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Headspace-solid phase microextraction: useful technique to characterize volatile and semi-volatile organic compounds in water reuse applications

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ABSTRACT

Sample preparation is an essential step in analysis, greatly influencing the reliability and accuracy, the time and cost of analysis. Solid-phase microextraction (SPME) is a very simple and efficient, solventless sample preparation technique, which has been widely used in different fields of analytical chemistry. In this study, four different polarity SPME fibres coupled with gas chromatography-mass spectrometry have been used for the determination of volatile and semi-volatile organic substances from the reverse osmosis (RO) influent in water reuse applications and the results have been compared with those obtained with conventional liquid–liquid extraction. Adsorption of organic foulants on the membrane surface causes organic and biological fouling which also produces flow loss and consequently pressure must be high to maintain the flow. PA and PDMS/DVB/CAR were complementary fibres which together could characterize the organic compounds in the influent water. Organic compounds characterized belong to different families including: aromatic hydrocarbons, linear hydrocarbons, ketones, alcohols, fatty acids, phenols, nitro-containing compounds, phthalates, fragrance allergens, hormones, halogenated compounds, acetate derivates, sulphur-containing compounds, amines and sugars. In addition, RO-influent water values of total organic carbon, chemical oxygen demand, biological oxygen demand and colour were analysed during the study in order to complement water analysis.

Keywords: Headspace solid phase microextraction; Gas chromatography-mass spectrometry; Organic compound; Reverse osmosis; Water reuse

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1. Introduction

In recent years, membrane processes, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membrane, have received an increasing attention as promising technologies for water treatment, such as drinking water treatment, wastewater treatment and sea water desalination since they can produce water with superior quality at low cost. This effect has been widely

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studied [1–4]. In spite of great advances in membrane technology, membrane fouling is still one of the major challenges faced by installations dealing with difficult waters. Membrane fouling is caused by the adsorption, accumulation or precipitation of dissolved constituents from the influent water on the membrane surfaces, as [5] Fang et al. mentioned in their paper. In particular, organic matter (OM) plays a crucial role in formation of RO fouling, being the organic fouling a serious problem for membrane processes and limiting the widespread use of membranes. Such fouling results in an increase in the energy and reduction of water production, well documented by [6–8].

Previous research reported that relatively hydrophilic and non-charged fractions, comprising of polysaccharides and protein-like substances, may be responsible for severe fouling formation in a membrane bioreactor (MBR) and NF membrane system which was tested with respect to water reclamation [9,10]. Some studies have also focused on the relationship between physical and chemical properties of OM and membrane fouling formation [11–14]. Although many studies have been conducted to determine or identify the most relevant factors contributing to fouling formation, understanding of membrane foulants in a large scale water reclamation plant is still incomplete as the majority of previous research has been performed under controlled laboratory conditions.

Previous research has been focused on OM characterization in the influent water by different analytical techniques which were focused on identifying major constituent of organic foulants and determining the natural organic matter (NOM) fraction and functional groups, as well as their molecular weight [15]. These analytical techniques included pyrolisis and mass spectroscopy [16], high-performance size exclusion chromatography with ultraviolet and dissolved organic carbon (DOC) detections and Fourier transform infrared spectroscopy (FTIR) [17,18]. Some studies have also applied advanced water characterization techniques, such as excitation emission matrix fluorescence spectroscopy (EEM) and liquid chromatography with organic carbon detection (LC-OCD) for the characterization of foulants [19], as well as high-resolution mass spectrometry for molecular characterization of dissolved organic matter [20]. These studies determined two fouling indexes: the total fouling index and the hydraulically irreversible fouling index, comparing them with the organic fouling results.

Several sample preparation techniques, such as liquid–liquid extraction (LLE), single drop microextraction and solid phase extraction can be used for the extraction of organic compounds from RO influent water samples, whereas headspace solid phase microextraction (HS-SPME) can selectively extract organic compounds and no solvents are required. Solid-phase microextraction (SPME) has been widely used in different fields of analytical chemistry since its first applications to environmental and food analysis and is ideally suited for coupling with mass spectrometry (MS). The SPME technique can be routinely used in combination with gas chromatography and it reduces the time needed for sample preparation. The organic compounds in the sample are directly extracted to the fibre coating. Some of the studies reported in the literature [21–24] have been analysed, different micropollutants by SPME, including pharmaceuticals and personal care products, which are continuously released into the environment. Therefore, advanced characterization of volatile and semi-volatile organic compounds is believed to provide valuable insights into the fouling characteristics in a large-scale application of UF and RO systems for municipal water reclamation.

