidium	
Agricultural food crops	20	<5	2-2-5 (Case by case)	<25	-	
Agricultural nonfood crops and processed food	20	20	-	<200	Giardia and Cryptosporidium	
Environmental	5	5	-	<200		
Industrial	20	<5	2-2-5 (Case by case)	<25	Giardia and Cryptosporidium	
Groundwater recharge (non-potable)	20	20	-	<200		<12 mg NO <sub>3</sub> /L
Indirect Potable Reuse (IPR)	20	<5	2-2-5 (Case by case)	<4	Giardia and Cryptosporidium	<10 mg TN/L

#### 1.4.1.2 Spanish Royal Decree (RD 1620/2007) of water reuse

The different reclaimed water uses included in the Spanish Royal Decree are listed in Table 12, Table 13, Table 14 and Table 15. The Spanish regulation was established in 2007 and regulates the reclaimed water quality delivered considering physico-chemical (SS and turbidity) and microbiological (E. Coli, Nematode eggs, Legionella) parameters, as well as other specific criteria defined case by case.

*Table 12. Review of the number of rules, regulation or guidelines addressing each reclaimed water use in the Spanish Royal Decree. This table has been from the Spanish Royal Decree in Water Reuse (2007).*

Parameter	QUALITY 1.1 RESIDENTIAL (Private garden irrigation, Toilet flushing)	QUALITY 1.2 SERVICES (Green areas irrigation, Streets cleaning, Firefighting, Vehicles cleaning)
SS [mg/L]	10	20
Turbidity [NTU]	2	10
E. Coli [CFU/100 mL]	0	200
Nematode eggs [egg/10 L]	1	1
Legionella [CFU/100 mL]	100	100
Other criteria	N/A	N/A



Table 12. Review of the number of rules, regulation or guidelines addressing each reclaimed water use in the Spanish Royal Degree. This table has been from the Spanish Royal Degree in Water Reuse (2007)

Parameter	<b>QUALITY 2.1</b> <i>Food crops in direct contact with irrigation (fresh vegetables)</i>	<b>QUALITY 2.2</b> <i>Processed food crops, crops used for pastures and aquiculture.</i>	<b>QUALITY 2.3</b> <i>Woody crops, ornamental flowers, and other industrial crops (non eatable)</i>
SS [mg/L]	20	35	35
Turbidity [NTU]	10	N/A	N/A
E. Coli [CFU/100 mL]	100	1000	10000
Nematode eggs [egg/10 L]	1	1	1
Legionella [CFU/100 mL]	1000	N/A	100
Other criteria	Salmonella	Taenia saginata, Taenia solium, Salmonella	N/A

Table 13. Review of the number of rules, regulation or guidelines addressing each reclaim water use in the Spanish Royal Degree. This table has been from the Spanish Royal Degree in Water Reuse (2007)

INDUSTRIAL USES	<b>QUALITY 3.1</b>			<b>QUALITY 3.2</b>
Parameter	<i>Process and cleaning water (except Food and Beverage industry)</i>	<i>Process and cleaning water (including Food and Beverage industry)</i>	<i>Other industrial uses</i>	<i>Cooling towers and evaporative condensers</i>
SS [mg/L]	35	35	35	5
Turbidity [NTU]	15	N/A	15	1
E. Coli [CFU/100 mL]	10000	1000	10000	Absence
Nematode eggs [egg/10 L]	N/A	1	N/A	1
Legionella [CFU/100 mL]	100	100	100	Absence
Other criteria	N/A	Salmonella	N/A	N/A

Table 14. Review of the number of rules, regulation or guidelines addressing each reclaimed water use in the Spanish Royal Degree. This table has been from the Spanish Royal Degree in Water Reuse (2007)

Parameter	<b>QUALITY 4.1</b> <i>Golf courses irrigation</i>	<b>QUALITY 1.2</b> <i>Artificial lakes and fountains</i>
SS [mg/L]	20	35
Turbidity [NTU]	10	N/A
E. Coli [CFU/100 mL]	200	10000
Nematode eggs [egg/10 L]	1	N/A
Legionella [CFU/100 mL]	100	N/A



Parameter	<b>QUALITY 4.1</b> Golf courses irrigation	<b>QUALITY 1.2</b> Artificial lakes and fountains
Other criteria	In case of applying drip irrigation, it can be applied QUALITY 2.3 requirements	Total phosphorus < 2 mg/L

Table 15. Review of the number of rules, regulation or guidelines addressing each reclaimed water use in the Spanish Royal Degree. This table has been from the Spanish Royal Degree in Water Reuse (2007)

Parameter	<b>QUALITY 5.1</b> Aquifer recharge (percolation)	<b>QUALITY 5.2</b> Direct Aquifer recharge	<b>QUALITY 5.3</b> Woods and non-accessible areas irrigation	<b>QUALITY 5.4</b> Other uses (Wetlands and ecological river flow maintenance)
SS [mg/L]	35	10	35	Case by case
Turbidity [NTU]	N/A	2	N/A	
E. Coli [CFU/100 mL]	1000	Absence	N/A	
Nematode eggs [egg/10 L]	N/A	1	N/A	
Legionella [CFU/100 mL]	N/A	N/A	N/A	
Other criteria	Total Nitrogen <10 mg/L; Nitrates <25 mg/L		N/A	

#### 1.4.1.3 European Regulation (EU 2020/741)

On June 5<sup>th</sup>, 2020, a new European Regulation (EU 2020/741) was published, establishing minimum requirements for water reuse for agricultural irrigation, was and it entered into force on of June 25<sup>th</sup>, 2020. The regulation defines three types of irrigation (Table 16) and define the concentration limits for physico-chemical and microbiological parameters (Table 17 and Table 18)

Table 16. Review of the number of rules, regulation or guidelines addressing each reclaimed water use in the EU Regulation. This table has been from the new European Regulation (EU 2020/741).

Minimum reclaimed water quality class	Crop category	Irrigation method
<b>A</b>	All food crops consumed raw where the edible part is in direct contact with reclaimed water and root crops consumed raw	All irrigation methods
<b>B</b>	Food crops consumed raw where the edible part is produced above ground and is not in direct contact with reclaimed water, processed food crops and non-food crops including crops used to feed milk-or meat-producing animals	All irrigation methods
<b>C</b>	Food crops consumed raw where the edible part is produced above ground and is not in direct contact with reclaimed water, processed food crops and non-food crops including crops used to feed milk-or meat-producing animals	Drip irrigation (**) or other irrigation method that avoids direct contact with the edible part of the crop
<b>D</b>	Industrial, energy and seeded crops	All irrigation methods (***)

Table 17 Review of the number of rules, regulation or guidelines addressing each reclaimed water use in the EU Regulation. This table has been from the new European Regulation (EU 2020/741).

Reclaimed water quality class	Indicative technology target	E. Coli (number/100 MI)	BOD5 (mg/L)	SS (mg/L)	Turbidity (NTU)
<b>A</b>	Secondary treatment, filtration and disinfection	≤10	≤10	≤10	≤5
<b>B</b>	Secondary treatment, and disinfection	≤100	In accordance with Directive 91/271/EEC	In accordance with Directive 91/271/EEC	-
<b>C</b>	Secondary treatment, and disinfection	≤1000			-
<b>D</b>	Secondary treatment, and disinfection	≤10000			-

Additionally, *Legionella pneumophila* must be below 1000 CFU/L in those cases where there is a risk of aerosolization, and intestinal nematodes must be below 1 egg/L for irrigation of pastures or forage.

*Table 18 Review of the number of rules, regulation or guidelines addressing each water reuse category in the EU Regulation. This table has been from the new European Regulation (EU 2020/741)*

Reclaimed water quality class	Indicator microorganisms	Performance targets for the treatment chain (log10 reduction)
<b>A</b>	E. Coli	≥5
	Total coliphages/F-specific coliphages/somatic coliphages	≥6
	Clostridium perfringens spores/spore-forming sulfate-reducing bacteria	≥4 (in case of Clostridium perfringens) ≥5 (in case of spore-forming sulfate-reducing bacteria)

As additional requirements, it is necessary to develop a risk assessment study in each water reuse system. Depending on its outcome, the removal of other parameters of particular concern such as hazardous metals, disinfection by-products (DBP), OMP, microplastics or anti-microbial resistance may be requested by the correspondent administration.

### 1.4.2 Organic micro-pollutants

The growing concern in society and scientific community about OMP occurrence and fate pushed the institutions to define strategies to guarantee their removal prior reaching the natural bodies or reclaimed water. Two of the main regulatory frameworks are presented in this section, in which the current legislations or purposes are defined: (i) European Legislation and (ii) swiss legislation.

#### 1.4.2.1 European Legislation

Table 19 summarizes the different directives legislated in the European Union (EU) in terms of OMP monitoring and removal.

Table 19 EU legislation in terms of OMP monitoring and removal (Alvarino, 2016).

Directives	Priority substances under the WFD
Water Framework Directive (WFD)	Define “Strategies against pollution of water”
Directive on Environmental Quality Standards (2008/105/EC) EQSD	<ul style="list-style-type: none"> <li>Limits on concentration of the 33 priority substances.</li> <li>Diclofenac, <math>\beta</math>-estradiol and 17<math>\alpha</math>-ethinylestradiol should be included in the first watch of substances for which Union-wide monitoring data.</li> </ul>
Directive 2013/39/EU	<ul style="list-style-type: none"> <li>12 substances added to the WFD List of Priority Substances.</li> <li>The first watch list shall contain a maximum of 10 substances.</li> </ul>
Commission implementing decision (EU) 2015/495	<p>The watch list of substances includes the following:</p> <ul style="list-style-type: none"> <li><u>Pharmaceuticals</u>: <b>Diclofenac</b> (DFC) and <b>Macrolide antibiotics</b> (Erythromycin (ERY), Azitromycin (AZI) and Clarithromycin (CLA))</li> <li><u>Hormones</u>: <b>Estrone</b> (E1), <b>17-<math>\beta</math>-estradiol</b> (E2) and <b>17<math>\alpha</math>-ethinylestradiol</b> (EE2)</li> <li><u>PCP</u>: <b>2-Ethylhexyl 4-methoxycinnamate</b>.</li> <li><u>Industrial additives</u>: <b>2,6-Ditert-butyl-4-methylphenol</b></li> <li><u>Pesticides</u>: <b>Methiocarb, Neonicotinoids, Oxadiazon, Tri-allate</b>.</li> </ul>

Throughout 2014, the European Commission gathered information and consulted experts from Member States and stakeholders’ groups to include other substances (which had come close to being prioritized in Directive 2013/39/EU) in a first watch list.

In 2015, as indicated in Table 19, the EU included several substances in the called “Watch List” in order to monitor and evaluate potential risks caused by them in the aquatic environment. Impact assessment are being carried out in order to evaluate the need of include them in the priority substances list.

#### 1.4.2.2 Swiss Legislation

Switzerland is currently the most advanced country in OMP removal strategies and legislation around the world. In 2016, developed and applied a new Water Protection Ordinance that includes the following measures, in order to protect their sensitive waters and drinking water sources (De Boer et al., 2022):

As **global target**: OMP Removal rates of  $\geq 80\%$  of the final effluent regarding the primary clarified wastewater.

**Monitoring** 6 out of 12 indicator compounds (provisionally): Amisulprid, Carbamazepine, Citalopram, Clarithromycin, Diclofenac, Hydrochlorothiazide, Metoprolol, Venlafaxin, Benzotriazol, Candesartan, Irbesartan, Mecoprop.

24h or 48h composite samples

**Frequency** of sampling: 8 to 24 campaigns per year depending on the WWTP size.

To achieve these milestones, advanced wastewater treatments based on Powdered Activated Carbon (PAC) addition and separation or based in Advanced Oxidation Processes using ozonation are being implemented in several of the WWTP of the country.

Financing of this macro-project is divided in the following: 75% of the investment paid by national budget, which implies a payment of 9 CHF/person/year, and which starts in 2016 and ends in 2040. On the other hand, municipalities assume the remaining 25% of the investment and operational costs. Therefore, in 2040 from 120 to 130 WWTPs (out of total 650) will be equipped with advanced wastewater treatment technologies, representing the 50% of the total wastewater treatment in the country.

## 1.5 References

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# Chapter 2



## 2. Chapter 2: Objectives and methodology

### 2.1 General objective and thesis scope

The general objective of this PhD thesis is to evaluate and compare from a technical and economic point of view different advanced municipal wastewater reclamation schemes to produce cost-effective reclaimed water to be reused, considering the removal of organic micro-pollutants, scalability and the requirements of the end-users. A graphical abstract describing the PhD thesis is shown in Figure 9.

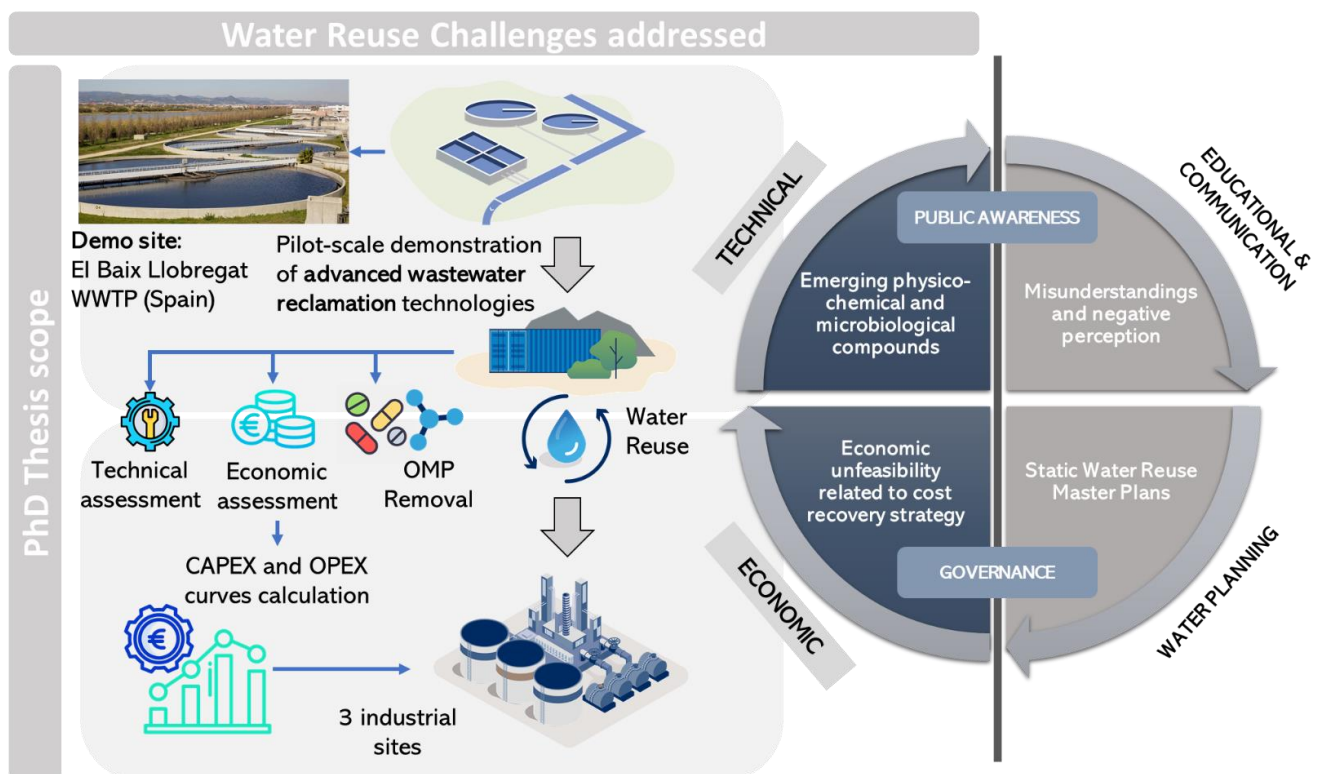


Figure 9. Graphical abstract describing the PhD thesis objectives

In Chapter 1, the different existing barriers in water reuse implementation have been explained. From one hand, public awareness needs to be tackled by demonstrating trust, safety and credibility in water reuse systems. This awareness is partially related to the concern of public authorities regarding the presence of emerging physico-chemical compounds such as OMP in natural bodies or in reclaimed water when is reused for the most sensitive uses. This thesis aims to demonstrate at industrial pilot-scale the removal efficiencies of selected organic compounds in different treatment trains and its associated cost, including PAC-MBR, ozonation-UV, PAC-UF, UF-RO and an innovative high-performance sorbent (CNM). On the other hand, tools to ease decision making in water reuse planning through a rapid estimation in costs need to be proposed. Cost curves for CAPEX and



OPEX for different reclamation technologies will be also calculated and applied to estimate implementation costs of reusing urban reclaimed water for industrial uses in three different case studies in the Barcelona (Spain) area. Thus, the ultimate goal is to provide knowledge to overcome some of the identified barriers and contribute to a higher implementation of water reuse.

## 2.2 Specific objectives

Specific objectives of the PhD thesis are listed in Table 20.

Table 20. Description of the specific objectives of the PhD Thesis

Specific Objective		Chapter
SO1	Critical revision of the state-of-the-art technologies for OMP removal in urban wastewater treatment.	#1
SO2	Experimental evaluation of an innovative hybrid system prototype (industrial pilot-scale) integrating MBR and PAC; and techno-economic comparison with a full-scale conventional treatment scheme configuration (CAS and BWRP).	#3
SO3	Experimental evaluation of an innovative hybrid system prototype (industrial pilot-scale) integrating tight UF and PAC; and techno-economic comparison with a full-scale AWRP (UF-RO 50% blend).	#4
SO4	Evaluation of PAC effect on membrane performance for in hybrid systems (PAC-MBR and PAC-UF) and quantification of OMP removal enhancement.	#3, #4
SO5	Experimental evaluation of an AOP based on ozonation + UV at bench-scale; and techno-economic comparison with the use of hybrid processes using PAC in terms of OMP removal efficiencies and cost	#3
SO6	Experimental evaluation of an innovative decentralized fit-for-use prototype (industrial pilot-scale) based in UF, CNM and RO, to boost the use of urban reclaimed water for industrial uses, considering end-users' water quality and quantity requirements.	#5
SO7	Evaluation from an operational an economic perspective the application of UF or CNM as suitable pre-treatment for RO.	#5

Specific Objective		Chapter
SO8	Calculation of cost curves (CAPEX and OPEX) for UF, CNM and RO, easing a rapid cost estimation at different scales.	#5

## 2.3 PhD thesis organization

The Chapters 3-5 provide the published results obtained according to the established specific objectives. Figure 10 shows graphically the scope and results of these Chapters.

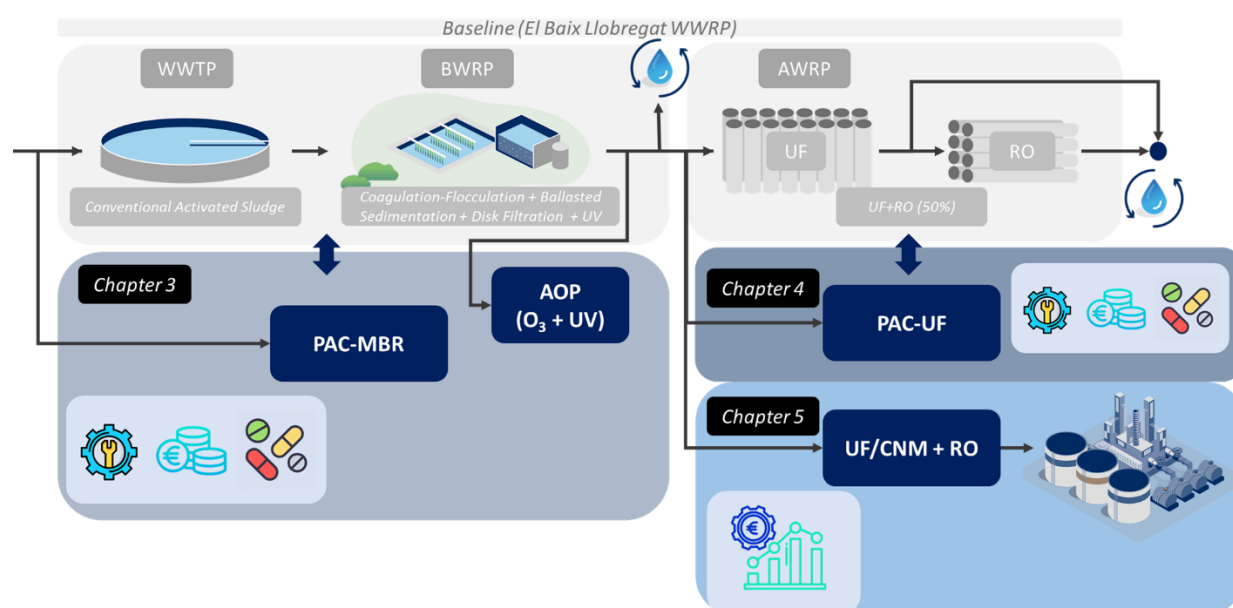


Figure 10. Graphical description of the PhD thesis links between the scope and results.

The different Chapters are briefly summarized in this section:

**Chapter 3:** *Techno-economic evaluation and comparison of PAC-MBR and ozonation-UV revamping for organic micro-pollutants removal from urban reclaimed wastewater.* Science of the Total Environment 671 (2019) 288-298. <https://doi.org/10.1016/j.scitotenv.2019.03.365>

The aim of Chapter 3 is to compare the technical and economic feasibility of different advanced treatment schemes for several OMP removal and water reuse in the El Baix Llobregat WRP, taking as reference the conventional system (CAS). A total of nine OMP have been monitored and evaluated, of which six are pharmaceuticals, two alkylphenols and one pesticide. The treatments considered are: (i) CAS upgraded with a basic water reclamation system (BWR) without salinity removal, (ii) the use of ozone-UV after the CAS and the BWR; (iii) the use of MBR and (iv) the integration of a hybrid adsorption/biological degradation process (PAC-

MBR). Finally, several decision support economic and technical indicators are estimated to address in the optimal way the OMP and water reclamation challenges.

**Chapter 4:** *Hybrid sorption and pressure-driven membrane technologies for organic micropollutants removal in advanced water reclamation: A techno-economic assessment.* Journal of Cleaner Production 273 (2020) 123108. <https://doi.org/10.1016/j.jclepro.2020.123108>

The aim of Chapter 4 is to compare, from a technical and economic point of view, the full-scale UF-RO system installed in the El Baix Llobregat WRP (currently used for groundwater recharge) with a prototype based on the use of capillary tight UF combined with the addition of PAC. Five target OMP commonly persistent in conventional systems (four pharmaceuticals and one pesticide) were monitored at the outlet of basic tertiary systems, and their concentrations were evaluated along mentioned schemes. An economic assessment was performed to scale-up the prototype results and compare both schemes.

**Chapter 5:** *Techno-economic assessment of decentralized polishing schemes for municipal water reclamation and reuse in the industrial sector in coastal semiarid regions: The case of Barcelona (Spain).* Science of the Total Environment, 815 (2022) 152842. <https://doi.org/10.1016/j.scitotenv.2021.152842>

The aim of Chapter 5 is to demonstrate the techno-economic reliability of a fit-for-use treatment train to reuse municipal reclaimed water from a Basic Water Reclamation system (BWR) for industrial uses. The performance of the different treatment units is assessed in terms of water quality and operation to identify the benefits of two potential pre-treatments for RO membranes. In addition, generic cost curves for the different technologies considered are provided and applied to estimate the CAPEX and OPEX required for scaling at three different industrial sites, e.g., chemical, waste management and electro-coating industries, to meet their different needs.

**Author Contribution** in published works. Taking into account that most of the work was developed through large research projects using EU funding schemes, Table 21 summarizes the specific contribution of the PhD candidate.

*Table 21 Summary of the specific contribution of the PhD candidate*

Chapter	Contribution
#3	Pilot plant operation Experimental plan direction and follow-up Operational and water quality results evaluation and analysis Scale-up and techno-economic comparison Discussion and conclusions Writing

<i>Chapter</i>	<i>Contribution</i>
#4	Pilot plant operation Experimental plan direction and follow-up Operational and water quality results evaluation and analysis Scale-up and techno-economic comparison Discussion and conclusions Writing
#5	Pilot plant operation Experimental plan direction and follow-up Operational and water quality results evaluation and analysis Quotation's collection and cost curves calculation Discussion and conclusions Writing

## 2.4 Methodology

The methodology is described in the following subsections. Table 22 summarize the main methods and indicates the corresponding Chapter.

*Table 22. Summary of the experimental methodologies used along the PhD thesis.*

<i>Subsection</i>		<i>Corresponding Chapter</i>
2.4.1	El Baix Llobregt WWTP/WRP description	#3, #4, #5
2.4.2	PAC-MBR prototype description	#3
2.4.2	Ozonation-UV system description	#3
2.4.2	PAC-UF prototype description	#4
2.4.2	Fit-for-use UF-CNM-RO prototype description	#5
2.4.3	Water quality analysis	#3, #4, #5
2.4.4	Economic analysis	#3, #4
2.4.5	Cost curves calculation	#5

### 2.4.1 El Baix Llobregat WWTP/WRP

The WWTP/WRP of “El Baix Llobregat” is located in Barcelona (Spain). It has a design treatment capacity of 330000 m<sup>3</sup>/d and counts with a CAS with biological nitrogen removal, followed by a BWRP capable of treating 100% of the effluent. Potential reclaimed water uses defined by the main water regulator are environmental (river flow and wetlands maintenance), agricultural irrigation, green areas irrigation in Montjuic and industrial uses (Pratenc Industrial Park). It also accounts with an AWRP, which is fed by the effluent from the BWRP and produces 15000 m<sup>3</sup>/d of high-quality reclaimed water for groundwater recharge (deep well injection) to protect it against sweater intrusion. The current treatment schemes are shown in Figure 11.

The BWRP combines a first coagulation-flocculation stage followed by a ballasted settling and a disk-filtration process. In the coagulation tank, poli-aluminum chloride (PAC) is added, which acts as a coagulant forming colloidal suspensions. Then, water is directed into an injection tank where micro-sand is added. Sand particles are added in the flocculation stage to create floccules of larger specific weight, increasing the settling velocity up to 60 times. In the maturing tank an anionic polymeric flocculant is added, and a slow-rotating stirrer provides the optimal conditions for the formation of large floccules that easily settle.

The AWRP consists of a UF followed by RO. The influent is treated by submerged UF, and 50% of produced permeate is subsequently treated by a 2 stage RO with a recovery of 75%. Both UF and RO effluents are blended and disinfected by means of UV lamps prior its injection in the aquifer. A more detailed scheme is shown also in Chapter 4 and summarized in Figure 21.

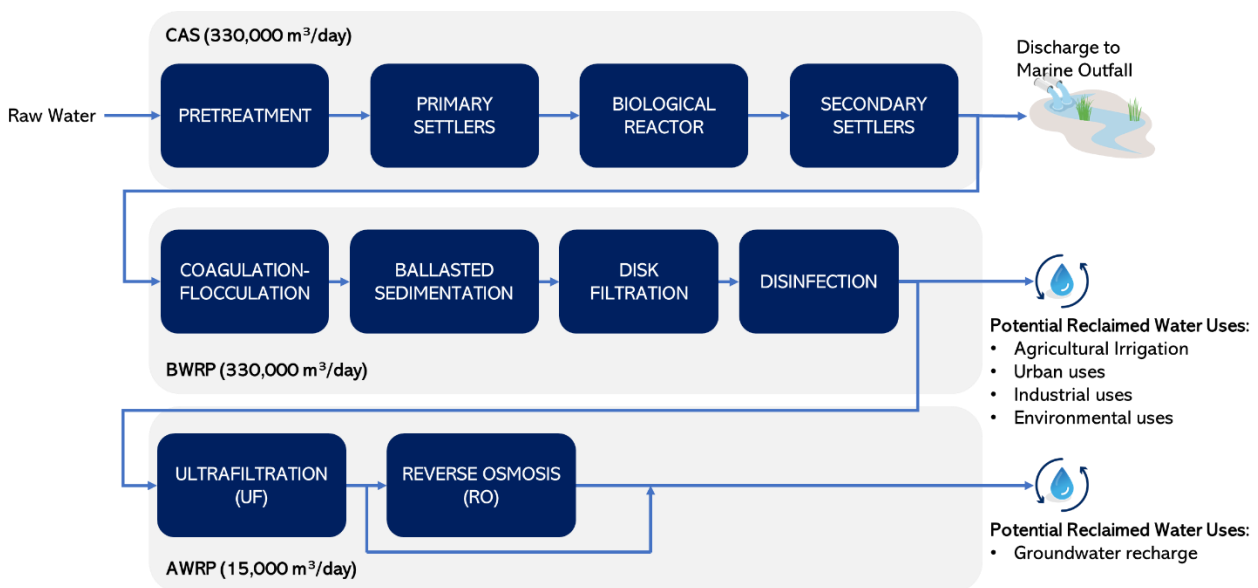


Figure 11 El Baix Llobregat WWTP and WRP treatment scheme (modified from [www.amb.cat](http://www.amb.cat)).

## 2.4.2 Pilot plants and experimental setups description

### 2.4.2.1 PAC-MBR prototype

The industrial pilot scale PAC-MBR prototype was operated for 18 months. Figure 12 shows an external view of the prototypes, which were constructed inside two different 40 ft. containers and located between the primary settlers and the secondary treatment of Baix Llobregat WWTP.

The MBR consisted of a biological reactor with a total volume of 24 m<sup>3</sup> (divided in four different tanks) and two external side stream tubular (PVDF) UF membrane modules (X.Flow, The Netherlands) with a total membrane area of 66 m<sup>2</sup> (Figure 13). The primary effluent (pretreated with a rotatory drum screen) was fed into a first anaerobic tank (3 m<sup>3</sup>) from where it flows by gravity first into the anoxic (5 m<sup>3</sup>) and then into the facultative (3 m<sup>3</sup>) and aerobic (13 m<sup>3</sup>) chambers. A more detailed scheme is shown also in Chapter 3 (Figure 16a).



Figure 12 External view of the PAC-MBR prototype

The side-stream UF modules applied operated in air-lift mode with inside-out filtration. The technical characteristics are collected in Table 23. The sludge from the anaerobic tank was pumped in crossflow (internal recirculation) mode across the UF membrane tubes while air was injected through bottom diffusers to scour membrane surface and control fouling. Backwashing was performed by pumping the permeate in the opposite direction to filtration, enhancing the removal of deposited foulants in the membrane. Chemical cleanings were performed manually every 15-20 days, adding 1 L of NaClO (15% w/w) for oxidizing cleanings and 3 L citric acid (50% w/w) for acid cleanings to 300 L of UF permeate water in the cleaning in place (CIP) tank.





Figure 13. Description of the two external side stream tubular (PVDF) UF membrane modules (X.Flow, The Netherlands) used in the MBR prototype, which account with a total membrane area of 66 m<sup>2</sup>.

The PAC (Norit CABOT, The Netherlands) was directly added to the aerobic tank achieving doses of 25 and 50 mg of PAC/L of raw wastewater. Physical and chemical properties of selected PAC are summarized in Table 24.

Table 23 Technical characteristics of the sidestream UF modules used in the MBR system

Technical characteristics	Value
Model	X-flow Airlift UF
Configuration	Tubular sidestream
Filtration mode	Inside-out
Membrane material	PVDF
Membrane surface area	33 m <sup>2</sup>
Pore diameter	20 nm
Internal fiber diameter	5.2 mm
Standard production	1.5 m <sup>3</sup> /h
Filtration flux	30-50 LMH
Air sparging flow	8-12 Nm <sup>3</sup> /h
Crossflow pump flow	8-15 m <sup>3</sup> /h

Table 24 Technical characteristics of the Powdered Activated Carbon added in the MBR system.

Technical characteristics	Value
Particle diameter	15
Specific surface area – BET (m <sup>2</sup> /g)	1093
Micropore area (m <sup>2</sup> /g)	828
Primary micropore (<0.8 nm) area (m <sup>2</sup> /g)	666
Secondary micropore (0.8-2 nm) area (m <sup>2</sup> /g)	162
Meso and macropore area (m <sup>2</sup> /g)	265
Total pore volume (cm <sup>3</sup> /g)	0.791
Micropore volume (cm <sup>3</sup> /g)	0.397
Primary micropore volume (cm <sup>3</sup> /g)	0.267
Secondary micropore volume (cm <sup>3</sup> /g)	0.130
Mesopore volume (cm <sup>3</sup> /g)	0.394

#### 2.4.2.2 Ozonation-UV system

A bench-scale AOP based in a combination of ozone and UV was validated. The setup included a contact chamber with a ceramic bubble diffuser on the bottom and a recirculation pump, which was employed for mixing water during the established contact time. The ozone was generated with an Ozone Generator from Zonosistem (G21.3 Spain), which produced it from oxygen (>99% of purity) via a corona discharge generator. The ozone rich gas stream (100 g O<sub>3</sub>/Nm<sup>3</sup>) was derived to the contact chamber and bubbled through the diffusers at a flow rate of 0.5 L/min. Doses of 6 and 9 mg O<sub>3</sub>(g)/L were validated.

The UV lamp (25 W) employed was conformed in a tubular reactor with a total volume of 1.5 L. The intensity of the lamp was monitored with a radiometer and the resulting intensity versus time curves was integrated in order to evaluate the dose provided (400 J/m<sup>2</sup>).

#### 2.4.2.3 PAC-UF prototype

The PAC-UF prototype was composed by two capillary HFW 1000 modules (X-Flow, The Netherlands), which could be considered as a tight poly-ether sulfone (PES) UF membrane commercialized as a NF membrane. The tight-UF membranes presented a MWCO of 1kDa and 0.8 mm internal diameter fibers. The main technical characteristics are summarized in Table 25. The two UF modules treated the MBR pilot effluent and the feed pump and a control valve that regulate the rejection stream control filtration flux. On the other hand, cross flow velocities (0-1 m/s) are controlled through an internal recirculation pump. A detailed scheme of the PAC-UF prototype is shown in Chapter 4 (Figure 20).

The validated capillary UF membrane modules allow the removal of macromolecules with MW higher than 1 kDa while do not allow the rejection of sulfates, phosphates or other dissolved inorganic ions. Tight-UF presented the flexibility of conventional UF regarding pre-treatment requirements regarding conventional spiral wound NF or RO and accounts with the possibility to perform backwashes by pumping produced permeate in the reverse direction to filtration, while at the same time performing forward flush, which consisted in pumping feed water across the membrane to scour removed foulants. Chemical cleanings need to be addressed in the feed-side of the membrane through Chemical Enhanced Forward Flush (CEFF) and alkaline cleanings were conducted manually by dosing 0.25 g/L of NaClO (15% w/w), keeping a soaking time of 1 h considering an internal recirculation of 4 m<sup>3</sup>/h. Acid cleanings were performed by adding citric acid (50% w/w) at 0.4 g/L following the same procedure than with alkaline CEFF.

PAC (Norit CABOT, The Netherlands) was directly added to the feed tank by means of a dosing pump. The sorbent physical and chemical properties are listed in Table 24. PAC doses in the feed side of the membrane



were monitored measuring SS and contact time was controlled by means of the tank level and the feed pump flow.

*Table 25 Technical characteristics of the Xflow UF modules used in the PAC-UF prototype*

Technical characteristics	Value
Model	X-flow HFW 1000
Configuration	Capillary (Cross-flow)
Filtration mode	Inside-out
Membrane material	PES
Membrane surface area	40 m <sup>2</sup>
MWCO	1 kDa
Internal fiber diameter	0.8 mm
Standard production	1 m <sup>3</sup> /h
Filtration flux	15-30 LMH
Crossflow pump flow	4-20 m <sup>3</sup> /h



#### 2.4.2.4 Fit-for-use UF-CNM-RO prototype

The prototype treated the BWRP effluent and consisted in two treatment lines in parallel, which fed a two-stage RO plant (1.5 m<sup>3</sup>/h): (i) a polymeric hollow fiber inside-out UF of 3.5 m<sup>3</sup>/h, and (ii) a high-performance sorbent column of 2.2 m<sup>3</sup>/h.

The UF unit consisted of one polymeric hollow fiber membrane module (AQUAFLEX 64, PENTAIR) operating in dead-end mode. The technical characteristics are collected in Table 26. Raw water was directly pumped to the UF membrane module through the feed pump and circulated across the fibers in inside-out mode, filtering the totality of the feed flow. Backwash were performed to control fouling, as well as chemical enhanced backwashes (CEB) in acid and alkaline conditions. For acid cleanings, 1.4 g/L of HCl (15% w/w) was used, while in alkaline cleanings a mixture of 0.2 g/L of NaClO (15%) and 1.4 g/L of NaOH (50%) was applied.

*Table 26 Technical characteristics of the UF membrane modules.*

Technical characteristics	Value
Model	X-flow AQUAFLEX 64
Configuration	Hollow fiber (Dead-end)
Filtration mode	Inside-Out
Membrane material	PES/PVP
Membrane surface area	64 m <sup>2</sup>

<i>Technical characteristics</i>	<i>Value</i>
<i>Pore's diameter</i>	20 nm
<i>Internal fiber diameter</i>	0.83 mm
<i>Standard production</i>	3.5 m <sup>3</sup> /h
<i>Filtration flux</i>	35-65 LMH

The sorbent column was filled with 115 kg of a high-performance carbon nanostructured material (CNM) from Blücher (SARATECH®). The filtration velocity applied varied between 8.5 and 10 m/s. Hydraulic cleanings based in controlled backwashes were applied every several days. Table 27 summarizes the physical and chemical properties of the CNM.

*Table 27 Technical characteristics of the Carbon Nanostructured Material*

<i>CNM properties</i>	<i>Value</i>
<i>BET-surface</i>	600-2100 m <sup>2</sup> /g
<i>Ball pan hardness</i>	99.5%
<i>Ash content</i>	0.1%
<i>Tap density</i>	250-800 kg/m <sup>3</sup>
<i>Bulk density</i>	250-800 kg/m <sup>3</sup>
<i>Water content</i>	<1%
<i>Abrasion strength</i>	>99%

Finally, the RO unit consists of a two-stages operated at a fixed recovery of 70%, allowing a permeate production of 1.5 m<sup>3</sup>/h. The technical characteristics are indicated in Table 28. The high-pressure pump accounted with a speed driver and recovery was fixed by means of a manual rejection valve.

*Table 28 Technical characteristics of the Reverse Osmosis membrane elements*

<i>Technical characteristics</i>	<i>Value</i>
<i>Model</i>	Hydranautics LFC3-LD-4040
<i>Configuration</i>	Spiral Wound
<i>Membrane material</i>	PA
<i>Membrane surface area</i>	7.4 m <sup>2</sup>
<i>Average NaCl rejection percentage</i>	99.7%

### 2.4.3 Water quality analysis

The characterization of the physico-chemical parameters of the different effluents is summarized in Table 29. In Chapter 3, the sampling points were the primary effluent, the CAS effluent, the BWRP effluent, the O<sub>3</sub>/UV effluent, the (PAC)-MBR permeate, and the (PAC)-MBR sludge. In Chapter 4, the sampling points were MBR permeate (feed water), the PAC contact tank, the (PAC)-UF permeate and the (PAC)-UF concentrate. Finally, in Chapter 5, the sampling points were the BWRP effluent (feed water), the UF permeate, the CNM permeate, and the RO permeate.

