

**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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**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 indirect potable reuse. During 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) in order 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 foot-print; 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.

**Keywords:** Organic micro-pollutants; Water Reclamation; Hybrid systems; Powder activated carbon; Membrane Bioreactor; recalcitrant.

## 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 & Anderson, 2018; Rock et al., 2018; Smith et al., 2018).

Several studies (Ávila & 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 Sulfametoxazole (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 ( $k_{\text{biol}} < 0.1 \text{ l/g}_{\text{SS}}/\text{d}$ ); (ii) moderately biodegradable ( $0.1 < k_{\text{biol}} < 10 \text{ l/g}_{\text{SS}}/\text{d}$ ); and (iii) highly biodegradable ( $k_{\text{biol}} > 10 \text{ l/g}_{\text{SS}}/\text{d}$ ). 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 adsorbents. 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 adsorbents 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 adsorbents); (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 adsorbents 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  $0.08 \text{ €/m}^3$ , thus the use of this sorbent increases significantly 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 asses deeply capital and operational expenditures (CAPEX & 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 1. 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 estimate to address in the optimal way the OMP and water reclamation challenges.

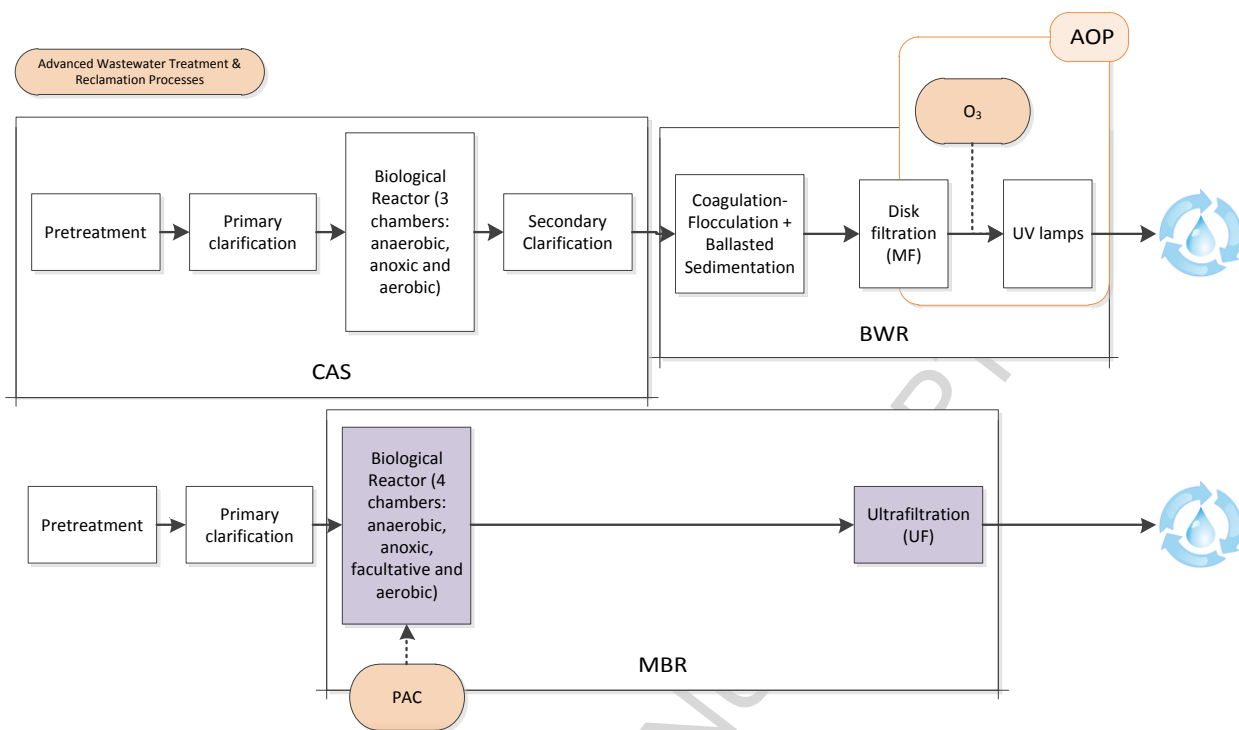


Figure 1 Evaluated advanced reclamation systems for OMP removal. On top, current reclamation system of Baix Llobregat revamped with ozone-UV system. Below, PAC-MBR prototype scheme evaluated in El Baix Llobregat.