The objective of this study was to evaluate the potential of the headspace HS-SPME technique for the water characterization. The advantage of HS techniques when volatile or semivolatile compounds are analysed is that the extraction is more selective and the matrix influence becomes lower [25]. A study of four different polarity SPME fibres was done in order to sequentially identify individually the organic compounds from the RO influent water. In addition, a comparison with the conventional LLE was also performed.

Furthermore, classical organic characterization of the influent water, such as chemical oxygen demand (COD), colour, UV254, biological oxygen demand (BOD), total organic carbon (TOC) and specific light absorbance (SUVA), was done in order to correlate with the volatile and semi-volatile organic compound results and to have supplementary information regarding the fouling.

2. Methods

2.1. Chemicals and materials

Dichloromethane (DCM) and isopropanol (IPA) solvents were GC grade with purity > 99.9% from Prolabo, (Barcelona, Spain). Helium gas 99.999% was supplied from Praxair (Barcelona, Spain).

Four commercial extraction fibres including 100-μm polydimethylsiloxane (PDMS), 65-μm polydimethylsiloxane/divinylbenzene (PDMS/DVB), 50/30-μm polydimethylsiloxane/divinylbenzene/carboxen (PDMS/DVB/CAR) and 85-μm polyacrylate (PA) were purchased from Supelco, (Madrid, Spain).

2.2. Research unit

The study was carried out in a research unit which consists RO membranes with UF system used as a pretreatment. The research unit was operated using the secondary clarified water coming from a conventional urban WWTP located in the NE of Spain. The pretreatment of the conventional WWTP included: coarse screening (1 mm), sand filtration followed by primary sedimentation, secondary biological treatment and secondary sedimentation. Fig. 1 depicts the existing treatment squeme with the sampling point as a star. Influent RO water samples were collected weekly in amber glass bottles and were stored at 4°C until analysis, within 2 d.

The RO elements tested were operated for two months to investigate the organic and biofouling resistance, as well as the removal of organic compounds from the secondary effluent of the WWTP. The tested membranes were DOW FILMTEC™ XLE-440. They are extra low-energy RO elements designed to deliver high-quality water at low operating cost for urban and industrial water applications. The operational permeate flow was fixed between 330 and 360 L h^{-1}, feed pressure was fixed between 6.27 and 6.30 bar and the pressure drop was also fixed between 0.14 and 0.32 bar. In addition, conductivity, temperature and pH were also monitored. These selected parameters are worldwide recognized as standard operational conditions for RO systems in wastewater application treatments [26].

2.3. Water analysis

Thirty millilitres of water sample was introduced into a 50-mL PTFE/silicone screw-cap glass vial. Then, 0.4 g mL^{-1} of sodium chloride (saturated solution) was added, the vial was closed and put over a magnetic stirrer in a water thermostatic bath at 50°C. The magnetic stirring was applied at 1,000 rpm and the SPME fibre was exposed to the headspace during 30 min. After the extraction, the fibre was inserted into the injection port of the gas chromatograph for the thermal desorption and analysis. Fibre was desorbed at 280°C during the chromatographic analysis in the splitless mode.

LLE was also performed to water samples in order to compare the results with the SPME extraction. The conventional standard method is described elsewhere [27]. Samples were acidified with 10% hydrochloric acid to pH 2 and extracted with 2 × 100 mL of DCM/IPA (90:10 v/v) and the extracts were concentrated in the R-210 Büchi rotavapor (Flawil, Switzerland) down to 250 μL as a final volume. Then, 1 μL was injected into the GC injector port.