*Table 29 Analytical methods used on the determination of the physico-chemical parameters of the water quality analysis.*

Parameters	Analytical Method	Chapter 3	Chapter 4	Chapter 5
pH	Electrometry (Mettler Toledo, INPRO 4260/SG/120)	X	X	X
Conductivity	Electrometry (Mettler Toledo, INPRO 4260/SG/120)	X	X	X
Temperature	Electrometry (Mettler Toledo, INPRO 4260/SG/120)	X	X	X
REDOX	Electrometry (Mettler Toledo, INPRO 4260/SG/120)	X		
COD	Test kits (Hach-Lange LCI)	X	X	X
BOD <sub>5</sub>	Standard Methods 5210 B	X	X	X
DOC	Shimadzu VSH-TOC analyzer	X	X	X
SS	Standard Methods 2540	X	X	X
Turbidity	Hach Lange 2100 Turbidimeter	X	X	X
TN	Test kits (Merck Spectroquant)	X	X	X
Na <sup>+</sup>	ICP/MS (Pekin-Elmer Nexion 300x)			X
Ca <sup>2+</sup>	ICP/MS (Pekin-Elmer Nexion 300x)			X
Cu <sup>2+</sup>	ICP/MS (Pekin-Elmer Nexion 300x)			X
Cl <sup>-</sup>	ICP/MS (Pekin-Elmer Nexion 300x)			X
SO <sub>4</sub> <sup>2-</sup>	ICP/MS (Pekin-Elmer Nexion 300x)			X
HCO <sub>3</sub> <sup>-</sup>	ICP/MS (Pekin-Elmer Nexion 300x)			X
Total aerobic (36°C)	UNE-EN-ISO 62222-1999			
Legionella	Enzyme immunoassay	X	X	X
E. Coli	Colillert kits	X	X	X
Nematode eggs	Bailenger method	X		X

Regarding OMP removal assessment, in Chapter 3, nine OMP were analyzed, including six pharmaceuticals, two alkylphenols and one pesticide. In Chapter 4, those recalcitrant compounds still detected in the MBR effluent, were analyzed (four pharmaceuticals and one pesticide). Finally, in Chapter 5, seven different compounds were analyzed, including three triazine pesticides and four PAH. Table 30 collects the list of measured OMP.

Table 30 Description of the OMP analyzed including CAS number, molecular weight and the industrial use.

Parameters	CAS n°	MW [g/mol]	Type	Chapter 3	Chapter 4	Chapter 5
Acetaminophen (ACET)	103-90-2	151	Pharmaceutical	X		
Atenolol (ATN)	29122-68-7	266	Pharmaceutical	X		
Carbamazepine (CBZ)	298-46-4	236	Pharmaceutical	X	X	
Diclofenac (DCF)	15307-86-5	296	Pharmaceutical	X	X	
Erythromycin (ERY)	114-07-8	734	Pharmaceutical	X	X	
Sulphametoxazole (SMX)	723-46-6	253	Pharmaceutical	X	X	
Nonylphenol (NP)	25154-52-3	220	Alkylphenol	X		
Octylphenol (OP)	67554-50-1	206	Alkylphenol	X		
Diuron (DIU)	330-54-1	232	Pesticide	X	X	
Terbutylazine	5915-41-3	230	Pesticide			X
Atrazine	1912-24-9	216	Pesticide			X
Simazine	122-34-9	202	Pesticide			X
Anthracene	120-12-7	178	PAH			X
Fluorene	86-73-7	166	PAH			X
Pyrene	129-00-0	202	PAH			X
Naphthalene	91-20-3	128	PAH			X

The determination of the target OMP involved their analysis in matrixes of different complexities, from the primary effluent of the WWTP to the final treatments. The analysis of the samples was performed by solid phase extraction (SPE) coupled online with liquid chromatography and tandem mass spectrometry (LC-MS/MS) with electrospray ionization (ESI) as described elsewhere (Tiwari et al., 2017; Han Tran and Yew-Hoong Gin, 2017). Both methods are described in Table 35 and Table 36.

Before the SPE, all the samples were passed through a 0.2 µm glass fibre filter (Whatman, UK) in order to avoid any system blockages. In addition, the samples from primary effluents were diluted 10 times in order to reduce the matrix effect. Afterwards, a 10 mL aliquot of each sample or diluted sample was spiked with isotopically labelled standards used as surrogates (to achieve a concentration of 100 ng/L) and injected in the instrument to be analyzed following the methods described.

The on-line solid phase extractions and chromatographic separations were performed by using an automated on-line SPE Symbiosis Pico system from Spark Holland (Emmen, The Netherlands). The samples were pre-concentrated in OASIS HLB cartridges (Waters, Milford, MA, USA) at 2 mL/min after conditioning cartridges with 2mL of methanol (Method 1) or acetonitrile (Method 2) and 2mL of water at a flow rate of 5mL/min. Elution was then performed by using the focusing extraction mode either with 400 µL of methanol in 1 min (Method 1) or

with 200  $\mu$ L of acetonitrile with 0.1% formic acid in 2 min (Method 2). The eluate entered a Kinetex F5 (100mm  $\times$  4,6mm i.d., 2,6 $\mu$ m particle size) LC column (Phenomenex, Torrance, CA, USA), where the analytes were separated by means of a gradient flow at 1 mL/min from 100% water to 100% of either methanol in 7 minutes (Method 1) or acetonitrile with 0.1% formic acid in 10 minutes (Method 2).

Table 31 Optimized method for negative ionizable compounds

	Method 1			Method 2		
	Solvent	Vol. (mL)	Flow (mL/min)	Solvent	Vol. (mL)	Flow (mL/min)
<b>Conditioning</b>	Methanol	2	5	Acetonitrile + 0.1 Formic Ac.	2	5
<b>Equilibration</b>	Water	2	5	Water + 0.1 Formic Ac.	2	5
<b>Sample Load</b>	-	2	2	-	2	2
<b>Elution</b>	Methanol	0.4	0.4	Acetonitrile + 0.1 Formic Ac.	0.2	0.1

Table 32 Optimized method for positively ionizable compounds

Method 1				Method 2			
Time (min)	Methanol (%)	H2O (%)	Flow ( $\mu$ L/min)	Time (min)	Acetonitrile + 0,1% Formic Ac. (%)	Water + 0,1% Formic Ac. (%)	Flow ( $\mu$ L/min)
0	0	100	600	0	0	100	900
1	0	100	600	2	0	100	900
1.01	50	50	1000	2.01	10	90	1000
6.5	100	0	1000	10	100	0	1000
8	100	0	1000	12	100	0	1000
9	50	50	1000	13	10	90	1000
12	50	50	1000	16	10	90	1000

The detection and quantification of the analytes were achieved by means of a 3200 Qtrap hybrid triple quadrupole-linear ion trap mass spectrometer (Applied Biosystems, Foster City, CA, USA) with a turbo Ion Spray source used as a triple quadrupole in selected reaction monitoring (SRM) mode. The source parameters for each method, as well as the transitions monitored for each analyte (quantification and confirmation) are detailed in Table 37.

*Table 33 Detection and quantification parameters of the OMP*

Method	OMP	Ioniz. Mode	RT (min)	Q1 (m/z)	DP (V)	Quantification		Confirmation	
						Q3 (m/z)	EC (V)	Q3 (m/z)	EC (V)
Method 1	DCF		5.5	294	-25	250	-14	214	-26
	OP	ESI (-)	7.1	205	-70	133	-34	117	-82
	NP		7.5	219	-55	133	-44	117	-80
Method 2	ATN		3.9	267	46	145	33	190	25
	ACET		4.2	152	46	110	21	65	43
	SMX	ESI (+)	5.7	254	36	156	23	92	37
	ERY		5.8	735	46	158	41	576	29
	CBZ		6.2	237	41	194	27	192	45
	DIU		6.9	233	51	72	35	160	33

The performance of the optimized methodology was evaluated by the analysis of spiked samples. In Table 34 are described the limits of detection, limits of quantification and precisions obtained with the described methodology for the different matrixes. The LODs were determined as the analyte concentration for which a signal-to-noise (S/N) ratio of 3 was obtained (media of n=3 for each matrix). The LOQs were defined as those concentrations yielding a S/N ratio greater than 10 and for which the relative standard deviation was lower than 25%. The repeatability was calculated as the relative standard deviation (%RSD) of the calculated concentrations for three replicates analyzed on three different days.

*Table 34 Limits of detection (LOD), Limits of quantification (LOQ) and precision regarding the different analyzed OMP in the different effluents.*

OMP	LOD (ng/L)			LOQ (ng/L)			Precision (%)		
	Primary effluent	WWTP effluent	Advanced Reclamation schemes	Primary effluent	WWTP effluent	Advanced Reclamation schemes	Primary effluent	WWTP effluent	Advanced Reclamation schemes
DCF	1.5	1.2	1.0	5	5	5	22	16	6.8
ATN	2.6	1.5	3.2	10	10	10	4.0	4.7	6.4
ACET	78	31	24	300	100	100	29	19	16
SMX	1.9	3.0	2.3	10	10	10	21	14	13

OMP	LOD (ng/L)			LOQ (ng/L)			Precision (%)		
	Primary effluent	WWTP effluent	Advanced Reclamation schemes	Primary effluent	WWTP effluent	Advanced Reclamation schemes	Primary effluent	WWTP effluent	Advanced Reclamation schemes
ERY	30	11	11	100	50	50	27	25	21
CBZ	2.6	1.5	0.7	10	10	10	21	15	8.1
DIU	4.7	3.2	4.1	15	15	15	19	13	14
OP	10.2	7.2	6.5	50	25	25	21	10	12
NP	22	13	12	100	50	50	22	18	16

#### 2.4.4 Economic analysis

The method applied for the estimation of CAPEX and OPEX of the different treatment schemes in Chapter 3 and Chapter 4 is described as follows. From one hand, for CAPEX calculation, the optimal operational conditions validated at prototype scale were used to preliminary and theoretically scale-up the treatment scheme, considering the hydraulic circuit, intermediate elements (tanks and pumps), instrumentation and civil works. For both PAC-MBR and PAC-UF systems, data from the different manufacturers (e.g., X-Flow, Suez WTS) was gathered in order to account with a reference economic value and compare it with the full-scale installation in El Baix Llobregat WWTP/WRP. The items considered for the PAC-MBR upscaling were depicted in Chapter 3 (Echevarria et al., 2019): (i) rotatory drum screens as pre-treatment, (ii) biological reactor (tanks, turbo-blowers and dosing units for coagulation and foaming control), (iii) UF membrane skids, (iv) PAC slurry preparation tank. On the other hand, PAC-UF upscaling was depicted in Chapter 4 (Echevarria et al., 2020) considered the following items: (i) rotatory drum screen as pre-treatment, (ii) PAC slurry preparation tank, PAC contact tank and hydraulic cleanings tank, and (iii) UF membrane skids.

Regarding the AOP, the ozonation system (ozone generator, contact chamber and injectors) and UV lamps were scaled-up considering data from manufacturers (e.g., Ozonia). Finally, the CAPEX of the existing full-scale WWTP, BWRP and AWRP was obtained from the plant managers.

OPEX calculation was based on energy and chemical reagents consumption, as well as other consumables (e.g., membranes or lamps reposition). Field data obtained from the prototype's performance was used in Chapter 3 and Chapter 4, together with data provided by the WWTP/WRP managers, water treatment-engineering firms and technology and chemical reagents providers.

The economic analysis of the technologies demonstrated in Chapter 5 and its upscaling in the three different industrial case studies was done with cost curves, which calculation is described in section 2.4.5

### 2.4.5 Cost estimation methodology

William Law (Tribe and Alpine, 1986), in which costs (CAPEX and OPEX) follow an exponential trend considering economy of scale, is defined as  $C = \beta \cdot Q^\alpha$ , where C corresponds to Cost, Q to capacity and  $\beta$  and  $\alpha$  are constants. Raj Sharma (2010) and the USEPA (1979) have developed cost equations based on exponential regression lines. The accuracy is highly dependent on the assumptions and key variables defined. As described in Chapter 5 (Echevarria et al., 2022), in CAPEX curves, the items considered were: (i) Site work or site preparation, (ii) equipment and housing, and (iii) electrical and instrumentation; while in OPEX curves, the items considered were: (i) energy consumption, (ii) chemicals consumption, (iii) equipment replacement and maintenance, and (iv) waste and by-products management.

In Chapter 5, different quotations were compiled to calculate CAPEX and OPEX curves, which were used to estimate data or the three different capacities of the industrial case studies.



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# Chapter 3



### 3. Chapter 3: Techno-economic assessment and comparison of PAC-MBR and O<sub>3</sub>/UV revamping for OMP removal from urban reclaimed wastewater.

The following Chapter corresponds to the article published in Science of the Total Environment the 25<sup>th</sup> of March of 2019.

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Techno-economic evaluation and comparison of PAC-MBR and ozonation-UV revamping for organic micro-pollutants removal from urban reclaimed wastewater

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Figure 14 Screenshot of the published article in Science of the Total Environment.

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#### Abstract:

The presence of sewage-borne Organic Micro-Pollutants (OMP) in Wastewater Treatment Plants (WWTP) effluents represents an increasing concern when water is reclaimed for irrigation or even for indirect potable reuse (IPR). For eighteen months, an innovative hybrid water reclamation scheme based on a Membrane Biological Reactor (MBR) enhanced with Powder Activated Carbon (PAC) was operated at pilot-scale (70 m<sup>3</sup>/d) to compare it with state-of-the art Wastewater Reclamation System (WWRS) also revamped with a final step of ozonation-UV. Removal of persistent OMP, water quality and treatment costs were evaluated and compared for the different treatment schemes. OMP removal efficiency results for the different schemes concluded that established technologies, such as physico-chemical and filtration systems as well as MBR, do not remove significantly (>15%) the most recalcitrant compounds. The upgrading of these two systems through the addition

of ozonation-UV step and PAC dosing allowed improving average recalcitrant OMP removal to  $85\pm 2$  and  $75\pm 5$  %, respectively. In term of costs, PAC-MBR represents an increase of 37 % of costs regarding conventional systems but presents improvements of 50 % reduction in space and water quality. On the other hand, ozonation requires up to a 15% increase of footprint; nevertheless, represents lower costs and lower carbon footprint. Ozonation-UV seems to be the best option for upgrading existing facilities, while PAC- MBR should be considered when space represents a critical limitation and produced water is reused for high water quality purposes.

### 3.1 Introduction

The excessive and unregulated consumption or discharge of anthropogenic origin compounds in centralized sewage collectors has increased the presence of organic contaminants, at micro level contents, causing potential negative effects along the environment bodies (de Jesus Gaffney et al., 2015; Wilkinson et al., 2017; Thomaidi et al., 2015; Thomaidi et al., 2017). The main reason why some organic micro-pollutants (OMP) reach the environment is the limited removal capacity of conventional wastewater systems. Nowadays, most of wastewater treatment plants (WWTPs) are based on conventional biological treatment (e.g., conventional activated sludge (CAS)), which have achieved convincing results on the removal of organic pollution load and nutrients through the combination of anaerobic, anoxic and aerobic systems. Nevertheless, these conventional treatments were not specifically designed to achieve high removal efficiencies of OMP; especially, those recognized as recalcitrant as they could not be degraded or metabolized by conventional biological microorganisms (Fernández-López et al., 2016; Martínez-Alcalá et al., 2017; Tiwari et al., 2017).

On the other hand, the upgrading of CAS with tertiary systems (generally based on physico-chemical treatments, media filtration, membrane filtration and/or disinfection) does not always ensure the removal of the most recalcitrant OMP. Depending on the reclaimed water uses (e.g., agriculture, aquifer recharge, recreational and environmental) the uncertain effects on human health can be perceived as risks by public administration, creating reluctances in end-users and, thus, generating barriers on water reuse implementation (Khan and Anderson, 2018; Rock et al., 2018; Smith et al., 2018).

Several studies (Ávila and García, 2015; Carballa et al., 2005; Gros et al., 2017; Luo et al., 2014; Sipma et al., 2010) have described the high variability in removal efficiencies measured in several WWTPs incorporating CAS. The presence of easily removable compounds (mainly composed by OMP that present high biodegradability or high sorption potential) and recalcitrant compounds, generally considered on the Priority Substances List or on the European Commission (EC) Watch List have been highlighted. It has been

demonstrated the limited removal capacity (<20%) of constructed wetlands for some compounds such as Carbamazepine (CBZ) or Sulphametoxazole (SMX) (Tondera et al., 2018), both of them very persistent in CAS. Luo et al., (2014) in their critical review reported the low efficiencies found in filtration systems such as microfiltration (MF) and ultrafiltration (UF). The limited removal capacity of recalcitrant compounds such as CBZ in sand filtration systems followed by UV has been demonstrated (Besha et al., 2017). Other studies have demonstrated the persistency of some OMP after conventional tertiary treatments based on physico-chemical system followed by disk filtration as it is the case of El Baix Llobregat Water Reclamation Plant (WRP) (Cabeza et al., 2012).

In order to provide a better understanding on the fate of OMP, Suárez et al., (2008) defined, as preliminary hypothesis, two main OMP removal mechanisms in conventional WWTPs incorporating CAS: (i) biological and/or chemical transformation and (ii) sorption. Although, volatilization has been considered as a third potential mechanism; nevertheless, aeration in CAS treatments usually is not capable to strip from water OMP unless they are particularly volatile. These two main removal mechanisms are dependent on the physico-chemical properties of the target compound and have been extensively studied by many authors. Transformation is related to metabolic reactions caused by the presence of microorganisms in the WWTP reactors (Ngoc et al., 2018; Park, et al., 2017). Joss et al., (2006) determined the pseudo first order degradation kinetics ( $k_{\text{biol}}$ ) for a large number of compounds. Accordingly, OMPs could be classified into three categories: (i) hardly biodegradable ( $k_{\text{biol}} < 0.1$  l/g (SS)/d); (ii) moderately biodegradable ( $0.1 < k_{\text{biol}} < 10$  l/g SS/d); and (iii) highly biodegradable ( $k_{\text{biol}} > 10$  l/g (SS)/d). Sorption, on the other hand, includes two main mechanisms (Suárez et al., 2008; Verlicchi et al., 2015; Verlicchi et al., 2010): (i) absorption onto living structures, which potential can be evaluated through octanol-water partition coefficient ( $k_{\text{ow}}$ ) (Omil et al., 2010); and (ii) adsorption onto solid phase, which refers to the electrostatic interactions between positively charged groups of OMP with negatively charged surfaces of sludge or sorbents. Extension of adsorption capacity could be quantified by using the distribution coefficient (D), dependent on pH, OMP acidity dissociation constant ( $k_a$ ) and octanol-water partition coefficient. It is used as indicator to assess the adsorption potential of OMP on sorbents such as activated carbon. OMP with  $\log D > 1$  have a high tendency to be adsorbed (Alvarino et al 2017).

Following these fundamental mechanisms, several technologies have been visualized as the most feasible technical solutions for ensuring high removal rates of persistent OMP. These technologies can be divided in four groups: (i) dense membrane filtration systems, such as nanofiltration (NF) or Reverse Osmosis (RO); (ii) adsorption processes (activated carbon or other sorbents); (iii) Advanced Oxidation Processes (AOP); and (iv) hybrid systems including combination of the previous options.

Hybrid systems seek for synergies between technologies in order to maximize the removal efficiency of OMP as well as to reduce, when possible, specific energy consumption and reagent costs associated. One example is the use of sorbents combined with biological processes, particularly the addition of powdered activated carbon (PAC) in a membrane biological reactor (MBR). Several authors demonstrated the improvements in PAC-MBR in terms of sludge filterability and fouling reduction, being able to improve twice critical fluxes. Remy et al., (2010) reported that PAC addition represents an operation cost of 0.08 €/m<sup>3</sup>, thus the use of this sorbent significantly increases the treatment cost. This increase should be compensated by taking advantage from the operational benefits expected in terms of higher flux, lower specific energy demand (more production and lower transmembrane pressure (TMP) ranges) and, finally, lower chemicals consumption (by enlarging the operation period between chemical cleanings).

Advanced wastewater treatments focused on OMP removal have been extensively evaluated from a technical point of view, understanding the removal mechanisms and the fate of different target compounds. Margot et al., (2013) compared at pilot scale the use of transformation mechanisms such as ozonation followed by sand filtration and the use of separation mechanisms such as PAC followed by UF. Moreover, Bourgin et al., (2017) demonstrated removal efficiencies >80% for persistent OMP through the use of ozone (0.55 g O<sub>3</sub>/ g DOC) in the secondary effluent of the Swiss WWTP of Neugut. Three possible post-treatments (sand filtration, moving bed and fixed bed) were compared with a direct GAC filtration of the secondary effluent. Nevertheless, there is still needed to assess deeply capital and operational expenditures (CAPEX and OPEX) associated to them in order to facilitate decision making.

The aim of this research is to compare the technical and economic feasibility of different advanced treatment schemes for several OMP removal and water reuse in the El Baix Llobregat WRP, taking as reference the conventional system (CAS) as it is depicted in Figure 15. A total of nine OMP have been monitored and evaluated, from them, six are pharmaceuticals, two alkylphenols and one pesticide. The treatments considered are: (i) CAS upgraded with a basic water reclamation system (BWR) without salinity removal, (ii) the use of ozone-UV after the CAS and the BWR; (iii) the use of MBR and (iv) the integration of a hybrid adsorption/biological degradation process (PAC-MBR). Finally, several decision support economic and technical indicators are estimated to address in the optimal way the OMP and water reclamation challenges.

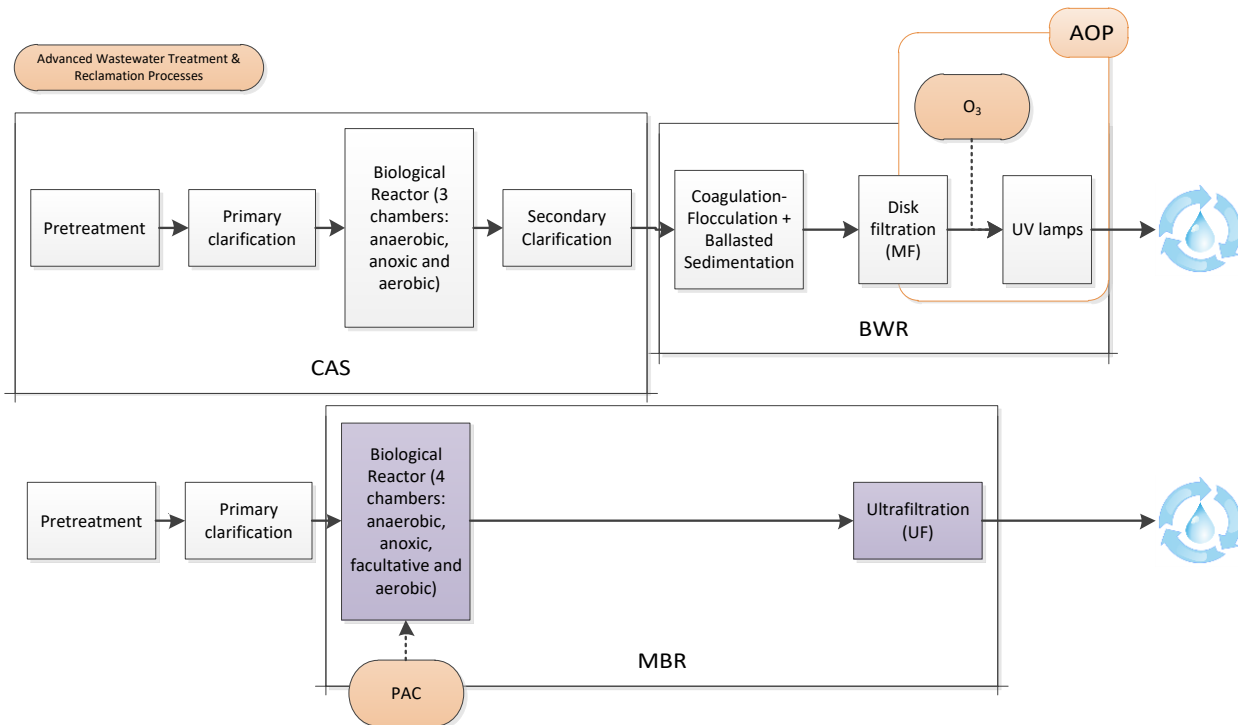


Figure 15 Evaluated advanced reclamation systems for OMP removal. On top, current reclamation systems of Baix Llobregat revamped with ozone-UV system. Below, PAC-MBR prototype scheme evaluated in El Baix Llobregat.

## 3.2 Materials and Methods

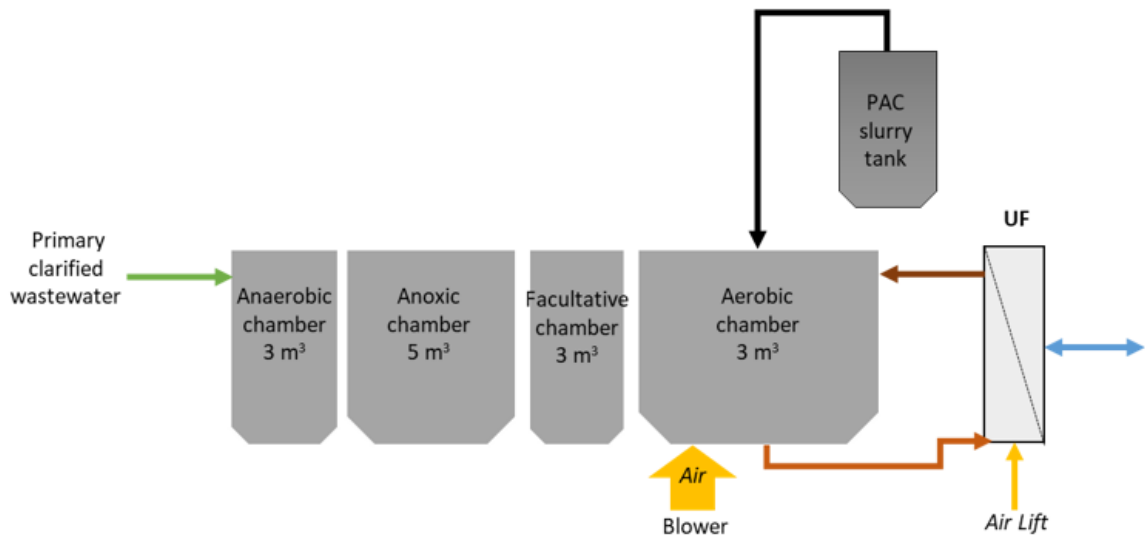
### 3.2.1 Pilot plant treatment description

The El Baix Llobregat WWTP has a treatment capacity of 330000 m<sup>3</sup>/d and counts with a CAS system with biological nitrogen removal and chemical phosphorus precipitation. Secondary treatment is followed by a BWR system which combines a coagulation-flocculation system followed by ballasted settling stage, a micro-filtration process and a final disinfection based on UV and chlorination. The BWR system can treat 100% of the influent flow and reuse reclaimed water in environmental, urban, agricultural, and industrial uses.

A PAC-MBR prototype (Figure 16a) with a capacity between 2 and 3 m<sup>3</sup>/h was operated steady for a total period of 12 months in the El Baix Llobregat WWTP. The MBR consisted in a biological treatment with a total working volume of 24 m<sup>3</sup> divided in four tanks and two external side-stream ultrafiltration membrane modules with a membrane area of 33 m<sup>2</sup>/module. The primary effluent (pre-treated with a rotatory drum screen) was fed into a first anaerobic tank (3 m<sup>3</sup>) from where it flows by gravity first into the anoxic (5 m<sup>3</sup>) and then into the facultative (3 m<sup>3</sup>) and aerobic (13 m<sup>3</sup>) chambers.



a



b

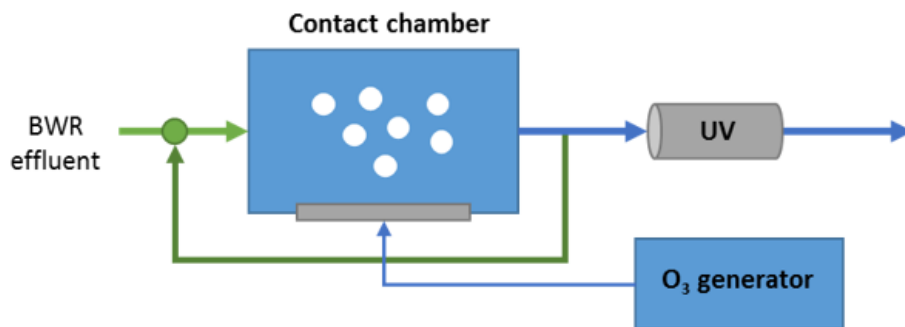


Figure 16 a) PAC-MBR prototype scheme where 4 tanks with a total volume of 24 m<sup>3</sup> compose the biological reactor which feeds the UF membrane in crossflow mode, and b) AOP bench-scale set up, composed by a contact chamber with recirculation, O<sub>3</sub> generator and a final step of UV.

The side-stream UF-modules employed were tubular PVDF membranes (X-Fflow, Netherlands) operated in air-lift mode with inside-out filtration. This mode consists in pumping the sludge from the aerobic chamber in cross flow across the UF membrane tubes while air is injected through the bottom diffusers of the modules in order to scour membrane surface and control fouling. The two membrane modules were operated in constant flux mode (which could be varied from 30 to 60 LMH), controlling the permeate production through the suction pressure generated by the permeate pumps. For backwashing, permeate was pumped in the opposite direction to filtration with the airlift and sludge crossflow pumping in operation in order to enhance the removal of deposited foulants on the membrane.

The PAC (Norit, Holland) was added to the aerobic tank achieving doses of 25 and 50 mg PAC/L of wastewater. Chemical cleanings were performed every 15-20 days and were conducted manually by adding either 1 L of

sodium hypochlorite (15 % w/w) for the oxidizing cleanings and 3 L of citric acid (50 % w/w) for the acid cleanings to 300 L of UF permeate water in the cleaning in place (CIP) tank.

Finally, a bench-scale AOP set-up was tested in BWR system after disk filtration. AOP unit, based on the combination of ozone and UV (Figure 16b), included a contact chamber with a ceramic bubble diffuser on the bottom. Additionally, a recirculation pump was employed for mixing and cycling the water samples in a circulation loop and through a tubular UV reactor. The ozone was generated with an Ozone Generator from Zonosistem, (G2L3, Spain), which produced it from oxygen via a corona discharge generator. The  $O_3(g)$  generator used quality grade oxygen with a purity of > 99 % with concentrations of ca.  $100 \text{ gO}_3/\text{Nm}^3$ . The  $O_3(g)$  rich gas stream was bubbled through the base of a contact chamber through ceramic bubble diffusers at a flow rate of 0.5 L/min using a ceramic fine bubble diffuser, during periods of 2 and 3 minutes, for target  $O_3(g)$  doses of 6, and 9 mg/L, respectively. After the end of the ozonation process 10 minutes contact time were applied before the beginning of disinfection with UV. The 25 W UV lamp employed for the test was installed in a U tube stainless still tubular reactor with a total volume of 1.5 L. The intensity of the lamp was monitored with a radiometer and the resulting intensity versus time curves was integrated in order to evaluate the dose provided. A target dose:  $400 \text{ J/m}^2$  was used.

### 3.2.2 Sampling and analysis

To characterize the produced water quality, different sampling points for off-line analysis were set. Primary effluent (wastewater inlet), CAS effluent, BWR effluent and MBR permeate, and sludge were monitored twice per week.

SS and  $BOD_5$  were analyzed through standard methods (2540 and 5210 B, respectively). Turbidity was measured using a Hach Lange 2100 Turbidimeter (Hach, USA). Test kits were used for COD (Hach-Lange LCI test kits) and total nitrogen containing species (Merck spectroquant test kits). DOC was analyzed with a Shimadzu VSH-TOC analyzer. Temperature, pH and redox potential were monitored online.

Finally, nine OMP were selected and analyzed as target compounds to understand their behavior in tested wastewater treatment and reclamation systems. Eighteen sampling campaigns were carried out along nine months, including warm and cold seasons. Twelve samples were analyzed for CAS (secondary effluent) and CAS+BWR, ten samples for CAS+BWR+ $O_3$ -UV, seven samples for MBR without PAC and ten samples for PAC-MBR. From these nine target compounds, six of them were pharmaceuticals: (Acetaminophen (ACET), Atenolol (ATN), Carbamazepine (CBZ), Diclofenac (DCF), Erythromycin (ERY) and Sulphametoxazole (SMX)); two of them were alkylphenols (Nonylphenol (NP) and Octylphenol (OP)) and finally a pesticide (Diuron (DIU)). The

selection of these compounds for the further discussion included easily removable and OMPs others with a strong recalcitrant character.

The determination of the target analytes involved the analysis in matrixes of different complexities, from the primary effluent of the WWTP to the final treatments. The analysis of the samples was performed by solid phase extraction (SPE) coupled online with liquid chromatography and tandem mass spectrometry (LC-MS/MS) with electrospray ionization (ESI) as described elsewhere (Tiwari et al., 2017; Han Tran and Yew-Hoong Gin, 2017). Two different methods were optimized for negative (Method 1) and positively (Method 2) ionizable compounds. Both methods are described in Table 35 and Table 36.

*Table 35 Optimized method for negative ionizable compounds*

	Method 1			Method 2		
	Solvent	Vol. (mL)	Flow (mL/min)	Solvent	Vol. (mL)	Flow (mL/min)
<b>Conditioning</b>	Methanol	2	5	Acetonitrile + 0.1 Formic Ac.	2	5
<b>Equilibration</b>	Water	2	5	Water + 0.1 Formic Ac.	2	5
<b>Sample Load</b>	-	2	2	-	2	2
<b>Elution</b>	Methanol	0.4	0.4	Acetonitrile + 0.1 Formic Ac.	0.2	0.1

*Table 36 Optimized method for positively ionizable compounds*

Method 1				Method 2			
Time (min)	Methanol (%)	H2O (%)	Flow (μL/min)	Time (min)	Acetonitrile + 0,1% Formic Ac. (%)	Water + 0,1% Formic Ac. (%)	Flow (μL/min)
0	0	100	600	0	0	100	900
1	0	100	600	2	0	100	900
1.01	50	50	1000	2.01	10	90	1000
6.5	100	0	1000	10	100	0	1000
8	100	0	1000	12	100	0	1000
9	50	50	1000	13	10	90	1000
12	50	50	1000	16	10	90	1000

Before the SPE, all the samples were passed through a 0,2  $\mu\text{m}$  glass fibre filter (Whatman, UK) in order to avoid any system blockages. In addition, the samples from primary effluents were diluted 10 times in order to reduce the matrix effect. Afterwards, a 10 mL aliquot of each sample or diluted sample was spiked with isotopically labelled standards used as surrogates (to achieve a concentration of 100 ng/L) and injected in the instrument to be analyzed following the methods described.

The on-line solid phase extractions and chromatographic separations were performed by using an automated on-line SPE Symbiosis Pico system from Spark Holland (Emmen, The Netherlands).

The samples were pre-concentrated in OASIS HLB cartridges (Waters, Milford, MA, USA) at 2 mL/min after conditioning cartridges with 2mL of methanol (Method 1) or acetonitrile (Method 2) and 2mL of water at a flow rate of 5mL/min. Elution was then performed by using the focusing extraction mode either with 400  $\mu\text{L}$  of methanol in 1 min (Method 1) or with 200  $\mu\text{L}$  of acetonitrile with 0.1% formic acid in 2 min (Method 2). The eluate entered a Kinetex F5 (100mm  $\times$  4,6mm i.d., 2,6 $\mu\text{m}$  particle size) LC column (Phenomenex, Torrance, CA, USA), where the analytes were separated by means of a gradient flow at 1 mL/min from 100% water to 100% of either methanol in 7 minutes (Method 1) or acetonitrile with 0.1% formic acid in 10 minutes (Method 2).

The detection and quantification of the analytes were achieved by means of a 3200 Qtrap hybrid triple quadrupole-linear ion trap mass spectrometer (Applied Biosystems, Foster City, CA, USA) with a turbo Ion Spray source used as a triple quadrupole in selected reaction monitoring (SRM) mode. The source parameters for each method, as well as the transitions monitored for each analyte (quantification and confirmation) are detailed in Table 37.

Table 37 Detection and quantification parameters of the OMP

Method	OMP	Ioniz. Mode	RT (min)	Q1 (m/z)	DP (V)	Quantification		Confirmation	
						Q3 (m/z)	EC (V)	Q3 (m/z)	EC (V)
Method 1	DCF	ESI (-)	5.5	294	-25	250	-14	214	-26
	OP		7.1	205	-70	133	-34	117	-82
	NP		7.5	219	-55	133	-44	117	-80
Method 2	ATN	ESI (+)	3.9	267	46	145	33	190	25
	ACET		4.2	152	46	110	21	65	43
	SMX		5.7	254	36	156	23	92	37
	ERY		5.8	735	46	158	41	576	29
	CBZ		6.2	237	41	194	27	192	45

Method	OMP	Ioniz. Mode	RT (min)	Q1 (m/z)	DP (V)	Quantification		Confirmation	
						Q3 (m/z)	EC (V)	Q3 (m/z)	EC (V)
	DIU		6.9	233	51	72	35	160	33

The performance of the optimized methodology was evaluated by the analysis of spiked samples. Table 38 shows the limits of detection, limits of quantification and precisions obtained with the described methodology for the different matrixes. The LODs were determined as the analyte concentration for which a signal-to-noise (S/N) ratio of 3 was obtained (media of  $n=3$  for each matrix). The LOQs were defined as those concentrations yielding a S/N ratio greater than 10 and for which the relative standard deviation was lower than 25%. The repeatability was calculated as the relative standard deviation (%RSD) of the calculated concentrations for three replicates analyzed on three different days.

*Table 38 Limits of detection (LOD), Limits of quantification (LOQ) and precision regarding the different analyzed OMP in the different effluents.*

OMP	LOD (ng/L)			LOQ (ng/L)			Precision (%)		
	Primary effluent	WWTP effluent	Advanced Reclamation schemes	Primary effluent	WWTP effluent	Advanced Reclamation schemes	Primary effluent	WWTP effluent	Advanced Reclamation schemes
Diclofenac	1.5	1.2	1.0	5	5	5	22	16	6.8
Atenolol	2.6	1.5	3.2	10	10	10	4.0	4.7	6.4
Acetaminophen	78	31	24	300	100	100	29	19	16
Sulfametoxazol	1.9	3.0	2.3	10	10	10	21	14	13
Erythromycin	30	11	11	100	50	50	27	25	21
Carbamazepine	2.6	1.5	0.7	10	10	10	21	15	8.1
Diuron	4.7	3.2	4.1	15	15	15	19	13	14
Octylphenol	10.2	7.2	6.5	50	25	25	21	10	12
Nonylphenol	22	13	12	100	50	50	22	18	16

ANOVA was applied as statistical method in order to evaluate significant variances in the removal rates obtained in the different treatment trains evaluated. Turkey method was used in order to statistically group the different treatment trains and evaluate with a 95% of confidence differences on the removal of a specific compound.

### 3.2.3 Economic analysis

The methodology applied for the estimation of operational expenditures (OPEX) and capital expenditures (CAPEX) for the different treatment schemes is described in this section.

#### 3.2.3.1 Capital expenditures (CAPEX)

Optimal operational conditions for the different treatment trains tested at prototype scale were used to design (in terms of hydraulic circuit, electric installation, monitoring, required modules and civil works) and estimate capital expenditures (CAPEX). For the MBR full-scale projection, data from different manufacturers (e.g. X-Flow, Suez WTS) were gathered in order to have a range of investment cost for a design flow of 330000 m<sup>3</sup>/d. The following elements have been considered for the MBR treatment:

- **Pre-treatment** composed by the intermediate pumps fed by the primary effluent and the rotatory drum screens.
- **Biological treatment**, composed by biological tanks, turbo-blowers and chemical dosing units for coagulation and foaming control.
- **UF membranes** composed by the different units that take part in the different operational sequences, including circulation/feed, permeate extraction, air injection, chemical dosing and backwash units.

Finally, it was considered a **PAC preparation tank** and its corresponding dosing unit.

On the other hand, for the final AOP treatment step, an ozonation system followed by a UV lamps channel were up scaled based on data from manufacturers. The ozonation plant accounts with the ozone generator system, its respective injectors and contact chamber.

Both treatment trains were directly compared or added to the total cost of the CAS system followed by the BWR plant from the El Baix Llobregat WRP described in section 3.2.1.