## 2 MATERIALS and METHODS

### 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 is capable of treating 100% of the influent flow and reuse reclaimed water in environmental, urban, agricultural and industrial uses.

A PAC-MBR prototype (Figure 2a) 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.

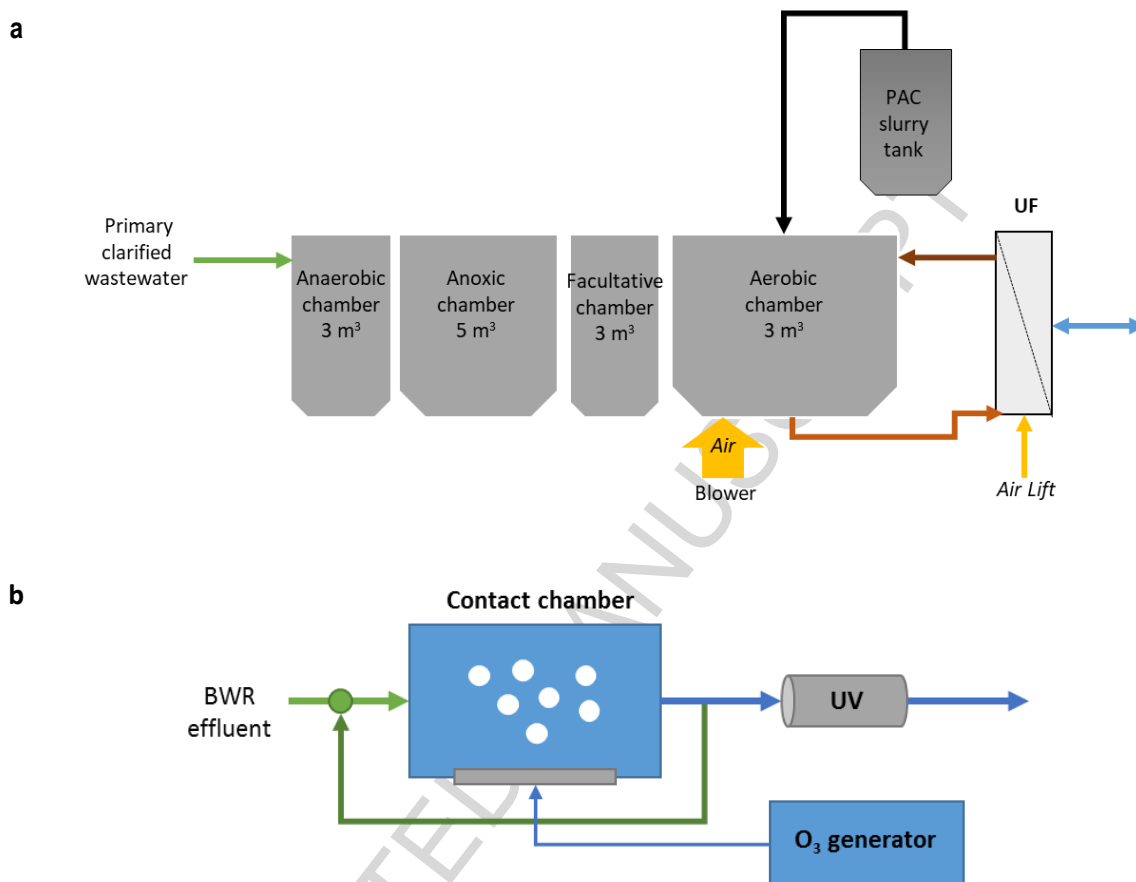


Figure 2. a) PAC-MBR prototype scheme where 4 tanks with a total volume of 24 m<sup>3</sup> compose the biological reactor which feeds the UF membrane in crossflow mode; and b) AOP bench-scale set up, composed by a contact chamber with recirculation, O<sub>3</sub> generator and a final step of UV.