The gas chromatography analysis of the SPME and LLE extracts were performed with a GCMS-QP2010 Ultra/GCMS-QP2010 SE from Shimadzu (Kyoto, Japan), equipped with a split/splitless injector and coupled to a mass spectrometer detector. Helium was employed as a carrier gas at constant column flow of 1.4 mL min^{-1}. Analytes were separated with TRB-5MS

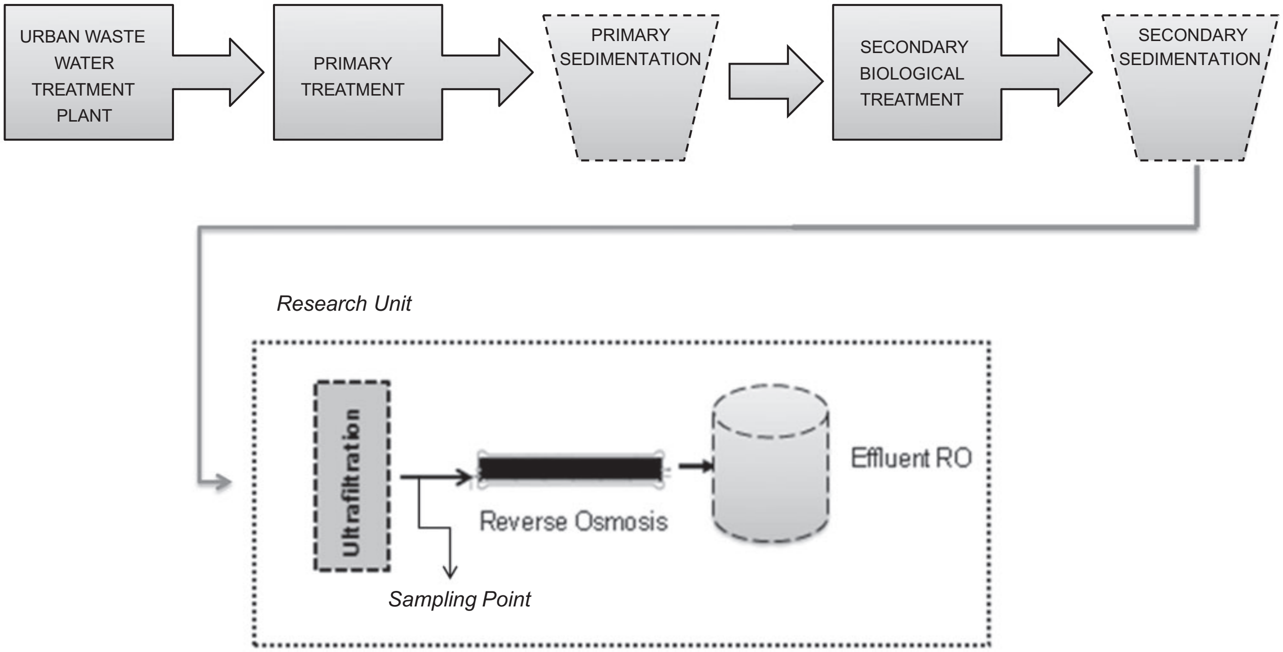

Fig. 1. Set-up of WWTP and research unit.

