



Study of reverse osmosis treatment for micropollutants rejection in advanced water reuse applications

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ABSTRACT

Reverse osmosis (RO) membranes have made a breakthrough in waste water reclamation for the rejection of micropollutants in multiple applications such as reuse. Since these compounds are not completely eliminated using conventional treatments. This paper offers an overview of a waste water treatment plant using RO membrane treatment to study the rejection of 75 micropollutants from different families. The 75 selected micropollutants include some emerging and persistent compounds like volatile organic compounds (52), endocrine disrupting compounds (2), odor compounds (8), fragrance allergens (10), and some pesticides (3). Experimental results indicated that secondary effluents from conventional treatments contained most of the micropollutants studied; showing that conventional treatments such as activated sludge are not able to completely eliminate them. The rejection of these organic compounds was studied after the RO system. In addition, the relation between the micropollutant's rejection, the molecular weight, and the octanol-water partition coefficients was also evaluated.

Keywords: Advanced waste water treatment; GC-MS; Organic micropollutants; Reverse osmosis.

1. Introduction

The occurrence of trace organic contaminants in treated and untreated domestic waste water has been identified as a significant environmental health concern. Currently, treated industrial and municipal waste water is discharged to the environment and generally considered as a waste. However, municipal

waste water effluent should be considered a resource from which high quality water could be produced [1].

It is recognized that current waste water treatment technologies are very often unable to entirely degrade such persistent micropollutants. Consequently, some of the micropollutants and/or their metabolites are being accumulated in the aquatic environment where they may result in an ecological risk [2]. Therefore, alternative advanced technologies for tertiary treatment of waste water treatment plant (WWTP)

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effluents are necessary. At present, these micropollutants are not routinely monitored by water treatment companies due to the lack of regulatory requirements. Furthermore, there is an extreme cost involved in monitoring thousands of potential contaminants that are expected to be removed after the treatment, although in reality they are not included in the literature. The most common families of micropollutants studied include volatile organic compounds (VOCs), disinfection by-products, steroids and hormones, anti-septics, personal care products (sun creams, fragrances, odors, etc.), petrol additives, drugs, heavy metals and metalloids, pesticides, surfactants, and endocrine disruptors [3,4]. Therefore, few studies either have looked at the occurrence of these compounds in groundwater or have evaluated their rejection in WWTPs [5–7]. However, some experimental flat sheet and pilot plant studies have been reporting other types of organic compounds, such as organic colloidal particles which are classified as contaminants and could cause performance problems in the reverse osmosis (RO) membranes [8,9].

Viable solutions for improving the removal of these micropollutants from water are pressurized membrane processes. The WWTP effluents can be then further treated with an array of advanced treatment processes, including microfiltration, ultrafiltration (UF), RO, or nanofiltration [10]. Recent developments in membrane bioreactor systems have led to the availability of these systems as an alternative to conventional activated sludge treatment processes [11].

This article presents a study where the presence of 75 organic micropollutants was evaluated and monitored to assess the effectiveness of a conventional WWTP using a thin film composite polyamide RO membrane as a tertiary treatment. In addition, the micropollutants rejection was also related to their physico-chemical properties. Since limited data exist in the literature for meaningful comparison of solute properties and rejection, the results obtained in this study can contribute to an improved understanding of micropollutants rejection by RO membranes. The 75 target compounds monitored ranged in variety from VOCs (e.g. chlorobenzenes, chloroalkanes), endocrine disrupting compounds (EDCs) (e.g. tri(2-chloroethyl) phosphate, and tributyl phosphate), odor compounds (e.g. limonene, phenol), fragrance allergens (e.g. geraniol, eugenol), and some pesticides (e.g. heptachlor, terbutryn).

2. Methods

2.1 Studied compounds

The different compounds selected have physico-chemical properties that are representative of a wide

range of organic compounds present in impaired water sources. The 75 selected micropollutants, provided by Dr Ehrenstorfer (Augsburg, Germany) and Sigma-Aldrich, Supelco (Madrid, Spain), included VOCs (52), EDCs (2), odor compounds (8), fragrance allergens (10), and some pesticides (3). Table 1 summarizes the physico-chemical properties of the compounds determined in this study.