#### 3.2.3.2 Operational expenditures (OPEX)

Energy and chemicals consumption data were gathered in order to estimate operational expenditures (OPEX) of the different schemes. Additionally, a membrane lifespan of 8 years was considered for UF modules and was coupled with the modules cost (provided by the membrane manufacturer) to calculate a membrane replacement relative cost. The same cost of electricity 0.111 €/kWh (average price provided by the WWTP managers) was considered for both projections and the actual cost of the full-scale plant for chemicals and sludge transportation were also taken into account. Operational expenditures should be adapted regarding the European country, taking into account that Germany, Denmark or the Netherlands account with higher average electricity costs (0.31, 0.30 and 0.25 €/kWh, respectively).

## 3.3 Results

### 3.3.1 Effect of PAC on MBR performance

The MBR was operated during 4 months without PAC addition during summer season (average temperature of  $27 \pm 3$  °C). The prototype treated between 2.0-2.5 m<sup>3</sup>/h of primary clarified wastewater, which corresponds to hydraulic retention time (HRT) between 10-14 hours. Through the periodical sludge purges, Mixed Liquor Suspended Solids (MLSS) were set between 8-10 g/L, achieving a sludge retention time (SRT) that ranged from 12 and 21 days. Airflow was set at 10 Nm<sup>3</sup>/h and BW were performed every 10 min at 8 m<sup>3</sup>/h. Fouling rates were evaluated by calculating the slope between CIPs, which were applied approximately every 15-20 days.

In a second phase, with a duration of 8 months, PAC was added to the aerobic tank at different concentrations (25 and 50 mg PAC/L of wastewater), reaching a TSS concentration of 9-11 g/L. A fixed concentration of 1-1.5 g PAC/L of sludge was also maintained in the reactor through periodical purges.

The average fouling velocities, as variation of the TMP with time (dTMP/dt) is compared according to the temperature (summer and winter seasons) and the operation (with and without PAC dosage) regimes (Figure 3). As can be seen in Figure 3a, despite temperature decrease and the consequent change in the diffusion of water, the addition of PAC implied a 10% decrease in average membrane fouling.

After 6 months from the beginning of phase 2, in summer (warm season), a reduction of 45% in fouling velocity (expressed as dTMP/dt) was achieved in PAC-MBR regarding MBR without PAC. Figure 3b, on the other hand, shows the TMP profile of two random periods in summer conditions with and without PAC addition. Initial values of TMP ranged between 50 and 60 mbar in PAC-MBR while in conventional MBR (without PAC) ranged between 100-120 mbar. Additionally, in this case, after 14 days of operation, MBR without PAC reached a TMP peak of 500 mbar (maximum TMP recommended), while PAC-MBR maintained a stable profile. COD and TOC were measured in the sludge supernatant operating with and without PAC addition and minor differences were found. Ying and Ping, (2006) reported similar results and suggested that a possible explanation is that a large fraction of organic matter could be present as high molecular weight compounds that could not be adsorbed onto the PAC pores (meso and microporosity) or that they do not having a high affinity to react with the active surface of the sorbent. While a high surface area is advantageous for adsorption, the presence of bulky organic matter can pose a problem when using PAC composed of mainly micro-pores. As some of the surface area available for adsorption on or within PAC may not be accessible to the larger organic matter (Wu and Zhao 2011) CST was also measured and no differences were found, allowing to conclude that the reduction of TMP levels may be provoked by a strengthening of the sludge flocks by PAC.

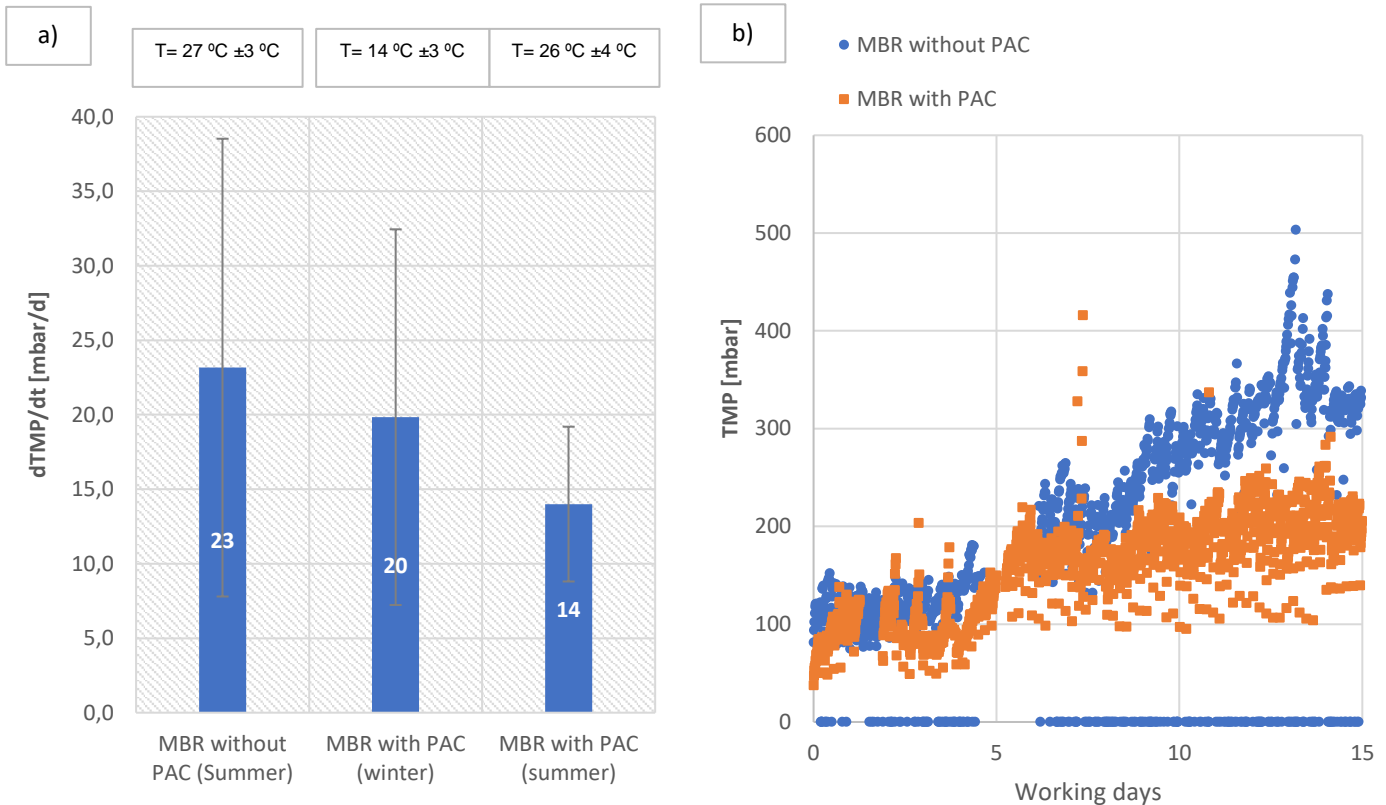


Figure 17 (a) Average UF fouling velocities expressed as  $dTMP/dt$  (mbar/d) for MBR along different phases covering cold and warm seasons (b) TMP evolution at 42-45 LMH with and without PAC addition.

Results obtained are consistent with those reported by (Remy et al., 2009), who operated two lab-scale MBRs at SRT's of 50 days and at 50 LMH, one with PAC addition and the other one with a constant dosage of 4 mg PAC/L of wastewater, leading to a constant PAC concentration in the reactor of 0.5 g PAC/L. Authors found that PAC addition contributed to an improvement of critical flux of 10% and an important improvement of filtration time (at least twice) without increase in fouling. The membrane inspection and measured COD, polysaccharides and proteins concentrations were three times lower in the sludge with PAC addition, which could explain the lower fouling (Remy et al., 2009).

Torretta et al. (2013) explained the different permeate flux loss observed by applying different low PAC dosages. An improvement of  $26 \pm 1\%$  and  $16 \pm 1\%$  was obtained for 5 and 2 mg PAC/L of wastewater, respectively. Moreover, by increasing the dose to 10 and 20 mg PAC/L, no further fouling reduction was obtained. This last fact is consistent with evidence found in this study operating at 25 or 50 mg PAC/L in terms of membrane fouling, where no differences were observed.

The relative cost of PAC dosing, which is accounted between 0.06 and 0.1 €/m<sup>3</sup>, depending on PAC dosage and considering a PAC cost of 2.5 €/kg, represents a significant increase in OPEX and should be compensated



with other savings to guarantee the economic feasibility and competitiveness of the system. Despite the improvement found, the high variability in fouling velocity hampered to change the membrane chemical cleanings procedure and did not represent a reduction in the cost of chemicals. Moreover, to increase in PAC-MBR filtration flux from 42-45 to 48-50 LMH with a constant air flow of 10 Nm<sup>3</sup>/h promoted a rapid increase of the TMP, which reached 500 mbar (maximum TMP established) in less than one day and resulting unfeasible to operate under these conditions. Thus, PAC did not allow to improve filtration flux and the consequent membrane area reduction needed to compensate the additional cost of the sorbent was not achieved.

Only by increasing the air flow from 10 to 15 Nm<sup>3</sup>/h, an improvement in terms of fouling is achieved; allowing to increase the flux from 42-45 to 55 LMH, also applying CIP's every 15 days. Additionally, the increase on the permeate production implied a reduction of the energy consumption of the UF system from 0.36 to 0.33 kWh/m<sup>3</sup>, where feed and recirculation (crossflow) pumping represent 57-61% of the total energy consumption, followed by the aeration applied for the airlift (27-30%). Finally, permeate extraction and backwash pumping represent the remaining consumption.

### 3.3.2 Evaluation of the physico-chemical water quality parameters

The wastewater influent and different effluents characterization, as well as the number of samples analysed, and calculated removal efficiencies are summarized in Table 39. Wastewater influent (primary settling effluent) presented average COD and BOD<sub>5</sub> concentrations of 415±85 mg O<sub>2</sub>/L and 195±38 mg O<sub>2</sub>/L, respectively. Measured SS and turbidity average were 154±23 mg/L and 186±42 NTU. On the other hand, in terms of nutrients, average TN and TP were 66±11 mg N/L and 9±2 mg P/L, respectively.

*Table 39 Basic water quality parameters for evaluated advanced treatment schemes. Average concentrations and removal efficiencies.*

OMP		Nº of samples	SS (mg/L)	Turbidity (NTU)	COD (mg O <sub>2</sub> /L)	BOD <sub>5</sub> (mg O <sub>2</sub> /L)	TN (mg N/L)	TP (mg P/L)
Influent concentrations [mg/L] (primary clarified effluent)		45	154 ± 23	186 ± 42	415 ± 85	195 ± 38	66 ± 11	9 ± 2
Effluent concentrations (removal efficiencies)	CAS + BWR	45	9 ± 5 (95%±2%)	3 ± 3 (98%±4%)	32 ± 18 (92%±3%)	3 ± 2 (97%± 1%)	10 ± 5 (85%± 4%)	1 ± 2
	MBR without PAC	45	<2 (>99%)	0.4 ± 0.2 (>99%)	33 ± 12 (91%±2%)	<2 (>99%)	11 ± 6 (83%± 6%)	1 ± 1

OMP		Nº of samples	SS (mg/L)	Turbidity (NTU)	COD (mg O <sub>2</sub> /L)	BOD <sub>5</sub> (mg O <sub>2</sub> /L)	TN (mg N/L)	TP (mg P/L)
	PAC-MBR (25 mg/L)	12	<2 (>99%)	0.3 ± 0.3 (>99%)	29 ± 16 (93%±5%)	<2 (>99%)	9 ± 2 (87%± 4%)	2 ± 1
	PAC-MBR (50 mg/L)	12	<2 (>99%)	0.5 ± 0.2 (>99%)	28 ± 19 (94%±4%)	<2 (>99%)	10 ± 1 (86%± 5%)	1 ± 2
	CAS + BWR + (O <sub>3</sub> -UV) <sub>1</sub>	10	5 ± 3 (96%±4%)	2 ± 3 (98%±2%)	29 ± 20 (93%±6%)	-	-	-
	CAS + BWR + (O <sub>3</sub> -UV) <sub>2</sub>	10	6 ± 4 (96%±3%)	3 ± 2 (98%±1%)	28 ± 10 (94%±1%)	-	-	-

The application of a secondary treatment enhanced with a basic reclamation system, allowed global removal efficiencies of 92%±3 and 97%±1% for COD and BOD<sub>5</sub>, respectively. (De)-Nitrification of the biological reactor reduced TN to 10±5 mg N/L. Phosphorus precipitation through FeCl<sub>3</sub> dosing allowed to achieve TP concentrations of 1±2 mg P/L. Turbidity and SS were 3±3 NTU and 9±5 mg/L, respectively, after the disk filtration.

ANOVA confirmed that no statistically significant improvements were obtained for COD, SS and turbidity removals by revamping the basic reclamation system with an ozonation-UV step based on ozonation (6-9 mg O<sub>3</sub>/L) and a fixed dosed of UV (400 J/m<sup>2</sup>).

On the other hand, the use of MBR achieved 9%±2 and >99% average removal efficiencies for COD and BOD<sub>5</sub>, respectively. Suspended solids were removed under the limit of detection (<2 mg SS/L) and turbidity was reduced below 0.5 NTU, which represents a known advantage when UF membranes are used (Judd, 2006). Average TN measured in the membrane permeate was 11-15 mg N/L. The addition of PAC (25-50 mg/L of influent) allowed an improvement on the TN removal of 10% approximately, which could be attributed to the formation and growth of a biofilm layer on the sorbent surface that creates anoxic zones enabling denitrification (Alvarino et al., 2016; Serrano et al., 2011).

On the other hand, in terms of organic matter, ANOVA allowed to confirm that no statistically significant differences were found between PAC-MBR and conventional MBR.

### 3.3.3 Evaluation of OMP removals

The removal efficiencies for OMP were defined in three groups and are collected in Table 40: (i) low removals (<20%), corresponding to the most recalcitrant OMP; (ii) medium removals (20-70%) and (iii) high removals (>70%).

As it can be seen in Table 40, in the conventional scheme based on CAS-BWR, removal efficiencies higher than 70% were obtained for 4 out of 9 of the detected compounds. These compounds correspond to reported easily removable OMP, which are easily bio-transformed (ACET, ATN) in the biological reactor or attached into the sludge particles due to its lipophilic character (NP, OCT). ACET for example, is a highly hydrophilic compound (low  $\log k_{ow}$  of  $0.46 < 2.5$ ); nevertheless, presents a  $k_{biol}$  of  $80 \text{ L}\cdot\text{g}^{-1} \text{ SS}\cdot\text{d}^{-1} > 10 \text{ L}\cdot\text{g}^{-1} \text{ SS}\cdot\text{d}^{-1}$ , which is an indicator of its high tendency to biotransformation (Suarez et al., 2010). Its removal can be also explained by the dominance of electron donating groups, concretely hydroxyl (-OH) and amide (-NH-CO-CH<sub>3</sub>) groups (Han Tran and Yew-Hoong Gin, 2017). In a similar way, ATN removal can be explained by the hydrolysis of the amide bond. On the other hand, the high removal of NP and OP can be explained by their high lipophilicity resulting in a great tendency to adsorb on sludge surface ( $\log k_{ow}$  of 5.8 and 5.5 respectively, which is identified with a high sorption potential). Moreover, based on Stasinakis et al., (2010), higher sorption potential is expected for NP when SRT is increased.

CBZ and DIU presented very low removal rates, which, can be related to their relatively low lipophilicity ( $\log K_{ow}$  of 2.5 and 2.7 respectively) and hard biodegradation ( $k_{biol} < 0.01$ ) (Serrano et al., 2011; Suarez et al., 2010). Additionally, the difficult biological transformation of CBZ is provoked by the heterocyclic N-containing aromatic rings (Alvariño Pererira, 2016). The presence of chlorine atoms in DIU makes difficult its biodegradation in aerobic conditions due to an electron deficiency (Phan et al., 2018). Similar behaviour has been observed for Diazepam, which has not been analysed in this study but contains also chlorine atoms and a high consequent persistence in conventional wastewater treatments (Jelic et al., 2012; Joss et al., 2006).

Table 40 Inlet concentrations [ng/L] and Removal efficiencies [%] obtained in 18 sampling campaigns for different target compounds (Carbamazepine (CBZ), Diuron (DIU), Erythromycin (ERY), Diclofenac (DCF), Sulfamethoxazole (SMX); Octylphenol (OP); Atenolol (ATN) Nonylphenol (NP) and Acetaminophen (ACET)) and the different treatment schemes evaluated. Low (<20%); Medium (20-70%), High (>70%). (O<sub>3</sub>-UV)<sub>1</sub> refers to 6 mg O<sub>3</sub>/L and 400 J/m<sup>2</sup> and (O<sub>3</sub>-UV)<sub>2</sub> refers to 9 mg O<sub>3</sub>/L and 400 J/m<sup>2</sup>

OMP		N° of samples	CBZ	DIU	ERY	DCF	SMX	OP	ATN	NP	ACET
Influent concentrations [ng/L] (primary clarified effluent)		18	177±38	140±48	152±95	614±258	313±112	190±102	1723±508	2158±1116	118118±40888
Treatment schemes removal [%]	CAS	12	4%±5%	6%±12%	22%±30%	22%±21%	60%±14%	84%±23%	82%±4%	92%±2%	>99%
	CAS + BWR	12	6%±7%	9%±15%	19%±28%	49%±35%	61%±15%	96%±1%	84%±7%	93%±3%	>99%
	MBR without PAC	7	2%±4%	13%±21%	73%±24%	72%±19%	60%±13%	89%±8%	95%±5%	95%±1%	>99%
	PAC-MBR (25 mg/L)	5	67%±16%	93%±5%	80%±9%	75%±14%	54%±28%	96%±1%	95%±2%	97%±2%	>99%
	PAC-MBR (50 mg/L)	6	76%±13%	89%±6%	N.d	77%±10%	82%±9%	89%±2%	97%±3%	93%±2%	>99%
	CAS + BWR + (O <sub>3</sub> -UV) <sub>1</sub>	5	97%±12%	80%±5%	72%±8%	>99%	96%±1%	-	-	-	-
	CAS + BWR + (O <sub>3</sub> -UV) <sub>2</sub>	5	96%±9%	89%±9%	94%±5%	>99%	98%±1%	-	-	-	-

The additional steps after the secondary settling do not show statistically significant improvement for removal of the recalcitrant compounds (based on ANOVA), which is consistent with the results obtained by Cabeza et al. (2012) in the El Baix Llobregat WRP.

MBR treatment, despite being considered state-of-the-art water reclamation technology, presents several advantages in terms of OMP removal over CAS and other BWR systems without salinity reduction. Significant improvements in the removal of ERY, DCF, SMX and COD were obtained through MBR technology. UF membrane pore exclusion cannot explain the higher removals in ERY and DCF, since the molecular weight cut off (MWCO) of those compounds (0.232 and 0.734 kDa) are lower than the range in UF membranes (1-10kDa). Gu et al. (2018) and Reif et al. (2011) proved that high SRT imply a higher biodegradability of some compounds, related to a higher microbial activity powered by a higher biomass growth. Additionally, Alvarino et al. (2017) correlated in their study an increase of ERY biodegradation with higher nitrification. CBZ, on the other hand, did not show an improvement in terms of removal despite higher SRT applied in MBR, which is in agreement with results found for this compound in literature (Besha et al., 2017; Tiwari et al., 2017).

The addition of PAC in the MBR system improved significantly the removal of recalcitrant compounds. Removals of  $67\% \pm 16\%$  and  $92\% \pm 5\%$  were obtained for CBZ and DIU, respectively, by applying low PAC doses (25 mg/L). This can be explained through log D values (1.9 and 2.7, respectively) of both compounds, which define their adsorption potential on the active surface ( $\log D > 1$ ). Moreover, by increasing PAC dose to 50 mg/L, it was measured a statistical significant improvement (ANOVA) for CBZ, which increased its removal efficiency from  $67\% \pm 16\%$  to  $76\% \pm 13\%$ . Nguyen et al. (2014) and Serrano et al. (2011) demonstrated that the use of PAC in biological systems leads to a slower and more efficient biodegradation due to the retention of soluble compounds on the activated layer. In this study, those compounds which were identified as sensible to biological reactor operational conditions (ERY and DCF) did not improve their removal efficiency with 25 mg PAC/L dosage. However, increasing PAC dosage to 50 mg/L reported a positive effect on SMX removal despite its logD is 0.5 ( $< 1$ ), probably due to a fostering of the liquid-solid equilibrium. In general, results obtained for (PAC-) MBR are consistent with those reported in literature and summarized in Table 41.

In AOP tests performed in this study, only moderate and highly recalcitrant compounds (CBZ, DIU, ERY, DCF and SMX) in conventional systems were analysed in this paper. Ozone doses of 6 and 9 mg  $O_3$ /L were applied maintaining a constant UV dose of 400 J/m<sup>2</sup>. In AOP processes, OMP may be degraded by a direct reaction with ozone, which is a selective agent, or by reacting with generated hydroxyl radicals, which are highly reactive and present an unselective oxidation power (Hansen et al., 2016). UV itself is not considered an efficient treatment for OMP removal; nevertheless, its combination with ozone aids to generate hydroxyl radicals. Therefore, the combination of both reaction kinetics, defined as a second order reaction between OMP, ozone and hydroxyl

radicals, can contribute to understand and predict their behavior and have a first approach on design these systems (Gomes et al., 2017).

CBZ, DIU, DCF and SMX exhibited statistical significant improvement regarding conventional treatments, and according to Gomes et al. (2017), these compounds are highly degraded by ozonation with higher kinetic constants ( $k_{O_3}$ ) than  $10^4 \text{ M}^{-1}\cdot\text{s}^{-1}$ . ERY showed lower removal rate at 6 mg/L than at 9 mg/L, which could be explained by its lower average concentration (62 Ng/L) regarding the rest of analysed OMP (100-300 ng/L). Results obtained are consistent with those reported by authors referenced at Table 41 for a similar  $O_3$  dosage of 2-6 mg/L.

Hansen et al. (2016) discussed that ozone dose necessary to achieve a 90% of removal is compound specific regarding DOC concentration. For concentrations between 7 and 16 mg C/L, which is in the range of the BWR effluent, 0.57, 0.51 and 0.52 mg  $O_3$ /mg DOC are required to be added for high removal of CBZ, DFC and SMX, respectively, consistent with doses applied and results obtained in this study (Table 40)

Table 41 Comparison between measured removal efficiencies and reported by literature for the different evaluated advanced treatment schemes

PHAR	MBR		PAC-MBR (10-60 mg/L)		CAS+BWR + Ozonation (2-6 mg/L)	
	Measured	Reference	Measured (25-50 mg/L)	Reference	Measured (6-9 mg/L)	Reference
CBZ	10%±1 %	28% (Tiwari et al., 2017) <10% (Alvarino et al., 2017) 13% (Tadkaew, Hai, McDonald, Khan, and Nghiem, 2011)	67%±2% - 76%±3%	>90% (Alvarino et al., 2017) 60-90 % (Nguyen et al., 2014)	97%±2% - 96%±2 %	97%±4 % (Margot et al., 2013) 100% (Yang et al., 2017)
DCF	79%±3 %	15-87 % (Besha et al., 2017) >60% (Alvarino et al., 2017) 17±4 % (Tadkaew et al., 2011)	67%±3% - 77%±5%	>98% (Besha et al., 2017) >95% (Alvarino et al., 2017) 95-60% (Nguyen et al., 2014)	>99%	100% (Moreira et al., 2015) 100% (Rivera-utrilla et al., 2013) >96% (Ternes et al., 2003) 94±3 (Margot et al., 2013)
ERY	80%±4 %	>80% (Dolar, Gros, Rodriguez-mozaz, Moreno, and Comas, 2012) >80% (Alvarino et al., 2017) 91% (Reif, Suárez, Omil, and Lema, 2008)	59%±2 %	>88% (Besha et al., 2017) >99% (Alvarino et al., 2017)	72%±1% - 94%±4 %	>92 % (Ternes et al., 2003) >95% (Yang et al., 2017)
SMX	64%±3 %	81% (Tiwari et al., 2017) >70% ((Alvarino et al., 2017) 92% (Tadkaew et al., 2011)	53%±4% - 88%±2 %	70% (Alvarino et al., 2017)	96%±1% - 98%±1 %	93%±7 % (Margot et al., 2013) 99% (Rivera-utrilla et al., 2013) >92% (Ternes et al., 2003) 100% (Yang et al., 2017)

### 3.3.4 Technical and economic assessment

A technical and economic evaluation was performed for the studied treatment trains (Table 42). Optimal conditions were applied for the base design necessary to estimate capital and operational costs for a total capacity of 330000 m<sup>3</sup>/d.

For MBR, a projection for a flux of 55 LMH with a crossflow operation mode of 15 m<sup>3</sup>/h and air flow/module of 15 Nm<sup>3</sup>/h was considered, which corresponds to 11232 modules (370656 m<sup>2</sup>) grouped in 52 skids. Energy consumption and reagents consumption were obtained from the prototype performance and through the unitary costs provided by the full-scale plant managers and completed with manufacturer's data, total reagent and energy costs could be calculated (Table 43). OPEX was calculated for two levels of PAC dosages (25 and 50 mg/L of wastewater).

In the case of Ozonation-UV upgrading unit, ozone generator, contact chambers and UV lamps were also projected, connected to the disk filtration outlet. Two levels of ozone doses of 6 and 9 mg/L were also considered with a contact time of 15 min.

*Table 42 Technical and economic assessment for conventional and advanced water reclamation systems evaluated in this research.*

Treatment scheme	Conventional Water Reclamation Systems		Advanced Water Reclamation Systems			
	CAS - BWR	MBR	CAS - BWR – Ozonation-UV		PAC-MBR	
PAC / O <sub>3</sub> - UV doses	-	-	6 mg/L + 400 J/m <sup>2</sup>	9 mg/L + 400 J/m <sup>2</sup>	25 mg PAC/L	50 mg PAC/L
Energy consumption Sludge treatment line) [€/m <sup>3</sup> ] (kWh/m <sup>3</sup> )	0.011 (0.102)	0.008 (0.072)	0.011 (0.102)	0.011 (0.102)	0.008 (0.072)	0.008 (0.072)
Energy consumption (Water treatment line) [€/m <sup>3</sup> ] (kWh/m <sup>3</sup> )	0.051 (0.530)	0.065 (0.584)	0.065 (0.640)	0.068 (0.680)	0.065 (0.584)	0.065 (0.584)
Chemical Reagents consumption [€/m <sup>3</sup> ]	0.053	0.035	0.060	0.063	0.098	0.160
Waste to landfill [€/m <sup>3</sup> ]	0.021	0.017	0.021	0.021	0.017	0.017
Membrane replacement [€/m <sup>3</sup> ]	-	0.036	-		0.036	0.036
UV lamps replacement [€/m <sup>3</sup> ]	0.002	-	0.002		-	
OPEX [€/m <sup>3</sup> ] without depreciation	0.138	0.161	0.158	0.165	0.223	0.286
CAPEX [€/m <sup>3</sup> /d]	579	623	655	677	624	
Relative footprint regarding CAS - BR [%]	-	-50%	15%		-45%	

From point of view of energy consumption, MBR presents 10% higher consumption than CAS-BWR (0.58 kWh/m<sup>3</sup> regarding 0.53 kWh/m<sup>3</sup>) in water treatment line due to a greater aeration in the biological reactor and



the additional energy demand in UF membranes through air scouring, crossflow and permeate extraction pumping. Moreover, in sludge treatment line, since MBR sludge production is around 30% lower than in CAS (higher SRT), a decrease from 0.102 to 0.072 kWh/m<sup>3</sup> is achieved.

Regarding chemicals consumption, the CAS-BWR accounts with a 14% higher consumption due to the use of coagulants and flocculants (PAX, anionic polymer (Hydrex 6161) and Microsand) in the physicochemical system and a higher flow in sludge treatment line (e.g., cationic electrolyte, FeCl<sub>3</sub> and liquid nitrogen) compared with MBR, which reagents consumption is generated by the use of oxidants agents (e.g., NaClO) and acids (e.g., Citric Acid) for the periodical membrane cleanings (CIP). Nevertheless, an annual replacement of 13% of the UF modules was considered for MBR.

From an economic point of view, the energy cost associated for CAS-BWR and MBR is 0.052 and 0.073 €/m<sup>3</sup> respectively, assuming an electricity cost of 0.111€/kWh. Additionally, in terms of chemicals, CAS-BWR account to 0.053 €/m<sup>3</sup> for the, while MBR accounts to 0.035 €/m<sup>3</sup>, taking into account the consumptions and unitary costs listed in Table 5. A reduction from 0.021 to 0.017 €/m<sup>3</sup> for sludge disposal (e.g., waste to cement plant) was also considered in MBR due to lower sludge production. On the other hand, UF modules replacement represents and associated cost of 0.036 €/m<sup>3</sup> while the replacement cost of UV lamps in CAS-BWR is 0.002 €/m<sup>3</sup>. Thus, MBR presents a higher OPEX (0.161 €/m<sup>3</sup>) regarding CAS-BWR (0.138 €/m<sup>3</sup>).

By upgrading the conventional system with ozonation, an increase in OPEX of 15% is achieved (0.158 €/m<sup>3</sup>) for O<sub>3</sub> dose of 6 mg/L and 20% (0.165 €/m<sup>3</sup>) for a dose of 9 mg/L. Applying O<sub>3</sub> doses of 9 mg/L accounts with an increase of 5% of the energy demand in water line, related to the ozone generation. CAPEX was accounted to be 655 €/m<sup>3</sup>/d for 6 mg O<sub>3</sub>/L, while an increase in O<sub>3</sub> dose to 9 mg/L resulted in 677 €/d.m<sup>3</sup> due to the need of larger contact chambers and an ozone generator with more capacity. Additionally, in terms of space, advanced reclamation process based on AOP is estimated to require an additional 15% of space regarding CAS-BWR.

Finally, to upgrade MBR performance by dosing PAC (25 and 50 mg/L of wastewater) accounts with 0.223 and 0.286 €/m<sup>3</sup> of OPEX, which represents an increase of 38 and 47% regarding conventional MBR, respectively. PAC-MBR does not account with a reduction in the energy demand since no flux improvement was achieved with PAC addition (only by enhancing air scouring). The increase in OPEX is related to the chemicals consumption, where PAC is considered a reagent with an estimated cost of 2.5 €/m<sup>3</sup>; considering the benefits in terms of OMP removals for both PAC doses and the associated cost, 25 mg PAC /L of wastewater was considered as the optimal dose. In terms of CAPEX, PAC-MBR accounts with 624 €/m<sup>3</sup>/d. On the other hand,

regarding required space, only an additional 5% regarding conventional MBR is required for PAC slurry preparation and dosing units.

In comparison to the use of AOP, 25 mg/L of PAC-MBR accounts with an operational cost 35% higher, nevertheless, it presents benefits in terms of CAPEX, which was 8% lower, and in terms of space requirements (60% lower).

Table 43 Advanced Wastewater and Reclamation systems reagent costs

Water Line	Treatment step	Reagent	Unitary Cost	Reference cost provided by	CAS + BWR + AOP		PAC-MBR		
					Consumption*	Cost	Consumption**	Cost	
Sludge Line	Thickeners (primary sludge)	Cationic polyelectrolyte (Flocculant)	0.249 €/kg	El Baix Llobregat WWRP	1.35 g/m <sup>3</sup>	0.00034 €/m <sup>3</sup>	1.164 g/m <sup>3</sup>	0.00029 €/m <sup>3</sup>	
	Anaerobic digestion	FeCl <sub>3</sub> (Sulphur's removal and deodorization)	0.238 €/kg	Apliclor	14.97 g/m <sup>3</sup>	0.00356 €/m <sup>3</sup>	12.87 g/m <sup>3</sup>	0.00306 €/m <sup>3</sup>	
		Liquid Nitrogen (Inertization)	0.150 €/kg	El Baix Llobregat WWRP	0.37 g/m <sup>3</sup>	0.00006 €/m <sup>3</sup>	0.318 g/m <sup>3</sup>	0.00005 €/m <sup>3</sup>	
Water Line	Biological reactors	FeCl <sub>3</sub> (Phosphorus removal)	0.238 €/kg	Apliclor	80.00 g/m <sup>3</sup>	0.01904 €/m <sup>3</sup>	80 g/m <sup>3</sup>	0.01904 €/m <sup>3</sup>	
		PAC (Micropollutants removal)		2.500 €/kg	Norit CABOT			25 g/m <sup>3</sup>	0.06250 €/m <sup>3</sup>
								50 g/m <sup>3</sup>	0.12500 €/m <sup>3</sup>
	Physico-chemical Treatment	PAX (Coagulant)	0.265 €/kg	El Baix Llobregat WWRP	79.20 g/m <sup>3</sup>	0.02099 €/m <sup>3</sup>	-	-	
		Anionic polymer (Coagulant)	1.989 €/kg	Hydrex 6161	3.45 g/m <sup>3</sup>	0.00686 €/m <sup>3</sup>	-	-	
		Microsand (Flocculant)	0.238 €/kg	El Baix Llobregat WWRP	5.25 g/m <sup>3</sup>	0.00125 €/m <sup>3</sup>	-	-	
	Disk filters / UF membranes	NaClO (Membrane cleaning)	0.130 €/kg	Apliclor	4.53 g/m <sup>3</sup>	0.00009 €/m <sup>3</sup>	1.7 ml/m <sup>3</sup>	0.00003 €/m <sup>3</sup>	
		Citric Acid (Membrane cleaning)	0.968 €/kg	Apliclor			10.3 ml/m <sup>3</sup>	0.01198 €/m <sup>3</sup>	
	Ozonation (6 mg O <sub>3</sub> /L)	Liquid Oxygen (ozone generation)	0.100 €/kg	El Baix Llobregat WWRP	66 g/m <sup>3</sup>	0.00660 €/m <sup>3</sup>	-	-	
		Liquid Nitrogen (ozone generation)	0.150 €/kg	El Baix Llobregat WWRP	2 g/m <sup>3</sup>	0.00030 €/m <sup>3</sup>	-	-	
	Ozonation (9 mg O <sub>3</sub> /L)	Liquid Oxygen (ozone generation)	0.100 €/kg	El Baix Llobregat WWRP	99 g/m <sup>3</sup>	0.00990 €/m <sup>3</sup>	-	-	
		Liquid Nitrogen (ozone generation)	0.150 €/kg	El Baix Llobregat WWRP	2 g/m <sup>3</sup>	0.00030 €/m <sup>3</sup>	-	-	

### **3.4 Conclusions**

Results obtained in this study demonstrated the limited removal capacity obtained for some OMP with conventional wastewater treatment and reclamation systems (CAS-BWR and MBR), and how, by upgrading these systems with an additional ozonation-UV step or by adding a sorbent (PAC), it is possible to achieve, for these recalcitrant OMP, removal efficiencies over  $85\pm 2$  and  $75\pm 5\%$ , respectively.

The addition of PAC in MBR achieved promising results in terms of OMP removal and membrane fouling improvement; nevertheless, PAC operational benefits were not enough to allow higher filtration fluxes and consequently to reduce installed membrane area required (and replacement), as well as energy and chemicals consumption, which would have compensated the additional PAC cost. Thus, based on these results, PAC should not be added unless OMP removal is required. On the other hand, MBR and PAC-MBR account with some benefits in terms of space reduction and water quality regarding other schemes evaluated in this study. To replace settlers by membranes accounts with a 50-45% of space reduction, and the water obtained through UF filtration is better than after CAS-BWR in terms of solids, turbidity and microbiological parameters. Additionally, no intensive disinfection (UV-Cl<sub>2</sub> / O<sub>3</sub>-UV) is needed.

In terms of the economic analysis OPEX results indicated that PAC-MBR is the most expensive option regarding conventional systems or the inclusion of ozonation-UV post-treatment. Ozonation-UV as a final polishing step presented several advantages regarding PAC-MBR in terms of OPEX, although it has a higher CAPEX. Unlike the use of PAC, ozonation presents beforehand the advantage of mineralizing OMP rather than separating or concentrating them. Additionally, compared to PAC-MBR, removal efficiencies were better for both ozone doses tested.

Summing-up, ozonation-UV seems to be the best option for upgrading existing projects, where only an additional 15% of space is required and the post-treatment is assembled directly to the conventional system. On the contrary, PAC-MBR should be considered when space represents a critical limitation, produced water is reused on high quality water uses (such as industrial uses), and can present advantages in terms of adequate pre-treatment for a potential RO post-step. It can be useful in decentralized systems such as in target industries (e.g. pharma, chemical, petrochemical, food and beverage) and hospitals. However, it has to be taken into account that CAPEX accounted for PAC-MBR not included the cost of remodelling an existing facility, only the cost of constructing it from zero.

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# Chapter 4



## 4. Chapter 4: Hybrid sorption and pressure-driven membrane technologies for OMP removal in advanced water reclamation: A techno-economic assessment.

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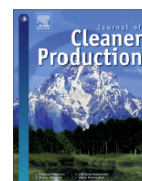
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### Hybrid sorption and pressure-driven membrane technologies for organic micropollutants removal in advanced water reclamation: A techno-economic assessment



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Figure 18 Screenshot of the article published in Journal of Cleaner Production

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#### Abstract:

The persistence of certain organic-micropollutants (OMP) in conventional wastewater and reclamation treatments represents a growing concern due to its associated uncertain effects on human health and the environment. This issue highlights the need to resort to advanced treatment technologies to ensure the maximum removal of these compounds. A prototype (1.5–2 m<sup>3</sup>/h) based on the combination of powdered activated carbon (PAC) with tight ultrafiltration (UF) membranes was operated in El Baix Llobregat Water Reclamation Plant (WRP) for 18 months. Its performance was compared from a technical and economic point of view with the current full-scale ultrafiltration and reverse osmosis system (UF-RO with 50% blend). The application of a PAC concentration of 20 mg/L and its separation with UF membrane resulted in an average removal up to 81±13% of the most recalcitrant OMP detected (Carbamazepine (CBZ), Diuron (DIU), Diclofenac (DCF), Erythromycin (ERY) and Sulphametoxazole (SMX)), while in UF-RO (50% blend), the average removal

was  $55 \pm 11\%$ . PAC-tight UF presented promising advantages for when these post-treatments need to be implemented in inland WRP and where brine management can represent a drawback. Moreover, PAC-tight UF presents 22% higher Operational Expenditures (OPEX) than UF-RO (50% blend), although in terms of Capital Expenditure (CAPEX), it appears as the less expensive option.

## 4.1 Introduction

The persistence of organic-micropollutants (OMP) in urban reclaimed water and their uncertain effects on human health have risen important concern in authorities, especially when Indirect Potable Reuse (IPR) schemes are proposed in water scarcity regions. IPR schemes consist of the addition of reclaimed water into a natural water body (surface water or groundwater) in order to store it and then reuse it for drinking water supply (Furlong et al., 2019).

The high variability found (Gros et al. 2017) in removal efficiencies for OMP in conventional activated sludge (CAS) systems indicates the need to resort to advanced technologies in wastewater reclamation plants (WWRP) to guarantee the removal of the most recalcitrant compounds (Avila and Garcia 2015).

Recently, the application of direct pressure-driven membrane filtration for centralized municipal wastewater reclamation has been paid more attention. Pressure driven membrane operations can be divided into four overlapping categories of increasing selectivity: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). In RO, it is generally accepted that the solution-diffusion mechanism is responsible for solute and solvent flux through the membrane. The size exclusion mechanism is the one contemplated to explain solute transport through UF membranes, and in the case of NF membranes, both solution-diffusion and size exclusion are considered to be involved together with other mechanisms such as electrostatic interactions. However, membrane composition combined with solvent and solute characteristics can influence rejection via electrostatic double layer interactions or other hindrances. In fact, when a solution containing ions is brought in contact with membranes possessing a fixed surface charge, the passage of ions possessing the same charge as the membrane (co-ion) can be inhibited. This condition is termed Donnan Exclusion (Macedonio and Drioli, 2008).