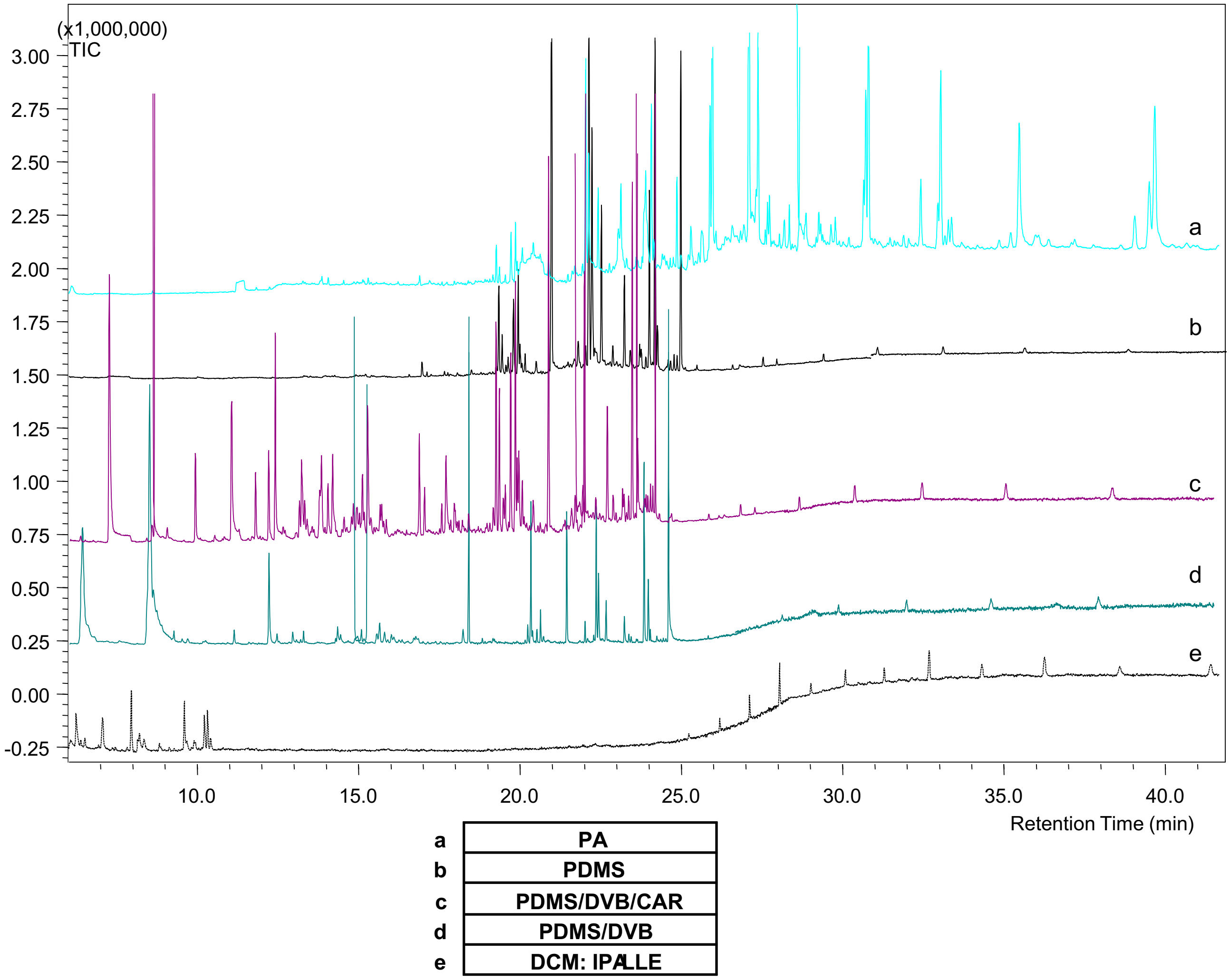

Fig. 2. GC-MS chromatograms for the four different SPME fibres and the LLE of the RO influent water.

column (60 m × 0.32 mm id, 1 μm film thickness) from Teknokroma (Barcelona, Spain). The split/splitless injection port was equipped with a 0.75 mm ID liner from Supelco, and operated at 280˚C, allowing direct injection or SPME desorption. The oven temperature programme was started at 80˚C, held for 5 min; and then increased by 10˚C min^{-1} up to 300˚C and held for 10 min. The total GC-MS analysis run was 42 min. The MS analyses were conducted 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 (EI) mode at 70 eV. The transfer line temperature was maintained at 300˚C and the ion source temperature at 250˚C.

The organic compounds were identified by the mass spectrum library, NIST08.LIB, considering only those compounds with match spectra higher o equal than 95%. Other compounds with match between 85 and 95% were also tentatively identified.

In addition, the performance of the RO membranes was monitored in terms of several operational and organic basic parameters such as TOC, colour, UV254, COD and BOD following Standard Methods [28].

3. Results and discussion

3.1. Basic organic water analysis

OM is much more relevant in water reuse applications than in other types of water samples such as river or sea water, having a TOC content approximately three times higher [29], which is not being totally eliminated by conventional water treatments. In this study, changes in water characteristics through

