

Elimination of trace organics in an MBR/RO system for water reuse

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ABSTRACT

An intensive programme for detection of trace organics was performed in a membrane bioreactor (MBR) plant in Almuñécar (south of Spain) over 1 year. The compounds investigated included 15 pharmaceutically active compounds, 12 polycyclic aromatic hydrocarbons and eight other compounds (nonylphenols, linear alkylbenzene sulphonates and phthalates). The MBR operated with two lines in parallel using a hollow fibre and a flat sheet membrane respectively. Additionally, a reverse osmosis (RO) plant treated the MBR permeate over 1 month and the elimination of trace organics by the MBR/RO system was assessed. The elimination efficiency of trace organics by the MBR was similar to that found in a conventional activated sludge plant treating the same influent. The concentration of trace organics was reduced after the MBR to a great extent and no significant differences were found between the two lines operating in parallel. The elimination efficiency increased up to 80–100% after passing the RO system. The results indicated that the MBR effluent reached the standard required by the Spanish Royal Decree for Water Reuse and can therefore be reused for multiple purposes, but advanced treatment like RO is necessary when the highest effluent quality is required.

Key words | membrane bioreactor, micropollutants, reverse osmosis, trace organics, water reuse

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INTRODUCTION

Implementation of membrane bioreactor (MBR) technology has increased rapidly in Spain in recent years (Huisjes *et al.* 2009) due to important factors like water scarcity and the recently approved Spanish Water Reuse regulation (RD 1620/2007). Nevertheless, this regulation only establishes limits for conventional parameters like suspended solids, pathogens, metals and conductivity of the effluent, but it does not regulate the concentration of trace organics. Apart from the possible effects of discharge of some of these contaminants in soil and in water for reuse, it is well known that they are harmful to aquatic life (Santos *et al.* 2007a). It is generally agreed that MBRs achieve better removal of suspended solids, bacteria, viruses and nutrients compared to conventional activated sludge (CAS), but increased removal of trace organics by the MBR with respect to CAS is still controversial. Some years ago, various studies reported better trace organics removal by MBR technology (Lesjean *et al.* 2005; Radjenovic *et al.* 2009).

Nevertheless, these studies were performed generally at a higher sludge retention time (SRT) than a CAS plant, with a consequently increased biodegradation of slowly biodegradable compounds. Later studies (Bouju *et al.* 2009) concluded that MBR may achieve higher elimination for those compounds which are neither effectively removed by CAS nor are recalcitrant. De Wever *et al.* (2007) found that, although MBRs could not always make a difference in the overall removal efficiencies achieved, they showed reduced lag phases for degradation and a stronger memory effect, which implies that they may respond quicker to variable influent concentrations.

Trace organics are removed in secondary treatment using micro- or ultrafiltration mainly through two mechanisms, biodegradation and adsorption, as membrane retention may be neglected (Tambosi *et al.* 2010). However, the reason why some compounds are removed to a greater extent than others is still unclear. Tadkaew *et al.* (2011)

studied the connection between specific molecular features of 40 trace organic contaminants and their removal efficiencies in a laboratory-scale MBR. They could explain the elimination of most of the micropollutants studied based on their molecular properties. Highly hydrophobic compounds showed removal of at least 98%. In contrast, those compounds with high or medium hydrophilic characteristics which possessed electron withdrawal functional groups consistently showed low removal (<20%).

The introduction of a reverse osmosis (RO) membrane in the removal process greatly increases the efficiency of the elimination. Several studies of RO reported greater than 90% elimination of micropollutants (Al-Rifai *et al.* 2011; Sahar *et al.* 2011). Van Der Bruggen *et al.* (1999) reported the following main removal mechanisms for RO: size exclusion, hydrophobic adsorption, molecule solubility and electrostatic repulsion/attraction. Thus, the main parameters determining the elimination of compounds are molecular size, solubility, octanol-water partition coefficient, charge of the molecule and the acid dissociation constant (pK_a). Understanding the main mechanism governing the elimination of each contaminant would help in the selection of an adequate complementary treatment process prior to water reuse (Nghiem *et al.* 2009).