2.2 Analytical method

This study was focused on the simultaneous characterization of 75 micropollutants in waste water samples with an analytical method based on headspace solid phase microextraction and gas chromatography-mass spectrometry, which was optimized in a previous paper [12].

Analytes were extracted using a volume of 30 mL of waste water, placing it into a 50 mL PTFE/silicone screw-cap glass vial and mixed with 400 g L⁻¹ of sodium chloride (saturated solution). The vial was hermetically closed, heated up to 50°C within a thermostatic water bath and put over a magnetic stirrer. A fiber of PDMS/DVB was exposed to the headspace above the aqueous solution and the magnetic stirring was fixed at 1,000 rpm during the 30 min of extraction. At the end of the extraction, the fiber was inserted into the injection port of the gas chromatograph for the thermal desorption and analysis. Fiber was desorbed at 270°C during the chromatographic analysis in the splitless mode to avoid carryover.

Micropollutants were analyzed by using Shimadzu GCMS-QP2010 Ultra/GCMS-QP2010 SE gas chromatography analysis, equipped with a split/splitless injector and coupled to a mass spectrometer detector. Helium was employed at constant column flow of 1 mL min⁻¹. Analytes were separated with TRB-5MS column (60 m × 0.32 mm i.d., 1 µm film thickness) from Tecknokra, (Barcelona, Spain). The split/splitless injection port was equipped with a 0.75 mm ID liner from Supelco, and operated at 270°C, allowing direct injection of SPME. The oven temperature program was started at 40°C, held for 2 min; then increased by 6°C min⁻¹ up to 150°C and by 20°C min⁻¹ up to 300°C, and held for 12 min. The total run was 39 min.

Mass spectrometry was performed in full-scan mode with a single quadrupole and monitored masses were between 40 and 280 m/z. Ionization was carried out in the electron impact mode at 70 eV. The transfer line temperature was maintained at 300°C and the ion source temperature at 250°C.

In addition, complementary analysis of some basic organic water parameters was performed such as total

Table 1

Target compounds and their retention time, log K_{ow} partition coefficients, molecular weight, and detection limits [12].

Family	Compound	t_R (min)	log K_{ow}	Molecular weight (g mol ⁻¹)	LOD (µg L ⁻¹)
VOCs	1,1-dichloroethene	5.17	2.13	96	0.100
	(Z)-1,2-dichloroethene	6.35	1.86	96	0.033
	1,1-dichloroethane	6.40	1.79	98	0.033
	2,2-dichloropropane	6.60	2.28	112	0.033
	Trichloromethane	6.67	1.97	118	0.001
	(E)-1,2-dichloroethene	7.16	2.09	96	0.033
	Bromochloromethane	7.41	1.41	129	0.100
	1,1,1-trichloroethane	7.69	2.48	132	0.033
	1,2-dichloroethane	7.74	1.48	98	0.033
	1,1-dichloro-1-propene	8.05	2.03	110	0.017
	Benzene	8.26	2.13	78	0.001
	Carbon tetrachloride	8.38	2.73	152	0.003
	1,2-dichloropropane	9.44	1.97	112	0.017
	Trichloroethene	9.59	2.71	130	0.003
	Dibromomethane	9.78	1.70	172	0.003
	Bromodichloromethane	10.11	1.70	162	0.100
	(E)-1,3-dichloro-1-propene	11.14	2.06	110	0.001
	(Z)-1,3-dichloro-1-propene	11.65	2.06	110	0.003
	Toluene	12.13	2.75	92	0.0005
	1,1,2-trichloroethane	12.23	2.05	132	0.100
	1,3-dichloropropane	12.64	2.00	112	0.010
	Dibromochloromethane	13.12	2.04	206	0.001
	1,2-dibromoethane	13.49	1.96	186	0.017
	Tetrachloroethene	13.62	2.67	164	0.033
	Chlorobenzene	14.85	2.86	112	0.001
	1,1,1,2-tetrachloroethane	14.92	2.62	166	0.010
	Ethylbenzene	15.31	3.14	106	0.0005
	o-xylene	15.56	3.13	106	0.001
	Tribromomethane	16.17	2.35	250	0.100
	Styrene	16.27	2.87	104	0.0005
	p-xylene/m-xylene	16.38	3.17	106	0.0005
	1,1,2,2-tetrachloroethane	16.83	2.39	166	0.010
	1,2,3-trichloropropane	17.10	2.29	146	0.010
	Isopropylbenzene	17.35	3.48	120	0.001
	Bromobenzene	17.71	2.71	156	0.0005
	1-chloro-2-methylbenzene	18.32	3.42	126	0.001
	1-chloro-4-methylbenzene	18.47	3.33	126	0.010
	1,2,4-trimethylbenzene	18.72	3.65	120	0.0005
	1,3,5-trimethylbenzene	18.95	3.42	120	0.010
	Tert-butylbenzene	19.52	4.11	134	0.0005
	Sec-Butylbenzene	20.07	4.57	134	0.0005
	1,3-dichlorobenzene	20.20	3.52	146	0.010
	p-isopropylbenzene	20.43	4.38	134	0.0005
	1,2-dichlorobenzene	20.92	3.43	146	0.001
	1,4-dichlorobenzene	21.02	3.42	146	0.010
	Butylbenzene	21.30	4.26	134	0.0005
	1,2-dibromo-3-chloropropane	22.05	2.95	234	0.001
	1,2,4-trichlorobenzene	23.95	4.01	180	0.001
	Naphthalene	24.14	3.35	128	0.0005
	Hexachlorobutadiene	24.52	4.78	258	0.010
	1,2,3-trichlorobenzene	24.55	4.05	180	0.010