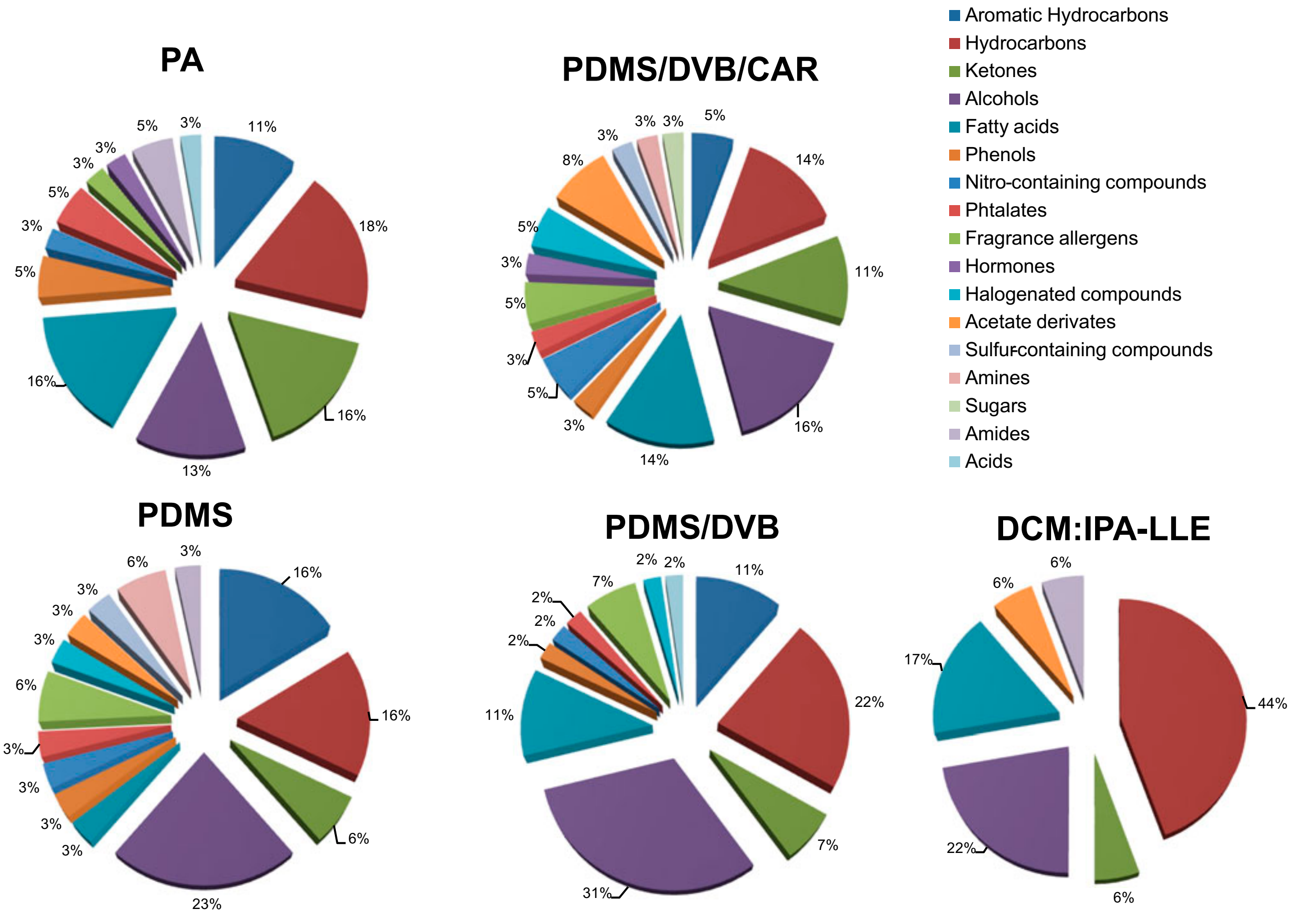

Fig. 3. Families of organic compounds found by the different SPME fibres and the LLE.

the RO membranes in terms of organic presence were monitored in order to investigate the RO influent water characteristics. Characteristics of RO influent water and operational parameters can be found in Table 1, showing the variability in terms of water quality measured weekly. The values are presented as the result range of the whole experiment.

The DOC was also measured. The combined expression of UV254/DOC as SUVA is a good representation of humic content. Humic substances exhibits relatively high SUVA values and contain relatively large amounts of aromatic carbons. However, microbial by-products, such as acids, polysaccharides, aminosugars and proteins, generally have relatively low SUVA values [30]. In this study, SUVA in the RO influent water had values less than 4 L (mg m)$^{-1}$, therefore the main DOC content was formed by microbial by-products (acids, aminosugars, polysaccharides and sugars).