The factors influencing the permeate quality and membrane performance during direct pressure-driven membrane filtration are the membrane type and material, pore size, pre-treatment of feed water and fouling control methods (Hube et al., 2020). Fouling is a major challenge due to the relatively higher amounts of organic matter and particulates when treating wastewater. It can lead to an increase of operation cost due to higher feed pressures and a decrease of membrane lifetime due to more frequent physical/chemical cleanings. Therefore,

proper membrane fouling control strategies are necessary to improve direct pressure-driven membrane filtration performance (Anis et al., 2019).

Asymmetric membranes such as nanofiltration (NF) or reverse osmosis (RO) represent a highly efficient technology in terms of removal of organic and inorganic compounds. As stated by Bellona et al. (2004), the rejection of solutes in membranes is driven by the combination of feed water and membrane properties, as well as operational conditions applied. Solute-solute, solute-liquid and membrane-solute are the main mechanisms governing solute rejections and interactions, which usually determine the mechanisms limiting the removal processes. (Teodosiu et al., 2011).

Van der Bruggen et al. (1999) calculated retention ratios for different asymmetric membranes (NF/RO) of different organic compounds as function of molecular weight (MW). Results obtained showed very high removal efficiencies (>90%) for those compounds with MW higher than 0.2kDa (which corresponds approximately to the molecular weight cut off (MWCO) of RO and NF tested membranes). Furthermore, as also stated by Kimura et al. (2003), in NF/RO, MWCO results more useful than 'salt passage' to evaluate OMP removal capacities.

In water reclamation, NF/RO typically requires substantial pre-treatment to reduce the fouling and clogging potential of secondary effluent (Kazner, 2011). MF or UF are commonly recommended pre-treatments for RO since they provide total removal of suspended solids (SS) that could clog the spiral wound configuration of NF/RO as well as significantly reduce turbidity and the microbiological load (Judd, 2006). Additionally, it is usual (when quality requirements allow it) to blend the UF permeate with the RO permeate in order to reduce operational costs (Gu et al., 2019).

Moreover, the concentrated rejection or brine stream generated in RO systems, represents one of the main drawbacks for its implementation, together with the associated high treatment cost. Typically, resulting intensive in energy and chemicals consumption. Rejection streams with high salinity and high OMP concentration usually cannot be recirculated to Wastewater Reclamation Plant (WWRP) headworks due to an inhibition of the biological activity. Thus, in inland areas, where discharge to the sea is not a possibility, the brine management represents a significant technical, economic and environmental issue.

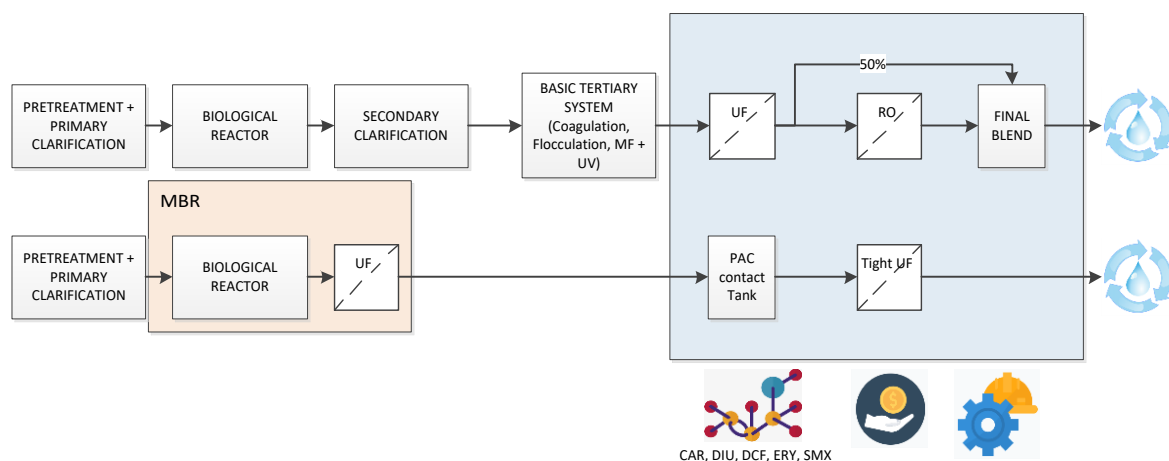
Hybrid treatment processes such as the combination of Powdered Activated Carbon (PAC) and UF could have several advantages over the use of simple membrane systems. The synergies achieved through the combination of an sorbent and a membrane barrier might be comparable to UF-RO systems in terms of OMP removal (Liu et al., 2019). Meier and Melin (2005) reported several advantages of PAC-UF combination, such as: (i) the pre-cleaning effect of activated carbon through the adsorption of organic foulants when applied before the



membrane; (ii) PAC acting as a filter layer and apparently having a scouring effect that protects the membrane and (iii) the adjustment of water quality through the regulation of PAC doses. Additionally, high OMP removal efficiencies might be achieved (Sheng et al., 2016). In PAC-UF systems, the rejected and partially saturated PAC might be recirculated to WRP headworks in order to act as biological support for microorganisms as well as a potential sorbent for OMP (Alvarino et al., 2017).

Echevarría et al. (2019) indicated the need to deeply assess the technical and economic feasibility for advanced wastewater reclamation technologies focused on OMP removal. Most hybrid membrane processes for OMP removal research are tested at lab or bench scale (Alvarino et al., 2016). Thus, industrial pilot scale studies are required in order to evaluate stable and critical fluxes, as well as permeability's variation (Rezaej et al., 2019). This information is highly useful in order to understand better the proper implementation of large-scale systems as well as to assess, in terms of energy, chemical consumption and its correspondent operational cost.

The aim of this study is to compare, from a technical and economic point of view, the UF-RO system installed in the El Baix Llobregat WRP (currently used for deep well injection to protect against seawater intrusion) with a prototype based on the use of capillary tight UF combined with the addition of PAC. Five target OMP commonly persistent in conventional systems (four pharmaceuticals and one pesticide) were monitored at the outlet of basic tertiary systems, and their concentrations were evaluated along mentioned schemes. An economic assessment was performed in order to scale-up the prototype results and compare both schemes as shown in Figure 19.



*Figure 19 Evaluated advanced reclamation scheme for OMP removal. On the top: the current advanced treatment of the El Baix Llobregat, currently focused on deep well injection of UF-RO blended water. Below: the PAC-tight UF prototype tested in the EL Baix Llobregat WRPDiscussion*

## 4.2 Materials and Methods

The materials and methods used in this research are described below, including (i) the description of the pilot plant operated and the full-scale facilities of the case study, (ii) the analytical methods employed for analysis of specific organic micropollutants and physico-chemical parameters and (ii) the assumptions made for the economic and footprint analysis.

### 4.2.1 Advanced Water Reclamation Pilot Plant description

The advanced water reclamation pilot was composed of two main units. The PAC-UF pilot plant (Figure 20) comprised two HFW 1000 modules (X-Flow, The Netherlands), which could be considered as a tight poly-ether sulfone (PES) UF membrane commercialized as a NF membrane. Tight UF were defined by Cassano et al. (2018) as those membranes with a MWCO that range between 1 to 3 kDa, while conventional UF ranges between 4 and 150 kDa. Their development has been devoted to potentially achieving the removal of organic compounds with MW above 1 kDa. The operated tight UF modules present a MWCO of 1 kDa and 0.8 mm internal diameter fibres, which operate at constant flux, with inside-out filtration. Each UF module presents a total membrane area of 40 m<sup>2</sup> operated in parallel (2 m<sup>3</sup>/h) in order to treat the effluent produced by an MBR pilot. Details on the performance of the MBR with and without PAC addition could be found elsewhere (Echevarría et al., 2019). Feed pump pressure regulates permeate flow, while cross flow velocities (0 -1 m/s) are controlled through an internal recirculation pump and the permeate recovery ratio is fixed by regulating the rejection stream with a control valve. The plant might be operated with or without crossflow, maintaining the permeate recovery ratio.

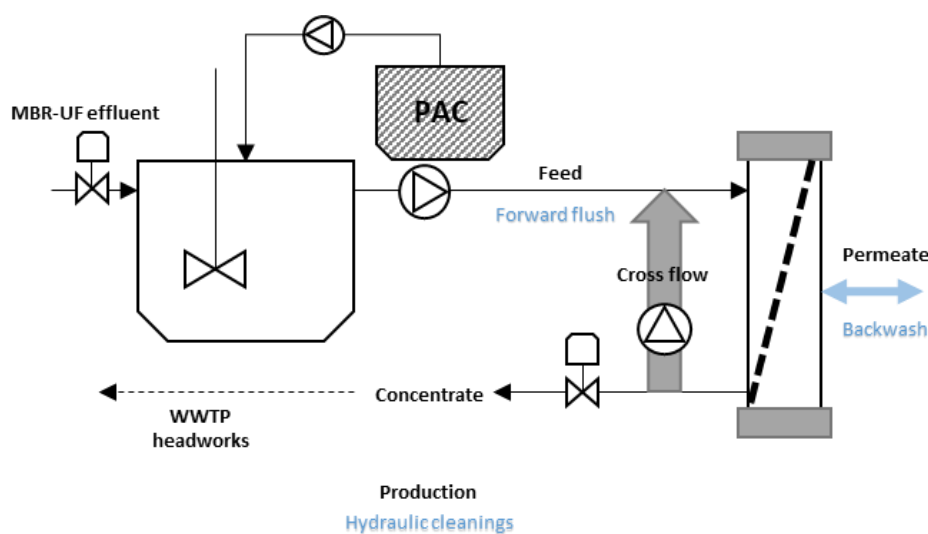


Figure 20 Description of the PAC-UF pilot. Arrows indicate the flow direction of the different hydraulic circuits.

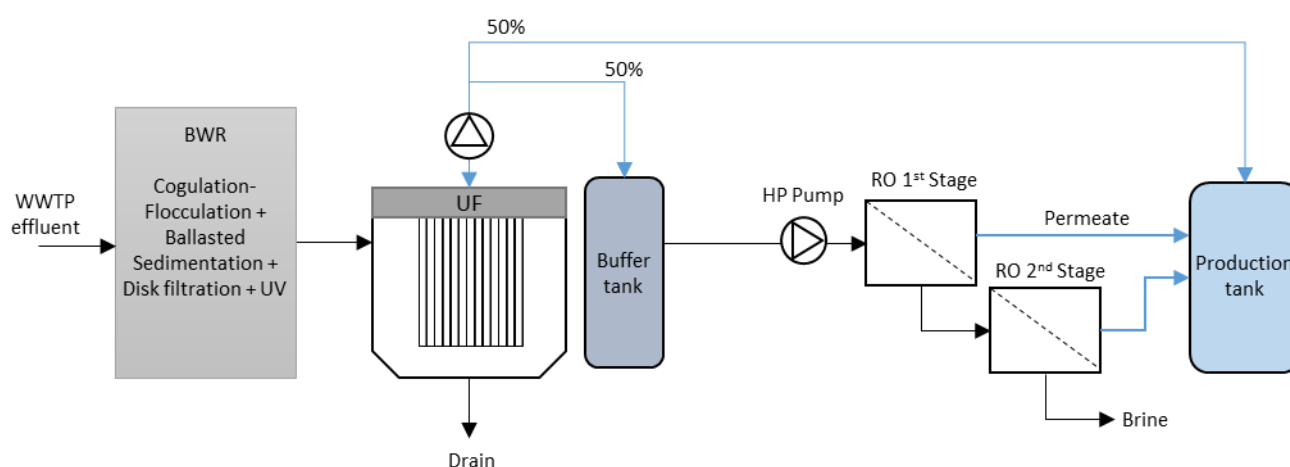
The capillary UF membrane modules do not reject sulphates, phosphates or other dissolved inorganic ions; nevertheless, as previously mentioned, they provide higher rejection of organic macromolecules with MW >1kDa. Additionally, they present the flexibility and advantages of conventional UF in terms of physical and chemical cleaning for fouling control strategies, and influent pre-treatment requirements are lower in comparison with conventional spiral wound RO and NF membranes. For backwashing (BW), produced permeate is pumped into the UF membrane module in reverse direction to filtration direction, and at the same time, forward flush (FF) is employed during the hydraulic cleaning (HC) sequence by pumping MBR-UF effluent from the feed water tanks.

A powder activated carbon (PAC) slurry was prepared in a secondary tank and pumped to the feed tank. PAC from Norit CABOT (The Netherlands) was used for this purpose. Physical and chemical properties of selected PAC are summarized in Table 44. PAC doses were monitored periodically by measuring the suspended solid (SS) as surrogate parameter in the tight UF feed tank, while contact time was set by controlling the tank level through a feed valve. Hydraulic membrane cleaning protocols consisted of a combination of BW and FF sequences (30 and 60 seconds of duration, respectively). On the other hand, alkaline chemical cleanings in the Chemical Enhanced Forward Flush (CEFF) mode were conducted manually by dosing 0.25 g/L of NaOCl (15% w/w), keeping a soaking time of 1 h (with an internal recirculation of 4 m<sup>3</sup>/h). When specific acid cleanings were required, citric acid (50% w/w) at 0.4 g/L was applied, following the same operational conditions as alkaline CEFF.

*Table 44 Physical and chemical properties of selected PAC*

Properties	Norit CABOT SAE SUPER
Particle diameter (µm)	15
Specific surface area – BET (m <sup>2</sup> /g)	1093
Micropore area (m <sup>2</sup> /g)	828
Primary micropore (<0.8 nm) area (m <sup>2</sup> /g)	666
Secondary micropore (0.8-2 nm) area (m <sup>2</sup> /g)	162
Meso and macropore area (m <sup>2</sup> /g)	265
Total pore volume (cm <sup>3</sup> /g)	0.791
Micropore volume (cm <sup>3</sup> /g)	0.397
Primary micropore volume (cm <sup>3</sup> /g)	0.267
Secondary micropore volume (cm <sup>3</sup> /g)	0.130
Mesopore volume (cm <sup>3</sup> /g)	0.394
PAC surface charge (pHpzc) (Moreno-Castilla's et al. (2000))	9.9

Furthermore, an on-site full-scale UF/RO (50% blend of the permeate and feed RO circuit) system was evaluated in terms of consumption (energy and chemicals) and water quality (physico-chemical parameters and OMP). The UF/RO treatment train is used as advanced water reclamation scheme (15,000 m<sup>3</sup>/d) to produce high quality reclaimed water for aquifer direct injection in the El Baix Llobregat WRP to protect against seawater intrusion. The system directly treats the basic water reclamation (BWR) effluent (100% of the UF/RO system capacity) by submerged UF (Polyvinylidene fluoride (PVDF), ZW500, pore size of 0.04 μm). A subsequent treatment of the 50% of UF effluent is treated by a two stage RO (BW30LE-440, Dow Filmtec, 0.2 kDa) with 75% of water recovery as it is depicted in Figure 21.



*Figure 21* Advanced reclamation system (UF/RO) of the El Baix Llobregat WRP (treated water is used for direct aquifer injection to protect against the seawater intrusion)

#### 4.2.2 Analytical Methodology

A water quality monitoring program to characterize the treated water included different sampling points for off-line analysis. Samples from the MBR effluent (inlet to PAC-UF system), BWR effluent (inlet to UF-RO system), PAC-tight UF permeate, tight UF without PAC effluent, conventional UF permeate, and RO permeate were collected twice per week for off-line analysis.

Standard methods (2540 and 5210 B) were used to analyse the suspended solids (SS) content and biological oxygen demand (BOD<sub>5</sub>), respectively. Turbidity was measured by means of a Hach Lange 2100 Turbidimeter (Hach, USA). The total chemical Oxygen Demand (COD) and total nitrogen were measured with test kits (Hach-Lange LCI test kits and Merck Spectroquant test kits, respectively). The Dissolved Organic Content (DOC) was measured through Shimadzu VSH-TOC analyzer. The redox potential, pH and temperature were monitored online.

Finally, five target OMP compounds were selected and analyzed in order to understand their behavior in the wastewater treatment and reclamation systems evaluated. In the monitoring program, 18 sampling campaigns were completed over nine months, including both warm (up to 32°C) and cold (up to -3°C) seasons. There were 18 samples analyzed from the MBR and the tight UF without PAC, six samples from the PAC-UF (20 mg/L), nine samples from the PAC-UF (50 mg/L) and three samples from the PAC-UF (100 mg/L).

From these five target model compounds (Table 45), four of them were classified as pharmaceuticals: (Carbamazepine (CBZ), Diclofenac (DCF), Erythromycin (ERY) and Sulphametoxazole (SMX)), and one was classified as a pesticide (Diuron (DIU)). The selection of these target compounds was based on their recalcitrant performance described elsewhere (Echevarría et al., 2019). These OMP were analyzed in the inlet and out-let effluents from both treatment trains, considering the complexity of the water matrixes in terms of dissolved, colloidal and suspended solids content. Solid phase extraction (SPE) coupled on-line with high pressure liquid chromatography and tandem mass spectrometry (LC-MS/MS) with electrospray ionization (ESI) were used for the determination of the different analytes. The optimization of two different methodologies for negative (Method 1) and positively (Method 2) ionizable compounds was applied. Details on the analytical procedures are included as supplementary material. The methods followed for the analysis of these organic compounds were depicted in Chapter 2 (Table 31 and Table 32).

*Table 45 Physico-chemical properties of target OMP*

Target OMP	CAS	Type of compound	MWCO	pKa	Log Kow	Log D (pH=7)*	Charge (pH=7)**
DCF	15307-86-5	Pain killer (PHAR)	296	4.1	4.5	1.8	-
SMX	723-46-6	Antibiotic (PHAR)	253	5.6-6.0	0.9	0.1	-
ERY	114-07-8	Antibiotics (PHAR)	734	8.8	3.0	2.1	+
CBZ	298-46-4	Antiepileptic (PHAR)	236	13.9	2.4	1.9	0
DIU	330-54-1	Herbicide (PEST)	232	-	2.7	2.7	

\*Alvarino. (2016)

\*\*Kazner. (2011)

With the aim to evaluate significant variances in the removal efficiencies obtained along the operation of the different treatment plants, Analysis of Variance (ANOVA) was applied as well as the Tukey method with a 95% confidence level.

### 4.2.3 Economic and footprint analysis methodology

In this section is summarized the assumptions taken for the Capital Expenditures (CAPEX), Operational expenditures (OPEX) and footprint estimation.

#### 4.2.3.1 Capital Expenditure (CAPEX)

Optimal operational conditions in terms of water flux, water yield, PAC doses and contact times obtained in the prototype performance were used to define the design of a full-scale PAC-UF treatment train (15,000 m<sup>3</sup>/d). The following considerations were considered:

- Pre-treatment based on a rotary drum screen to guarantee the absence of large size particles in the system.
- PAC slurry preparation tank, PAC contact tank including the mixing system and FF tank for hydraulic cleanings.
- UF membrane skids, including external units such as feed, cross flow and backwash pumps, chemicals dosing units and production tank.

In addition, data from the full-scale UF-RO system was gathered in order to directly compare it with the PAC-UF projection. The CAPEX associated to UF-RO plant include:

- Submerged UF system (ZW500), associated pumps, chemicals dosing units and production tanks
- RO skids, associated pumps and chemical dosing units, permeate and concentrate tanks.

Regarding the PAC-UF plant, quotations of its projection at full-scale capacity (15,000 m<sup>3</sup>/day) were gathered from different providers in order to have an indicative estimate in terms of associated capital expenditures. Layouts indicating the footprint, in terms of space, were obtained by the different quotations. On the other hand, regarding the existing installation (UF-RO), the constructive budgets were gathered from the WWTP managers to compare them with PAC-UF system, as well as the plant footprint.

#### 4.2.3.1 Operational Expenditures (OPEX)

Relevant data in terms of energy and chemicals consumption was obtained for OPEX calculation from both the prototype performance (PAC-UF) and full-scale UF-RO plant. Chemical reagents cost was estimated based on the cost provided by the different suppliers. These costs could vary depending on the location and the volume or weight supplied. Regarding the energy consumption, a fixed cost of 0.11 €/kWh was considered (mean cost provided by the WWTP managers). In the same way, the energy cost might change depending on the tariff and the geography. Countries such as the Netherlands, Denmark or Germany have higher electricity costs (0.25–0.31 €/kWh). Finally, regarding membrane replacement cost, a membrane lifespan of eight and six years were

considered for UF and RO modules, respectively. Equipment and infrastructures depreciation were not included in the operational expenditures.

## 4.3 Results

This section presents the results obtained from the optimization of the PAC-UF performance, the long-term membrane performance, the water quality monitoring (both physico-chemical parameters and OMP), and the economic assessment of both treatment schemes.

### 4.3.1 Optimization of PAC-UF performance

In the tests operated without PAC addition, the capillary tight UF module was continuously operated in filtration mode without hydraulic cleanings. Several water filtration fluxes were evaluated for crossflow velocities of 0.6 m/s (12 m<sup>3</sup>/h), and water recovery ratio was fixed at 75%, as it is depicted in Figure 22 and then compared without internal recirculation. By applying a crossflow velocity of 0.6 m/s, it is possible to operate the membrane at a sustainable fouling velocity (31–38 mbar/d) at fluxes of 25 or 30 LMH. Significant decrease in energy consumption (70–80%) can be achieved by operating the module without crossflow; nevertheless, it is not recommended to reach higher fluxes than 20 LMH, since fouling velocity values are over 100 mbar/d.

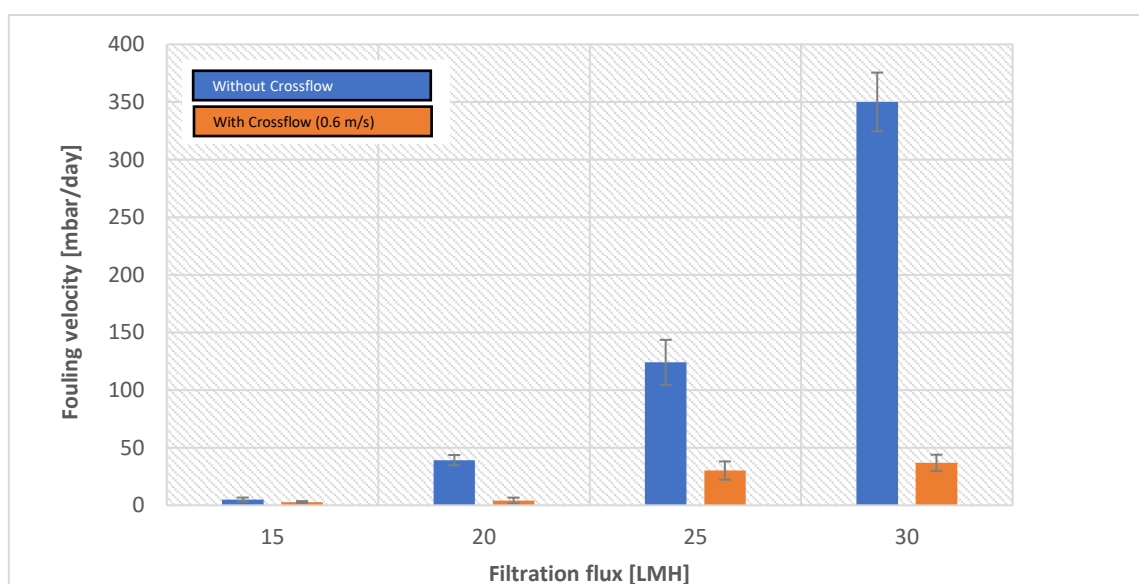


Figure 22 Average Fouling velocities measured ( $n=5$ ) in UF system for different filtration fluxes (15–30 LMH) with and without crossflow ( $X_{flow}$ )

A set of tests (Figure 23) applying different PAC doses (25, 50 and 100 mg/L) were conducted at a constant crossflow velocity of 0.6 m/s. The used PAC dosages were recommended by the UF module manufacturer for the applied range of SS to evaluate different fouling velocities obtained when membrane flux was gradually



increased from 15 to 30 LMH at a fixed 75% water recovery ratio. The module was operated in each test for at least one week of continuous operation, applying hydraulic cleanings (forward flush and back-wash) every 30 min and followed by CEFF including a sequence of alkaline and acidic stages. This cleaning sequence was applied after every test in order to recover the membrane performance to the initial permeability values (20–25 LMH/bar).

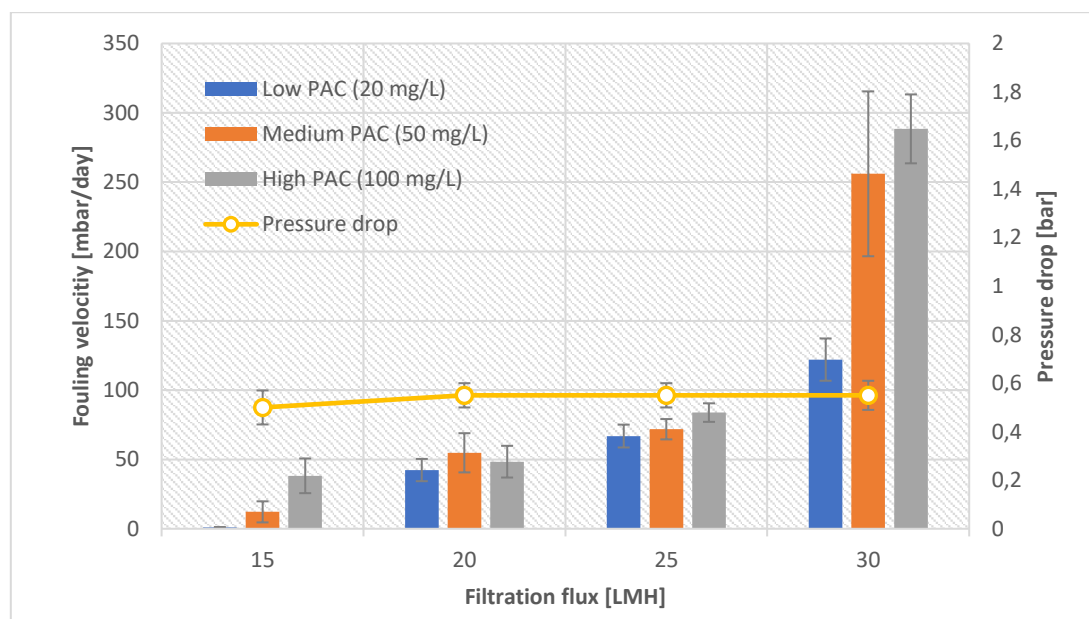


Figure 23 Average Fouling velocities measured ( $n=5$ ) in PAC-UF system for different filtration fluxes (15–30 LMH), crossflow velocity (0.6 m/s), at different PAC dosages (20, 50 and 100 mg/L) and pressure drop mean evolution over the experiments.

Among other authors, Torretta et al. (2013) assessed the hydraulic performance of UF with PAC dosage in MBRs. Nevertheless, scarce studies devoted to the PAC dosage for UF membranes have been reported. Krashtover et al. (2018) indicated in their review of the state of the art on this technology the contradictory results reported by different authors regarding the expected operational benefits (Meier and Melin, 2005).

Lee et al., (2007) reported the improvement in permeate flux decline (30%–40%) by comparing bench-scale PAC-UF performance at different doses (0, 50, 100 and 150 mg PAC/L). Despite the best improvement achieved at a dose of 100 mg PAC/L, regarding baseline conditions, practical operational time was relatively short with a total filtration time of 80 minutes. Additionally, despite applied backwash allowing a successful recovery of the permeability values, the irreversible fouling was not assessed deeply as the operational runs were very short. Yiantios and Karabelas, (2001) reported no significant flux decline at 10 mg PAC/L nor a measurable improvement associated to PAC addition. Authors concluded that the dissolved and colloidal organic matter reduced the PAC deposition onto the membrane surface. This effect was attributed to electrostatic and steric



stabilization effects promoting the reduction of the adhesion energy imparted on the particles and the membrane surface by the adsorbed organic matter. Moreover, Campinas and Joa (2010) suggested that the PAC effect on membrane fouling seems to be mainly driven by membrane properties, with their hydrophobicity being the main factor.

In this study, results (Figure 23) showed that PAC doses applied in the feed tank provided negative effects in terms of membrane fouling when compared with the same conditions without PAC uses (Figure 22). The membrane was operated up to fluxes of 25 LMH reaching a fouling velocity below 100 mbar/d for the target established based on the permeability recovery after rapidly reaching TMP levels over 2.5 bar. In this direction, Lin et al. (1999) stated that the use of PAC dosage in combination with UF to reduce membrane fouling yields negative effects, being ineffective in removing the organic matter with MWs lower than 0.3 kDa or greater than 17 kDa. Additionally, Li and Chen (2004) also reported higher membrane fouling indicators when PAC was applied.

#### 4.3.2 Long-term UF membrane performance

The optimal conditions obtained for different PAC dosages, which were divided into low (20 mg/L), medium (50 mg/L) and high (100 mg/L), along with a constant PAC contact time of 30 min, are summarized in Table 46. Long-term performance tests of at least one month were performed after the optimal conditions, in terms of flux and internal recirculation, were set. Filtration tests were carried out at 20 LMH. Crossflow velocity was varied to mitigate the fouling increase, especially for the higher PAC dosages.

Table 46 Operational results obtained for the different PAC doses tested along the prototype operation.

PAC dosage range (average) [mg/L]	Low ( $\approx 20$ mg/L)	Medium ( $\approx 50$ mg/L)	High ( $\approx 100$ mg/L)
	14–29 (21)	47–52 (49)	110–125 (113)
PAC contact time [min]	30	30	30
Filtration flux [LMH]	20	20	20
Recovery [%]	75	75	75
Crossflow [m <sup>3</sup> /h] (m/s)	12 (0.6)	14 (0.7)	16 (0.8)
Filtration time [min] (Hydraulic cleaning (HC) frequency)	60 (1 HC/h)	15 (4 HC/h)	15 (4 HC/h)
Pressure drop across the module [bar]	0.45–0.50	0.45–0.50	0.95–1.00
Water yield [%]	71	45	45
Feed pump energy consumption [kWh/m <sup>3</sup> ]	0.07	0.09	0.09
Recirculation pump energy consumption [kWh/m <sup>3</sup> ]	0.28	0.4	0.57
Total energy consumption [kWh/m <sup>3</sup> ]	<b>0.35</b>	<b>0.49</b>	<b>0.66</b>

PAC dosage range (average) [mg/L]	Low ( $\approx 20$ mg/L)	Medium ( $\approx 50$ mg/L)	High ( $\approx 100$ mg/L)
		14–29 (21)	47–52 (49)
NaOCl (15%) consumption range (average) [mL/m <sup>3</sup> ]	2–4 (3)	4–6 (5)	7–6 (7)
Citric Acid (50%) consumption range (average) [mL/m <sup>3</sup> ]	15–31 (23)	47–52 (49)	49–52 (50)

For low PAC dosages (20 mg/L), applying a constant flux of 20 LMH (75% of water recovery), cross flow velocity of 0.6 m/s and performing hydraulic cleanings every 60 min, no irreversible fouling was detected (Figure 24). Permeability values were maintained between 20 and 15 LMH/bar, and no irreversible fouling was detected after CEFF, which were applied every seven days. Water yield under these conditions resulted as 71% with a total energy consumption of 0.35 kWh/m<sup>3</sup>.

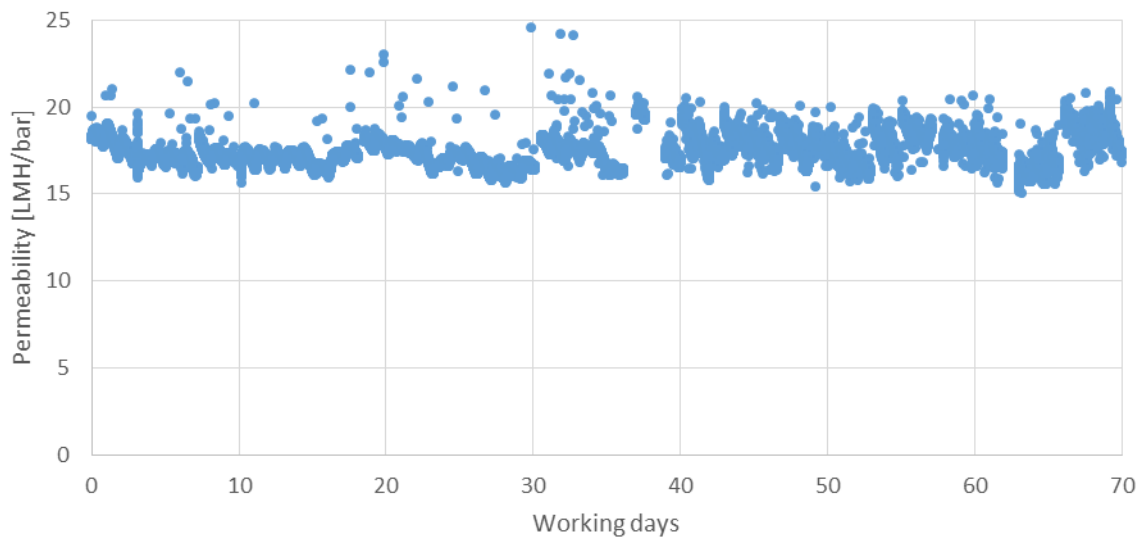
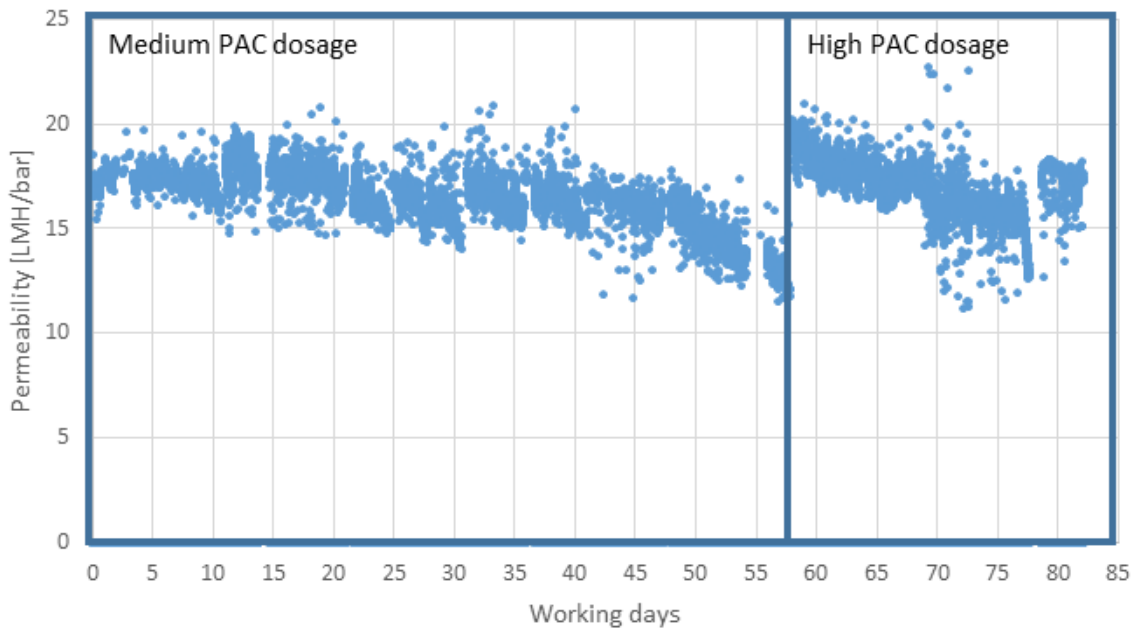


Figure 24 PAC-UF Long term membrane performance. Low PAC dosage (20 mg/L), 20 LMH, 75% recovery, cross flow velocity 0.6 m/s, hydraulic cleanings frequency of 60 min<sup>-1</sup> and CEFF frequency of seven days<sup>-1</sup>.

The permeability evolution of the capillary tight UF membrane operated at a constant flux of 20 LMH at medium and high PAC dosages is depicted in Figure 25. For medium PAC dosages, based on the clogging observed, crossflow velocity was increased to 0.7 m/s, and hydraulic cleanings were performed every 15 minutes in order avoid the cumulative deposition of PAC on the membrane surface. Moreover, the CEFF (alkaline followed by acid) were performed every 4–5 days.

As it can be seen in Figure 25, permeability was not completely recovered after the hydraulic and chemical cleanings, existing an irreversible fouling on the membrane that led to reaching permeability levels between 12 and 15 LMH/bar after 50–55 days. The increase of the crossflow velocity implied an increase of the specific energy consumption associated to the recirculation pump, which represents around 80% of the total energy

consumption of the plant ( $0.49 \text{ kWh/m}^3$ ). Any increase of the pressure drop across the module was observed by applying this crossflow velocity. Additionally, water yield decreased significantly from 71 to 45% due to the increase of hydraulic cleanings frequency. Moreover, when the high PAC dosage was tested, also at 20 LMH, 75% water recovery was achieved by applying hydraulic cleanings every 15 min, and crossflow was increased to  $16 \text{ m}^3/\text{h}$  (Table 46). Under these conditions, a permeability decrease from 20–18 LMH/bar to 15–13 LMH/bar was observed. Moreover, an increase of total energy consumption up to  $0.66 \text{ kWh/m}^3$  was reached, and water yield was reduced to 45%. In this case, no increase in pressure drop was also observed. Therefore, cross flow tested for medium and high PAC dosages ( $14$  and  $16 \text{ m}^3/\text{h}$ ), coupled with an increase of hydraulic cleanings frequency up to  $15 \text{ min}^{-1}$ , did not allow the operation of the membranes at 20 LMH and 75% of recovery without resulting in irreversible fouling events and an unsustainable decrease in permeability.



*Figure 25 PAC-UF Long term membrane performance. Medium PAC dosage (50 mg/L) and High PAC dosage (100 mg/L), 20 LMH, 75% recovery, cross flow velocity 0.7 and 0.8 m/s, hydraulic cleanings frequency of  $60 \text{ min}^{-1}$  and CEFF frequency of seven days<sup>-1</sup>.*

### 4.3.3 Evaluation of physico-chemical parameters of the treated water

Physico-chemical parameters of the treated water were evaluated for both treatment schemes (UF-RO and PAC-tight UF) and are listed in Table 47. For respective influents, inlet concentrations are indicated as the removal or reduction efficiency for each water quality parameter. Removal efficiencies were calculated from the measured values in the feed and permeate streams.

The conventional UF-RO system was fed with the BWR effluent, which presented SS concentration of  $9\pm 5$  mg/L and turbidity of  $3\pm 3$  NTU. Additionally, COD and BOD<sub>5</sub> presented average concentrations of  $32\pm 18$  and  $3\pm 2$  mg O<sub>2</sub>/L, respectively. Electrical conductivity, Total Nitrogen (TN) and Total Phosphorus (TP) were  $2,093 \pm 79$   $\mu$ s/cm and  $10\pm 5$  and  $1\pm 2$  mg/L, respectively.

UF-RO (50% blend) effluent presented an SS concentration below the limit of detection and turbidity of  $0.2\pm 0.1$  NTU. Additionally, COD was reduced to  $11\pm 5$  mg O<sub>2</sub>/L and BOD<sub>5</sub> was reduced to  $<2$  mg O<sub>2</sub>/L. As expected, the high rejection of dissolved ions (97–99%) provided by RO enables the reduction of electrical conductivity to  $41\pm 27$   $\mu$ s/cm in the RO permeate and results in  $1,091\pm 30$   $\mu$ s/cm after the 50% blending with the filtered UF stream. In this stream, dissolved TN and TP were reduced to  $4\pm 2$  and  $0.5\pm 0.2$  mg/L, respectively, which corresponds to the mix (50%) of very high and negligible removal efficiencies obtained with RO and UF stages, respectively.

The PAC-UF prototype was fed directly with the MBR-UF effluent, and the performance was evaluated by Echevarría et al. (2019). The inlet water was free of SS and presented turbidity levels of  $0.4\pm 0.2$  NTU. In terms of organic matter, the biodegradable fraction (BOD<sub>5</sub>) was under the limit of detection, and COD and DOC were  $33\pm 12$  mg O<sub>2</sub>/L and  $14\pm 8$  mg C/L, respectively. Regarding nutrients, TN was  $11\pm 6$  mg N/L and TP was  $1\pm 1$  mg/L. Moreover, measured electric conductivity was  $2,065 \pm 94$   $\mu$ s/cm.