In this study, the operation and effluent of an MBR/RO pilot plant with two units operating in parallel was evaluated for water reuse purposes over 1 year. The elimination of 35 trace organics of both the MBR and the subsequent RO

system was investigated. The removal efficiencies achieved by the two lines of the MBR were compared. Furthermore, the elimination of trace organics of a CAS system treating the same influent over 1 month was compared to those of the MBR. The molecular properties of the compounds studied were evaluated in order to find any explanation of their elimination efficiency.

METHODS

Pilot plant

The wastewater treatment plant of Almuñécar (Granada, Spain) treats municipal wastewater with CAS technology without primary settling at a SRT of approximately 10 d. After grit and grease removal, the wastewater passes through an automatic disc filter (0.4 mm mesh) and enters the MBR. As it can be seen in Figure 1, the plant consists of two lines operating in parallel with a hollow fibre (HF) membrane and flat sheet (FS) module respectively.

Sulphuric acid and anti-scalant is dosed to the permeate obtained in the HF line and this is further treated using RO. The mean operating parameters for the MBR and the RO are presented in Table 1 and Table 2 respectively. A low-fouling membrane made of aromatic polyamide was selected for the RO system. The recovery of the RO was limited to 50% due to mechanical limitations of the plant.

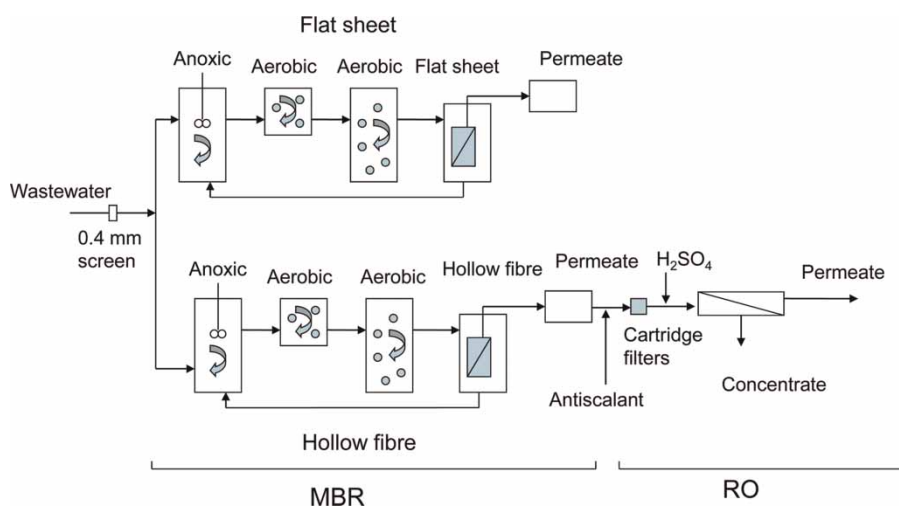


Figure 1 | Scheme of the pilot plant.

Table 1 | Parameters of the MBR

Line	Supplier	Mean pore size (μm)	Membrane surface (m^2)	Total volume line (m^3)	SRT (days)	TSS (g/L)	Filtered COD influent ($\text{mg O}_2/\text{L}$)	Temperature ($^{\circ}\text{C}$)
HF	Koch membrane systems	0.01	250	29	20	6–9	15–830	11–29
FS	Kubota	0.4	160	37	20	4–7	15–830	12–30

Table 2 | Parameters of the RO system

Membranes	Permeability ($\text{L}/(\text{m}^2 \text{ d bar})$)	Area (m^2)	Temperature ($^{\circ}\text{C}$)	No. elements/tube	Recovery (%)
TRISEP 4040-X201-TSA	40	165.9	18–20	7	50

Analytical methods

Dissolved oxygen, temperature and pH were regularly monitored in the plant. Chemical oxygen demand (COD), nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), total phosphorus and phosphates of incoming water and effluent were analysed daily (Hach-Lange, Germany). Total suspended solids (TSS) were measured according to standard methods (Clesceri *et al.* 1998).

Pharmaceutical compounds were simultaneously extracted by solid-phase extraction (SPE) according to Camacho-Muñoz *et al.* (2009). Determination was carried out by high performance liquid chromatography (HPLC) with diode array and fluorescence detectors sited on line. Separation of pharmaceutical compounds was carried out using a Zorbax Eclipse XDB-C18 ($150 \times 4.6 \text{ mm}$, particle size $5 \mu\text{m}$) cartridge column (Agilent, USA) protected by a XDB-C18 ($4 \times 4 \text{ mm i.d.}$, $5 \mu\text{m}$) guard column (Agilent).