(Continued)

Table 1 (Continued)

Family	Compound	t_R (min)	$\log K_{ow}$	Molecular weight (g mol^{-1})	LOD ($\mu\text{g L}^{-1}$)
Odors	Dimethyl disulfide	11.40	1.77	94	0.017
	Phenol	18.62	1.50	94	0.001
	D-limonene	20.60	4.57	136	0.001
	3-methyl-phenol	21.40	1.98	108	0.100
	Carvone	24.81	2.71	150	0.001
	Indole	25.48	2.14	117	0.100
	Skatole	26.56	2.60	131	0.010
	Geosmin	26.98	3.57	182	0.0005
Allergens	Benzyl alcohol	20.54	1.05	108	0.001
	Citral	24.62	3.76	152	0.010
	Geraniol	24.72	3.56	154	0.033
	Hidroxicitronellal	25.16	1.41	172	0.100
	Cinnamyl alcohol	25.84	1.95	134	0.100
	Eugenol	26.12	2.49	164	0.010
	Isoeugenol	27.04	3.04	164	0.100
	Coumarin	27.18	1.39	146	0.0005
	Ammylcinamaldehyd	28.67	4.16	202	0.0005
	Benzil salizicate	30.49	4.67	228	0.017
Pesticides	Terbutryn	30.87	3.74	241	0.010
	Heptachlor	31.17	6.66	370	0.017
	Dicofol	31.64	4.28	371	0.017
EDCs	Tributyl phosphate	28.37	4.00	266	0.001
	Tri(2-chloroethyl) phosphate	29.35	0.5	284	0.001

organic carbon (TOC), chemical oxygen demand (COD), biological oxygen demand (BOD), absorbance at 254 nm (UV 254), and color, following their standard methods [13].

2.3 WWTP overview

The study was carried out in an urban WWTP located in the NE of Spain. Primary and secondary

biological treatments were designed to treat $15,000 \text{ m}^3 \text{ d}^{-1}$ of water during winter time and $47,500 \text{ m}^3 \text{ d}^{-1}$ during summer time. The effluent of the secondary treatment was connected to a research unit comprising UF system (as a RO pretreatment) followed by RO treatment. Fig. 1 depicts the existing treatment scheme.