Turbidity was reduced due to the lower MWCO obtained, by using the capillary tight UF without PAC addition, to  $0.2\pm 0.2$  NTU, COD to  $16\pm 5$  mg O<sub>2</sub>/L and DOC to  $6\pm 1$  mg C/L. Lee et al. (2007) classified the MW distribution of DOC in urban WWTP secondary effluent, in which 40% was  $<1$  kDa, 20% was between 1–3 kDa and the rest was  $>3$  kDa; this was consistent with the MWCO characteristics of the tight UF membrane used in this study and the dissolved organic matter removal efficiencies achieved. In addition, Li and Chen (2004) evaluated the performance of different UF membranes, including tight UF (1–3 kDa), and achieving removal efficiencies over 85% of the dissolved organic matter quantified using the molecular absorption values of UV at 254 nm. It should be stated that the use of such surrogate to quantify DOC removal should be considered as a semi-quantitative indicator.



Through the application of an Analysis of Variance (ANOVA), no significant statistical variances were found in the removal of turbidity or COD with and without PAC addition. Additionally, DOC was reduced to  $4\pm 1$  mg C/L and  $3\pm 1$  mg C/L for 20–50 and 100 mg/L, respectively. No variation regarding MBR effluent was found for electrical conductivity since tested tight UF does not reject dissolved single or multi-charged species, nor does it reject inorganic species associated with nutritional value (nitrogen, phosphorous and potassium-based species).

Table 47 Evaluation of the removal of physicochemical parameters in the different treatment schemes.

	Technology	N° of samples	SS (mg/L)	Turbidity (NTU)	COD (mg O <sub>2</sub> /L)	BOD <sub>5</sub> (mg O <sub>2</sub> /L)	DOC (mg C/L)	Conductivity [μS/cm]	TN (mg N/L)	TP (mg P/L)
UF-RO	Inlet (CAS-BWR effluent)	45	9 ± 5	3 ± 3	32 ± 18	3 ± 2	-	2093 ± 79	10 ± 5	1 ± 2
	50% blend UF-RO	-	<2 (90%±2%)	0.2 ± 0.1 (93%±1%)	11±5 (65%±7%)	<2 (65%±1%)	-	1091 ± 30 (48%±5%)	4 ± 2 (58%±21%)	0.5 ± 0.2 (53%±15%)
PAC-UF	Inlet (MBR effluent)	45	<2	0.4 ± 0.2	33 ± 12	<2	14 ± 8	2065 ± 94	11 ± 6	1 ± 1
	Tight UF without PAC	30	<2	0.2 ± 0.2 (48%±21%)	16 ± 5 (49%±23%)	<2	6 ± 1 (43%±21%)	2045 ± 62	-	-
	PAC-UF (20 mg/L)	20	<2	0.2 ± 0.1 (56%±19%)	15 ± 2 (52%±22%)	<2	4 ± 1 (60%±22%)	2137 ± 57	-	-
	PAC-UF (50 mg/L)	20	<2	0.2 ± 0.1 (45%±19%)	15 ± 5 (75%±23%)	<2	4 ± 1 (55%±14%)	2163 ± 94	-	-
	PAC-UF (100 mg/L)	20	<2	0.2 ± 0.1 (66%±34%)	15 ± 5 (67%±20%)	<2	3 ± 1 (75%±14%)	2085 ± 43	-	-

#### 4.3.4 Evaluation of Organic Micro-Pollutants (OMO) Removal in the advanced treatment trains

As it has been explained, UF-RO and PAC-UF systems were fed by CAS-BWR and MBR effluents respectively, of which the performance and removal capacity were explained by Echevarría et al., (2019). Since both pre-treatments could remove significantly biodegradable OMP below their correspondent LODs, only the most persistent compounds were evaluated. Inlet concentrations as well as the associated removal efficiencies for the different OMP analyzed are summarized in Table 48.

*Table 48 Inlet concentrations and removal efficiencies found in the different treatment schemes in 18 sampling campaigns for selected persistent OMP (Carbamazepine (CBZ), Diuron (DIU), Diclofenac (DCF), Erythromycin (ERY) and Sulphametoxazole (SMX)). Effluent concentrations are summarized in the supplementary material (Table SP3.1)*

	Removal efficiency [%]	N° of samples	CBZ	DIU	DCF	ERY	SMX
UF-RO	Inlet (CAS-BWR effluent) [ng/L]	12	189 ± 29	189 ± 20	362 ± 162	144 ± 41	127 ± 34
	UF	5	10% ± 1%	15% ± 12%	2% ± 2%	10% ± 3%	4% ± 2%
	RO	5	98% ± 1%	97% ± 1%	99% ± 0%	96% ± 1%	96% ± 2%
	50% blend UF-RO	5	54% ± 6%	56% ± 10%	44% ± 14%	53% ± 7%	49% ± 3%
PAC-UF	Inlet (MBR effluent) [ng/L]	18	166 ± 24	127 ± 25	195 ± 70	37 ± 13	124 ± 35
	Tight UF without PAC	18	11% ± 9%	4% ± 3%	10% ± 8%	12% ± 7%	8% ± 7%
	PAC-UF (20 mg/L)	6	88% ± 10%	85% ± 15%	70% ± 26%	67% ± 36%	25% ± 18%
	PAC-UF (50 mg/L)	9	88% ± 9%	92% ± 6%	66% ± 24%	69% ± 31%	57% ± 23%
	PAC-UF (100 mg/L)	3	89% ± 8%	N.d	73% ± 17%	N.d	82% ± 8%

Conventional UF presented removal efficiencies below 15% for the five target OMP evaluated. These low removal ratios are related to the MWCO of the UF membrane (>3 kDa), which is significantly higher than the MW of the evaluated compounds (described in Table 45). Vona et al. (2015) indicated that only partial sorption of highly hydrophobic compounds can be expected on the membrane surface due to weak Van der Waals and London interactions. Additionally, López-Fernandez et al. (2016) proposed the potential adsorption of lipophilic compounds ( $\log k_{ow} > 2.5$ ) to poly-vinyl difluoride (PVDF) groups of the UF membranes.

The thin-film composite RO membranes used presented an aromatic polyamide-based active layer, although being a non-porous structure, some authors assigned MWCO < 0.25 kDa. A filtration test allowed the reduction of concentration values below the LOD of all evaluated target OMP and achieved a removal efficiency over 95%. The high efficiencies of RO membranes for OMP removal have been largely reported in literature. Taheran et al. (2016) reported the rejection of target OMP through the use of RO and FO in several studies for MBR and groundwater filtration. Comerton et al., 2008 and Radjenovic et al., 2009 achieved removal efficiencies over 97%

for CBZ, DFC and SMX. Moreover, Foureaux et al. (2019) achieved concentrations in the permeate stream below the LOD for all measured compounds when applied to surface water filtration.

Undoubtedly, RO represents the most robust option in terms of OMP removal efficiency; nevertheless, its relatively high associated treatment cost (as it will be stated in section 3.5) leads to by-pass UF permeate and produce tailored blends that account with lower costs. As it has been explained, the El Baix Llobregat WRP has a 50% blend UF-RO system; thus, since UF presents very limited OMP removal capacity, removal capacities for the UF-RO system did not exceed 60% for evaluated compounds. Tight UF without PAC presented similar behavior in terms of target OMP removal efficiencies to UF, which is also related to its associated MWCO (1kDa).

By upgrading the tight UF performance with PAC addition, CBZ and DIU, which were highly recalcitrant OMPs in conventional systems (Luo et al., 2014) reported removal efficiencies of  $88\% \pm 10\%$  and  $85\% \pm 15\%$ , respectively. DCF and ERY, which are moderately removable compounds, presented similar performance to PAC, achieving removal efficiencies over 70%. The increase of PAC concentration did not significantly improve removal efficiency in CBZ, DIU, DCF or ERY; the absence of statistically significant variances was verified by ANOVA. Sheng et al. (2016) evaluated the removal efficiencies of mentioned OMP among others at different PAC doses (10, 50 and 100 mg/L) through the application of PAC-UF systems, achieving similar results with the exception of DCF (which was found to present removal efficiencies below 20% for PAC dose of 10 mg/L).

Furthermore, SMX presented relatively low removal efficiencies ( $25\% \pm 18\%$ ) when PAC doses of 20 mg/L were applied. Its relatively low sorption constant (e.g., LogD (0.14)) indicates that this compound does not present a high tendency for being sorbed to the activated carbon structure. The results on the removal of SMX are consistent with those obtained by Sheng et al. (2016) who reported a lower removal for PAC doses of 10 mg/L, in the same way Löwenberg et al. (2014), reported similar values for PAC doses of 20 mg/L. Increasing the PAC concentration to 50 and 100 mg/L, lead to an increase in removal efficiency to  $57\% \pm 23\%$  and  $82\% \pm 8\%$ ; this positive effect, which might be related to a fostering of the liquid-solid equilibrium, was also observed in PAC-MBR systems in a previous study (Echevarría et al., 2019).

Table 49 summarizes different reported efficiencies found in PAC-UF and RO systems, which are aligned to the results obtained in this study.



Table 49 Review of reported removal efficiencies in literature for OMP removal (CBZ, DCF and SMX) in evaluated treatment schemes

PAC-UF						
Raw Water	Membrane Configuration	PAC	Scale	Operational conditions	Reported Removal (%)	Reference
Secondary Effluent (WWTP)	- Hollow Fibre—Zeeweed® 10 - PVDF - Nominal pore size: (40 nm)	PAC—SAE Super (Norit Activated Carbon) BET: 1,300 m <sup>2</sup> /g d <sub>50</sub> : 15	Bench-scale (1 m <sup>2</sup> of membrane—23 L/h)	- PAC concentration: 15–20 mg/L - Previous coagulation (4 mg Fe <sup>3+</sup> /L) - PAC contact time: 30 min - Filtration flux: 23 LMH	CBZ: >95% DFC: 80–85% SMX: 65–70%	(Löwenberg et al., 2014)
	- Pressurised—A/G - PES - MWCO: 100 kDa	PAC—DETOX 1,600 USP (Charcoal House Ltd) BET: 1550-1600 m <sup>2</sup> /g d <sub>50</sub> : 8-15	Bench scale (240 cm <sup>2</sup> )	- PAC concentration: 10 mg/L - PAC contact time: 1 h	CBZ: 40% DFC: 20% SMX: 25%	(Sheng et al., 2016)
				- PAC concentration: 50 mg/L - PAC contact time: 1 h	CBZ: 80% DFC: 50% SMX: 50%	
	- PAC concentration: 50 mg/L - PAC contact time: 1 h	CBZ: 85% DFC: 100% SMX: 100%				
- Pressurised—IRIS - PES - MWCO: 3 kDa	PAC—Clarimex 061 CAE (Chemivall, Spain)	Bench scale (90 cm <sup>2</sup> )	- PAC concentration: 50 mg/L - PAC contact time: 4 h	DCF: 95% SMX: 68%	(Vona et al., 2015)	
			- PAC concentration: 50 mg/L - PAC contact time: 4 h	DCF: >99% SMX: 95%		
RO						
Raw water	Membrane Configuration		Scale	Operational conditions	Reported Removal (%)	Reference
Surface water (Ontario Lake, USA)	Flat sheet X20 (TriSep, 4040-X201-TFS) 155 cm <sup>2</sup> MWCO <0.2 kDa		Bench-scale	Filtration flux: 30 LMH Feed pressure: 10 bars	CBZ: 98±1% SMX: 99±1%	(Comerton et al., 2008)
MBR effluent					CBZ: 97±1% SMX: 99±1%	
Surface Water (Besòs River, Spain)	Spiral Wound RO BW30LE-440, Dow Filmtec (44 m <sup>2</sup> ) MWCO <0.2 kDa		Full-scale	Filtration flux: 25 LMH Feed pressure: 8 bar	CBZ: 98% DCF: >99% SMX: >99%	Radjenovic et al., 2009

### 4.3.5 Technical and economic evaluation

A technical and economic evaluation was performed for both treatment schemes. OPEX and CAPEX were evaluated and compared for both treatment schemes considering a wastewater reclamation plant projection of 15,000 m<sup>3</sup>/d (Table 50). Additionally, infrastructure cost for deep well injection technology applied on the El Baix Llobregat WRP was omitted in order to simplify the technological comparison.

*Table 50 Technical and economic assessment for advanced water reclamation systems (PAC-UF and UF-RO) evaluated in this research. PAC-UF shows the results associated to 20 mg PAC/L, considering operational conditions depicted in Table 46; meanwhile, UF-RO has been divided considering different UF/RO permeate volume blends.*

Treatment scheme Production capacity: 15,000 m <sup>3</sup> /d	UF-RO blend*			PAC-tight UF
UF-RO (%) blend / PAC doses applied	50% UF 50% RO	25% UF 75% RO	100% RO*	20 mg PAC/L
Energy consumption [€/m <sup>3</sup> ] (kWh/m <sup>3</sup> )	0.08 (0.7)	0.11 (1.0)	0.14 (1.3)	0.04 (0.35)
Chemical reagents consumption [€/m <sup>3</sup> ]	0.06	0.09	0.11	0.09
Membrane replacement [€/m <sup>3</sup> ]	0.04	0.05	0.06	0.09
OPEX [€/m <sup>3</sup> ] without depreciation	0.18	0.24	0.31	0.22
CAPEX [€/m <sup>3</sup> /d]	594	628	662	548
Relative footprint (regarding CAS-BWR)	+20%	+25%	+30%	+30%

\*Using UF as pre-treatment

Operational data of UF-RO treatment trains were collected from the full-scale system and complemented with operational data and recommendations provided by technology and chemicals suppliers (Table 51). In terms of energy, the UF-RO (50% blend) system is expected to consume 0.7 kWh/m<sup>3</sup>, which accounts to 0.08 €/m<sup>3</sup>. Chemical consumption and membrane replacement account for 0.06 and 0.04 €/m<sup>3</sup>, respectively, considering a six-year lifespan for RO membranes and eight-year lifespan for UF and resulting in OPEX of 0.18 €/m<sup>3</sup>. RO is highly intensive in terms of energy and reagents; thus, while RO treatment capacity and blend is increased to 75 or 100%, the associated OPEX increases to 0.24 and 0.31 €/m<sup>3</sup>, respectively (based on El Baix Llobregat WRP data).

In addition, operational conditions established as optimal along the prototype operation test were used for PAC-tight UF projection, using design codes from X-Flow, as well as measured consumptions (energy and chemicals). A PAC contact tank of 330 m<sup>3</sup> was projected, imposing a contact time of 30 min and considering the required PAC preparation and dosing units. A filtration flux of 20 LMH was considered as a preliminary hypothesis with a theoretical water recovery of 75% (Table 46), which results in a required total membrane area of 44,014 m<sup>2</sup>. This implies 1,101 pressurized tight UF modules grouped into 18 skids. Moreover, a crossflow velocity of 0.6 m/s (12 m<sup>3</sup>/h/module) was considered for a 20 mg PAC/L dose.

As it has been described in sections 3.2 and 3.4, in order to achieve high removal (>70%) of recalcitrant compounds in a sustainable way in terms of irreversible fouling, it is required to dose 20 mg/L of PAC. The associated electrical energy consumption of 0.35 kWh/m<sup>3</sup> corresponds to 0.04 €/m<sup>3</sup>, while the chemical consumption corresponds to 0.09 €/m<sup>3</sup>, from where PAC dosing represents 90% of the cost, considering a PAC cost of 2.5 €/kg (Remy et al., 2009). Additionally, the UF membrane lifespan of six years was considered, corresponding to 15% of modules replacement per year, with an associated cost of 0.09 €/m<sup>3</sup>. Thus, a total OPEX of 0.22 €/m<sup>3</sup> was obtained without considering depreciation, labour and maintenance costs.

For higher PAC doses (50 and 100 mg/L), as it was shown in section 3.2, crossflow velocities of 0.7 and 0.8 m/s were not enough to avoid irreversible fouling; thus, no definitive operational conditions can be provided. Nevertheless, it can be assessed that for 50 and 100 mg PAC/L doses, reagents consumption accounts for 0.28 and 0.56 €/m<sup>3</sup>, resulting in a total OPEX higher than 0.48 and 0.78 €/m<sup>3</sup>.

Another interesting point of view to tackle in the technical-economic comparison is the by-products generation of both systems. In this study, this is mainly associated to the separation and concentration mechanisms associated to the target OMP. UF-RO systems present a limitation related to the generation of brine streams with high salinity. Advanced reclamation plants located in coastal areas present the possibility to pump brines to the sea through a submarine pipeline. Nevertheless, in inland areas, brines need to be recirculated to WWTP headworks, which might provoke disarrangement in biological reactors performance, or treated in advanced high organic load and salinity removal schemes such as Zero Liquid Discharge (ZLD) systems (Bluetech Research, 2018). Therefore, PAC-tight UF presents the advantage of not removing dissolvent ions from the treated stream and thus the possibility to recirculate the concentrate stream (with PAC) to WWTP headworks without affecting the microbiological activity. Additionally, recirculated PAC might not be saturated and can contribute to the organic matter, nutrients and OMP removal in conventional activated sludge or MBR. Alvarino et al., (2017) indicated in their studies that PAC acts as substrate for microbiological growth in biological processes and allowing the diversification of the reactor microbiology through the development of slow growth biomass. Additionally, an increase in OMP biodegradability was detected in several compounds as has been also described by Serrano et al., (2011) in a similar study. In the same line, Echevarria et al., 2019 reported an increase in the removal of TN in MBR associated to the generation of a biofilm layer on the sorbent surface, which creates anoxic zones enabling denitrification. Moreover, an increase in sludge filterability was observed, reaching improvements in terms of membrane performance. Regarding sludge generation, based on the optimal PAC dose applied (20 mg/L), and considering a concentration factor derived to WWTP headworks (100 mg/L), it represents a minor impact in the MBR operational suspended solids level (8-10 g/L).



Table 51 Chemical's consumption and cost for the different evaluated advanced treatment trains

Advanced Treatment Train	Reagent	Unitary Cost	Reference cost provided by	Consumption*	Cost
PAC-UF	PAC (Micropollutants Removal)	2.5 €/kg	Norit CABOT	20 g/m <sup>3</sup> influent	0.07 €/m <sup>3</sup> permeate
	NaClO (15%) (UF chemical cleaning)	0.130 €/kg	Apliclor	3 mL/m <sup>3</sup> permeate	0.0001 €/m <sup>3</sup> permeate
	Citric Acid (40%) (UF chemical cleaning)	0.938 €/kg	Apliclor	2 mL/m <sup>3</sup> permeate	0.0023 €/m <sup>3</sup> permeate
UF-RO	NaClO (15%) (UF chemical cleaning)	0.130 €/kg	Apliclor	15 mL/m <sup>3</sup> permeate	0.0003 €/m <sup>3</sup> permeate
	NaOH (40%) (UF chemical cleaning)	0.177 €/kg	Apliclor	21 mL/m <sup>3</sup> permeate	0.0057 €/m <sup>3</sup> permeate
	HCl (15%) (UF chemical cleaning)	0.220 €/kg	Apliclor	23 mL/m <sup>3</sup> permeate	
	Genesys RED (Sodium bisulfite to compensate the oxidant effect in RO)	0.244 €/kg	Genesys	0.07 kg/m <sup>3</sup> permeate	0.017 €/ m <sup>3</sup> permeate
	Genesys LF (antiscalant to prevent precipitation in RO)	5 €/kg	Genesys	0.012 kg/m <sup>3</sup> permeate	0.060 €/m <sup>3</sup> permeate
	HCl (15%) (pH adjustment)	0.220 €/kg	Apliclor	64 mL/m <sup>3</sup> permeate	0.015 €/m <sup>3</sup> permeate

## 4.4 Conclusions

The pilot scale demonstration of the PAC-tight UF allowed a long-term evaluation of the system as an advanced treatment scheme and demonstrated that PAC doses of 20 mg/L can be applied without achieving progressive irreversible fouling, unlike PAC doses of 50 and 100 mg/L. Moreover, the treatment train was compared from a technical and economic point of view to the large-scale UF-RO system considering the full-scale potential of the pilot, which represents the main scientific contribution of this work.

From a technical point of view, the treatment scheme based on UF-RO (50% blend) allowed to achieve average removal efficiencies between 50 and 60% for analyzed OMP, taking into account the limited removal efficiency of conventional UF membranes (<15%) and the very high rejections achieved with RO (>95%). Additionally, PAC-tight UF applying a PAC dose of 20 mg/L achieved average removal efficiencies over 80% for CBZ and DIU and over 70% for DCF and ERY. In the case of SMX, the removal efficiency found was relatively low (<30%), since the compound does not have a high tendency to be sorbed by the activated carbon. Regarding operation, PAC presented a negative effect in terms of membrane fouling, and cross flow velocity and the application of periodical hydraulic cleanings were required.

On the other hand, from an economic point of view, PAC-tight UF (20 mg/L) presents 22% higher OPEX than UF-RO (50% blend), although in terms of CAPEX, it appears to be the less expensive option. OMP removal efficiencies are higher for PAC-tight UF, and, to increase UF-RO removal efficiencies to its range, a 75% RO blend would be required, which accounts for 0.24 €/m<sup>3</sup> (9% higher in OPEX). Moreover, based on results found, PAC concentrations higher than 20 mg/L do not seem to be economically feasible, and from a technical point of view, the improvements in terms of OMP and DOC removal are limited. Only the removal of peak inlet concentrations of highly recalcitrant compounds with high sorption tendency (LogD>1) might justify, from an economic point of view, the application of 50–100 mg/L doses in urban wastewater reclamation systems.

The possibility of cycling generated brines to WWTP headworks is associated to economic savings in brine management and can be perceived as an environmental driver. On the other hand, UF-RO seems to be an adequate system for coastal areas, where brine generation does not represent a drawback since marine disposal is the main management alternative. Additionally, in coastal areas, the application of these systems is also linked to groundwater overexploitation areas, where treated water with a low salinity content needs to be injected and create an artificial water barrier to protect against the seawater intrusion and preserve groundwater reservoirs from salinization.

Water reuse is one of the main vectors in bio-factories, together with energy, nutrients and resources (such as bio-methane, fertilizers or bioplastics). In water scarcity regions, and considering future previsions in terms of water availability, water reuse and the consequent concentration of recalcitrant pollutants in the water cycle has

raised the interest of authorities to ensure safety, especially when high water quality or sensitive applications are planned, such as IPR, agricultural or industrial uses. Beyond OMP removal efficiencies of conventional and advanced technologies, the associated cost from an economic point of view as well as footprint obtained in this study have been demonstrated to be key variables for decision makers.

Which strategy follow from a policy-making perspective and where and how (as centralized or decentralized treatment) it is necessary to deploy advanced reclamation systems, are questions that need to be answered in a consistent way. New paradigms to conceive water reuse and OMP removal strategies need to be developed and supported with robust decision support systems (DSS) fed with valuable data obtained on-field (efficiencies, cost and footprint).

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# Chapter 5



## 5. Chapter 5: Techno-economic assessment of decentralized polishing schemes for municipal water reclamation and reuse in the industrial sector in coastal semiarid regions: The case of Barcelona (Spain)

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Techno-economic assessment of decentralized polishing schemes for municipal water reclamation and reuse in the industrial sector in coastal semiarid regions: The case of Barcelona (Spain)



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Figure 26 Screenshot of the article published in Science of the Total Environment.

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### Abstract:

This study demonstrates the techno-economic reliability of an innovative fit-for-use treatment train to boost municipal reclaimed water reuse for industrial uses in the Barcelona Metropolitan Area (BMA). The relatively high conductivity (2090  $\mu\text{S}/\text{cm}$ ) and hardness (454 mg/L) of reclaimed water in the BMA (e.g. Water Reclamation Plant (WRP) of El Baix Llobregat, Barcelona, Spain), together with the restrictive water quality demands in industrial uses, claims for the implementation of advanced reclamation schemes based on desalination technologies such as reverse osmosis (RO). The study assesses the benefits of two potential pre-treatments of the RO stage: (i) ultrafiltration (UF) or (ii) an innovative high-performance nano-structured polymeric sorbent (CNM); in which a permeability decline of 5% was observed when CNM was used as a pre-treatment, while a stable permeability of RO was found when was fed by the UF effluent. On the other hand, generic cost curves have been calculated for the technologies evaluated and were applied to estimate capital and operational expenditures (CAPEX and OPEX) for the scale-up in three different industrial sites (e.g., chemical, waste

management and electro-coating industries). The economic assessment indicates that the use of municipal reclaimed water is economically competitive in front of the use of tap water in the BMA, providing savings between 0.13 and 0.52 €/m<sup>3</sup> for the waste management industry and between 0.49 and 0.98 €/m<sup>3</sup> for the electrocoating industry. On the other hand, the use of groundwater in one of the industrial sites and its relatively low cost implied that, although it is necessary a RO, the current cost of water is significantly lower.

## 5.1 Introduction

Water scarcity represents a growing challenge in the EU coastal regions, especially in the Mediterranean area, and it has been accentuated in recent decades due to extreme effects of climate change in terms of more frequent and prolonged droughts. This issue has evidenced the need to resort to more resilient strategies and incorporate alternative water resources in the water cycle.

Water reuse has become another key component for water planning together with freshwater resources and seawater desalination, allowing the increase in freshwater availability, and saving conventional resources for environmental maintenance and drinking water supply. In different water stressed regions, water reuse for non-potable uses has been proved from an economic and environmental point of view, as the most sustainable alternative to the use of freshwater resources (Allen et al., 2017). This is due to overexploitation or contamination of groundwater (e.g., nitrates and salinity), and the need to purchase imported water for potable water supply. Examples can be found in coastal Spanish regions such as Barcelona, Alicante, or Murcia, which present higher energy consumption and operation and maintenance (O&M) costs in water treatment than other regions, and water reclamation represents an attractive opportunity from a cost perspective (AEAS 2016).

Industrial water consumption in Europe represents the 32% of total water abstractions in the EU (EEA 2017). The need of industrial users to guarantee their production and protect themselves against water shortages has raised their interest in boosting water reuse projects. Nevertheless, despite its demonstrated benefits, water reuse is still far from its potential. The European Commission reported that only 2% of the total treated wastewater in Europe was reclaimed and reused (964 Hm<sup>3</sup>/year) (European Commission, 2021). Specifically, in Spain, the total water reclamation is estimated in 400 Hm<sup>3</sup>/year (Allen et al., 2017) and the use of municipal reclaimed water to cover industrial needs accounts to 12% of the total reclaimed water volume.

On the other hand, the reclamation and reuse of municipal wastewater faces different local transversal challenges such as social perception and the lack of economic and governance successful models. From the strictly techno-economic point of view, it is necessary to ensure the water quality demanded by both regulation and end-users and be able to demonstrate efficient fit-for-use water reclamation trains. While conventional

secondary and tertiary treatment trains have demonstrated consistent efficiency in organic matter and nutrients removal, salinity and some organic micropollutants (OMP) remain in the treated effluents and its elimination require the application of advanced technologies.

Salinity and hardness are highly restricted in industrial water uses, especially for sensitive applications such as boiler feed, closed-loop cooling circuits or process water, in which scaling and corrosion are the main concerns in the main industrial sectors (e.g Chemical, Oil and Gas, Mining and Metallurgy, Automotive, Food&Beverage, among others) (Barot et al., 2020; Löwenberg et al., 2015). Moreover, the presence of OMP in reclaimed water effluents represents a risk in terms of its concentration in the water cycle since these compounds are reincorporated again and again in the wastewater treatment plants (WWTPs).

The application of Reverse Osmosis (RO) membranes is relatively extended in industrial water supply in order to reduce total dissolved solids (TDS) from both groundwater or tap water sources. This allows to directly obtain a suitable water that meets with quality requirements. Borsani et al. (1996) assessed the use of RO to provide process water in a steel making plant in Woljisky (Volgograd, Russia). Additionally, Alanood et al. (2021) and Al-Obaidi et al. (2021) assessed the performance of medium sized RO plants to supply water for industrial applications.

Quevedo et al. (2012) investigated the use of RO for surface and groundwater water make-up for industrial water supply, as well as its pre-treatment needs. Nevertheless, when municipal reclaimed water is intended to be used for industrial applications, the selection and implementation of the correct pre-treatments for RO results even more challenging due to reclaimed water physico-chemical properties. Membrane filtration systems such as Microfiltration (MF) or Ultrafiltration (UF) are commonly applied as pre-treatment requirement to ensure the removal of particulate inorganic and organic matter and ensure a Silt Density Index (SDI) below 3 (Touati et al., 2018). In addition, media filters could be used and when based on anthracite or granular activated carbon (GAC) they provide the possibility of reducing the levels of dissolved organic matter (DOC) (Kavitha et al. 2019). In this direction, some authors have evaluated novel materials with claims on nanostructured properties that may act as high efficiency sorbents (Moradi et al., 2021). Some of them, in base to a polymeric structure, could be regenerated chemically on-site and then overcome the limitation of GAC that only could be thermally regenerated off-site (Larasati et al., 2021). As an example, Lewatit® AF 5 a microporous carbonaceous sorbent in bed form, derived from a synthetic polymer with a high surface area of 1300 m<sup>2</sup>/g, has been designed for downstream process separation and purification (Reczek et al., 2020).



The implementation of advanced reclamation schemes to supply municipal reclaimed water for industrial uses is not new and several successful case studies can be found at worldwide level (BlueTech 2016). In North-America, The Edward C. Little Water Recycling Facility (ECLWRF) is the main water reuse system of West Basin Municipal Water District (California), with a nominal capacity of 151500 m<sup>3</sup>/day. The ECLWRF is fed by the Hyperion WWTP secondary effluent and accounts with a multi-barrier system (physico-chemical system, UF, RO and UV disinfection), which provides different reclaimed water qualities for aquifer recharge, industrial (Oil&Gas sector) and urban uses (Lazarova et al. 2013). In South-East Asia, The Public Utilities Board (PUB) of Singapore boosted an innovative and referent water management system to guarantee the water supply of the country, including rainfall harvesting, seawater desalination and water reuse. Specifically, the new Tuas WRP will provide through a membrane bioreactor (MBR) followed by RO high quality reclaimed water for local industries and surface water replenishment as Indirect Potable Reuse (IPR) system (Lefebvre, 2018; Tortajada, 2006). In the north of Europe, Dow Water (Dupont) collaborated with a local water utility and the regional water manager of the city of Terneuzen (The Netherlands) to use local wastewater to cover the industrial water needs (30000 m<sup>3</sup>/day) of one of their world's largest chemical-industrial centers (Dow, 2021). Particularly in Spain, AITASA WRP (Tarragona) provides municipal reclaimed water to the petrochemical area (Pintilie et al., 2016), and Arroyo Culebro WRP (Madrid) supplies reclaimed water to a local Pulp and Paper industry.

Nevertheless, main references found in full-scale water reuse systems are associated to extreme water scarcity areas, with a large water demand and thus, a great necessity. With the aim to contribute to expand water reuse, Lee et al. 2020 investigated the drivers and barriers of water reuse, and as mentioned before, there is a need to provide to decision markers key information of which are the capital and operational expenditures (CAPEX and OPEX) of advanced reclamation technologies at different scales, which are the impacts (environmental or economic) and potential savings that can push industrial users to adopt them. Particularly, cost is a key variable in decision making in early stages of technologies implementation to evaluate its financial consistency. This issue takes importance when centralized or decentralized systems are planned, existing significant differences related to economies of scale for both CAPEX and OPEX. These uncertainties, are added to the existing governance and economic barriers, holding back private and public investment in water reuse projects.

The aim of this work is to demonstrate the techno-economic reliability of a fit-for-use treatment train to reuse municipal reclaimed water from a Basic Water Reclamation system (BWR) for industrial uses as depicted in Figure 27. The performance of the different treatment units is assessed in terms of water quality and operation to identify the benefits of two potential pre-treatments for RO membranes. In addition, generic cost curves for the different technologies considered are provided and applied to estimate the CAPEX and OPEX required for

scaling at three different industrial sites, e.g., chemical, waste management and electro-coating industries, to meet their different needs.

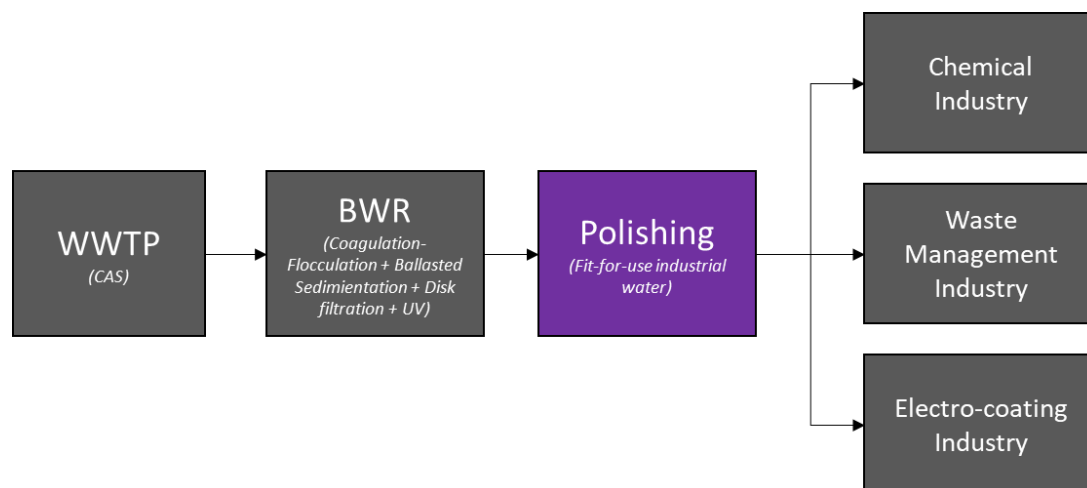


Figure 27 Overall scheme of the techno-economic analysis for three industries in the fit-for-use treatment scheme to reuse municipal reclaimed water.

## 5.2 Materials and Methods

The materials and methods used are described in the following section. From one side the technical assessment methodology is presented, in which the evaluated scenarios are defined, and the prototypes are described, as well as the analytical methods for characterization of water quality. On the other hand, the methods employed for the economic analysis are also described.

### 5.2.1 Polishing technologies assessment

#### 5.2.1.1 Scenarios defined and characterization

Three different target water reuse projects have been evaluated, consisting in different industries from representative market segments (chemical, waste management and electro-coating) interested in reuse municipal reclaimed water to cover their water needs. Valuable information was obtained from different stakeholders who shared their water quality requirements and demands (flow-rates). This characterization was used for the matching between users and tested technologies, and also to scale-up the selected decentralized treatment trains in order to assess them from an economic perspective and to compare the result with the current baseline scenario (current freshwater sources and water polishing systems).

#### 5.2.1.2 Baseline definition and treatment train characteristics

El Baix Llobregat WWRP accounts with a conventional activated sludge system followed by a BWR system composed by coagulation-flocculation, ballasted sedimentation, disk filtration and UV disinfection. The total capacity of the water treatment and reclamation plant is 3.25 m<sup>3</sup>/s. A treatment train with different water

reclamation technologies was operated at pilot scale for a total of 18 months in El Baix Llobregat WWRP (Barcelona, Spain) to assess from a techno-economic point of view two different treatment trains and scale them up at different levels based on the user's requirements.

The treatment train consisted of two lines in parallel: i) a polymeric hollow fiber inside-out UF of 3.5 m<sup>3</sup>/h and ii) a high-performance sorbent column of 2.2 m<sup>3</sup>/h. Both lines fed a two-stage RO plant with 1.5 m<sup>3</sup>/h of capacity. Each one of the units had sampling points to validate the water qualities obtained and validate its reuse for industrial uses. The prototype was fully automatized and operational data (pressure and flow) were acquired from the SCADA system to guarantee the monitoring of the different unit's performance. The prototype scheme is shown in Figure 28.

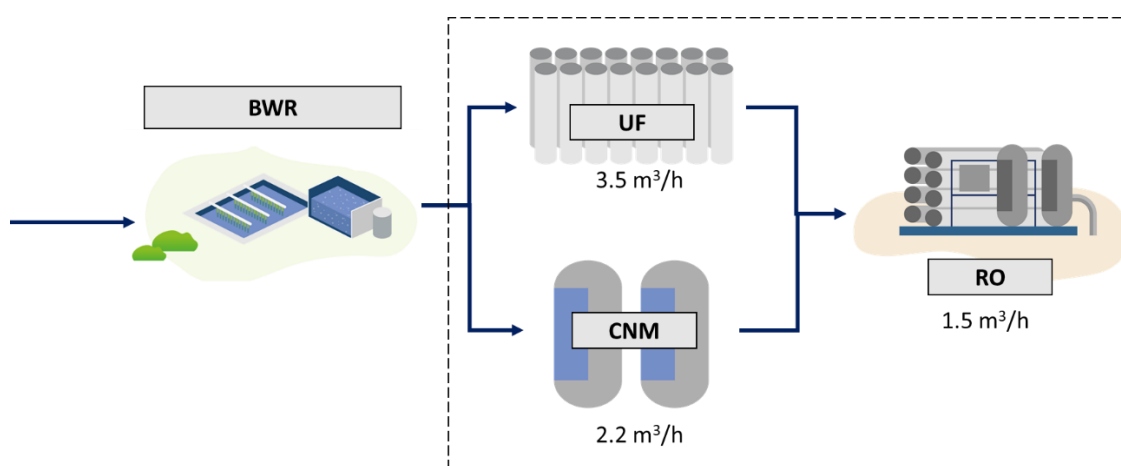


Figure 28 Experimental pilot scheme of two different RO pre-treatment: a) incorporating an UF membrane stage, and b) a carbon-based nanostructured material (CNM). The feed is treated municipal wastewater using a Basic Water Reclamation scheme.

The ultrafiltration unit consisted in a single module of polymeric hollow fiber membranes (AQUAFLEX 64, PENTAIR) with a total membrane area of 64 m<sup>2</sup> operated in dead-end mode. The technical characteristics are summarized in Table 52. The feed water was pumped and circulated through the membrane fibers in an inside-out filtration, collecting the produced permeate in the module shell. Hydraulic cleanings were performed consisting in a combination of a backwash (15 m<sup>3</sup>/h for 30 seconds) and the circulation of raw water in the feed side (4 m<sup>3</sup>/h for 30 seconds) to remove the cake layer and the organic matter accumulated in the module during filtration cycles. Additionally, chemical enhanced backwashes (CEB) were also applied periodically in acid (1.4g/L of HCl (15%)) and alkaline conditions (0.2g/L of NaOCl (15%) and 1.4g/L of NaOH (50%)) to recover permeability.

*Table 52 Technical characteristics of the UF membrane modules.*

<i>Technical characteristics</i>	<i>Value</i>
<i>Model</i>	X-flow AQUAFLEX 64
<i>Configuration</i>	Hollow fiber (Dead-end)
<i>Filtration mode</i>	Inside-Out
<i>Membrane material</i>	PES/PVP
<i>Membrane surface area</i>	64 m <sup>2</sup>
<i>Pore's diameter</i>	20 nm
<i>Internal fiber diameter</i>	0.83 mm
<i>Standard production</i>	3.5 m <sup>3</sup> /h
<i>Filtration flux</i>	35-65 LMH

On the other hand, the sorbent column accounted with a load of 115 kg of a high-performance material. This material was an innovative carbon-based nanostructured material (CNM) from Blücher (SARATECH®), which technical characteristics (provided by the manufacturer) are summarized in Table 53. The filter was operated with a filtration velocity between 8.5 and 10 m/s and allowed the possibility to perform controlled backwashes (BW) several times per day, at a fixed flow of 4 m<sup>3</sup>/h.