Table 1
Operational and organic water parameters in the RO study

Parameters	Values
Permeate Flow (L/h)	336–352
Feed Pressure (bar)	6.27–6.30
Pressure drop (bar)	0.14–0.32
Conductivity (μS/cm)	1,964–2,012
Temperature (°C)	24.5–26.8
pH	7.2–7.3
Total COD (mg L^{-1} O_2)	15.6–32.3
Color (Pt-Co)	28–42
UV 254 (cm^{-1})	0.13–0.15
BOD (mg L^{-1} O_2)	<1.5–3.68
TOC (mg L^{-1})	5.7–7.7
DOC (mg L^{-1})	5.7–7.7
SUVA (L (mg m)$^{-1}$)	<4

Table 2
Organic compounds found by using the PDMS/DVB/CAR and PA SPME fibres

SPME fibre	Compounds	Family	Match (%)
	p-Benzoquinone, 2,6-di-tert-butyl-; *Butylated Hydroxytoluene*[a]	Aromatic Hydrocarbons	>95
PDMS/ DVB/ CAR	Decane; Eicosane, 3-methyl; 2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-; 7-(1,3-Dimethylbuta-1,3-dienyl)-1,6,6-trimethyl-3,8-dioxatricyclo[5.1.0.0(2,4)]octane; *4-(2,2-Dimethyl-6-methylenecyclohexylidene)-3-methylbutan-2-one*[a]	Hydrocarbons	>90
	Ethanone, 1-(6,6-dimethylbicyclo[3.1.0]hex-2-en-2-yl)-; *5,8-Decadien-2-one, 5,9-dimethyl-*[a]; 1-Hydroxy-6-(3-isopropenyl-cycloprop-1-enyl)-6-methyl-heptan-2-one; 3-Ethyl-4,4-dimethyl-2-(2-methylpropenyl)cyclohex-2-enone	Ketones	>86
	1-Hexanol, 2-ethyl-; Ethanol, 2-[2-[2-[4-(1,1,3,3-tetramethylbutyl)phenoxy] ethoxy]ethoxy]; 1-Heptanol, 6-methyl-; 5,7-Octadien-3-ol, 2,4,4,7-tetramethyl-; 2,5-Pentadecadien-1-ol; 3-Cyclohexene-1-methanol, .alpha.,.alpha.4-trimethyl-	Alcohols	>89
	Benzoic acid, 5-acetyl-2-methoxy-, methyl ester; 1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester; 1,4-Benzenedicarboxylic acid, bis(2-methylpropyl) ester; Propanoic acid, 2-methyl-, 2,2-dimethyl-1-(1-methylethyl)-1,3-propanediyl ester; Acetic acid, (1,2,3,4,5,6,7,8-octahydro-3,8,8-trimethylnaphth-2-yl)methyl ester	Fatty acids	>91
	Di-tert-butylphenol[a]	Phenols	>95
	Benzonitrile, 4-(4-butyl-1-cyclohexen-1-yl)-[a]; Pyrido[2,3-g]indole, 5-methoxy-2,3,7,9-tetramethyl-	Nitro-containing compounds	>90
	Dibutyl phthalate [a]	Phtalates	>90
	Tonalide[a]; D-Limonene	Fragrance allergens	>90
	Diazoprogesterone	Hormones	>85
	Tetrachloroethylene; 4-(2,4-Dichloro-7,8,9,10-tetrahydro-6H-5-oxa-cyclohepta [b]naphthalen-5a-yl)-morpholine	Halogenated compounds	>85
	4-tert-Butylcyclohexyl acetate; Isopulegol acetate; Acetate, 2-cyclohexenyl-3-[1-(2-oxopropyl)ethenyl]-2,4,4-trimethyl	Acetate derivates	>90
	1-Propene-1-thiol	Sulphur-containing compounds	>91
	3,6-Bis(N-dimethylamino)-9-ethylcarbazole	Amines	>85
	d-Glucitol, 4-O-decyl-	Sugars	>93
	Butylated Hydroxytoluene[a]; 1,4-Benzenediol, 2-[(-octahydro-tetramethyl-1-naphthalenyl)methyl]-; Cyclopenta[g]-2-benzopyran, -hexahydro-hexamethyl-; 4-Acetylphenyl 5-acetyl-2-methoxyphenyl ether	Aromatic Hydrocarbons	>90
PA	trans-4,5-Epoxydecane; *4-(2,2-Dimethyl-6-methylenecyclohexylidene)-3-methylbutan-2-one*[a]; Tetrahydrofurfuryl acrylate; Oxirane, 2,2′-[1,4-butanediylbis(oxymethylene)]bis-; 4-Hydroxybutyl acrylate; Butanal, 4-[(tetrahydro-2H-pyran-2-yl)oxy]-; 1,3,5-Trioxane, 2,4,6-tripropyl-	Hydrocarbons	>90
	5,8-Decadien-2-one, 5,9-dimethyl-[a]; 4′-Ethoxy-2′-hydroxyoctadecanophenone; 1,3-Dioxolan-4-one, 2-(1,1-dimethylethyl)-5-(1-methylethyl)-; 2,5-Dimethyl-4-hydroxy-3-hexanone; 3-Methyl-hexahydro-pyrano[3,2-b]pyran-2-one; Hexamethylbenzophenone	Ketones	>85
	1-Butanol, 4-butoxy-; Undecanol-4; Tetraethylene glycol diethyl ether; 3-Nonanol, 3-methyl-; (7a-Isopropenyl-4,5-dimethyloctahydroinden-4-yl) methanol	Alcohols	>90
	Butyric acid, 3-tetradecyl ester; 2-Propenoic acid, tridecyl ester; Benzoic acid 2-ethoxyethyl ester; 2-Methoxy-3-methyl-butyric acid, methyl ester; 1,3,5-Trioxane, 2,4,6-tripropyl-; Sulfurous acid, pentadecyl 2-pentyl ester	Fatty acids	>95
	Di-tert-butylphenol[a]	Phenols	>95