Linear alkylbenzene sulphonates (LAS), nonylphenols (NP) and di-(2-ethylhexyl) phthalate (DEHP) were simultaneously extracted by SPE. Compounds were

simultaneously determined by HPLC as previously reported (González *et al.* 2010). Separation was carried out using an Inertsil Ph-3 ($150 \times 4.6 \text{ mm}$, particle size $5 \mu\text{m}$) column (GL Sciences, Tokyo, Japan) protected by an Inertsil Ph-3 ($4 \times 10 \text{ mm}$, $5 \mu\text{m}$) guard column (GL Sciences).

Polycyclic aromatic hydrocarbons (PAHs) were extracted by SPE and determined by HPLC as reported by Santos *et al.* (2007b). PAH separations were carried out using a Lichrospher[®] PAH column ($250 \times 3 \text{ mm i.d.}$, $5 \mu\text{m}$) protected by LiChropher[®] 100 RP-18 ($4 \times 4 \text{ mm i.d.}$, $5 \mu\text{m}$) guard columns (Merck, Darmstadt, Germany).

The compounds analysed during the study are listed in Tables 3–5.

RESULTS

MBR effluent quality

The mean values for COD and nutrients in the effluent obtained during the steady-state operation of the MBR

Table 3 | Pharmaceutically active compounds

Antibiotics	Anti-inflammatory drugs	Lipid regulating agents	β -blocker	Stimulant	Anticonvulsant	Estrogens
Trimethoprim	Diclofenac	Clofibric acid	Propanolol	Caffeine	Carbamazepine	17α -ethynylestradiol
	Ibuprofen	Gemfibrozil				17β -estradiol
	Naproxen					Estriol
	Ketoprofen					Estrone
	Salicylic acid					

Table 4 | Phthalate, linear alkylbenzene sulphonates and nonylphenols

Compound	Abbreviation
Di-(2-ethylhexyl)phthalate	DEHP
Linear alkylbenzene sulphonates	C10, C11, C12, C13
Nonylphenol	NP
Nonylphenol mono and diethoxylate	NP1EO and NP2EO

Table 5 | Polycyclic aromatic hydrocarbons

Compound	Abbreviation
Naphthalene	Nap
Phenanthrene	Phe
Fluoranthene	Fluo
Pyrene	Pyr
Anthracene	Ant
Benz[a]anthracene	BaA
Chrysene	Chr
Benz[b]fluoranthene	BbF
Benz[k]fluoranthene	BkF
Benz[a]pyrene	BaP
Dibenz[ah]anthracene	DahA
Benz[ghi]perylene	BghiP

pilot plant are presented in Table 6. Although the pilot plant faced numerous technical problems during the study and the influent wastewater was very variable, the effluent quality was consistently high. Pathogens, turbidity, metals and SAR (sodium adsorption ratio) were monitored in order to check if the MBR effluent reached the standard required by the Spanish Wastewater Reuse regulation (Table 7). The results indicated that the effluent obtained with the MBR can be reused as described in the standard for all industrial, agricultural and urban purposes. For other purposes, further treatment for enhanced nutrient removal should be applied.

Table 6 | Results from the MBR effluent; elimination of COD and nutrients

	NH ₄ ⁺		COD		Nitrogen total		Phosphorus total	
	Concentration (mg N/L)	Removal (%)	Concentration (mg O ₂ /L)	Removal (%)	Concentration (mg N/L)	Removal (%)	Concentration (mg P/L)	Removal (%)
Hollow fibre	0.7	98	55	96	12	87	6	69
Flat sheet	0.6	98	45	97	15	81	7	59

Concentration of trace organics in the incoming wastewater

Figure 2 and Figure 3 show the mean concentration values of the pharmaceutically active compounds (PhACs), nonylphenols, LAS and DEHP in the influent. The concentration of the compounds varies widely depending on the compound and also within the same compound, as shown by the large standard deviation. All compounds studied were detected in the incoming water except estrone and trimethoprim.