The plant was operated continuously in once-through mode and was operated for at least one week

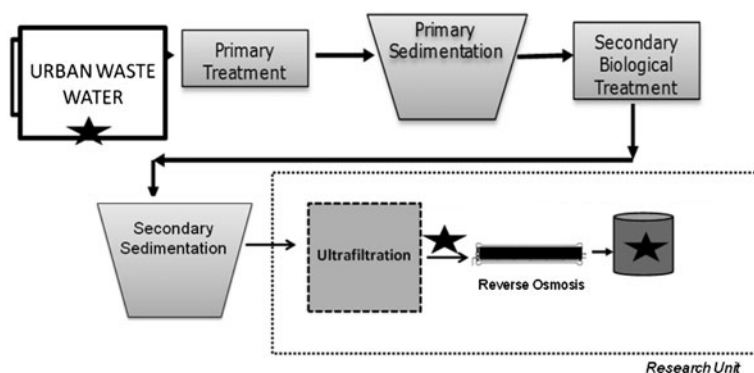


Fig. 1. Waste water plant overview. Sampling points are indicated by a star.

before water samples were taken. This ensured representative operation conditions for the RO plant with stabilized membrane performance. The tested RO membranes were DOW FILMTEC™ BW30 (A Trade-mark of the Dow Chemical Company or an affiliated company of Dow). These membranes were industrial standard rejection and high productivity brackish water membranes. The molecular weight cut-off of these membranes was in the range of 100 Dalton.

The process and sampling points (stars) are also shown schematically in Fig. 1. Samples belong to the influent and effluent of RO membrane treatment as well as the influent of the WWTP. Water samples were collected weekly in amber glass bottles and were stored in the dark at 4°C until analysis, within 2 d. A total of 30 samples were analyzed in the full study.

3. Results and discussion

3.1 Water characterization

When compared to other waters such as river water or sea water, waste water has a higher load of organic content. For this reason, its organic and biological fouling tendency in RO is higher. For the present study, the operational flow-rate through the RO membrane, which is the rate of influent water introduced to the

Table 2

RO experimental conditions during the study

Parameter	Unit	Experimental range
Temperature	°C	16–20
pH	–	7.0–7.8
Feed conductivity	mS/cm	2,500–3,800
Flow-rate	L/h	900–950
Recovery	%	50–51
Feed pressure	Bar	11–14
Salt Rejection	%	98.7–99.1

RO membrane, was fixed at 900–950 L h⁻¹ and the recovery, which is the percentage of RO influent water that emerges from the system as product water or effluent, was fixed at 50%. These selected parameters are worldwide recognized as standard operational conditions for RO systems in waste water application treatments. In addition, based on the flow-rate and recovery, the feed pressure was adjusted. Characteristics of RO influent water and operational parameters are collected in Table 2, where minimum and maximum values through the study period are indicated.

In addition, values of different organic parameters such as COD, TOC, BOD₅, and UV254 of the RO influent and effluent were analyzed. As expected, the values in the RO effluent samples were always lower than in the RO influent samples, as shown in Fig. 2. In