(*Continued*)

Table 2 (*Continued*)

SPME fibre	Compounds	Family	Match (%)
	Benzonitrile, 4-(4-butyl-1-cyclohexen-1-yl)-[a]	Nitro-containing compounds	>93
	Dibutyl phthalate[a]; Phthalic acid, butyl undecyl ester	Phtalates	>87
	Tonalide[a]	Fragrance allergens	>90
	Pseduosarsasapogenin-5,20-dien	Hormones	>90
	Propanamide, 2-methyl-; Hexanamide, N-tetrahydrofurfuryl-	Amides	>95
	Butanoic acid, anhydride	Acids	>89

[a]Italics compounds are found by both fibres.

3.2. Characterization of organic compounds

The presence of micropollutants and possible organic foulants on the RO influent water were determined by four different SPME polarity fibres and also compared with a conventional LLE, both followed by GC-MS analysis. The tested fibres were PDMS with low polarity, PDMS/DVB and PDMS/DVB/CAR with intermediate polarity and PA with high polarity. Chromatograms of the RO influent water tested with the SPME fibres are depicted in Fig. 2.

PA fibre extracted more polar compounds which eluted after the first 20 min of the GC analysis such as some fatty acids including butyric acid 3-tetradecyl ester, 2-propenoic acid tridecyl ester and benzoic acid 2-ethoxyethyl ester. PDMS/DVB/CAR fibre extracted a higher number of organic compounds, such as 1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester (fatty acid), diazoprogesterone (hormone) and d-glucitol, 4-o-decyl (sugar) compared to the PDMS/DVB fibre. This is due to the fact that the intermediate polarity of PDMS/DVB/CAR fibre can also extract the polar compounds. It can be concluded that PA and PDMS/DVB/CAR can together characterize from very polar compounds such as fatty acids to very apolar compounds such as hydrocarbons.

The organic compounds found by the different fibres were also classified into different families of compounds. All families of organic compounds found by the different fibres are shown in Fig. 3.

In the case of the PA fibre, it could be observed that it extracted more polar compounds such as fatty acids, acids and amides (16, 3 and 5% of the total organic compounds extracted), than the other types of fibres. For example, only 3% of the extracted compounds by PDMS fibre were fatty acids, (because it is the less polar fibre). A detailed list of identified compounds of the two complementary fibres (PDMS/DVB/CAR and PA) is presented in Table 2.