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 2b), 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  $gO_3/Nm^3$ . 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  $J/m^2$  was used.

## 2.2. Sampling and analysis

In order 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 analysed 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 analysed with a Shimadzu VSH-TOC analyser. Temperature, pH and redox potential were monitored online.



Finally, nine OMP were selected and analysed as target compounds to understand their behaviour in tested wastewater treatment and reclamation systems. Eighteen sampling campaigns were carried out along nine months, including warm and cold seasons. Twelve samples were analysed for CAS (secondary effluent) and CAS+BWR, ten samples for CAS+BWR+O<sub>3</sub>-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 & Yew-Hoong Gin, 2017). Two different methods were optimized for negative (Method 1) and positively (Method 2) ionisable compounds.

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 analysed following the methods described (Tables SP1.1 and SP1.2).

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 µL of acetonitrile with 0.1% formic acid in 2 min (Method 2). The eluate entered a Kinetex F5

(100mm × 4,6mm i.d., 2,6µm 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 SP1.3.

The performance of the optimized methodology was evaluated by the analysis of spiked samples. Table SP1.4 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 analysed on three different days.

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.

### **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.

#### **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 1.

### **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. RESULTS AND DISCUSSION

#### 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.

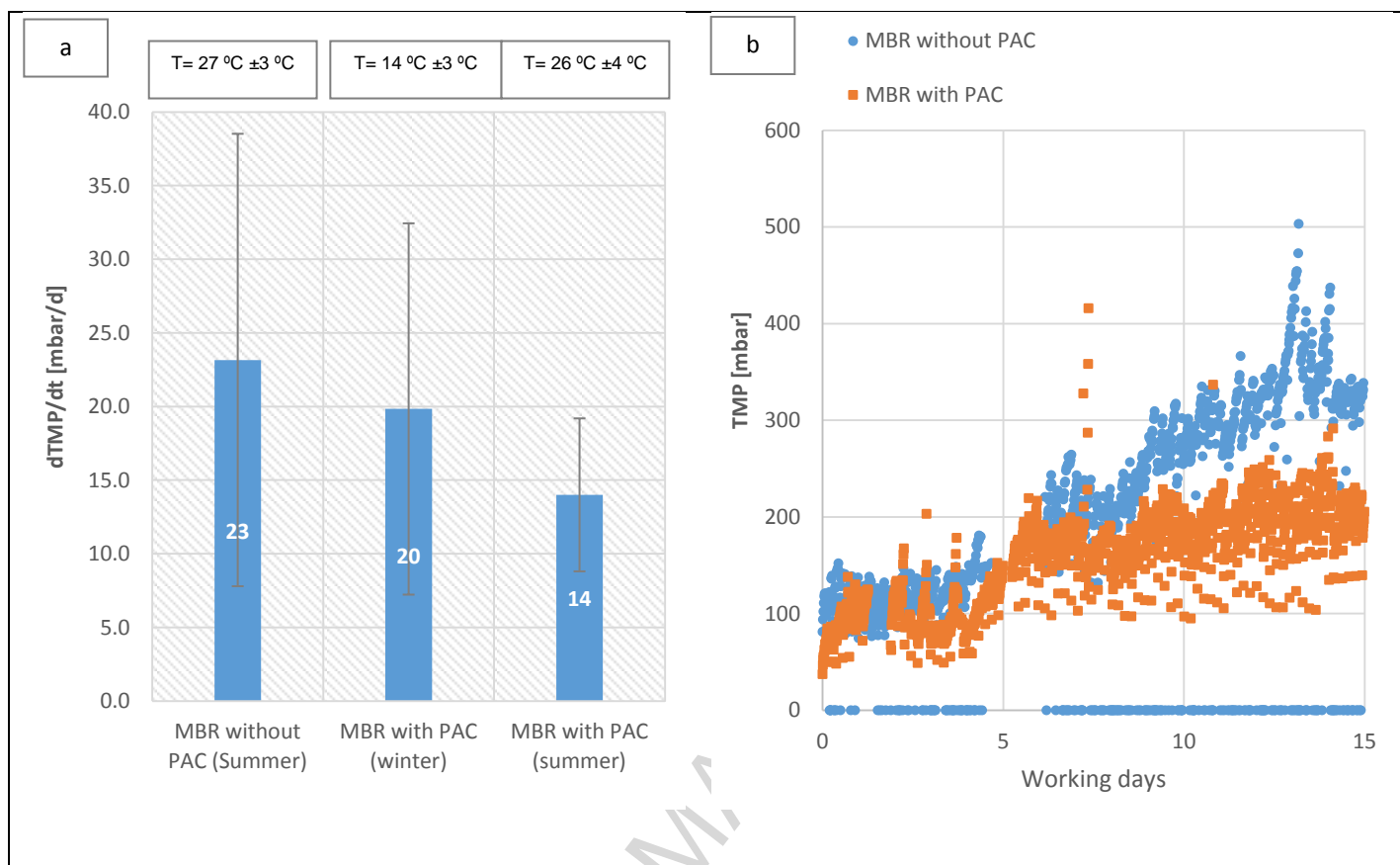


Figure 3. (a) Average UF fouling velocities expressed as  $dTMP/dt$  (mbar/d) for MBR along different phases covering cold and warm seasons (b) TMP evolution at 42-45 LMH with and without PAC addition.

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 & 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 adsorbent. 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.

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 evidences 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 in order 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 adsorbent 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, applying also 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.

### 3.2 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 1. 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.

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 statistical 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 mgSS/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 adsorbent 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 statistical significant differences were found between PAC-MBR and conventional MBR.

Table 1 Basic water quality parameters for evaluated advanced treatment schemes. Average concentrations and removal efficiencies.

OMP		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)	TN (mg N/L)	TP (mg P/L)