*Table 53 Technical characteristics of the Carbon Nanostructured Material*

<i>CNM properties</i>	<i>Value</i>
<i>BET-surface</i>	600-2100 m <sup>2</sup> /g
<i>Ball pan hardness</i>	99.5%
<i>Ash content</i>	0.1%
<i>Tap density</i>	250-800 kg/m <sup>3</sup>
<i>Bulk density</i>	250-800 kg/m <sup>3</sup>
<i>Water content</i>	<1%
<i>Abrasion strength</i>	>99%

Finally, the two-stage RO unit was designed to be operated with a permeate production of 1.5 m<sup>3</sup>/h at a fixed recovery of 70%. It consists of two pressure vessels and the first and second stage contained 4 and 2 membrane elements (Hydranautics LFC3-LD-4040), respectively. The technical characteristics are included in Table 54. The high-pressure pump accounted with a speed driver to adjust pressure and flow to a fixed set point, and the rejection valve was manually controlled.

*Table 54 Technical characteristics of the Reverse Osmosis membrane elements*

<i>Technical characteristics</i>	<i>Value</i>
<i>Model</i>	Hydranautics LFC3-LD-4040

Technical characteristics	Value
Configuration	Spiral Wound
Membrane material	PA
Membrane surface area	7.4 m <sup>2</sup>
Average NaCl rejection percentage	99.7%

### 5.2.1.3 Analytical methods

In order to have a complete characterization of the different generated effluents, samples were taken weekly. Regarding physico-chemical parameters, pH and conductivity were measured online (Mettler Toledo, INPRO 4260/SG/120). Turbidity was measured through a turbidimeter Hach Lange 2100, and SS were analyzed using standard methods 2540 (APHA, 1995). COD was analyzed using test kits (Hatch Lange LCI test) and TOC was measured with a Shimadzu VSH-TOC analyzer. Sodium, Calcium and Copper were measured through ICP/MS (Pekin-Elmer Nexion 300x).

Total aerobic colonies were counted on a nutrient agar culture medium after 48 h of inoculation at 36°C (UNE-EN-ISO 6222:1999). *E. Coli* was measured through Colilert kits (Minimal Media ONPG-MUG Test) and *Legionella* was measured through enzyme immunoassay (Kazandjian et al. 2021). Finally, the presence or absence of *Nematode* eggs was determined through Bailenger method (WHO, 1989).

Additionally, seven OMP (three pesticides from the triazines family and four Polycyclic Aromatic Hydrocarbon (PAH) compounds) were selected (Table 55) and analyzed through C18-Solid phase extraction Gas Chromatography- Triple Quadrupole Mass Spectrometry (7000 GC/MS/MS Agilent Technologies).

Table 55 List of the seven OMP selected and measured

OMP	CAS	Type
<i>Terbuthylazine</i>	5915-41-3	Triazine pesticide
<i>Atrazine</i>	1912-24-9	Triazine pesticide
<i>Simazine</i>	122-34-9	Triazine pesticide
<i>Anthracene</i>	120-12-7	PAH
<i>Fluorene</i>	86-73-7	PAH
<i>Pyrene</i>	129-00-0	PAH
<i>Naphthalene</i>	91-20-3	PAH

Three samples of the CNM were analyzed to characterize their porous textural properties such as surface area, micropores volume, outer surface, and porosity distribution. Characterization was done through the determination of adsorption and desorption isotherms of N<sub>2</sub> (-196°C) and adsorption of CO<sub>2</sub> (0°C) using a volumetric adsorption equipment (Autosorb 6 y 6B, Quantachrome).

Finally, Silt Density Index (SDI) was measured in both UF and CNM effluents using standard methods ASTM D4189-07 in order to identify how suitable is to feed the RO membrane.

### 5.2.2 Economic Assessment

Historically, the calculation of CAPEX in wastewater reclamation plants and distribution networks has been based on a detailed engineering project assessment, being considered specific aspects such as sizing and selection of commercial equipment, construction materials and instrumentation, and the evaluation of site adaptation requirements (Raj Sharma 2010). The preparation of these assessments is time consuming and requires the implication of experts from technologies providers.

In this study, analysis was based on Williams Law, in which cost functions follow an exponential trend,  $C = \beta \cdot Q^\alpha$ , in which C is cost, Q is capacity and  $\beta$  and  $\alpha$  are constants (Guo et al., 2014). This approach considers the economy of scale, being applicable for both capital and O&M expenditures. Tribe and Alpine (1986) explained that the scale coefficient ( $\alpha$ ) ranges between 0.5 and 1 and represents the scalability factor, which may vary depending on the technology nature, being  $\alpha=0.6$  in many cases the best adjustment in cost curves. Nevertheless, it has been observed and reported that not all technologies scale-up following the “0.6 rule”.

On the other hand, OPEX (expressed as €/m<sup>3</sup> of produced water) is not a constant value associated to each technology and presents a range of variation related to scale economies. It depends on energy consumption; beyond depending on water quality and operational conditions applied, pumping efficiency varies significantly regarding capacity, as well as the indirect energy costs associated to the installed power of building and control room. Additionally, based on the volumes of chemical reagents purchased and distribution logistics, the associated market price changes.

During the eighties, to boost a rapid decision making, the US Environmental Protection Agency (USEPA) developed cost curves based on actual and conceptual designs of different capacities (USEPA, 1979). Several authors, in recent decades, have applied this method and developed corresponding cost equations based on regression lines, which can also be integrated in computer programs in order to interpolate a CAPEX or OPEX value regarding the required capacity (Raj Sharma 2010). The accuracy in the estimation of costs, both CAPEX and OPEX, depends on how key variables and assumptions are defined. Regarding CAPEX estimation, the following items have been considered: i) Site work or site preparation, ii) Equipment and housing, iii) Electrical and Instrumentation. On the other hand, the following variables are considered for OPEX estimation: i) Energy consumption, ii) Chemicals consumption, iii) Equipment replacement and maintenance, iv) Waste and By-products management.

Different quotations have been identified and compiled to calculate CAPEX and OPEX curves, which were extrapolated for the different treatment capacities defined by the end-users (1890, 215 and 100 m<sup>3</sup>/day for chemical, waste management and electro-coating industries, respectively). In all quotations, the Consumer Price Index (CPI) has been updated to 2021. On the other hand, detailed engineering, manpower and contingency plan have been excluded to ease the comparison among quotations compiled. This also answers to the worldwide variability in salary ranges for workers and engineers.

## 5.3 Results and discussion

In the following section the results obtained are described and discussed. Firstly, a water quality evaluation (section 1) is presented, considering both physico-chemical parameters and OMP removal. Secondly, the prototype performance results (section 2) are described, in which UF and CNM are evaluated, together with the RO. Finally, in section 3, CAPEX and OPEX cost curves are used to estimate the full-scale cost of the defined industrial water reuse projects and assess them from a techno-economic perspective.

### 5.3.1 Water quality assessment

The different effluents produced by the prototypes were assessed in terms of water quality with the aim to compare them with the regulations considered and the end-user's requirements. Conventional physico-chemical parameters and selected OMP were analyzed, and removal efficiencies were estimated.

#### 5.3.1.1 Evaluation of conventional physico-chemical stages of pollution load removal

The characterization of the basic reclaimed water influent and the effluents from the different process units of the prototype are summarized in Table 56 and Table 57. The current basic reclamation scheme of El Baix Llobregat was designed for the removal of suspended solids, turbidity, organic matter, and microbiological indicators. Its mean turbidity and SS values were  $0.7 \pm 0.2$  NTU and  $2.5 \pm 1.0$  mg/L, respectively. Additionally, in terms of COD and TOC, mean concentrations of  $23 \pm 4$  mg O<sub>2</sub>/L and  $8 \pm 1$  mg C/L were measured. Nevertheless, the treatment units integrating the BWR do not account with desalination steps and as it will be depicted in section 0, despite that it is not considered in the Spanish regulation for water reuse (RD1620/2007), the target industrial end-users' requirements demand the removal of salinity measured as electrical conductivity and the total reduction of hardness. In this sense, the application of a post-treatment based on desalination (RO) to achieve these objectives is required, together with the proper pre-treatments (CNM or UF) to guarantee the correct performance and lifespan of RO membranes.

The BWR effluent presented average conductivity of  $2090 \pm 94$   $\mu$ S/cm and total hardness was  $454 \pm 39$  mg CaCO<sub>3</sub>/L. Main measured cations were sodium and calcium, which mean concentrations were  $255 \pm 30$  mg/L

and  $119 \pm 11$  mg/L, respectively. In addition, main measured anions were chlorides, sulfates and bicarbonates, which mean concentrations were  $388 \pm 53$  mg/L,  $181 \pm 97$  mg/L and  $331 \pm 28$  mg/L, respectively. Finally, due to the disinfection step through UV and chlorination, the microbiological indicators were below the limit of detection.

Regarding the CNM filter and UF, the main objective was to remove dissolved organic matter. An average removal efficiency of 30% of COD and 32% of TOC was measured for CNM. On the other hand, the removal efficiency found in UF was 21% and 15% for COD and TOC, respectively.

Finally, the RO step allowed a reduction of conductivity from  $2090 \pm 94$   $\mu$ S/cm to  $25 \pm 6$   $\mu$ S/cm, which was one of the main objectives of this treatment step. Sulfate concentrations were reduced below the detection limit, as well as bicarbonates and calcium, which represented a total removal of hardness (>99%). Sodium and calcium were reduced to  $4.8 \pm 1.0$  and  $4.7 \pm 2.0$ , respectively.



Table 56 Evaluation of the removal of physico-chemical and microbiological parameters in the different treatment schemes

Effluent	N samples	pH [-]	Turbidity [NTU]	SS [mg/L]	COD [mg O <sub>2</sub> /L]	TOC [mg C/L]	Total aerobic (36°C) [CFU/100 mL]	Legionella [CFU/100 mL]	E.Coli [CFU/100 mL]	Nematode eggs
BWR	35	7.7 ± 1.0	0.7 ± 0.2	2.5 ± 1.0	23 ± 4	8.6 ± 1.0	<1.0	<100	<1.0	Absence
CNM	26	7.5 ± 1.0	0.4 ± 0.2	<2.0	16 ± 5	5.8 ± 1.0	<1.0	<100	<1.0	Absence
UF	21	7.7 ± 1.0	0.11 ± 0.02	<2.0	18 ± 3	7.3 ± 1.0	<1.0	<100	<1.0	Absence
RO	18	5.8 ± 1.0	0.11 ± 0.02	<2.0	<4.0	<0.5	<1.0	<100	<1.0	Absence

Table 57 Evaluation of the removal of physico-chemical and microbiological parameters in the different treatment schemes

Effluent	N samples	Conductivity [μS/cm]	Na <sup>+</sup> [mg/L]	Ca <sup>2+</sup> [mg/L]	Cu <sup>2+</sup> [μg/L]	Cl <sup>-</sup> [mg/L]	SO <sub>4</sub> <sup>2-</sup> [mg/L]	HCO <sub>3</sub> <sup>-</sup> [mg/L]	Total Hardness [mg CaCO <sub>3</sub> /L]
BWR	35	2090 ± 95	255 ± 30	119 ± 11	<2.0	388 ± 53	181 ± 97	332 ± 28	45 ± 39
CNM	26	2087 ± 89	255 ± 73	118 ± 11	<2.0	388 ± 53	164 ± 33	315 ± 30	454 ± 39
UF	21	2064 ± 94	246 ± 73	115 ± 8	<2.0	365 ± 8	150 ± 34	320 ± 25	440 ± 32
RO	18	25 ± 6	5 ± 1	<0.5	<2.0	5 ± 2.0	<3.0	7 ± 1	<1.0

### 5.3.1.2 Evaluation of OMP removal

Average removal efficiencies for triazine pesticides and PAH analyzed are collected for the different process units in Table 58.

*Table 58 Effluent concentrations (ng/L) and removal efficiencies (%) for the selected OMP in the different technologies evaluated.*

OMP	BWR effluent	CNM permeate	UF permeate	RO permeate
Number of samples	10	5	5	10
Terbutylazine	15 ± 7	6 ± 1 (67% ± 25%)	14 ± 1 (5% ± 5%)	1 ± 1 (98% ± 5%)
Atrazine	26 ± 4	1 ± 1 (97% ± 10%)	19.5 ± 1 (25% ± 5%)	1 ± 1 (96% ± 1%)
Anthracene	8 ± 5	5.1 ± 1 (46% ± 25%)	4.6 ± 1 (8% ± 6%)	5.3 ± 1 (33% ± 25%)
Fluorene	6 ± 4	4.6 ± 1 (27% ± 20%)	5 ± 1 (7% ± 6%)	4.2 ± 1 (32% ± 13%)
Pyrene	7 ± 4	6 ± 1 (5% ± 2%)	6 ± 1 (10% ± 8%)	5 ± 1 (23% ± 12%)
Naphthalene	6 ± 2	6 ± 1 (3% ± 1%)	6 ± 1 (5% ± 5%)	5 ± 1 (30% ± 15%)

CNM allowed high removal efficiencies for triazine pesticides, in which terbutylazine presented removal efficiencies of 67% and atrazine of 97%. Similar results were found by Borrull et al. (2021) who reported efficiencies of total triazines between 95.3% and 68.0% at the outlet of a GAC filter in a DWTP when inlet concentrations were above 10 ng/L. Regarding PAH, moderate efficiencies were found for anthracene and fluorene (46% and 27%, respectively), while in the case of pyrene and naphthalene low efficiencies were achieved (5% and 3%, respectively). Scarce data have been found for the CNM sorbents and only a similar material as Lewatit® AF 5 reported it is used for adsorptive polishing in water treatment applications for traces of organic substances such as chlorinated hydrocarbons, MTBE, organic phosphates, amines, pesticides, herbicides, and metabolites (Reckek,2020).

UF presented low efficiencies (<15%) for the different OMP analysed. This is associated to the molecular weight cut off (MWCO) of UF membranes, in which those OMP with higher molecular weight (MW) than 3 kDa can easily pass through the membrane. Similar behaviour in pharmaceutical compounds in UF membranes was reported by Echevarria et al., (2020). On the other hand, atrazine presented moderate removal efficiency (25%) which, as suggested by López-Fernandez et al. (2016), might be associated to its relatively high lipophilicity (log Kow>2.5) and the potential sorption to the membrane layer, composed by poly-vinyl difluoride (PVDF) or onto the cake layer formed along the filtration stages.

In the case of RO, very high removal efficiencies (>95%) were found for triazine pesticides. Nevertheless, limited efficiencies between 20% and 35% were found for PAH. Argun et al., (2020) indicated that the main removal mechanism of PAH with low molecular weight and high volatility such as naphthalene and anthracene is stripping

when investigated strategies for the removal of organic compounds from leachates; thus, these compounds present high removal efficiencies in bioreactors. On the other hand, their low MW difficult their removal in dense membranes such as RO or NF.

### 5.3.2 Pilot treatment train performance

#### 5.3.2.1 Ultrafiltration stage

The optimization of the UF system was based on maximize the production and reduce the main operational expenditures. Different steps were followed to achieve this objective, considering as main variables the water yield and production rate. Water yield (WY) was calculated as the net production volume over the total filtered volume, and production rate (PR) was calculated as the amount of time in which the membrane was in filtration mode over the total operational time.

Fouling velocity, expressed as permeability decline (PD) over time (dK/dt) and measured as the slope of the liner regression of permeability in five chemical cycles, was calculated for each operational condition set. A maximum PD of 10 LMH/bar/day was established based on membrane design recommendations to define whether the operational conditions applied were sustainable in terms of fouling or not. After each step, an intensive chemical cleaning was applied to recover permeability to baseline conditions. The different steps followed, and the results obtained in terms of WY (%) and PR (%) are plotted in Figure 29.

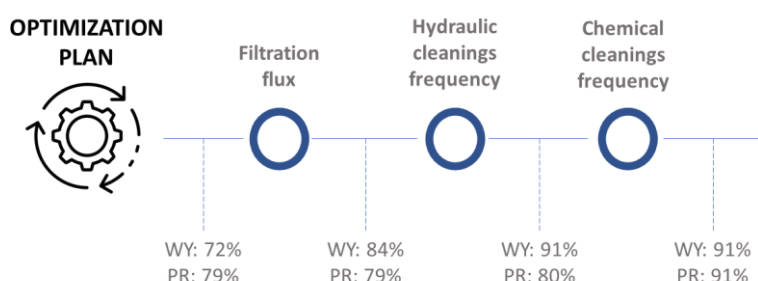


Figure 29. Details of the optimization plan of the ultrafiltration stage including the WY (%) and PR (%) along the filtration operation cycles including the hydraulic and chemical cleanings frequencies.

Firstly, filtration flux was gradually increased from 31 to 62 LMH, applying a fixed filtration time of 30 min and thus performing two hydraulic cleanings per hour, as it can be seen in Figure 30. Additionally, one CEB was applied every 10 hours. As result, WY increased from 72% to 84% while PR was kept in 79%, since it is associated to operational time and not produced volume. Fouling slopes suggested that applying 62 LMH there was PD of 18 LMH/bar/day, representing a risk on the integrity of the membranes. Thus, 55 LMH was selected as the most suitable flux, allowing to increase water yield to 84%.

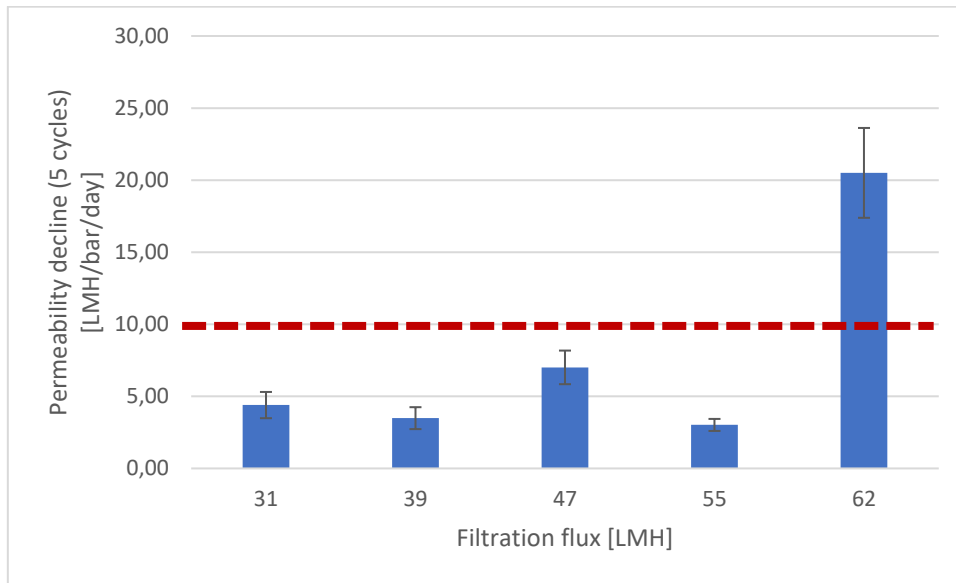


Figure 30 Variation of the permeability decline (PD) (LMH/bar/day) as function of the filtration flux (LMH) along the UF optimization stage including 5 operation cycles.

In a second step, fixing 55 LMH as the optimal flux, filtration time was varied from 20 to 60 min. Based on the fouling slopes obtained, to keep 30 min as filtration seem to be the best option as it can be seen in Figure 31. Moreover, a trial to reduce the hydraulic cleaning duration from 60 to 30 seconds was done, obtaining promising results in terms of fouling and implying a WY of 91% and a PR of 80%.

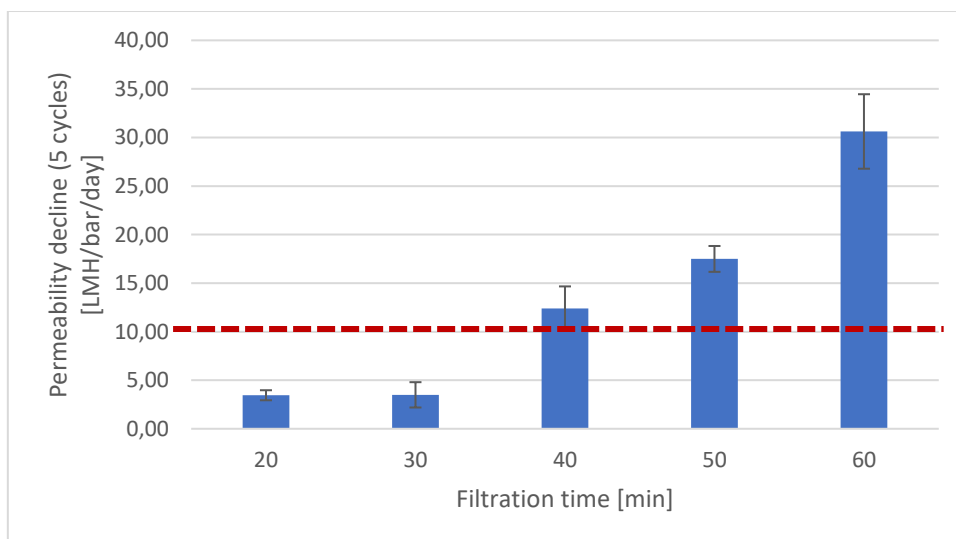
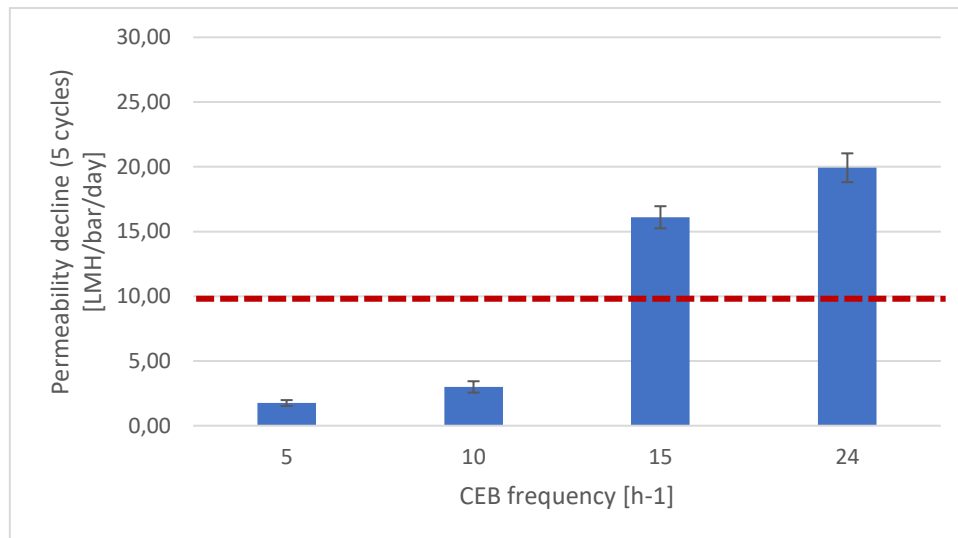


Figure 31 Variation of the permeability decline (PD) (LMH/bar/day) as function of the filtration time (min) along the UF optimization stage including 5 operation cycles.

Finally, in a third step, chemical cleanings frequency was varied from 5 to 24 h<sup>-1</sup>. In this case, as it is depicted in Figure 32, results clearly indicated that 10 h<sup>-1</sup> was the most suitable option, considering that higher frequencies led to not completely recover permeability and the risk of accumulated fouling. Additionally, different soaking

times were applied (60, 30 and 15 min) in order to increase production time. No significant variances were found in permeability recovery by applying the soaking time of 15 min, thus it resulted the optimal option, implying an increase of PR to 91%.



*Figure 32 Variation of the permeability decline (PD) (LMH/bar/day) as function of the CEB frequency (h<sup>-1</sup>) along the UF optimization stage including 5 operation cycles.*

Based on these results, the operational conditions selected as the optimal to apply them in a long-term membrane performance test consist of a filtration flux of 55 LMH (which corresponds to a net production of 3.5 m<sup>3</sup>/h), applying a filtration time of 30 min and performing CEBs every 10 hours (and 15 min of soaking per cleaning type).

Once the optimal operating conditions were obtained, long term membrane performance was evaluated operating the UF module under optimal conditions for 270 hours. During this period, permeability remained stable between 200 and 100 LMH/bar (Figure 33).

After 180 hours of operation, it was detected a fouling event in which permeability reached lower values than 100 LMH/bar. This decline was clearly correlated to an excess of turbidity associated to a rainfall event that compromised the performance of the basic reclamation system and thus the inlet water quality in the UF.

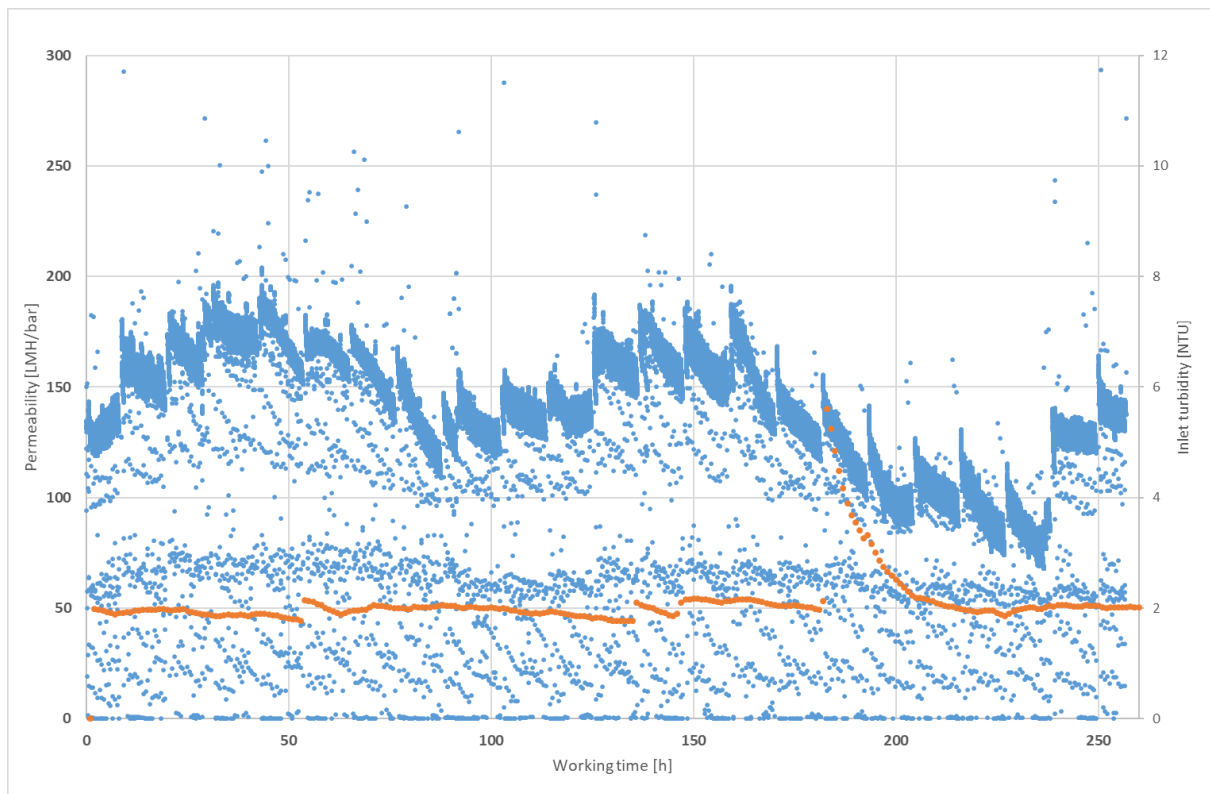


Figure 33 Long-term UF Permeability (blue) and turbidity (orange) evolution.

### 5.3.2.2 CNM adsorption stage

The CNM filter was operated at a filtration velocity between 8.5 and 10 m/h (1.7 - 2.2 m<sup>3</sup>/h) for approximately 25000 bed volumes. Hydraulic cleanings consisting in a backwash (BW) were performed when pressure drop, measured as the difference between the inlet and outlet pressure, reached 1.5 bar.

During this period, COD, TOC and absorbance at 254 nm were monitored in the inlet and outlet of the filter, in order to calculate C/C<sub>0</sub> curve and decide when regeneration was required. These three parameters were selected as surrogates of the organic to evaluate the removal of organic matter as they were easily monitored. As it can be seen in Figure 34, under the flow-rate conditions, at the initial stages <1000 BV, a removal of 90, 85 and 80% of COD, TOC and absorbance 254 nm were obtained, respectively for the first samples. Nevertheless, as the filtration time increases (e.g., after 8000 BV) the removal efficiency decreased approximately to 25, 30 and 40%, respectively.

Results found in this research were compared with those reported by Mailler et al. (2016), who assessed conventional GAC in municipal wastewater. COD, TOC and UV 254 removal efficiencies of 21-48%, 13-44% and 22-48%, respectively were reported for GAC. On the other hand, in this study, CNM allowed a removal efficiency for COD, TOC and UV 254 nm of 75-10%, 76-20%, 90-19%, respectively.

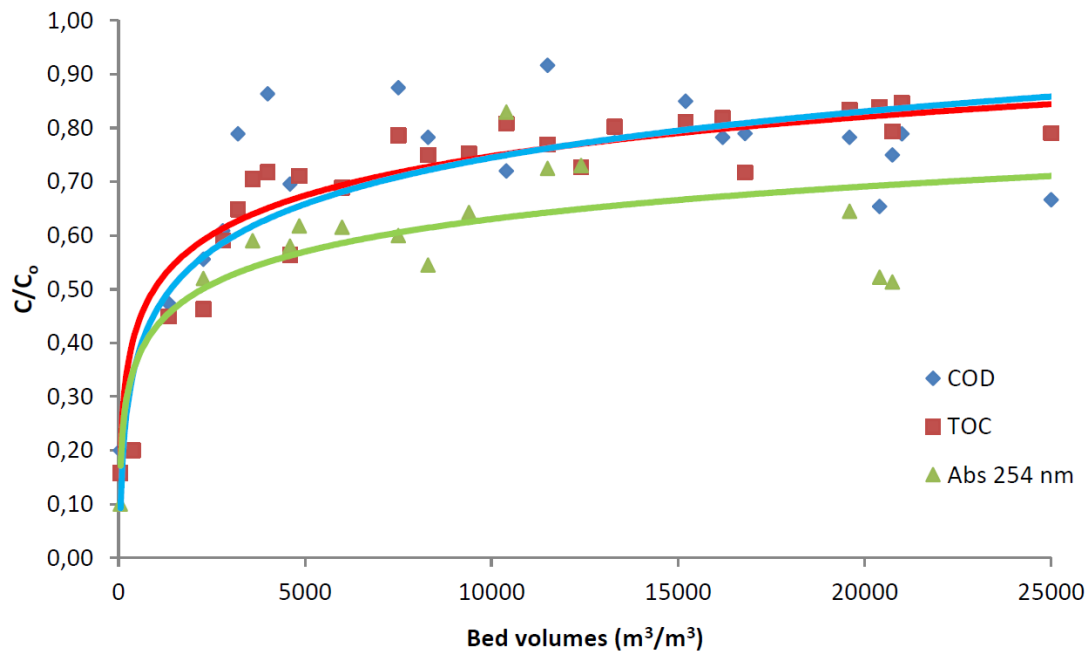


Figure 34 Variation of the COD, TOC and Absorbance values at 254, expressed as  $(C/C_0)$  for the sorption stage using Carbon Nanostructured Material (CNM)

Once  $C/C_0$  reached 0.8 for COD and TOC, the filter still operated stable and was able to feed RO; nevertheless, in order to reach more detail on the technical performance of this innovative material, CNM was regenerated by the manufacturer. According to literature a similar microporous carbonaceous sorbent as Lewatit® AF 5 regeneration could be achieved using steam or hot water or other organic solvents as the separation mechanism is partially via low energy hydrogen bonding (Kaleh et al., 2016; Reczek et al., 2020) After its regeneration, the sorbent was characterized, and results are listed in Table 59.

Table 59 CNM characterization of the three analyzed samples, where  $S_{BET}$  is the surface area,  $V_{DRN_2}$  is the total volume of micropores,  $V_{DRCO_2}$  is the total volume of narrow micropores,  $A_S$  is the outer surface and  $V_S$  is the micropores volume.

Sample	$S_{BET}$ [m <sup>2</sup> /g]	$V_{DRN_2}$ [cm <sup>3</sup> /g]	$V_{DRCO_2}$ [cm <sup>3</sup> /g]	$V_{meso}$ [cm <sup>3</sup> /g]	$A_S$ [m <sup>2</sup> /g]	$V_S$ [cm <sup>3</sup> /g]
Virgin CNM	1720	0.67	0.36	0.1	75	0.71
Saturated CNM	1000	0.38	0.22	0.07	53	0.41
Regenerated CNM	1720	0.65	0.36	0.13	100	0.71

Both virgin and regenerated samples presented similar textural properties, which indicates that the regeneration was effective. On the other hand, as expected, the saturated sample showed a significant lower surface area BET and micropores volume.

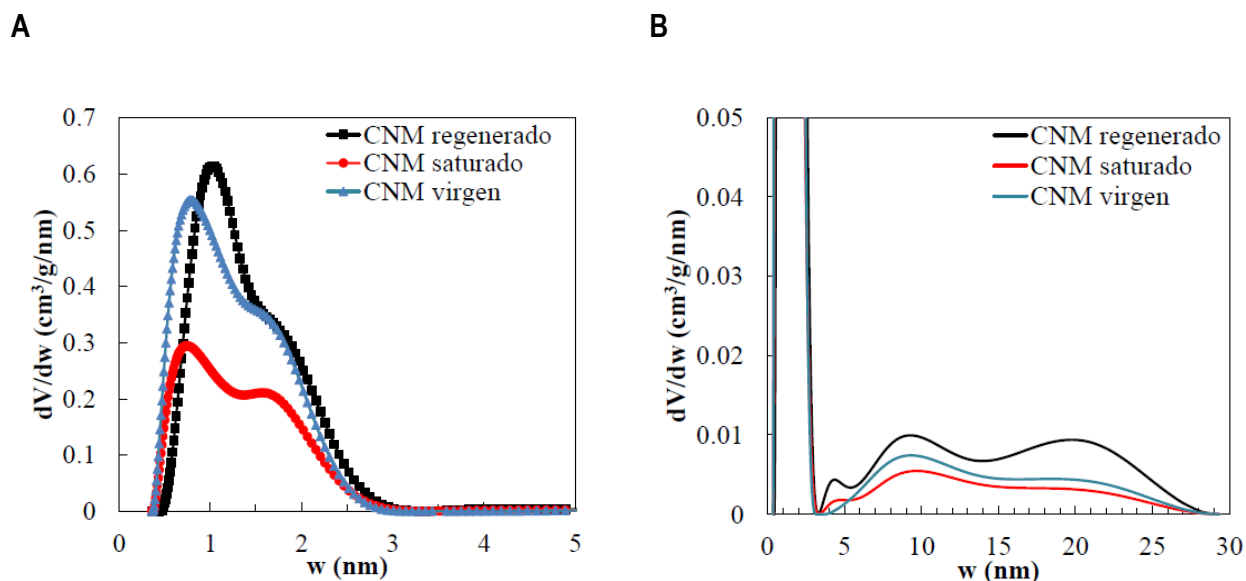


Figure 35 Pore size distribution of the micropore (A) and mesopore (B) regions.

Figure 35 shows the distribution of the pore size of the analysed samples. Most probable size ranges between 0.7 and 1 nm in all samples with a second size of wide micropores with a pore size around 1.6 nm (Figure 35A). A small contribution of mesopores (Figure 35B) between 5 and 30 nm was found also for the three samples. The results obtained suggest that the saturation is mainly associated to the filling of micropores. Once the regeneration is done, the surface area for adsorption is recovered (1720 m<sup>2</sup>/g), with a slightly increase of its mesoporosity (from 0.10 to 0.13 cm<sup>3</sup>/g) and outer area (from 75 to 100 m<sup>2</sup>/g). Additionally, a slight widening of the microporosity was observed.

### 5.3.2.3 Reverse Osmosis stage

The RO prototype was operated fixing a recovery of 70% for approximately 500 hours. During the first 250 hours it was fed with the CNM permeate (phase 1), while the rest of the period was fed with the UF permeate (phase 2) as shown in Figure 36.

Despite COD and TOC values were slightly lower in CNM permeate (Table SM6), the average SDI found after 10 samples was  $4.0 \pm 0.5$ , while in UF permeate mean SDI was  $2.0 \pm 0.5$ . As it can be seen in Figure 36, during the first phase TC Permeability declined from mean values of 37 LMH/bar to 35 LMH/bar. Moreover, when the RO prototype was fed with UF permeate, the TC permeability remained stable, even was slightly improved.



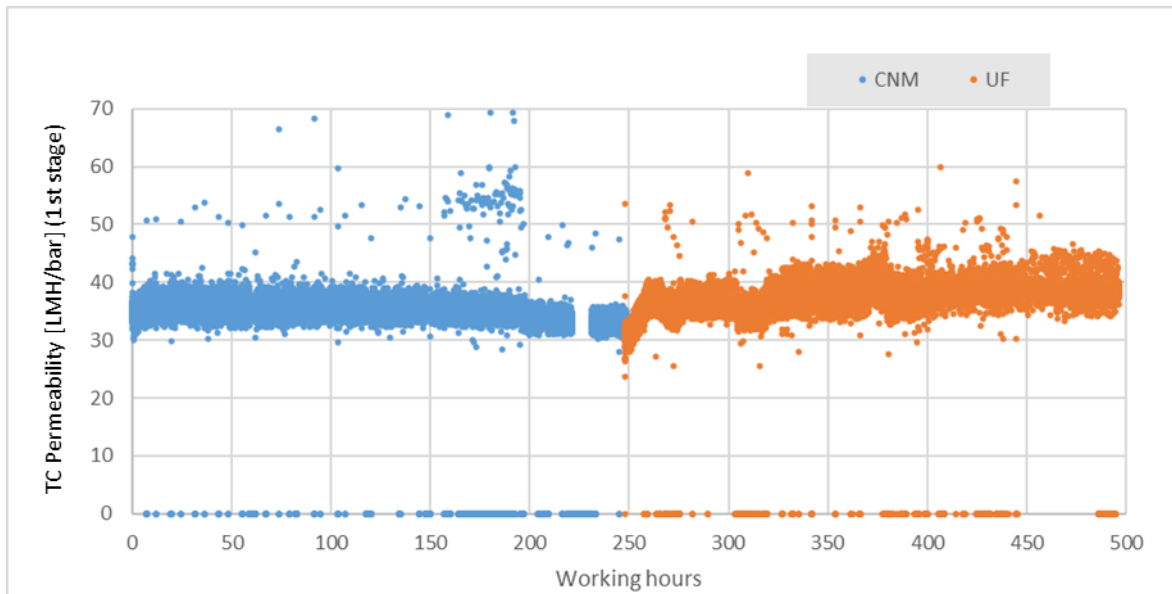


Figure 36 Long-term RO Permeability evolution regarding feed water (UF or CNM)

Recently Cai et al. (2021) evaluated two different pre-treatments (biofiltration, coagulation and microfiber filtration (BCMF) vs. UF) to reduce fouling in RO. The results showed that UF pre-treatment process allowed a more controlled permeability evolution, and it was correlated with a lower modified fouling index ( $MFI_{0.45}$ ). Similar results were found by Benito-Alcázar et al. (2010), who investigated different pre-treatments (GAC and UF) for RO applied for industrial water reclamation in the petrochemical sector. In their work, TOC, COD, turbidity and  $SDI_{15}$ , were used to determine the better pre-treatment in terms of fouling mitigation in the RO membranes. Due to a lower SDI, UF was also postulated as better pre-treatment than GAC despite presenting higher TOC and COD values.

### 5.3.3 Techno-economic assessment

In this section the techno-economic assessment is described. In section 5.3.3.1, cost curves for UF, sorbent filters and RO are calculated. These curves are used in section 0 for estimating CAPEX and OPEX for the scenarios defined in section 5.3.3.3, allowing to estimate the potential savings or over costs associated to potential water reuse projects for industrial water supply.

#### 5.3.3.1 Cost curves calculation

Cost curves were calculated (Table 60) for the different reclamation technologies evaluated. As it has been explained, different quotations were obtained from different engineering firms to estimate CAPEX. On the other hand, data from industrial O&M contracts was obtained to estimate OPEX. The list of quotations collected in this

study, maintaining the confidentiality of the provider, is depicted in Table 61 for CAPEX curves calculation, and Table 62 for OPEX curves calculation.