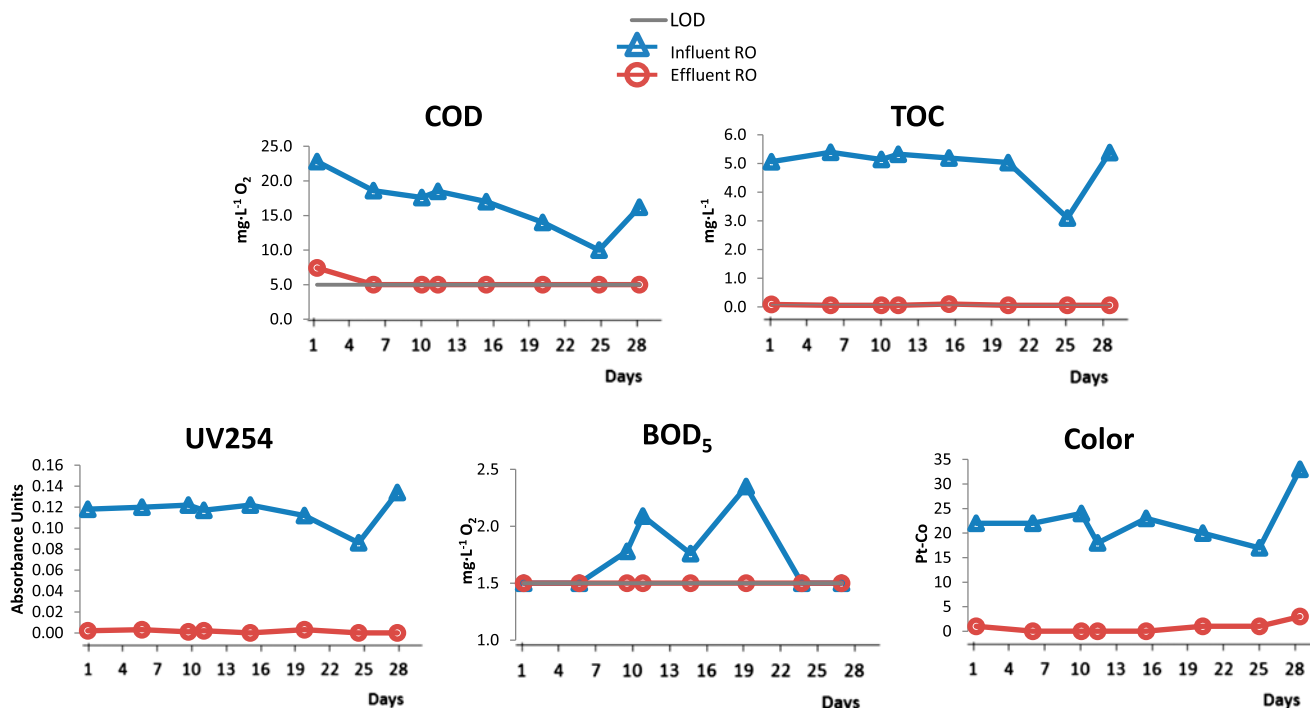


Fig. 2. Organic parameters of the RO influent and effluent water.

addition, the limit of detection (LOD) of the COD and BOD₅ were represented in the figure.

It could be observed that the COD of the RO influent water varied from 24 mg L⁻¹ of O₂ on the day 1 to 10 mg L⁻¹ of O₂ on day 25, while the BOD₅ was less than 2.5 mg L⁻¹ of O₂ over the entire period. This gives a BOD₅/COD ratio of less than 0.2, which indicates that most of the organic compounds in the waste water are poorly biodegradable [14,15]. In addition, the COD and the BOD₅ results of the effluent samples were lower than the LOD of the method in all cases.

There was a trend in some of the parameters, such as TOC, COD, and UV254, where their concentrations in the RO influent consistently decreased during the study, probably because of some unexpected issues in the conventional treatment, such as rainy days which diluted the organic content in the primary and secondary treatment. Moreover, there was an unexpected shutdown of the RO membrane treatment, which was also reflected on the water analysis showing higher concentrations in the last sampling point (day 28).

3.2 Rejection of micropollutants

The rejection percentage or rejection efficiency of every compound via RO treatment was calculated as presented using equation:

$$\text{Rejection} = \left(1 - \frac{C_e}{C_i} \times 100 \right) \quad (1)$$

where C_e is the concentration of the analyte in the effluent of the RO membrane system and C_i is the concentration of the analyte in the RO influent.

The target micropollutants belong to different families (VOCs, fragrance allergens, odors, EDCs, and

pesticides), shown previously in Table 1, with different physico-chemical properties which could result in different RO performance. Analyte rejection by RO membranes will be affected by the analyte and membrane properties, RO influent composition, and operating conditions [16,17]. The micropollutants could be rejected by one of a combination of three basic mechanisms: size exclusion, charge exclusion and physico-chemical interactions between analyte, solvent, and membrane. For organic molecules, especially for uncharged compounds, the most commonly used parameter is the molecular weight because it is assumed that transport through the membrane is mainly related to size exclusion as well as its polarity.