Influent concentrations [ng/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
	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%)	-	-	-

### 3.3. Evaluation of OMP removals



The removal efficiencies for OMP were defined in three groups and are collected in Table 2: (i) low removals (<20%), corresponding to the most recalcitrant OMP; (ii) medium removals (20-70%) and (iii) high removals (>70%).

Additionally, influent and effluent concentrations are depicted in Table SP2.1.

Table 2 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%). ( $O_3$ -UV)<sub>1</sub> refers to 6 mg O<sub>3</sub>/L and 400 J/m<sup>2</sup> and ( $O_3$ -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 + ( $O_3$ -UV) <sub>1</sub>	5	97%±12%	80%±5%	72%±8%	>99%	96%±1%	-	-	-	-
	CAS + BWR + ( $O_3$ -UV) <sub>2</sub>	5	96%±9%	89%±9%	94%±5%	>99%	98%±1%	-	-	-	-

As it can be seen in Table 2, 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  $k_{bio}$  of 80 L·g<sup>-1</sup> SS·d<sup>-1</sup> > 10 L·g<sup>-1</sup> SS·d<sup>-1</sup>, which is an indicator of its high tendency to bio-transformation (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 & 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).

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 3.

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 behaviour 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 mg/L) regarding the rest of analysed OMP (100-300 mg/L). Results obtained are consistent with those reported by authors referenced at Table 3 for a similar O<sub>3</sub> 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<sub>3</sub>/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 2).

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Table 3 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, & 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, & Comas, 2012) >80% (Alvarino et al., 2017) 91% (Reif, Suárez, Omil, & 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)

### 3.5 Technical and economic assessment

A technical and economic evaluation was performed for the studied treatment trains (Table 4). 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 5). 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 4 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)
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 5 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> (Sulphurs 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 reference	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>	-	-
Liquid Oxygen (ozone generation)		0.100 €/kg	El Baix Llobregat	99 g/m <sup>3</sup>	0.00990 €/m <sup>3</sup>	-	-	

	(9 mg O <sub>3</sub> /L	WWRP					
	Liquid Nitrogen (ozone generation)	0.150 €/kg	El Baix Llobregat WWRP	2 g/m <sup>3</sup>	0.00030 €/m <sup>3</sup>	-	-

\* Consumption values provided by the WWRP managers, estimated as the average consumption along yearly operation and complemented with manufacturers data.

\*\* Consumption values obtained from the PAC-MBR prototype operation and evaluation

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#### 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 an adsorbent (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.