The LAS were abundant in the incoming water, which is quite usual in wastewater as they are surfactants commonly found in high amounts in domestic and industrial wastewaters discharged from textile, leather, food, paint, polymer, cosmetics, mining, oil recovery and paper industries (Hellsten 1986). However, their concentration in the effluent is reduced because they are highly biodegradable (Khleifat 2006). This is clearly shown in Figure 4, where even for peaks of LAS in the influent the concentration of LAS in the effluent is consistently low.

The results for the PAHs are presented in Table 8. Only naphthalene, phenanthrene, anthracene, pyrene, benz[a]anthracene and chrysene were found in the influent at concentrations higher than the detection limits. In the effluent, the mean concentration of most of the PAHs analysed was generally below the detection limits. Only phenanthrene was found in FS effluent in a measurable concentration.

Elimination efficiency of trace organics

The elimination of the different compounds can be seen in Figure 5. Some bars are missing in the figure because, as the RO and the CAS systems were only monitored over 1 month, some compounds present no data for these two treatment systems, as they were constantly below the

Table 7 | Results from the MBR effluent (mean values from HF and FS). Relevant parameters for water reuse for the most restrictive agricultural purposes (quality 2.1. from RD 1620/2007)

Parameter	Limit RD1620/2007	MBR effluent
Conductivity (dS/m)	3	1.2
SAR (meq/L)	6	3.2
Metals		<limit of the RD1620/2007
TSS (mg/L)	20	<1
<i>Escherichia coli</i> (cfu/100 mL)	100	<1
Intestinal nematodes (egg/L)	1	0
Turbidity (NTU)	10	<0.1

detection limits during the sampling period. An improvement in efficiency can be observed from the two MBR lines compared to the CAS system for propranolol, estradiol, NP and DEHP whereas other compounds like estriol and salicylic acid showed higher removal for the CAS.

It can be generally stated that no significant difference was found between the removal by the FS and the HF membrane. This is already expected because, as mentioned in the introduction, the main removal mechanisms in these systems are biodegradation and adsorption, and the

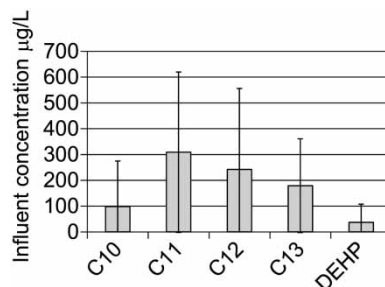


Figure 3 | Mean concentration of LAS and DEHP in the influent.

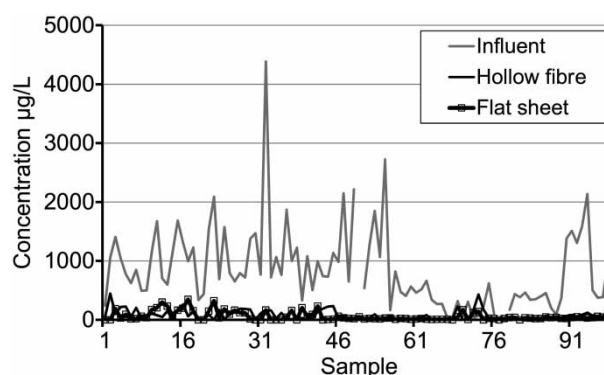


Figure 4 | Evolution of the LAS concentration.

membrane step can be neglected. An important improvement in elimination efficiency can be observed when RO was applied, with a mean removal of 87%.