As expected, all RO effluents showed less concentration of micropollutants than the RO influent in all the families studied. Almost all the micropollutants found correspond to VOCs, the biggest group (with 54 compounds). VOCs (77% in the influent and 86% in the effluent of the total micropollutants identified) and odor compounds (10.9% in the influent and 14% in the effluent of the total micropollutants identified) could be properly quantified in the influent and effluent samples. On the other hand, fragrance allergens (11.6% in the influent of the total micropollutants identified) and EDCs (0.5% in the influent of the total micropollutants identified), the concentration in the RO effluents was lower than 1 µg L⁻¹ in both families. Fig. 3 shows the concentration of the micropollutants found in the RO influent and effluent classified by families. The pesticide group is not shown in the figure, as its concentration was lower than the detection limit in all samples tested.

The micropollutants families with consistently higher rejection were the fragrance allergens and EDCs because of their polarity as well as their molecular

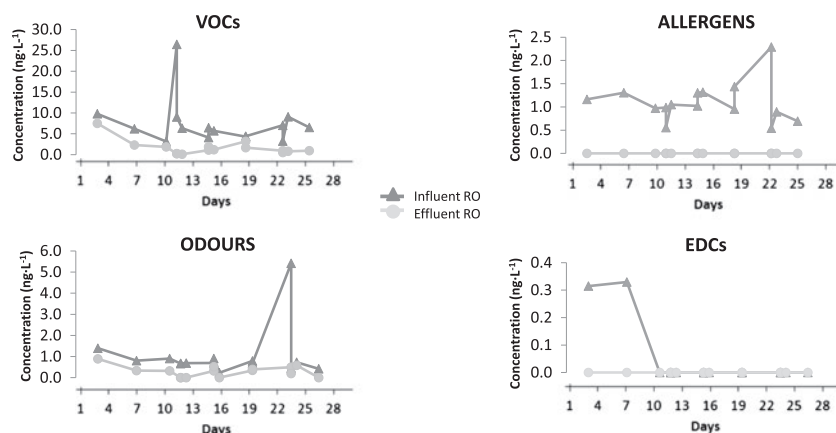


Fig. 3. Concentration of the micropollutants found classified by families.

Table 3

Organic parameters and micropollutants analyzed (in $\mu\text{g L}^{-1}$) found in the WWTP influent and RO influent and effluent samples ($n = 30$).

	Organic parameters	Average influent WWTP	Average RO influent	Average RO effluent	Average rejection %
	Color (Pt-Co)	–	23	0.5	98
	UV254 (cm^{-1})	–	0.120	0.002	98
	BOD5 (ppm O_2)	–	1.593	<1.500	53*
	TOC (ppm)	–	5.20	0.07	99
	COD (ppm O_2)	–	19.7	5.8	71
	Micropollutants				
VOCs	Trichloromethane	2.50	2.47	<0.001	99*
	E-1,2-Dichloroethane	0.30	0.13	<0.033	88*
	Carbon tetrachloride	n.d.	0.11	<0.003	99*
	Trichloroethene	0.26	0.12	<0.003	99*
	Methane, bromodichloro-	n.d.	0.80	0.14	83
	Toluene	1.08	0.07	0.06	16
	Ethane, 1,1,2-trichloro-	6.59	2.71	0.47	83
	Methane, dibromochloro-	n.d.	0.28	0.14	49
	Tetrachloroethene	<0.001	0.86	2.27	<5
	Benzene, chloro-	n.d.	0.07	0.19	<5
	Ethylbenzene	0.05	0.05	0.03	25
	o-xylene	0.09	0.08	<0.001	99*
	Styrene	0.20	0.20	<0.0005	99*
	p-xylene/m-xylene	0.09	0.09	<0.0005	99*
	Benzene, (1-methylethyl)-	0.14	0.14	0.14	<5
	Benzene, 1,2,4-trimethyl-	0.17	0.16	0.15	6
	Benzene, 1,3,5-trimethyl-	0.21	0.17	0.16	5
	Benzene, tert-butyl-	0.24	0.23	<0.0005	98*
	Benzene, 1,3-dichloro-	0.18	0.18	<0.010	97*
	Benzene, 1,2-dichloro-	n.d.	0.34	<0.001	99*
	Benzene, 1,4-dichloro-	0.23	0.34	<0.010	99*
	Benzene, 1,2,4-trichloro-	n.d.	0.22	<0.001	98*
	Naphthalene	0.13	0.11	0.10	3
Odors	Disulfide, dimethyl	0.66	0.27	0.18	32
	Phenol	3.00	0.42	0.43	<5
	Phenol, 3-methyl-	0.75	3.27	<0.100	98*
	Geosmin	0.27	0.23	<0.005	99*
	Citral	0.33	0.30	<0.010	98*
Allergens	Cinnamyl Alcohol	11.52	1.37	<0.100	96*
	Eugenol	0.51	0.30	<0.010	98*
	Isoeugenol	0.96	0.48	<0.100	90*
	Benzil Salizicate	0.21	0.11	<0.017	93*
EDC	Tributyl phosphate	n.d.	0.32	<0.001	99*