## 5. Acknowledgements

This research has been done through LIFE Aware Project (LIFE11 ENV/ES/000606 aWARE) with a total budget of 2.6 M€ co-funded with the financial support of the LIFE+ Programme of the European Commission (60%) and the participation of Aigües de Barcelona, CETAQUA and LNEC.

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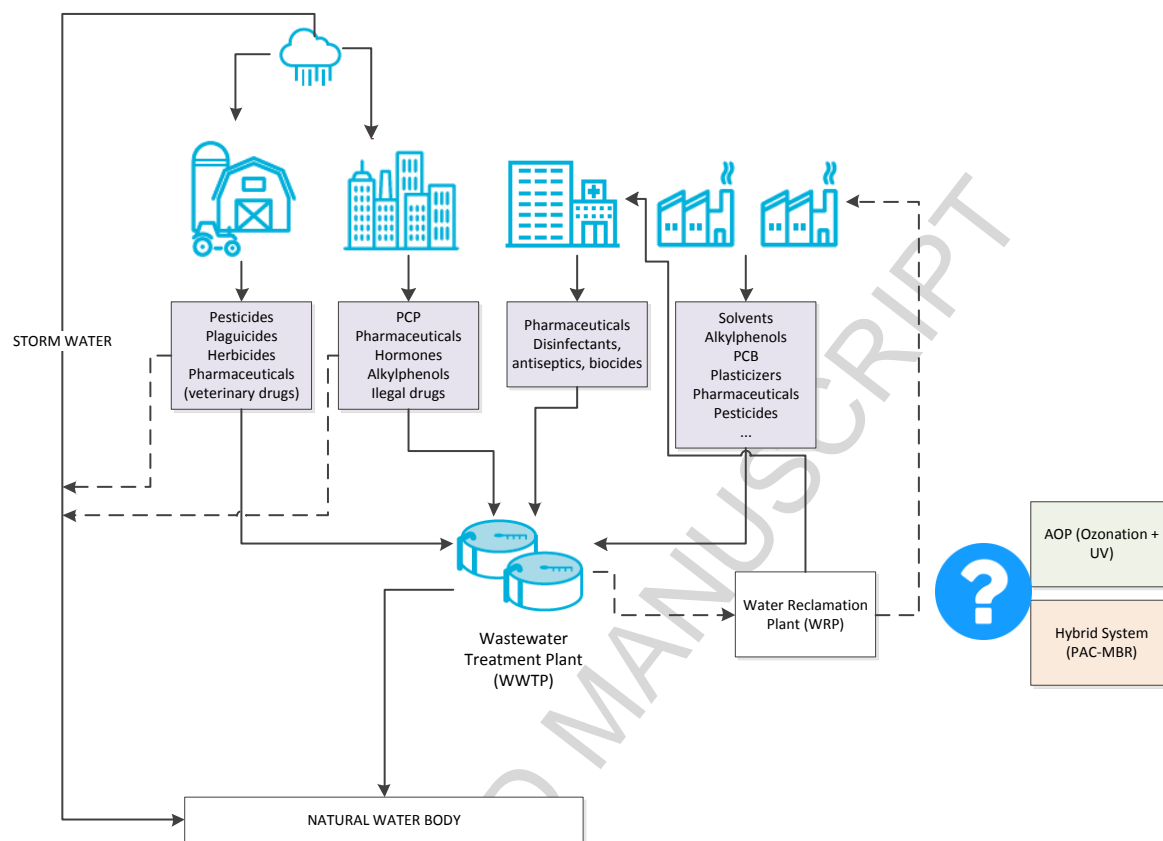
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## Graphical abstract



**Highlights**

- OMP Removal in advanced wastewater reclamation schemes was evaluated
- Evaluation of a hybrid system based on PAC and membrane bioreactor for OMP removal
- The operational benefits of PAC applied in MBR were estimated.
- Technical and economic evaluation for PAC-MBR and tertiary ozonation-UV
- OMP Removal over 80% and 75% for ozonation-UV and PAC-MBR, respectively were achieved

ACCEPTED MANUSCRIPT