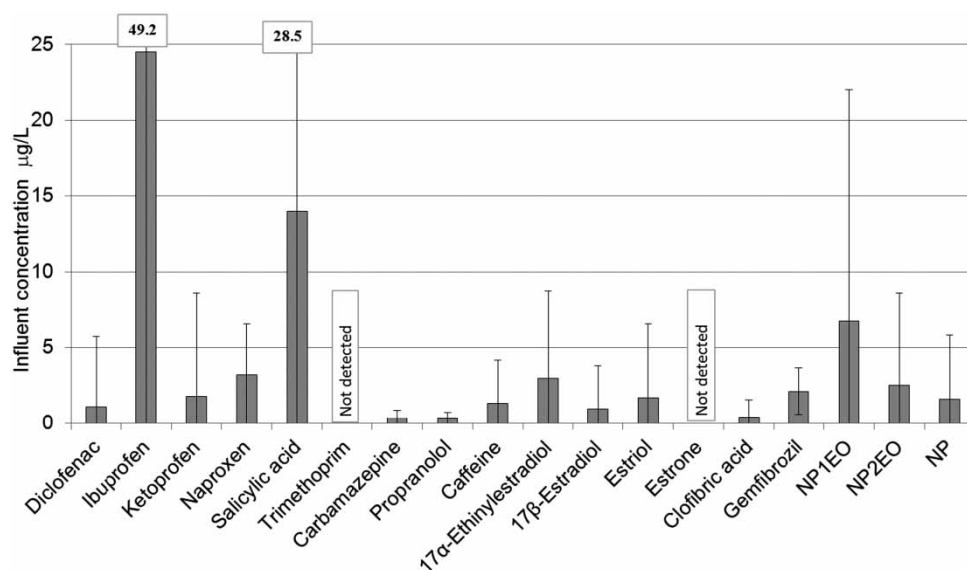


Figure 2 | Mean concentration and standard deviation of PhACs and nonylphenols in the influent.

Table 8 | Results from the PAHs analysis

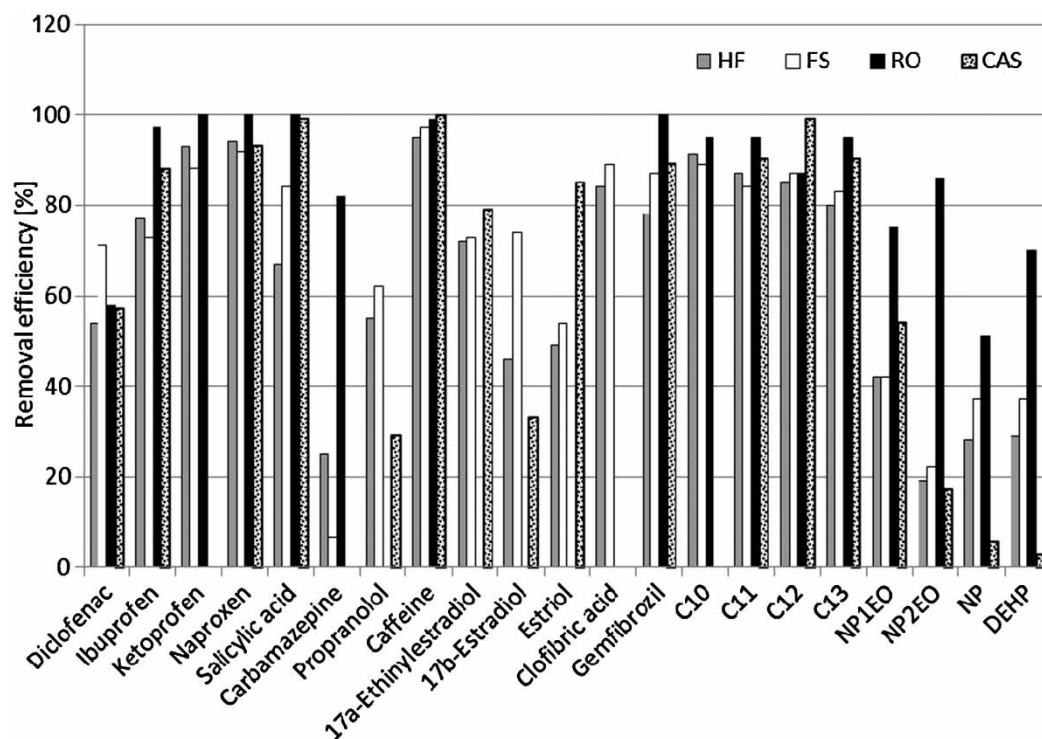
Compound	LD ($\mu\text{g L}^{-1}$)	Influent concentration ($\mu\text{g L}^{-1}$)	MBR effluent concentration	
			HF ($\mu\text{g L}^{-1}$)	FS ($\mu\text{g L}^{-1}$)
Nap	0.029	0.042	<LD	<LD
Phe	0.005	0.015	<LD	0.007
Ant	0.001	0.001	<LD	<LD
Fluo	0.004	<LD	<LD	<LD
Pyr	0.078	0.008	<LD	<LD
BaA	0.006	0.001	<LD	<LD
Chr	0.0002	0.002	<LD	<LD
BbF	0.001	<LD	<LD	<LD
BkF	0.002	<LD	<LD	<LD
BaP	0.024	<LD	<LD	<LD
DahA	0.011	<LD	<LD	<LD
BghiP	0.045	<LD	<LD	<LD