*Table 60 CAPEX and OPEX cost curve equations for evaluated reclamation technologies.*

Treatment Unit	CAPEX Cost Curve			OPEX Cost Curve		
	Number of quotations	Equation	R <sup>2</sup>	Number of quotations	Equation	R <sup>2</sup>
UF	8	$CAPEX = 4268 \cdot x^{-0.34}$	0.899	13	$OPEX = 2.06 \cdot x^{-0.30}$	0.875
Sorbent column (GAC)	10	$CAPEX = 8250 \cdot x^{-0.59}$	0.897	7	$OPEX = 0.13 \cdot x^{-0.03}$	0.813
RO	29	$CAPEX = 3275 \cdot x^{-0.46}$	0.954	10	$OPEX = 7.92 \cdot x^{-0.38}$	0.868

Firstly, regarding UF, 8 and 13 quotations were used to calculate CAPEX and OPEX cost curves, respectively (Figure 37 and Figure 38). These correspond to ultrafiltration plants which capacity ranged from 80 to 2800 m<sup>3</sup>/day. Considered UF plants are based on side stream pressurized filtration modules (both hollow fiber or tubular) operating in dead-end configuration and the maximum turbidity allowed is 20 NTU. Based on the obtained results and considering mentioned capacity range, UF CAPEX and OPEX might vary between 1150 and 255 €/m<sup>3</sup>/day and 0.59 and 0.21 €/m<sup>3</sup>, respectively. Iglesias (2017) reported a CAPEX range between 312 and 158 €/m<sup>3</sup>/day for UF plants in municipal water plants with capacities ranging from 1000 to 25000 m<sup>3</sup>/day, which are consistent with the results obtained in this study.

Secondly, quotations for sorbent columns with capacities ranging from 95 to 3000 m<sup>3</sup>/day were collected. Due to the lack of available data, these quotations include both drinking water and water reclamation applications and only those plants operating at a filtration velocity between 10 and 15 m/h were considered. Additionally, these results correspond to conventional commercial products, which price ranges between 3 and 4 €/kg of sorbent, including transport, commissioning, and disposal. Obtained results indicated that CAPEX and OPEX might vary between 445 and 55 €/m<sup>3</sup>/day and 0.13 and 0.11 €/m<sup>3</sup>, respectively. Similar results were obtained by Plumlee et al. (2014), who provided also OPEX cost curves for biological activated carbon (BAC) filters ranging from 0.15 to 0.10 €/m<sup>3</sup>. On the other hand, when advanced sorbents such as CNM are used, the impact on OPEX needs to be considered due to its significantly higher price (50 €/kg of sorbent). In this case, OPEX might vary from 1.03 and 1.01 €/m<sup>3</sup>, considering that sorbent purchase and regeneration costs represent more than 95% of OPEX.

Finally, for RO, quotations of water reclamation plants presenting recoveries between 50 and 75% and capacities between 28 and 2760 m<sup>3</sup>/day were used. In this case, CAPEX and OPEX varied from 675 to 91 €/m<sup>3</sup>/day and 5.92 to 0.49 €/m<sup>3</sup>.

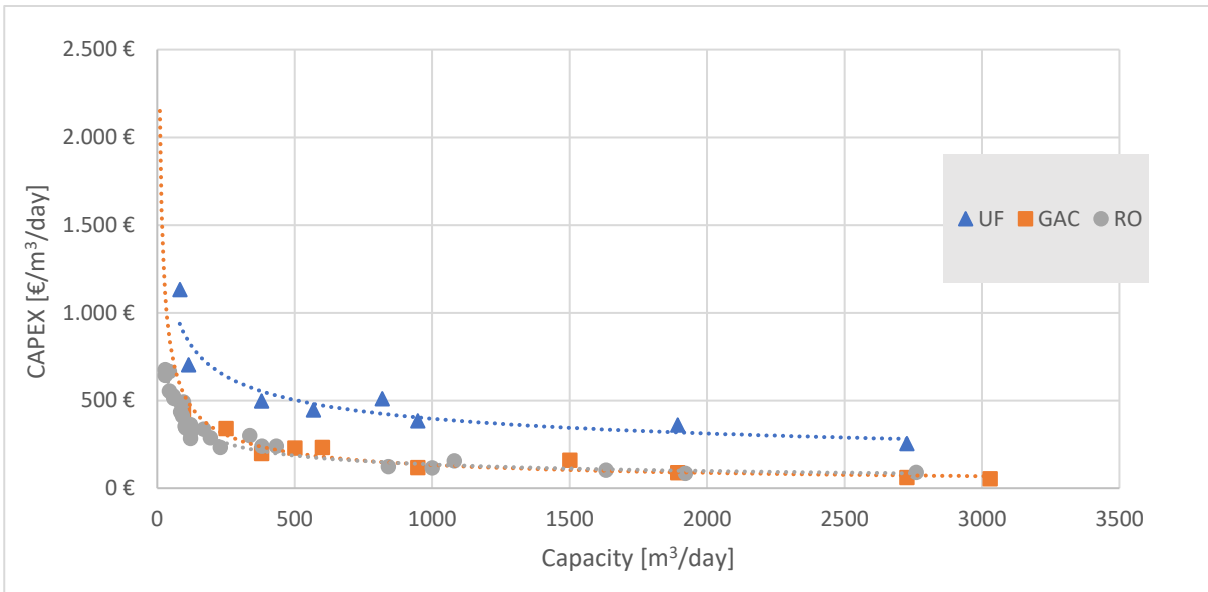


Figure 37 CAPEX curves for the different evaluated technologies (UF, GAC and RO)

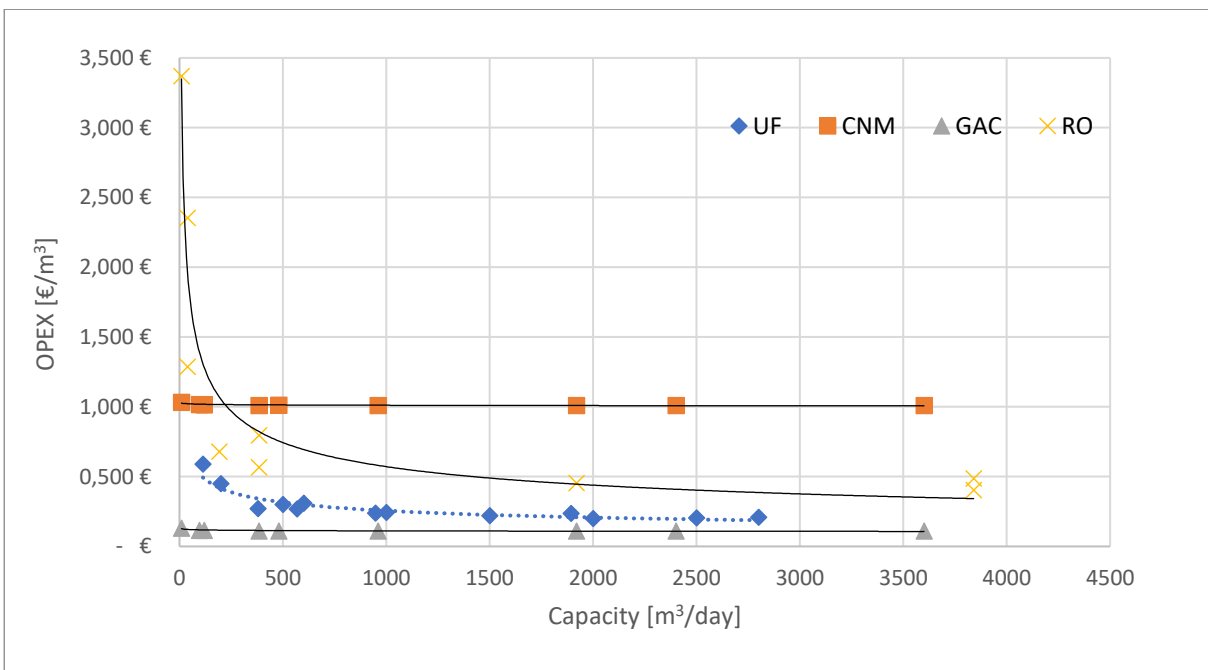


Figure 38 OPEX curves for the different evaluated technologies (UF, GAC, CNM and RO)

Table 61 Raw data used for CAPEX curves calculation

Technology	Capacity (m <sup>3</sup> /day)	CAPEX (€/m <sup>3</sup> /day)	Reference
UF	114	703	USEPA 1986
UF	379	497	USEPA 1986
UF	568	447	USEPA 1986
UF	947	385	USEPA 1986
UF	1893	360	USEPA 1986
UF	82	1132	Engineering firm 1
UF	818	509	Engineering firm 1
UF	2726	255	Engineering firm 1
GAC	95	445	USEPA 1986
GAC	379	198	USEPA 1986
GAC	947	119	USEPA 1986
GAC	1893	88	USEPA 1986
GAC	2726	61	Engineering firm 2
GAC	3029	55	Engineering firm 2
GAC	500	230	Engineering firm 3
GAC	600	233	Engineering firm 3
GAC	250	340	Engineering firm 3
GAC	1500	160	Engineering firm 3
RO	7	336	Engineering firm 1
RO	18	240	Engineering firm 1
RO	45	156	Engineering firm 1
RO	336	299	Engineering firm 1
RO	840	123	Engineering firm 1
RO	1632	103	Engineering firm 1
RO	28	675	Engineering firm 4
RO	103	344	Engineering firm 4
RO	228	233	Engineering firm 4
RO	91	411	Engineering firm 4
RO	120	347	Engineering firm 4
RO	120	284	Engineering firm 5
RO	130	315	Engineering firm 5
RO	29	643	Engineering firm 6
RO	43	554	Engineering firm 6
RO	58	526	Engineering firm 6
RO	43	664	Engineering firm 6
RO	60	512	Engineering firm 6
RO	84	436	Engineering firm 6
RO	120	362	Engineering firm 6
RO	192	288	Engineering firm 6
RO	95	491	USEPA 1986
RO	380	239	USEPA 1986
RO	100	352	Raj Sharma 2010
RO	1000	116	Raj Sharma 2010

Table 62 Raw data used for OPEX curves calculation

Technology	Capacity (m <sup>3</sup> /day)	OPEX (€/m <sup>3</sup> )	Reference
UF	114	0.591	USEPA 1986
UF	379	0.271	USEPA 1986
UF	568	0.270	USEPA 1986
UF	947	0.240	USEPA 1986
UF	1893	0.236	USEPA 1986
UF	2800	0.210	USEPA 1986
UF	200	0.450	Industrial O&M contract
UF	600	0.310	Industrial O&M contract
UF	1500	0.220	Industrial O&M contract
UF	2500	0.205	Industrial O&M contract
UF	1000	0.245	Industrial O&M contract
UF	500	0.301	Industrial O&M contract
UF	2000	0.201	Industrial O&M contract
GAC	10	0.13	USEPA 1986
GAC	96	0.12	USEPA 1986
GAC	384	0.11	USEPA 1986
GAC	960	0.11	USEPA 1986
GAC	1920	0.11	USEPA 1986
GAC	480	0.11	Industrial O&M contract
GAC	120	0.12	Industrial O&M contract
GAC	2400	0.10	Industrial O&M contract
GAC	3600	0.10	Industrial O&M contract
RO	10	5.92	USEPA 1986
RO	38	2.35	USEPA 1986
RO	384	0.80	USEPA 1986
RO	3840	0.49	USEPA 1986
RO	10	3.37	Industrial O&M contract
RO	38	1.29	Industrial O&M contract
RO	192	0.68	Industrial O&M contract
RO	384	0.57	Industrial O&M contract
RO	1920	0.45	Industrial O&M contract
RO	3840	0.40	Industrial O&M contract

### 5.3.3.2 Water fit-for-use strategy

With the aim to size the treatment scheme for the defined scenarios, the three industrial sites (Figure SM 6) were evaluated in terms of non-potable water quality requirements and demands Table 63. Additionally, based on the results summarized in Table 56 and Table 57, it has been indicated if the evaluated technologies meet the water quality requirements or not. A water yield of 90 and 99% has been considered for both UF and CNM (or GAC) pre-treatments and a recovery of 70% has been estimated for RO.

As it is indicated in Table 63, the chemical industry presented a process water demand of 1500 m<sup>3</sup>/day, which required a conductivity below 250 µS/cm, chloride levels below 60 mg/L and a total hardness of 15 mg CaCO<sub>3</sub>/L. Additionally, COD and TOC maximum levels were 4 mg O<sub>2</sub>/L and 1.2 mg C/L. The same requirements were established for cleaning operations for stainless steel equipment (130 m<sup>3</sup>/day) and cooling towers supply (160 m<sup>3</sup>/day). Thus, to meet this water quality and cover these demands, quality of RO permeate was required. On the other hand, the cleaning operations for pavements (100 m<sup>3</sup>/day) presented lower quality requirements, with a maximum conductivity and chloride concentration of 4000 µS/cm and 1200 mg/L, respectively, which could be met with treated water with UF or CNM. Two different lines (UF+RO and CNM+RO) have been projected and are described in Figure 39, in which net production capacities of 2657 m<sup>3</sup> of UF or CNM permeate/day and 1790 m<sup>3</sup> of RO permeate/day are needed.

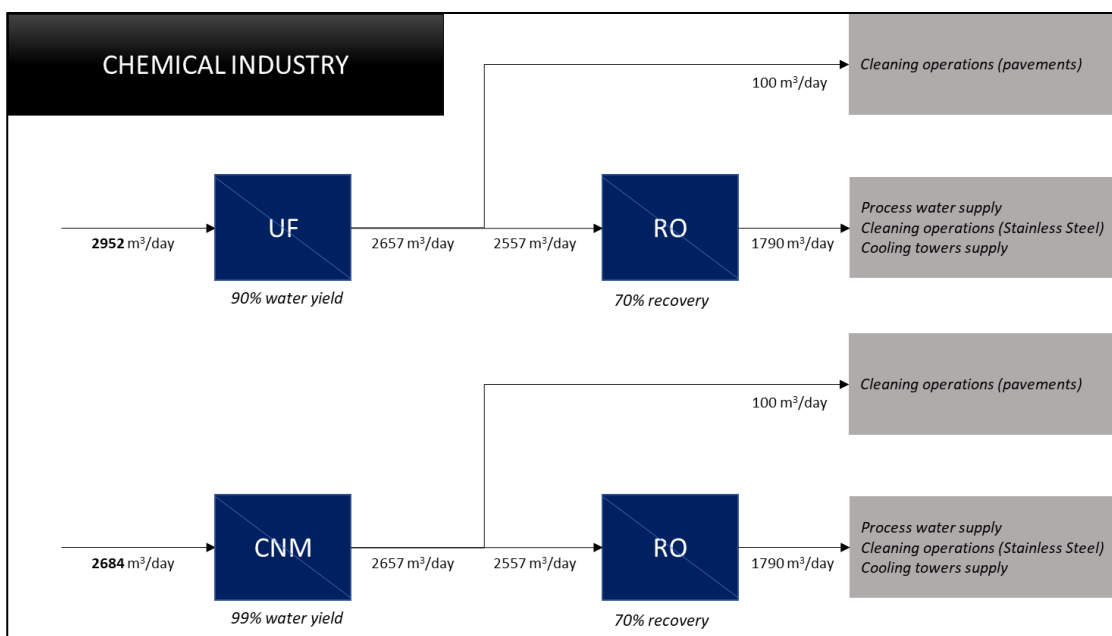


Figure 39 Projection of the decentralized water reclamation schemes in the chemical industry.

In the waste management industry (Figure 40), the main water consumption was for boiler feed (140 m<sup>3</sup>/day), in which lower conductivity and total hardness values lower than 700 µS/cm and 1 mg CaCO<sub>3</sub>/L were required.

Additionally, the industrial site had a daily consumption for cooling towers and reagents consumption of 50 and 25 m<sup>3</sup>/day, respectively, and had the same requirements for conductivity, apart from a limitation on turbidity. The possibility to blend both UF and RO permeates in a buffer tank to achieve the reduction of conductivity (but minimize the RO capacity) was excluded under request of the site, since it implied a higher control in order to minimize potential microbiological risk. Thus, the whole demand (215 m<sup>3</sup>/day) needs to be covered with RO permeate, which requires UF/CNM net permeate capacity of 307 m<sup>3</sup>/day.

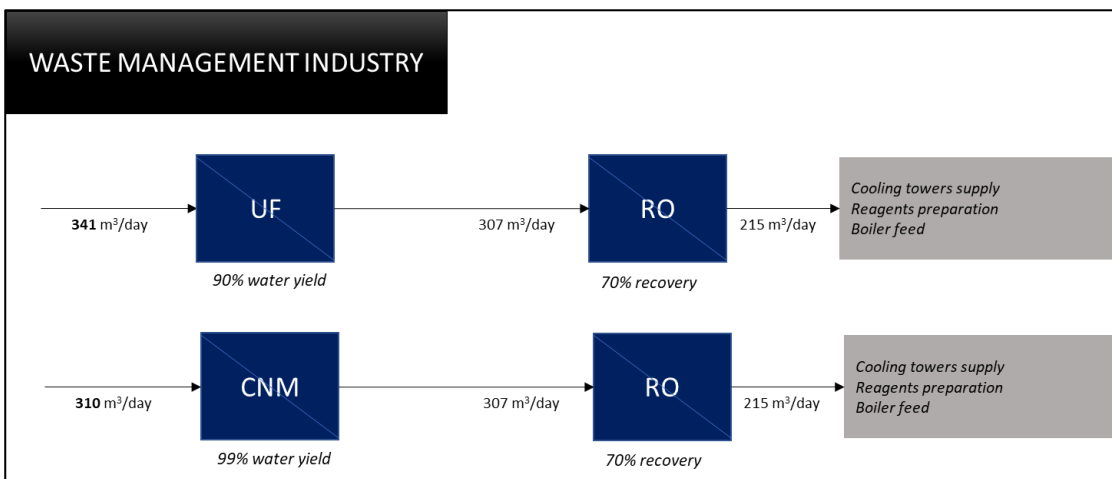


Figure 40 Projection of the decentralized water reclamation schemes in the waste management industry.

Finally, the electro-coating industry (Figure 41), requested 100 m<sup>3</sup>/day of process water supply, which requirements were lower conductivity than 250 μS/cm, lower chloride and total hardness concentrations than 250 mg/L and 1 mg CaCO<sub>3</sub>/L, respectively, and COD and turbidity values below 5 mg O<sub>2</sub>/L and 1 NTU, respectively. Based on the water quality, 100 m<sup>3</sup>/day of RO permeate are needed, which needs from 143 m<sup>3</sup>/day of UF/CNM net permeate.

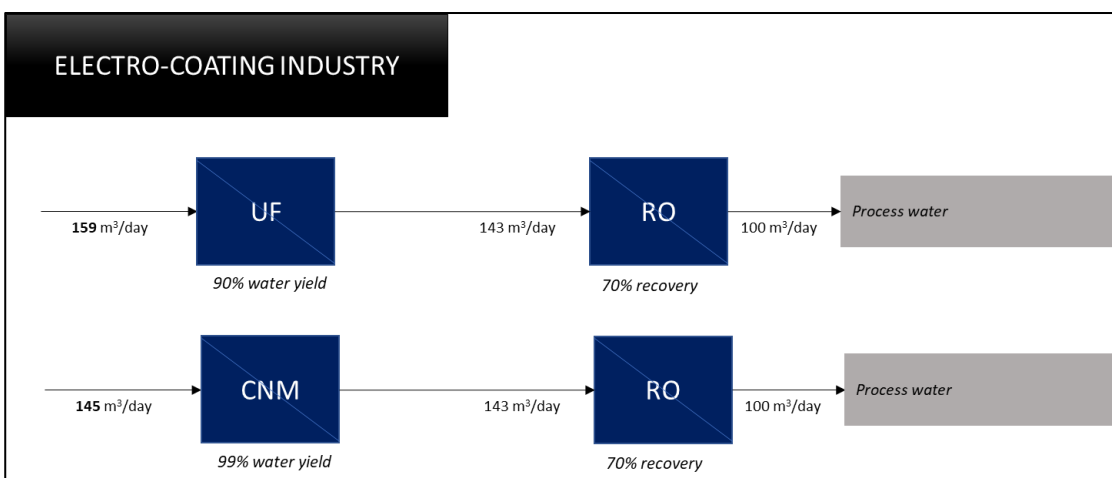


Figure 41 Projection of the decentralized water reclamation schemes in the electro-coating industry.

The water quality requirements provided by the industrial users are significantly more restrictive than the Spanish regulation (Royal Decree 1620/2007) for water reuse in industrial applications. The RD 1620/2007 limits the SS and turbidity concentration and microbiological activity but does not limit salinity, hardness, or chloride, which as it has been seen, are of major concern for industrial key players.



Table 63 Industrial water quality requirements regarding market segment and Spanish Royal Decree regulation

Industrial Market Segment / Effluent	Industrial Uses	Flow [m <sup>3</sup> /day]	pH [-]	Conductivity [μS/cm]	Chloride [mg/L]	Total Hardness (mg CaCO <sub>3</sub> /L)	Turbidity [NTU]	SS [mg/L]	COD [mg O <sub>2</sub> /L]	TOC [mg C/L]	UF	CNM	UF+RO	CNM + RO
Chemical	Process water (reactors)	1500	6.0 - 7.5	<250.0	<65.0	15.0	-	-	<4.0	<1.2	N	N	Y	Y
	Cleaning operations (Stainless steel equipment)	130	6.0 - 7.5	<250.0	<65.0	15.0	-	-	<4.0	<1.2	N	N	Y	Y
	Cleaning operations (pavements)	100	6.0 - 7.5	<4000.0	<1200.0	-	-	-	-	-	Y	Y	Y	Y
	Cooling towers supply	160	6.0 – 8.0	<250.0	<65.0	15.0	-	-	<4.0	<1.2	N	N	Y	Y
Waste Management	Cooling towers	50	6.5 - 9.0	<700.0	-	-	<15.0	-	-	-	N	N	Y	Y
	Chemical Reagents preparation	25	7.0 – 9.0	<700.0	-	-	<1.0	-	-	-	N	N	Y	Y

### 5.3.3.3 Economic analysis

The economic evaluation for the different industrial sites is described in Table 64. The current water source and demand of the industrial users is indicated, as well as its associated water cost. Moreover, the CAPEX and OPEX of the alternative decentralized schemes (UF+RO and GAC+RO) fed by municipal reclaimed water are depicted to estimate a total cost and potential savings.

These values have been calculated using the cost curves equations developed in this study and considering a depreciation for the electro-mechanical equipment of 10 years. A reclaimed water tariff of 1.26 €/m<sup>3</sup> has been used as mean indicative value suggested in a technical study (LEITAT, 2008) supported by the Catalan Water Agency, which is one of the main regulatory bodies in the territory.

Table 64 Economic evaluation for decentralized water reuse projects in the three industrial sites.

	Chemical Industry		Waste management industry		Electro-coating industry	
Current water source	Well + RO		Tap water + IEX		Tap water + RO	
Total water consumption for defined industrial uses	1890 m <sup>3</sup> /day		215 m <sup>3</sup> /day		100 m <sup>3</sup> /day	
Current water cost	1.05 €/m <sup>3</sup>		2.95 €/m <sup>3</sup>		3.80 €/m <sup>3</sup>	
Alternative water sources	UF + RO	GAC + RO	UF + RO	GAC + RO	UF + RO	GAC + RO
UF/CNM capacity	2657 m <sup>3</sup> /day	2657 m <sup>3</sup> /day	307 m <sup>3</sup> /day	307 m <sup>3</sup> /day	143 m <sup>3</sup> /day	143 m <sup>3</sup> /day
RO capacity	1790 m <sup>3</sup> /day	1790 m <sup>3</sup> /day	215 m <sup>3</sup> /day	215 m <sup>3</sup> /day	100 m <sup>3</sup> /day	100 m <sup>3</sup> /day
<b>Total CAPEX</b>	<b>963,786 €</b>	<b>396,110 €</b>	<b>219,941 €</b>	<b>146,757 €</b>	<b>136,934 €</b>	<b>102,270 €</b>
UF/GAC	776,824 €	209,148 €	147,786 €	74,603 €	89,171 €	54,507 €
RO	186,961 €	186,961 €	72,155 €	72,155 €	47,763 €	47,763 €
Depreciation UF/GAC	0.08 €/m <sup>3</sup>	0.02 €/m <sup>3</sup>	0.19 €/m <sup>3</sup>	0.10 €/m <sup>3</sup>	0.24 €/m <sup>3</sup>	0.15 €/m <sup>3</sup>
Depreciation RO	0.03 €/m <sup>3</sup>	0.03 €/m <sup>3</sup>	0.06 €/m <sup>3</sup>	0.06 €/m <sup>3</sup>	0.09 €/m <sup>3</sup>	0.09 €/m <sup>3</sup>
<b>Total OPEX</b>	<b>0.65 €/m<sup>3</sup></b>	<b>0.56 €/m<sup>3</sup></b>	<b>1.31 €/m<sup>3</sup></b>	<b>1.01 €/m<sup>3</sup></b>	<b>1.72 €/m<sup>3</sup></b>	<b>1.31 €/m<sup>3</sup></b>
UF/GAC	0.19 €/m <sup>3</sup>	0.10 €/m <sup>3</sup>	0.41 €/m <sup>3</sup>	0.11 €/m <sup>3</sup>	0.52 €/m <sup>3</sup>	0.11 €/m <sup>3</sup>
RO	0.46 €/m <sup>3</sup>	0.46 €/m <sup>3</sup>	0.90 €/m <sup>3</sup>	0.90 €/m <sup>3</sup>	1.20 €/m <sup>3</sup>	1.20 €/m <sup>3</sup>
<b>CAPEX + OPEX</b>	<b>0.76 €/m<sup>3</sup></b>	<b>0.61 €/m<sup>3</sup></b>	<b>1.56 €/m<sup>3</sup></b>	<b>1.17 €/m<sup>3</sup></b>	<b>2.05 €/m<sup>3</sup></b>	<b>1.56 €/m<sup>3</sup></b>
Reclaimed water tariff*	1.26 €/m <sup>3</sup>	1.26 €/m <sup>3</sup>	1.26 €/m <sup>3</sup>	1.26 €/m <sup>3</sup>	1.26 €/m <sup>3</sup>	1.26 €/m <sup>3</sup>
<b>Total Cost</b>	<b>2.02 €/m<sup>3</sup></b>	<b>1.87 €/m<sup>3</sup></b>	<b>2.82 €/m<sup>3</sup></b>	<b>2.43 €/m<sup>3</sup></b>	<b>3.31 €/m<sup>3</sup></b>	<b>2.82 €/m<sup>3</sup></b>
<b>Savings</b>	<b>-0.97 €/m<sup>3</sup></b>	<b>-0.82 €/m<sup>3</sup></b>	<b>+0.13 €/m<sup>3</sup></b>	<b>+0.52 €/m<sup>3</sup></b>	<b>+0.49 €/m<sup>3</sup></b>	<b>+0.98 €/m<sup>3</sup></b>

(\*) The reclaimed water tariff considered is an indicative value based on other references. An actual tariff has not been estimated in the demonstrated case study.

The chemical industry covers its current water demand (1890 m<sup>3</sup>/day) by applying a RO treatment on well-extracted water. Due to the relatively low costs of well exploitation in this area (compared with tap water supply),

their water cost was 1.05 €/m<sup>3</sup>. On the other hand, to use reclaimed water as an alternative requires an investment of 963.7 k€ for UF+RO and 396.1 k€ for GAC+RO. Additionally, considering both reclaimed water tariff and the exploitation cost (CAPEX + OPEX) of the polishing system, a total cost of 2.02 €/m<sup>3</sup> and 1.87 €/m<sup>3</sup>, respectively, is estimated. These costs are higher than the current one, thus instead of savings, to apply this reuse project would imply an additional economic cost for the industry.

In the case of the waste management industry, its current water demand (215 m<sup>3</sup>/day) is covered with tap water followed by an ion-exchange (IEX) stage for softening, which has a total cost of 2.95 €/m<sup>3</sup>. In this case, CAPEX was estimated in 219.9 k€ for the UF+RO and 146.7 k€ for the GAC+RO, and considering all exploitation costs and reclaimed water tariff, a total cost of 2.82 €/m<sup>3</sup> and 2.43 €/m<sup>3</sup> was estimated, which represent savings of 0.13 €/m<sup>3</sup> and 0.52 €/m<sup>3</sup>, respectively.

Finally, the electro-coating industry covers its demand for process water (100 m<sup>3</sup>/day) with tap water followed by RO, and accounts with a current cost of 3.80 €/m<sup>3</sup>. CAPEX of 136.9 k€ and 102.2 k€ have been estimated for UF+RO and GAC+RO, respectively, with a total cost of 3.31 €/m<sup>3</sup> and 2.82 €/m<sup>3</sup>, which represent savings of 0.49 €/m<sup>3</sup> and 0.98 €/m<sup>3</sup>, respectively.

## 5.4 Discussion

The novelty of the present study relies in the validation of a pilot-scale water reclamation scheme and the techno-economic assessment of decentralized water reuse systems to promote the use of municipal reclaimed water in the industrial sector. The two potential schemes (UF+RO and CNM+RO) are assessed from an operational perspective and a deep revision of economic data has been done to calculate generic cost curves for CAPEX and OPEX of the evaluated technologies, allowing the cost assessment in three industrial sites and providing relevant results to support decision making for new water reuse projects. A literature revision of similar published works has been done.

The technical feasibility and economic costs of several reclamation technologies has been reported by different authors, with special mention to water reuse projects in the agricultural sector. Racar et al. (2020) evaluated the use of MBR followed by NF/RO for crops irrigation, comparing with the WHO and EU 2020/741 guidelines the removal of main physico-chemical and microbiological parameters, and including also a revision of the detection and removal of organic micropollutants included in the Watch List (EU Decision 2015/495). Additionally, Nahim-Granados et al. (2020) assessed from a techno-economic perspective the implementation at industrial scale of different solar-based water purification processes for OMP removal and disinfection. Mendret et al. (2019) investigated the use of ozonation and RO for urban wastewater reclamation for a capacity of 125 m<sup>3</sup>/h and

assessed the economic savings of the potential reuse of the effluent. Moreover Uludag-Demirer et al. (2020) investigated Electrocoagulation for the reclamation of anaerobic digestion effluents, providing results of physico-chemical and microbiological parameters removal, as well as estimating its cost; and Zarebska-Molgaard et al. (2022) studied also the application of a combination between forward osmosis (FO) and Membrane Distillation (MD) to reclaim anaerobic digestion effluents, evaluating also generic costs.

Valuable information for the definition of DSS was obtained by Murashko et al. (2018) when analyzed the potential of implementing a closed-loop decentralized wastewater treatment and reclamation plant in a Finnish community. Four different scenarios were assessed considering two different technological setups, in which costs are estimated and compared in terms of CAPEX and OPEX. These results can be used to support the investment decision regarding different technological alternatives considering a fixed capacity; nevertheless, as well as previous mentioned works, these results do not consider the differences associated to scale and the added complexity of providing different qualities regarding considered uses.

Regarding promoting reuse in the industrial sector, Saidan (2020) quantified the water demand and reclamation needs in 395 industrial facilities in Jordan through a cross-sectional survey, obtaining valuable results regarding water consumption per employee and per ton of product, as well as wastewater disposal practices. Nevertheless, although potential volumes to be reused were identified, a very preliminary techno-economic analysis was provided, avoiding details on which technologies should be implemented and their CAPEX and OPEX. Wang et al. (2019) assessed the use of moving bed ceramic membrane bioreactor (MBCMBR) and reverse osmosis (RO) for municipal wastewater reclamation considering ultrapure water standards to be supplied to various industrial sectors in Singapore. In a similar work, Liu et al. (2020) assessed the use of an anaerobic fixed-film membrane bioreactor (AnfMBR) followed by RO for municipal water reclamation and compared its costs towards the existing NEWater facility in Singapore, concluding that about 37.5% reduction in total cost could be achieved due to an improvement in energy efficiency. Additionally, Shingwenyana et al. (2021) investigated a circular economy concept in the South African mining sector, specifically in the reclamation and valorization of acid mine drainage (AMD). CAPEX and OPEX was provided for a softening process followed by RO.

In a similar way to the present study, Pérez et al. 2022 evaluated a decentralized UF+RO system for municipal water reclamation in an industrial hub located nearby the Vuelta Ostrera WWTP (Spain). The authors assessed the optimal operational conditions and estimated the associated costs (CAPEX and OPEX) for three different scenarios (2.5, 5 and 20 m<sup>3</sup>/h) as well as potential savings regarding the current water cost.

## 5.5 Conclusions

The technical feasibility of the evaluated polishing treatment trains has been demonstrated through the operation and optimization during eighteen months of a treatment train located in El Baix Llobregat WWTP. Both pre-treatments, UF and CNM, allowed the removal of SS and turbidity, and a similar removal of dissolved organic matter. No significant differences were found in the RO performance in terms of organic fouling or scaling, regardless of the pre-treatment (UF or CNM) applied. In the case of CNM effluent, a permeability decline in RO of 5% was found, while in the case of UF effluent permeability remained steady.

On the other hand, regarding OMP, the use of advanced sorbents allowed high removals of triazines (67% and 97% for Terbutylazine and Atrazine respectively), while as expected UF presented relatively low removal efficiencies ( $\leq 25\%$ ).

Water quality requirements for the different uses of each of the three industrial sites have been gathered. The removal of dissolved salts (limited as maximum conductivity or chloride concentration) and hardness are the main requirements for most of the uses evaluated, as well as some limitations in COD or TOC. This clearly demands the use of desalination technologies such as RO, as it has been exposed in the full-scale treatment trains projection. On the other hand, it points out the non-alignment between regulation and end-users' requirements.

The economic feasibility has been evaluated for the three industrial scenarios, considering the water qualities and insights obtained from the prototype performance. In this line, the calculation of cost curves for both CAPEX and OPEX has allowed the estimation of economic scenarios for the three sites, considering both treatment schemes combinations (UF followed by RO and CNM/GAC followed by RO). Based on the results obtained, potential savings have been estimated considering the current cost of water accounted by the industrial users, and the estimated tariff of municipal reclaimed water that would feed the decentralized treatment.

The assessment indicates that the use of municipal reclaimed water for industrial applications is economically competitive in front of the use of tap water, which has the need to add polishing steps such as IEX or RO. On the other hand, the use of groundwater and its relatively low cost implied that, although it is necessary a RO step, the current cost of water is significantly lower than the one assumed for the water reuse project.

Beyond the economic results, and the fact that in one of the three cases the water reuse project was unfeasible from a cost perspective, other drivers need to be considered such as the preservation of freshwater resources and resilience strategies in front of climate change to guarantee water supply and industrial production.

## 5.6 Acknowledgments

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# Chapter 6



## 6. Chapter 6: Discussion

The novelty of this thesis relies in its contribution to the demonstration at industrial pilot scale of advanced reclamation technologies and its economic assessment. The work developed aids to compare from technical point of view different technological strategies for water reuse, providing tools to ease decision making through techno-economic indicators (OMP removal efficiency, CAPEX, OPEX and footprint) and contributing to unlock technical and economic barriers in its full-scale implementation.

Advanced wastewater treatments focused on OMP removal have been extensively evaluated from a technical point of view, understanding the removal mechanisms and the fate of different target compounds. Bourgin et al., (2017) demonstrated removal efficiencies higher than 80% for persistent OMP using ozone (0.55 g O<sub>3</sub>/g DOC) in the secondary effluent of the Swiss WWTP of Neugut. Regarding hybrid membrane processes for OMP removal, most of the results found were tested at lab or bench scale (Alvarino et al., 2016), claiming for the need to develop industrial pilot scale studies in order to evaluate stable and critical fluxes, long-term permeability's variation (Rezaej et al., 2019) and costs. Margot et al., (2013) compared at pilot scale the use of transformation mechanisms such as ozonation followed by sand filtration and the use of separation mechanisms such as PAC followed by UF; however, no economic assessment was provided. In this line, scarce data of pilot-scale or full-scale costs (CAPEX and OPEX) for advanced reclamation technologies for OMP removal has been found. **Chapter 3** and **Chapter 4** contribute to the demonstration and techno-economic assessment of a pilot scale PAC-MBR and tight UF system that were directly compared with a full-scale CAS+BWR system revamped with O<sub>3</sub>/UV and with a UF-RO (50% blend) treatment train.

Another key for the successful implementation of water reuse is the development of demonstration projects in coordination with key end-users to understand and guarantee their water needs (quality and quantity) through cost-effective treatment trains and match them with existing water quality regulations. Additionally, the development of tools for the rapid calculation of water reuse technologies cost represents a clear advantage in early stages of decision making to place value on the benefits (economic, environmental, and social) of using reclaimed water instead freshwater sources. Racar et al. (2020) evaluated the use of MBR followed by NF/RO for crops irrigation, comparing with the WHO and EU 2020/741 guidelines the removal of main physico-chemical and microbiological parameters, also including a revision of the detection and removal of organic micro-pollutants included in the Watch List (EU Decision 2015/495). Nahim-Granados et al. (2020) assessed from a techno-economic perspective the implementation at industrial scale of different solar-based water purification processes for OMP removal and disinfection. Mendret et al., (2019) investigated the use of ozonation and RO for urban wastewater reclamation for a capacity of 125 m<sup>3</sup>/h and assessed the economic savings of the potential

reuse of the effluent. Saidan (2020) quantified the water demand and reclamation needs in 395 industrial facilities in Jordan through a cross-sectional survey, obtaining valuable results regarding water consumption per employee and per ton of product, as well as wastewater disposal practices. Nevertheless, although potential volumes to be reused were identified, a very preliminary techno-economic analysis was provided, avoiding details on which technologies should be implemented and their CAPEX and OPEX. Wang et al. (2019) assessed the use of moving bed ceramic membrane bioreactor (MBCMBR) and reverse osmosis (RO) for municipal wastewater reclamation considering ultrapure water standards to be supplied to various industrial sectors in Singapore. In a similar work, Liu et al. (2020) assessed the use of an anaerobic fixed-film membrane bioreactor (AnfMBR) followed by RO for municipal water reclamation and compared its costs towards the existing NEWater facility in Singapore, concluding that about 37.5% reduction in total cost could be achieved due to an improvement in energy efficiency. Additionally, Shingwenyana et al., (2021) investigated a circular economy concept in the South African mining sector, specifically in the reclamation and valorization of acid mine drainage (AMD). CAPEX and OPEX was provided for a softening process followed by RO.

Valuable information for the definition of DSS was obtained by Murashko et al. (2018) when analyzed the potential of implementing a closed-loop decentralized wastewater treatment and reclamation plant in a Finnish community. Four different scenarios were assessed considering two different technological setups, in which costs are estimated and compared in terms of CAPEX and OPEX. Müller et al. (2020) explores in their research an innovative conceptual integration of water shortage risk and sustainability assessment as DSS in 'water scarcity-water reuse opportunities'. Ghafourian et al. (2021) evaluates the use of nature-based solutions (NBS) as suitable solution for water reuse, considering its economic impact and social-cultural benefits. Valizadeh et al. (2015) performed a cost analysis of a full-scale MF-RO system applied in an industrial WWTP treating oily wastewater. Foglia et al. (2021) and Canaj et al. (2021) assessed from an environmental (Life Cycle Assessment) and economic (Life Cycle Costing) perspective the implementation of an anaerobic MBR and disinfection system for reclaimed water reuse in agricultural irrigation in two different case studies in Italy. Moreover, Bolinches et al. (2021) proposes a method to quantify the CAPEX and OPEX and the benefits of boosting water reuse projects for agricultural irrigation in different WWTP of the Upper Guadiana area in Spain.