n.d.—No detected compound.

*Estimated rejection.

weight (see in Table 1). Two odor compounds (dimethyl-disulfide and phenol) were low rejected due to their low $\log K_{ow}$ partition coefficient and their low molecular weight.

It needs to be noted that close to the LOD, accuracy in detected concentrations might be affected. The target organic parameters as well as the specific micropollutants detected in the WWTP influent and RO influent and effluent samples as an average of all the sampling are presented in Table 3. Moreover, their rejection by RO membranes is also shown in the table. Some of the rejections were estimated in cases where the concentration in the RO effluent was lower than the LOD. Those rejections were estimated taking into account the half of the LOD. It is worth mentioning the presence of some halogenated VOCs, such as bromodichloromethane, dibromochloromethane, and 1,3-dichlorobenzene in the RO influent due to chlorination stages of the conventional treatment. These species

were finally reduced by the RO treatment. In addition, some micropollutants such as trichloromethane, 1,1,2-trichloroethane, phenol, and cinnamyl alcohol were present in the WWTP influent and not eliminated by the conventional treatment.

The molecular weight, the $\log K_{ow}$, and the RO rejections regarding some representative micropollutants found in the RO influents and effluents are represented and compared in Fig. 4. The molecular weight of some micropollutants vs. their rejections have a similar trend especially for uncharged compounds, because it is assumed that transport through the membrane is mainly related to size exclusion (Fig. 4(a)). The $\log K_{ow}$ partition coefficient compared with the micropollutants rejection is shown in Fig. 4(b). A similar trend has been observed for the majority of the compounds, especially those which have higher $\log K_{ow}$ partition coefficient and higher molecular weight. The higher to K_{ow} , the more