Major constituents of the RO-influent water can be categorized into different families: aromatic hydrocarbons and linear hydrocarbons (identified by the library with match spectra higher o equal than 90%), ketones and alcohols (with match spectra higher than 85%), fatty acids, phenols and nitro-containing compounds (with match spectra higher than 90%), phthalates, fragrance allergens (d-limonene and tonalide) and hormones (diazoprogesterone) (with match spectra higher than 85%). In addition, there were several specific compounds, including butylated hydroxytoluene, 5,8-decadien-2-one, 5,9-dimethyl-, di-tert-butylphenol, benzonitrile 4-(4-butyl-1-cyclohexen-1-yl)-, dibutyl phthalate and tonalide, which were extracted by both fibres. Benzonitrile is characteristic nitrogen containing aromatic compound [31] and aromatic aminoacid [32]. It could also be generated during the desorption of humic material [33]. Similarly, benzoic acid is a well-known fragment of humic-like material and might have more than one origin [34,35]. On the other hand, phthalates are compounds present in numerous plastic materials, and also could produce the peak of benzoic acid [36]. A probable pathway of benzoic acid formation from phthalates could be release of free phtalic acid, which is decarboxylated to benzoic acid. These findings partly support other previous study, which took place in the same research unit treating wastewater and analysing the fouling layers of the RO membranes [37].

There were some families of compounds extracted by PDMS/DVB/CAR and not by PA and vice versa. For instance, PDMS/DVB/CAR extracted halogenated hydrocarbons (tetrachloroethylene), acetate derivates (isopulegol acetate), sulphur-containing compounds (1-propene-1-thiol), amines and sugars (all of them with match spectra higher than 85%). On the other hand, PA fibre-extracted amides (propanamide, 2-methyl-) and acids (butanoic acid) were as well-extracted (with match spectra higher than 89%).

LLE with a mixture of DCM:IPA organic solvents was performed for the comparison with the SPME methodology. The GC chromatogram is presented in Fig. 2. It could be appreciated that SPME fibres extracted more compounds than the conventional LLE. In addition, the signal areas of the compounds extracted by LLE were always lower than those extracted by the SPME fibres. In Fig. 3 the number of families found by the LLE, being lower than with SPME, is also represented. The families of organic compounds found were hydrocarbons (being the 44% of the total organic compounds extracted), ketones, alcohols, fatty acids, phenols and amides. Therefore, as a general conclusion, the influent water was better characterized by the PDMS/DVB/CAR and PA SPME fibres than the LLE followed by GC-MS.

4. Conclusions

In the present study, the analysis of the organic compounds present in the influent water has been performed by different HS-SPME polarity fibres followed by GC-MS analysis. PA and PDMS/DVB/CAR were complementary fibres which together could mainly characterize the organic compounds in the influent water.

More families of compounds have been found with the powerful technique HS-SPME than LLE. In addition, SPME has the advantage of eliminating organic solvents and decreasing the steps for sample preparation.

However, more experiments are needed, such as flat sheet studies, in order to understand and confirm if these families of compounds could be possible strong organic foulants of RO membranes. In addition, it would be interesting to know their nature and the concentration limit in which they start to act as a foulants.

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Abbreviations

BOD_5 — biological oxygen demand
COD — chemical oxygen demand
EDC — endocrine disrupting compounds
EI — electron impact
EEM — excitation emission matrix fluorescence
FTIR — Fourier transform infra-red spectroscopy
GC-MS — gas chromatography-mass spectrometry
HS-SPME — headspace solid phase microextraction
LC-OCD — liquid chromatography with organic carbon detection
LLE — liquid–liquid extraction
MBR — membrane bioreactor
MF — microfiltration
NOM — natural organic matter
NF — nanofiltration
OM — organic matter
PA — polyacrilate
PDMS — polydimethylsiloxane
PDMS/DVB — polydimethylsiloxane/divinylbenzene
PDMS/DVB/CAR — polydimethylsiloxane/divinilbenzene/carboxene
RO — reverse osmosis
TOC — total organic carbon
UF — ultrafiltration
VOCs — volatile organic compounds
WWTP — wastewater treatment plant

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