All these results can be used to support the investment decisions regarding different technological alternatives considering a fixed capacity; nevertheless, as well as previous mentioned works, these results do not consider the differences associated to scale and the added complexity of providing different qualities regarding considered uses. In Chapter 5 two potential schemes (UF+RO and CNM+RO) were assessed from an operation perspective and a deep revision of economic data was done to calculate generic cost curves for CAPEX and

OPEX of the evaluated technologies, allowing a cost assessment in three industrial sites and providing relevant results to support decision making for new water reuse projects. In a similar way, Pérez et al. (2022) evaluated a decentralized UF+RO system for municipal water reclamation in an industrial hub located nearby the Vuelta Ostrera WWTP (Spain). The authors assessed the optimal operational conditions and estimated the associated costs (CAPEX and OPEX) for three different scenarios (2.5, 5 and 20 m<sup>3</sup>/h) as well as potential savings regarding the current water cost.

In the following sections, a revision of literature is done with the aim to compare the results obtained in the studies published in this thesis framework regarding specific topics. The effect of PAC addition in membrane performance is discussed in section 6.1 and compared with the results obtained in Chapter 3 and Chapter 4. In section 6.2, OMP removal mechanisms and efficiencies in reclamation technologies reported by several authors is compared with the results obtained in Chapter 3 and Chapter 4. In section 6.3, a revision of quality requirements of end-users is compared with the status of regulations and official guidelines, pointing out the non-alignment between regulation and end-users' requirements assessed in Chapter 5. Finally, in section 6.4, a revision of published works in which cost curves are calculated is done and compared with those obtained in Chapter 5. CAPEX and OPEX of technologies assessed in Chapter 3 and Chapter 4 are also compared with the results obtained from other authors.

## **6.1 Hybrid membrane systems: The effect of PAC addition in membrane performance.**

### **6.1.1 The effect of PAC addition in MBR systems**

Remy et al. (2009) reported bench-scale results of two MBR (submerged UF) set ups operated at 50 LMH for 50 days, one of them without PAC addition and the other one with a continuous dosing of 4 mg PAC/L of raw wastewater and a fixed concentration of 0.5 g PAC/L of reactor controlled through sludge purges. Improvements of 10% in critical flux and filtration time could be increased at least twice. Different PAC dosages (2 and 5 mg PAC/L of wastewater) were also validated by Torretta et al. (2013) at lab-scale, achieving an improvement between 16 and 26%. At industrial-pilot scale, Martí-Calatayud et al. (2020) validated the treatment of an industrial wastewater effluent (35 m<sup>3</sup>/day), which contained organic pesticides and reported a notably lower permeability decline when PAC was dosed. Hu et al. (2014) validated also at pilot-scale (1.2 m<sup>3</sup>/h) the application of high PAC doses in batch mode, demonstrating that a fixed PAC dose of 1 or 2 g/L in the reactor lead to a reduction of permeate flux. Regarding the role of PAC in foulants sorption, Ying and Ping (2006) found minor differences in the fraction of COD and TOC in an aged MBR sludge supernatant operating with and without PAC, which seem to indicate that large organic molecules may not react with the active surface, which is likely to



happen in microporous PAC. Additionally, according to Wu and Zhao (2011), PAC could lead to a strengthening of the sludge flocks. Results found in **Chapter 3** indicated that a more stable permeability is obtained when PAC is added; nevertheless, in discordance with other publications, PAC addition did not allow to improve filtration flux or reduce chemical cleanings needs.

### **6.1.2 The effect of PAC addition in tight UF systems**

Krashtover et al. (2018) indicated in their review of the state of the art on this technology the contradictory results reported by different authors regarding the expected operational benefits and synergistic effects of PAC addition in UF membrane systems (Meier and Melin, 2005).

From one hand, Lee et al., (2007) reported the improvement in permeate flux decline (30%–40%) by comparing bench-scale PAC-UF performance at different doses (0, 50, 100 and 150 mg PAC/L). Despite the best improvement achieved at a dose of 100 mg PAC/L, regarding baseline conditions, practical operational time was relatively short with a total filtration time of 80 minutes. Additionally, despite applied backwash allowing a successful recovery of the permeability values, the irreversible fouling was not assessed deeply as the operational runs were very short. Yiantsios and Karabelas, (2001) reported no significant flux decline at 10 mg PAC/L nor a measurable improvement associated to PAC addition. Authors concluded that the dissolved and colloidal organic matter reduced the PAC deposition onto the membrane surface.

On the other hand, results obtained in Chapter 4 clearly show that in terms of UF membrane permeability, a more rapid decline was found when PAC was added compared with tight UF operated without PAC addition. Moreover, it was mandatory to operate the PAC-UF system with moderate (0.6 m/s) crossflow velocity when low PAC doses were applied (20 mg/L) or high crossflow velocities (0.8-1.0 m/s) when medium or high PAC doses were applied (50-100 mg/L). In line with these results, Lin et al. (1999), was the first author describing that the PAC dosing in combination with UF to reduce membrane fouling yields negative effects, being ineffective in removing the organic matter with MWs lower than 0.3 kDa or greater than 17 kDa. Additionally, Li and Chen (2004) also reported higher membrane fouling indicators when PAC was applied. From these dates not too much effort has been described until the results generated in this work.

## **6.2 Conventional and Advanced reclamation technologies for OMP removal**

In the following section, the removal efficiency of four recalcitrant OMP is assessed in the different validated reclamation systems. From one hand, in Table 65, results obtained in Chapter 3 in PAC-MBR are compared with those obtained in conventional MBR (without PAC) and basic water reclamation systems based on coagulation-

flocculation, ballasted sedimentation, disk filtration and disinfection. A revision of the main results reported in literature has been done.

As it can be seen, low removal rates (<20%) were also found for CBZ in conventional MBR, finding no improvement regarding CAS+BWR. This can be related to its relatively low lipophilicity ( $\log K_{ow}$  of 2.5 and 2.7 respectively) and hard biodegradation ( $k_{biol} < 0.01$ ) (Serrano et al., 2011; Suarez et al., 2010). Additionally, Alvarino et al. (2016) indicates that its difficult biological transformation may be associated to the presence of heterocyclic N-containing aromatic rings. However, significant improvement was found in the removal of DCF, ERY and SMX. The use of UF membranes instead of settlers cannot explain the removal of OMP since the MW (from 0.232 to 0.734 kDa) of these compounds is lower than the MWCO of UF (1 to 10kDa). Gu et al. (2018) and Reif et al. (2011) proved that high SRT imply a higher biodegradability of some compounds, related to a higher microbial activity powered by a higher biomass growth. Additionally, Alvarino et al. (2017) indicated that the formation of biofilm on the sorbent surface could contribute to a higher biodegradation of OMP and correlated it with a higher nitrification.

The addition of PAC in the MBR allowed to significantly improve the removal of recalcitrant compounds as it was in this thesis, in consistence with the results reported in literature. CBZ removal was increased up to 76% by adding 50 mg of PAC/L of wastewater, which can be explained through its  $\log D$  value (1.9) which defines its adsorption potential on the active surface ( $\log D > 1$ ). In the present work, no significant improvement was found in DCF and ERY when PAC was dosed regarding MBR without PAC. Nevertheless, other authors such as Nguyen et al. (2014) and Serrano et al. (2011) demonstrated that the use of PAC in biological systems leads to a slower and more efficient biodegradation of soluble compounds. Zhang et al. (2019) reported an improvement in the microbial biodiversity when PAC was added, compared to conventional MBR. Finally, regarding SMX, despite its low adsorption potential ( $\log D < 1$ ), results obtained showed an improvement up to 88% of removal, which can be explained through a fostering of the liquid-solid equilibrium.

In Chapter 3, the application of AOP processes (e.g.,  $O_3/UV$ ) for OMP was demonstrated as potential revamping of conventional CAS+BWR and technological alternative to hybrid membrane systems (e.g., PAC-MBR or PAC-UF). OMP may be degraded by a direct reaction with ozone, which is a selective agent (Hansen et al., 2016), or by reacting with generated hydroxyl radicals produced spontaneously in its decomposition, which act unselectively (Lee et al., 2012). UV itself is not considered an efficient treatment for OMP removal; nevertheless, its combination with ozone aids to accelerate the generation of hydroxyl radicals (Gorito et al., 2021). Therefore, the combination of both reaction kinetics, defined as a second order reaction between OMP, ozone and hydroxyl

radicals, can contribute to understand and predict their behavior and have a first approach on design these systems (Gomes et al., 2017).

Ozone doses of 6 and 9 mg O<sub>3</sub>/L were applied (Chapter 3), maintaining a constant UV dose of 400 J/m<sup>2</sup>, obtaining very high removal efficiencies (>90%) for the analyzed OMP. Specifically, CBZ, DCF and SMX presented removal rates applying both ozone concentrations, which can be correlated to a kinetic constant ( $k_{O_3}$ ) higher than 10<sup>4</sup> M<sup>-1</sup>·s<sup>-1</sup> (Gomes et al. 2017). On the other hand, ERY showed lower removal rate at 6 mg/L than at 9 mg/L, which can be explained by its lower concentration measured in the inlet (62 ng/L) regarding the rest of analyzed OMP (100-300 ng/L).

In Chapter 4, OMP removal efficiencies measured in PAC-UF were compared with those obtained in conventional UF-RO (50% blend) quaternary systems. Conventional UF as RO pre-treatment presented removal efficiencies below 15% for the five target OMP evaluated. These low removal ratios are related to the MWCO of the UF membrane (>3 kDa), which is significantly higher than the MW of the evaluated compounds (Table 30; Chapter 2). Vona et al. (2015) indicated that only partial sorption of highly hydrophobic compounds can be expected on the membrane surface due to weak Van der Waals and London interactions. Additionally, López-Fernandez et al. (2016) proposed the potential adsorption of lipophilic compounds ( $\log k_{ow} > 2.5$ ) to poly-vinyl difluoride (PVDF) groups of the UF membranes

Tight UF without PAC presented similar behavior than conventional UF in terms of target OMP removal efficiencies, which is related to its associated MWCO (1kDa). Nevertheless, by upgrading the tight UF performance with PAC addition, removal efficiency for CBZ was raised to 88%. DCF and ERY, presented similar behavior, achieving removal efficiencies over 70%. Sheng et al. (2016) evaluated the removal efficiencies of mentioned OMP among others at different PAC doses (10, 50 and 100 mg/L) through the application of PAC-UF systems, achieving similar results with the exception of DCF. Regarding SMX, results found in Chapter 4 allowed relatively low removal efficiencies (25%±18%) when PAC doses of 20 mg/L were applied. Its low sorption constant (e.g.,  $\text{LogD} < 1$ ) indicates that this compound does not present a high tendency for being sorbed to the activated carbon structure. The results on the removal of SMX are consistent with those obtained by Sheng et al. (2016) who reported a lower removal for PAC doses of 10 mg/L, in the same way Löwenberg et al. (2014), reported similar values for PAC doses of 20 mg/L.

The thin-film composite RO membranes present an aromatic polyamide-based active layer, and although being a non-porous structure, some authors assigned MWCO<0.25 kDa (De Boer et al., 2022; Taheran et al., 2016) for providing a discussion oriented to consider the size of the compound. A filtration test allowed the reduction

of concentration values below the LOD of all evaluated target OMP and achieved a removal efficiency over 95%. The high efficiencies of RO membranes for OMP removal have been largely reported in literature. Taheran et al. (2016) reported the rejection of target OMP with RO and FO in several studies for MBR and groundwater filtration. Comerton et al., 2008 and Radjenovic et al., 2009 achieved removal efficiencies over 97% for CBZ, DFC and SMX. Moreover, Foureaux et al. (2019) achieved concentrations in the permeate stream below the LOD for all measured compounds when applied to surface water filtration.

Table 65

PHAR	Chapter 3				Chapter 4	
	CAS+BWR	CAS+BWR+AOP (2-6 mg/L)	MBR	PAC-MBR (10-60 mg/L)	PAC-UF (20-50 mg/L)	UF+RO
CBZ	6%±7% (Echevarria et al. 2019)	<b>97%±2% - 96%±2%</b> (Echevarria et al., 2019) >90% (Lee et al., 2012) 97%±4 % (Margot et al., 2013) 100% (Yang et al., 2017)	<b>10%±1%</b> (Echevarria et al. 2019) 28% (Tiwari et al., 2017) <10% (Alvarino et al., 2017) 13% (Tadkaew et al., 2011)	<b>76%±3%</b> (Echevarria et al. 2019) >90% (Alvarino et al., 2017) 60-90 % (Nguyen et al., 2014)	<b>88%±10%</b> (Echevarria et al. 2020) >95% (Löwenberg et al., 2014) 40%-85% (Sheng et al., 2016) 80-85% (Vona et al., 2015)	<b>98%±1%</b> (Echevarria et al. 2020) 98% (Comerton et al., 2008) 98% (Radjenovic et al., 2009)
DCF	49%±35% (Echevarria et al. 2019)	<b>&gt;99%</b> (Echevarria et al., 2019) 100% (Moreira et al., 2015) 100% (Rivera-utrilla et al., 2013) >96% (Ternes et al., 2003) 94±3 (Margot et al., 2013)	<b>79%±3%</b> (Echevarria et al. 2019) 15-87 % (Besha et al., 2017) >60% (Alvarino et al., 2017) 17±4 % (Tadkaew et al., 2011)	<b>77%±5%</b> (Echevarria et al., 2019) >98% (Besha et al., 2017) >95% (Alvarino et al., 2017) 95-60% (Nguyen et al., 2014)	<b>70%±26%</b> (Echevarria et al., 2020) 80-85% (Löwenberg et al., 2014) 20%-100% (Sheng et al., 2016) >99% (Vona et al., 2015)	<b>99%±0%</b> (Echevarria et al. 2020) >99% (Radjenovic et al., 2009)
ERY	19%±28% (Echevarria et al. 2019)	<b>72%±1% - 94%±4%</b> (Echevarria et al., 2019) >92 % (Ternes et al., 2003) >95% (Yang et al., 2017)	<b>80%±4%</b> (Echevarria et al. 2019) >80% (Dólar et al., 2012) >80% (Alvarino et al., 2017) 91% (Reif et al., 2008)	<b>59%±2%</b> (Echevarria et al. 2019) >88% (Besha et al., 2017) >99% (Alvarino et al., 2017)	<b>67%±36%</b> (Echevarria et al. 2020)	<b>96%±1%</b> (Echevarria et al. 2020)
SMX	61%±15% (Echevarria et al. 2019)	<b>96%±1% - 98%±1%</b> (Echevarria et al., 2019) 93%±7 % (Margot et al., 2013) 100% (Lee et al., 2012) 99% (Rivera-utrilla et al., 2013) >92% (Ternes et al., 2003) 100% (Yang et al., 2017)	<b>64%±3%</b> (Echevarria et al. 2019) 81% (Tiwari et al., 2017) >70% (Alvarino et al., 2017) 92% (Tadkaew et al., 2011)	<b>88%±2%</b> (Echevarria et al., 2019) 70% (Alvarino et al., 2017)	<b>25%±18%</b> (Echevarria et al., 2020) 65-70% (Löwenberg et al., 2014) 25%-100% (Sheng et al., 2016) 68%-95% (Vona et al., 2015)	<b>96%±2%</b> (Echevarria et al. 2020) 99% (Comerton et al., 2008) >99% (Radjenovic et al., 2009)

### 6.3 Fit for use water approach

The reclaimed water quality requirements of three industries were assessed in Chapter 5. A significant difference was found regarding the quality needs provided by the case studies and the current Spanish Regulation (RD 1620/2007), which only considered SS, Turbidity, and microbiological parameters, while hardness, iron, silica and salinity are the impurities of major concern, specifically in boiler feed and cooling water. In other water reuse regulations revised in Chapter 1 such as in California, Texas and Florida (USA), do not consider neither dissolved salts nor other ions for industrial uses.

In boiler feed, the concentration limit of impurities recommended by the APAVE (Association of electrical and steam unit owners), the ABMA (American Boiler Manufacturers Association) and water technology firms (e.g Lenntech, Suez Water Technologies and Solutions, Veolia Water Technologies) is dependent on the design conditions (flow, pressure, and heat transfer rate). Water quality requirements in boiler feed are summarized in Table 66.

Table 66 Water quality recommendations for boiler feed reported by APAVE and ABMA.

Reference	APAVE and ABMA			
Industrial use	Boiler feed			
Working pressure	0-20 bar	21-40 bar	40-60 bar	60-100 bar
pH	7.5-10	7.5-10	7.5-10	8.5-10
Dissolved Oxygen [mg/L]	0.040	0.040	0.007	0.007
Oily matter [mg/L]	1.0	1.0	0.5	0.5
Total Iron [mg/L]	0.10	0.05	0.03	0.01-0.02
Total copper [mg/L]	0.050	0.025	0.020	0.015-0.010
Total hardness (CaCO <sub>3</sub> ) [mg/L]	0.3	0.3	0.2	0.1-0.05
Non-volatile TOC [mg/L]	1	1	0.5	0.2

Most of industrial facilities account with demineralization units to adapt tap or groundwater quality to their industrial uses' standards. In this sense, it is usual to find RO, Electrodialysis Reversal (EDR) or Electrodeionization (EDI) plants operated by the end-users to guarantee water supply quality. When reclaimed water is intended to be reused, one possibility is to produce and distribute suitable reclaimed water to feed the existing polishing plants or boost the implementation of decentralized polishing schemes (**Chapter 5**) fed with a basic reclaimed water quality, easing the implementation when the same user requires different water qualities.

An emblematic case study for municipal reclaimed water reuse in industries is the case of West Basin Municipal District (California, USA). The water reuse system accounts with a centralized WRP (Edward C. Little Water Recycling Facility) and three satellite plants (Chevron Nitrification Plant, Juanita Millender-McDonald Carson

Regional Water Plant and Torrance Refinery Water Reclamation Plant) with a flexible scheme able to produce five different types of reclaimed water (Table 67). Based on the water type, a different tariff is applied. Similar results were obtained in **Chapter 5**.

*Table 67 Water Reclamation trains, reclaimed water uses and tariffs for the different facilities integrating the West Basin Municipal Water District*

<i>Water quality</i>	<i>Treatment train</i>	<i>Uses</i>	<i>Tariff [\$/m<sup>3</sup>]</i>
<i>Disinfected tertiary effluent (Tittle 22)</i>	Physicochemical + UV	Irrigation Industrial uses (cleaning)	0.74-0.77
<i>Denitrified effluent</i>	Biological nitrification-denitrification system	Industrial (Cooling towers)	0.76
<i>Advanced tertiary effluent</i>	MF+RO+UV/H <sub>2</sub> O <sub>2</sub>	Groundwater recharge	0.47-0.90
<i>RO (1 step) permeate</i>	RO (1 step)	Low pressure boiler feed	0.96
<i>RO (2 steps) permeate</i>	RO (2 step)	High pressure boiler feed	1.25

## 6.4 Cost estimation tools a useful tool for decision making

Historically, the calculation of CAPEX in wastewater reclamation plants and distribution networks has been based on a detailed engineering project assessment, being considered specific aspects such as sizing and selection of commercial equipment, construction materials and instrumentation, and the evaluation of site adaptation requirements (Raj Sharma 2010). The preparation of these assessments is time consuming and requires the implication of experts from technologies providers.

In Chapter 5, cost curves based on Williams Law were estimated for three different technologies (UF, GAC/CNM filters, and RO) applied for municipal wastewater reuse. Guo et al. (2014) provided cost curves for different technologies, most of them evaluated in this thesis such as MBR, UF, GAC and RO applying a logarithmic variant of the Williams Law cost function.

Regarding UF, to calculate CAPEX and OPEX cost curves, 8 and 13 quotations were used respectively (Figure 37 and Figure 38; Chapter 5). These correspond to ultrafiltration plants which capacity ranged from 80 to 2800 m<sup>3</sup>/day. Considering mentioned capacity range, UF CAPEX and OPEX might vary between 1150 and 255 €/m<sup>3</sup>/day and 0.59 and 0.21 €/m<sup>3</sup>, respectively. Iglesias (2017) reported a CAPEX range between 312 and 158 €/m<sup>3</sup>/day for UF plants in municipal water plants with capacities ranging from 1000 to 25000 m<sup>3</sup>/day, which are consistent with the results obtained in this study. Additionally, Perez et al., (2022) provided lower CAPEX values (232 €/m<sup>3</sup>/day) for a UF capacity of 480 m<sup>3</sup>/day, but similar OPEX (0.316 €/m<sup>3</sup>). Drouiche et al. (2001) reported

a UF system in a DWTP of the Kabylia region (Algeria) a total cost (CAPEX+OPEX) of 0.234 €/m<sup>3</sup>, being depreciation over 15 year period the largest expense (0.117 €/m<sup>3</sup>)

For sorbent filters (GAC/CNM), quotations for capacities ranging from 95 to 3000 m<sup>3</sup>/day were collected. Obtained results indicated that CAPEX and OPEX might vary between 445 and 55 €/m<sup>3</sup>/day and 0.13 and 0.11 €/m<sup>3</sup>, respectively. Similar results were obtained by Plumlee et al. (2014), who provided also OPEX cost curves for biological activated carbon (BAC) filters ranging from 0.15 to 0.10 €/m<sup>3</sup>.

In the case of RO cost curve calculation, quotations of water reclamation plants presenting recoveries between 50 and 75% and capacities between 28 and 2760 m<sup>3</sup>/day were used. CAPEX and OPEX varied from 675 to 91 €/m<sup>3</sup>/day and 5.92 to 0.49 €/m<sup>3</sup>. Lower costs were reported by Perez et al., (2022) when assessed RO costs for 480 m<sup>3</sup>/day (66 €/m<sup>3</sup>/day for CAPEX, and 0.256 €/m<sup>3</sup> for OPEX). This might be related to the assumptions made regarding pumping efficiency, since the authors considered pumping efficiency and the energy cost a fix cost (0.139 €/m<sup>3</sup>) nondependent on scale. In Chapter 4, results obtained from techno-economic assessment indicated an OPEX of 0.31 €/m<sup>3</sup> without depreciation, considering the whole UF+RO system (15,000 m<sup>3</sup>/day), from where RO accounted with 0.25 €/m<sup>3</sup>. Similar results were found by Akgul et al. (2008) who indicated a fixed OPEX of 0.24 €/m<sup>3</sup>.

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# Chapter 7

## 7. Conclusions and outlook

Water reuse needs to respond to rising water availability in front of water scarcity, but also represents an opportunity to capture economic benefits of wastewater and boost an economic return on the capital expenditures associated to the water cycle infrastructure and operation and maintenance costs. Reclaimed water and its reuse are one of the main vectors in bio-factories, together with energy, nutrients, and other valuable resources.

In **Chapter 1**, the main barriers in water reuse implementation were explained. Firstly, the presence of contaminants of emerging concern in the effluents of conventional wastewater and reclamation schemes, and their consequent concentration in the water cycle when water is reused, has awakened concern in public authorities, specifically when high water quality or sensitive applications are planned (e.g., IPR, agricultural or industrial uses). The occurrence and fate of OMP in conventional wastewater and reclamation systems have been reviewed, together with the main mechanisms involved in their removal, the main advanced treatment technologies available and the existing legal framework. The research developed in this PhD thesis framework tackles the demonstration of advanced reclamation trains for OMP removal and water reuse, considering its costs and technical advantages such as the non-generation of brines (e.g., PAC-MBR, PAC-UF or O<sub>3</sub>/UV), which account with added difficulties in their management. Additionally, the feasibility and economic benefits of boosting the use of municipal reclaimed wastewater for industrial uses was demonstrated, together with the calculation of cost curves for decision making.

The key findings and conclusions of this PhD thesis are depicted below, together with an outlook and future prospects proposal.

### 7.1 Advanced wastewater reclamation technologies for OMP removal

#### 7.1.1 How OMP removal should be addressed?

The removal mechanisms of OMP are driven by the physico-chemical properties of each compound. A single technology cannot guarantee the total removal of a wide range of OMP or avoid the generation of by-products (brines, spent sorbents or metabolites) that need to be properly managed. In this sense, it is necessary to combine different treatment steps in the most efficient way.

Many OMP are effectively removed in conventional biological processes since present a high biodegradability potential measured through their biological transformation rates ( $k_{\text{biol}}$ ). Those compounds that are not removed in CAS need to be tackled with advanced wastewater treatment (and reclamation) technologies to ensure their



removal, mostly prior to reuse reclaimed water. Where to tackle this recalcitrant compound to guarantee its removal is another important issue to consider. For example, a WRP may not be able to reuse a reclaimed water effluent due to an unacceptable concentration of a certain compound (included in the WFD Priority Pollutants List). In this sense, if this compound can be tracked and its source of pollution is detected, a decentralized advanced wastewater treatment scheme can be proposed. Some examples can be specific pharmaceuticals used in hospitals or present in industrial wastewater effluents (e.g., pharma, oil and gas, chemical industrial sectors), that could be directly removed or transformed prior to reach municipal WWTP/WRP. On the other hand, when OMP arrival is associated to the consumption of anthropogenic products in households, or pesticides from agricultural runoffs, centralized schemes need to be addressed

### **7.1.2 Evaluation of upgrading strategies for OMP removal.**

In Chapter 3, the removal of different OMP, including two compounds present in the EC Watch List (DCF, ERY), was assessed in a conventional wastewater treatment and reclamation scheme (CAS-BWR) in El Baix Llobregat WWTP/WRP and a pilot-scale MBR. The results obtained demonstrated the limited removal capacity for some OMP in CAS-BWR or MBR, and how by upgrading these systems with an additional ozonation-UV step or by adding a sorbent (PAC), it is possible to achieve, for these recalcitrant OMP, removal efficiencies over 85 and 75% respectively.

In Chapter 4 the removal of recalcitrant OMP was assessed, concluding that UF-RO (50% blend) allowed to achieve average removal efficiencies between 50 and 60% for analyzed OMP, taking into account the limited removal efficiency of conventional UF membranes (<15%) and the very high rejections achieved with RO (>95%). Additionally, PAC-tight UF applying a PAC dose of 20 mg/L achieved average removal efficiencies over 80% for CBZ and DIU and over 70% for DCF and ERY. In the case of SMX, the removal efficiency found was relatively low (<30%), since the compound does not have a high tendency to be sorbed by the activated carbon.

Figure 42 summarizes the treatment schemes evaluated.

From one hand, MBR account with some benefits in terms of space reduction and water quality regarding other schemes evaluated in this study. To replace settlers by membranes accounts with a 50-45% of space reduction, and the water obtained through UF filtration is better than after CAS-BWR in terms of solids, turbidity and microbiological parameters, suitable to feed RO. Additionally, no intensive disinfection (UV-Cl<sub>2</sub> / O<sub>3</sub>-UV) is needed. The upgrading of MBR through the dosage of PAC allowed significant advantages in terms of OMP removal and a more controlled membrane fouling. Additionally, sorbed OMP into the sludge are purged and after



the sludge thickening and drying can be disposed as a solid in landfills. The potential OMP desorption from PAC and sludge should be further investigated prior to propose the use of stabilized sludge in agricultural applications.

Ozonation-UV as transformation process presents the advantage of being possible to achieve mineralization of OMP instead of concentrating them in spent sorbents or brines. Nevertheless, the partial transformation would lead to the generation of metabolites, some of them potentially hazardous for human health or the environment. The inclusion of a final step based on Biologically Activated Carbon (BAC) filters can allow the removal of this compounds.

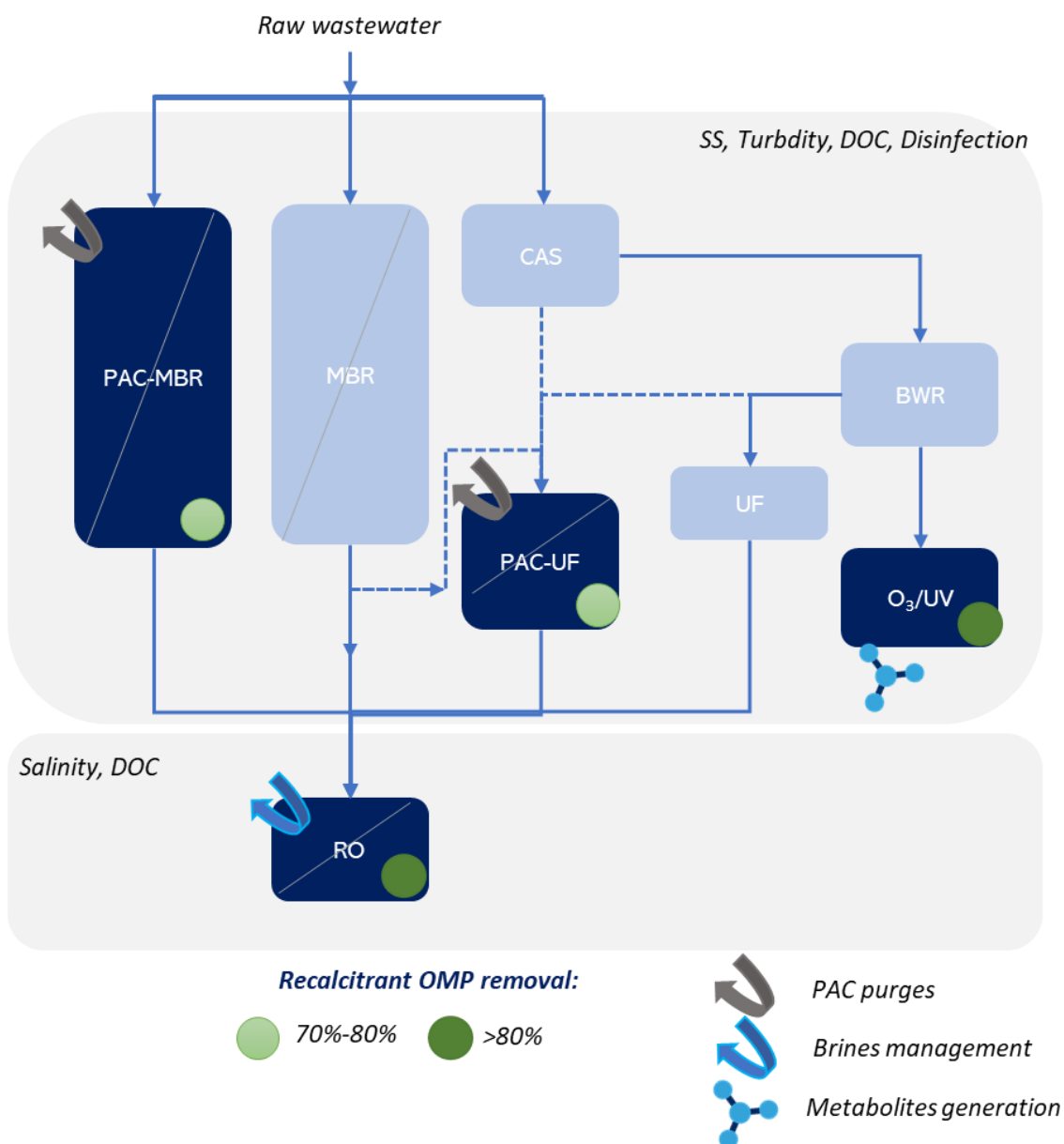


Figure 42 Treatment train proposal of upgrading strategies for OMP removal

In terms of the economic analysis, OPEX results indicated that PAC-MBR is the most expensive option regarding conventional systems (CAS-BWR) or the inclusion of ozonation-UV post-treatment. Ozonation-UV as a final polishing step presented several advantages regarding PAC-MBR in terms of OPEX, although it has a higher CAPEX. Additionally, compared to PAC-MBR, removal efficiencies were better for both ozone doses tested.

Summing-up, ozonation-UV seems to be the best option for upgrading existing projects, where only an additional 15% of space is required and the post-treatment is assembled directly to the conventional system. On the contrary, PAC-MBR should be considered when space represents a critical limitation; reclaimed water is intended to be reused in high quality water uses (e.g., industrial, potable reuse) by feeding a RO post-step to guarantee salinity removal. Additionally, as decentralized wastewater treatment to guarantee the removal of recalcitrant OMP in identified and complex wastewater sources such as target industries (e.g., pharma, oil and gas, chemical) and hospitals.

Undoubtedly, RO represents the most robust option in terms of OMP removal efficiency (>95% for most of recalcitrant OMP assessed); nevertheless, its relatively high associated treatment cost leads to by-pass UF permeate and produce tailored blends that account with lower costs. As it has been explained, the El Baix Llobregat WRP has a 50% blend UF-RO system; thus, since UF presents very limited OMP removal capacity, removal capacities for the UF-RO system did not exceed 60% for evaluated compounds. PAC-UF allowed relatively high OMP removal, comparable to UF-RO (50% blend) systems but did not allow the rejection of dissolved salts. In this sense, regarding the reclaimed water uses foreseen, one of the main advantages of PAC-UF is that rejection stream, which mainly contains used PAC and organic matter, can be recycled to upstream units (CAS or MBR), providing operational advantages if PAC still accounts with sorption capacity. On the other hand, the use of RO allowed the complete removal of most of the OMP evaluated together with salinity; however, these are concentrated in a brine that needs to be adequately managed. Thus, in coastal areas in which brine can be disposed through marine outfalls, UF-RO seem to be an adequate system, while in inland facilities, PAC-UF can present an advantage when reclaimed water is intended to be reused for groundwater recharge but salinity does not represent a limitation. A final combination could be the use of PAC-MBR or PAC-UF followed by a RO step, allowing the sorption of OMP into PAC instead of concentrating them into brines, easing brine management or disposal afterwards.

### **7.1.3 Evaluation of the synergistic effects in hybrid membrane systems**

The synergistic effects of adding PAC in MBR and UF were assessed (Chapter 3 and Chapter 4) with the aim to quantify the removal in OMP and the improvements in terms of reduction of membrane fouling and OPEX. Results obtained in Chapter 3 suggest that the use of PAC allow an average removal of 75% for recalcitrant

OMP such as CBZ, DIU, ERY, DCF and SMX. Nevertheless, despite achieving a more stable fouling profile, PAC addition do not allow to decrease membrane cleaning frequency or increase filtration flux, and thus, cannot compensate the OPEX increase associated to the relatively high cost of PAC (0.06 to 0.1€/m<sup>3</sup>) considering a PAC cost of 2.5 €/kg. Thus, based on these results, PAC should not be added unless OMP removal is required. As mentioned in the discussion section, some industrial pilot scale or full-scale PAC-MBR references (e.g., Marti-Calatayud et al. (2020) and Hu et al. (2014)) have been found, and despite reporting a lower permeability decrease due to PAC addition and a stronger sludge floc structure, no improvements from an economic perspective have been quantified.

On the other hand, similar results were obtained in Chapter 4, in which PAC dosage in combination with a separation step based on UF allowed to obtain average removal over 70% for the most recalcitrant OMP. The pilot-scale demonstration of PAC-UF allowed a long-term evaluation of the system as an advanced treatment scheme and demonstrated that PAC doses of 20 mg/L can be applied without achieving progressive irreversible fouling. Nevertheless, the use of PAC did not allow any improvement in filtration flux and, to guarantee the correct system operation, hydraulic cleanings need to be applied together with internal recirculation (crossflow), which is associated to an increase in the energy consumption. Moreover, when PAC dose was increased to 50 and 100 mg/L irreversible permeability decline was observed when moderate (0.6 m/s) crossflow were applied, and required a velocity increase up to 0.7-0.8 m/s. On the other hand, the combination of PAC and a separation step based on UF membranes compared to other technologies such as settling or sand filtration, allow the obtention of a higher water quality, free of solids and with low organic matter load, suitable for sensitive uses.

## 7.2 Boosting municipal reclaimed water reuse.

Beyond overcoming the public awareness associated to contaminants of emerging concern, other transversal barriers need to be addressed. As it has been explained, the experience in water reuse point to the importance of establishing effective channels of communication between government departments (environmental and public health) or regulatory bodies responsible for different parts of the integrated water cycle, with relevant local and territorial actors. Sustainable water reuse programs must integrate **public involvement campaigns**, particularly in potable reuse projects but also in non-potable applications. A water reuse project might fail due to a lack of involving from early stages the territorial stakeholders. According to the EPA (2012), a proposal done by the city of San Diego in 2011, presented great public opposition towards water reuse and it was necessary to boost stakeholder involvement through many years to reverse the situation. The work done by the PUB in Singapore is inspiring, also boosting a change of terminology that allowed a better acceptance. The word 'wastewater' was changed to 'treated water', WWTP were the new 'WRP', 'reclaimed water' was branded as

'NEWater or purified water' and existing WRP were renamed as 'NEWater Facilities'. By means of this strategy, these negative and stigmatizing words are more likely to promote public acceptance (Allen et al., 2017). In the case of Los Angeles City (California, USA), through a collaborative approach involving 14 city departments and 6 regional agencies, One Water L.A 2040 Plan aims to minimize its freshwater dependency in the following decades, looking for ambitious objectives such as potable reuse, non-potable reuse, and stormwater management.

Tools must be developed to achieve a flexible and dynamic master plan able to be continuously updated and adapted to water demand changes and forecasting, considering risk management as a pillar and allowing the rapid demonstration of water reuse benefits (from an environmental, economic and social point of view). It is necessary to be able to estimate water demand and the price elasticity based of demand (Worthington, 2010). As lower is the demand, the higher will be the relative cost of reclaimed water served. To anticipate end-users water demand and quality, will help public authorities and water utilities to stablish realistic tariffs that enable cost recovery and stimulate reclaimed water consumption. Capital and operational costs of water reuse need to be understood and explained to relevant local and territorial actors (through key benefit indicators) and financial opportunities should be explored and maximized. In this sense, the work developed in Chapter 5 allowed the calculation of cost curves for three different technologies (UF, GAC/CNM and RO) suitable to a rapid scale-up of treatment schemes and flexible estimation of CAPEX and OPEX.

Finally, in Chapter 5 the technical feasibility of decentralized schemes was demonstrated, concluding that the reuse of municipal wastewater for high quality applications such as industrial uses may generate significant economic savings (up to 0.98 €/m<sup>3</sup>) when compared to the use of tap water. Additionally, to reach a proper matching among reclaimed water (water utilities) and end-users, it is necessary to understand that water reclamation schemes must be projected according to the real needs and not only based on the minimum requirements established by regulation. Reclaimed water needs to account with the demanded water quality and adapt it beyond the limits established by water reuse regulations, which are usually focused on guarantee the reclaimed water safety in terms of human health, ensuring disinfection and the removal of suspended matter and turbidity, but do not consider pollutants such as salinity or other impurities that may compromise the acceptance of the end-users.

### **7.3 Outlook and future prospects**

Advanced wastewater reclamation technologies focused on OMP removal will gain importance in the following years since more restrictive limits are incorporated in the legal frameworks. Specifically, OMP removal will be

critical in potable reuse (indirect or direct) and agricultural irrigation (EPA, 2017). Although in Spain the extension in water reuse is still limited, the effects of climate change manifested as longer droughts and higher variability in rainfall, will lead to increase the dependency on reclaimed water and potable schemes to boost surface or groundwater augmentation will be boosted as it has happened in other regions in the world. Among them, USA accounts with large experience in adapting water reclamation schemes to the removal of OMP when reclaimed water is intended for potable applications. The pilot and full-scale demonstrations of MF/UF, RO and UV/H<sub>2</sub>O<sub>2</sub> as triple barrier trains have allowed reliability and a positive public and administrative perception towards water security (EPA, 2017). Other technological trends are the combination of the benefits of AOP and sorbents through ozonation followed by bio-filters. To keep leading and participating in demonstration projects is crucial to demonstrate to the public administration that technology is robust enough to guarantee the removal of target pollutants and water safety in reuse schemes.

The risk assessment of OMP in reclaimed water uses will shape the concentration limits established in wastewater and water reuse regulations. Additionally, to deploy risk assessment methodologies such as Sanitation Safety Plans (SSP) in existing or new WRP is one of the news included in the European Regulation for Water Reuse (EU 2020/741).

Finally, innovation will introduce in the following years new paradigms in water reuse, such as holistic tools and platforms that will tackle the main pillars and current existing barriers in its implementation (technical, economic, educational, and planning). In the last years, **Water Reuse Living Labs** are emerging as physical and virtual spaces in which all the main stakeholders in the water cycle can co-create new solutions to ease and accept the use of reclaimed water while boosting collaborative and demonstrative projects that step by step will lead to a more sustainable world.

## 7.4 References

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