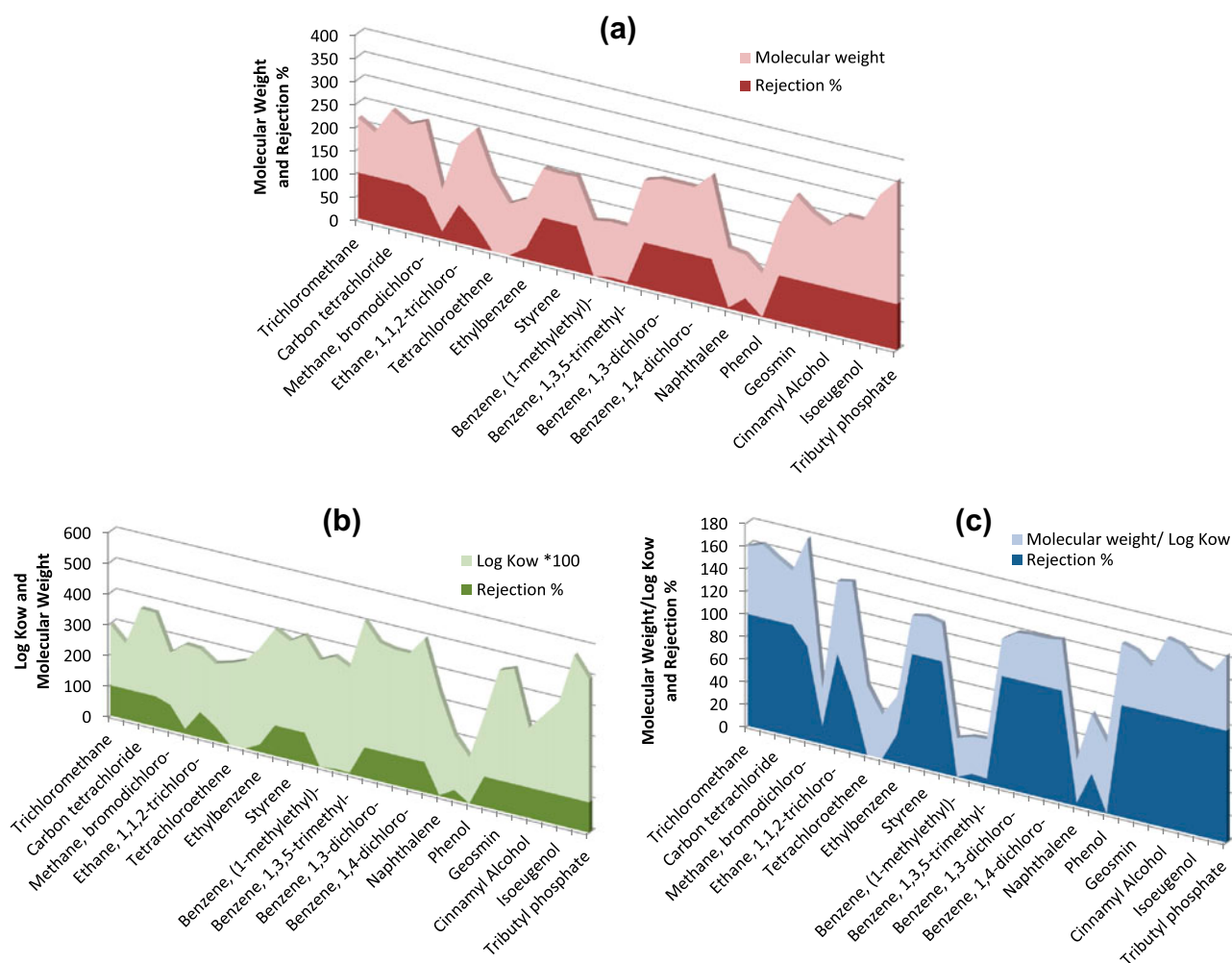


Fig. 4. Comparison between the molecular weight, the $\log K_{ow}$, and the rejection of some representative micropollutants.

non-polar the compound, being better rejected by RO membranes the less polar compounds. The log K_{ow} partition coefficients are generally inversely related to aqueous solubility and directly proportional to molecular weight. In addition, similar tendency was also observed for the micropollutants rejection by the relation between the molecular weight and the log K_{ow} and it is shown in Fig. 4(c).

As a general trend, the results reported indicate that RO membrane treatment can achieve an enhanced rejection efficiency of a wide range of trace organic contaminants, over conventional treatment methods, which is in agreement with other authors [18–21].

4. Conclusions

The presence and behavior of 75 micropollutants during RO membrane treatment has been evaluated in an urban WWTP. Results reported in this study indicate that RO membrane processes can achieve an enhanced rejection efficiency of a wide range of trace organic contaminants, since conventional processes alone are not sufficient to remove these micropollutants.

The majority of the present micropollutants are removed from the waste water using RO membrane treatment, improving the effluent quality in terms of micropollutants concentration. Fragrance allergens and EDCs were the families of the micropollutants with consistently high rejection, being higher than 83% because of their polarity as well as their molecular weight.

It is assumed that transport through the membrane is mainly related to size exclusion. Therefore, as a general trend, higher rejection was observed when increasing molecular weight.

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Abbreviations

BOD ₅	—	biological oxygen demand
COD	—	chemical oxygen demand
CIP	—	cleaning in place
EDC	—	endocrine disrupting compounds

EI	—	electron impact
GC-MS	—	gas chromatography-mass spectrometry
HS-SPME	—	headspace solid phase microextraction
LOD	—	limit of detection
MF	—	microfiltration
NF	—	nanofiltration
PDMS/DVB	—	polydimethylsiloxane/divinylbenzene
RO	—	reverse osmosis
TOC	—	total organic carbon
UF	—	ultrafiltration
VOCs	—	volatile organic compounds
WWTP	—	waste water treatment plant

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