Elimination efficiency and molecular properties

As shown in [Figure 5](#), compounds with electron-donating groups in their molecules (caffeine, gemfibrozil, ibuprofen,

naproxen, salicylic acid and ketoprofen) were significantly removed with elimination efficiencies ranging from 75 to 100%. These elimination efficiencies agree with those found in the literature, as reviewed by [Tadkaew *et al.* \(2011\)](#). According to their studies, the reason why these compounds are easily removed is that the presence of electron-donating groups in their molecules renders the molecule prone to electrophilic attack by oxygenases of aerobic bacteria. Propanolol is also included in this group but it shows slightly less removal than the other compounds with electron-donating groups. This may be attributed to the double ring of their molecule, as this has been associated with low removal efficiencies ([Jones *et al.* 2005](#)). However, [Tadkaew *et al.* \(2011\)](#) could not confirm this relationship.

Contrary to those with electron-donating groups, carbamazepine showed low removal efficiency consistent with the fact that it contains electron-withdrawal groups. Diclofenac and clofibric acid also contain electron-withdrawal groups in their molecules but they showed medium to high removal (60% for diclofenac and 80% clofibric acid). In the case of diclofenac, this might be attributed to the existence of anoxic-oxic zones in the plant that may lead to an

**Figure 5** | Elimination efficiency for PhACs studied for the HF line, FS line, RO and CAS.

increased removal of diclofenac (Zhang *et al.* 2008). In the case of clofibric acid, it not only contains electron-withdrawing groups but it is also hydrophilic and chlorinated, features which have been associated with low biodegradability (Kimura *et al.* 2003). Therefore, the high removal for this compound could not be explained by any of the properties that are found in the literature linked to removal efficiency.

According to Tadkaew *et al.* (2011), there is another group of compounds which are easily removed with MBR and these include estriol, 17 β -estradiol, 17 α -ethynylestradiol, NP and DEHP. Their biodegradability is related to their high hydrophobicity, as this property facilitates the sorption of the trace organics on the floc surface. Tadkaew *et al.* (2011) reported removal rates for these hormones ranging from 98 to 100%. In this study, hormones showed a mean removal efficiency ranging from 46 to 74%, which is lower than the removal commonly found in the literature for these compounds after secondary treatment. The same occurs with DEHP and NP, which are hydrophobic and important removal efficiencies of 94% for DEHP (Martinen *et al.* 2003) and more than 99% for NP (Nasu *et al.* 2001) have been reported in the literature, whereas low to medium removal values (6–37% for NP and 3–37% for DEHP) were found in this study. The reason for the lower removal of the hydrophobic compounds in this study is therefore still unclear.

CONCLUSIONS

The results from the monitoring programme showed that the MBR is a useful technology that produces an effluent which can be reused for most applications described in the Spanish Royal Decree for Water Reuse. Regarding the trace organics, the elimination using MBR ranged between 0 and 100% and showed a high variability. The LAS appeared at the highest concentration but their elimination efficiency was high due to their high biodegradability. In contrast, PAHs could only be detected in few samples and the concentration was close to the detection limit in most cases. The elimination efficiency of trace organics varied depending on the compound, and this variation could only be linked to their molecular properties in some cases. The elimination efficiency of trace organics by the MBR was similar to that of the CAS. No significant difference could be found in the

removal of the HF and the FS membrane, which demonstrated that the main removal mechanisms of trace organics by these systems are biodegradation and adsorption, and not membrane separation. This is not the case for the RO system, as its introduction increased significantly the elimination of the contaminants studied, achieving a mean removal of 87%. In conclusion, MBR technology produces a high quality effluent for reuse and it is able to remove most trace organics to a great extent but, when the highest effluent quality is required this may be insufficient and the combination of MBR and RO is a promising alternative.

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