Characterization of organic fouling in reverse osmosis membranes by headspace solid phase microextraction and gas chromatography–mass spectrometry

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ABSTRACT

Adsorption of organic substances on reverse osmosis (RO) membrane surfaces may form an organic film on the membrane, known as organic fouling, and cause flow-rate loss. This problem is mostly unavoidable as no pretreatment method exists for perfect removal of possible foulants, including organic compounds resulting from undesirable bioactivity. Understanding the characteristics of fouling layers is an essential step towards overall improvement of RO membrane operations. In this study, the organic fouling in RO membranes treating the effluent of a secondary treatment from an urban wastewater treatment plant was characterized. Headspace solid phase microextraction (HS-SPME) coupled with gas chromatography–mass spectrometry has been used for the first time, to provide valuable information of organic fouling. Different polarity SPME fibers were tested for this purpose. In addition, the characterization of the organic fouling obtained by HS-SPME was compared with the results obtained by extraction using several organic solvents. The results indicated that more compound families can be identified by HS-SPME than by organic solvent extraction. Moreover, complementary organic analyses were done for better understanding of the organic fouling in RO membranes, such as total organic carbon and loss on ignition.

Key words | extraction, gas chromatography–mass spectrometry, headspace solid phase microextraction, organic fouling characterization, reverse osmosis membranes, water treatment

INTRODUCTION

Reverse osmosis (RO) membranes have been applied as an advanced water treatment process for the removal of natural organic matter (NOM) and micropollutants throughout the world. Low-pressure membrane filtration systems, such as ultrafiltration (UF), have also been widely applied in water treatment as an RO pretreatment or as a filtration step. RO pretreatment should be considered when total organic carbon (TOC) exceeds 3 mg L$^{-1}$ (Pearce 2007). Membrane technologies, including RO and UF, have a wide range of applications, ranging from brackish water and seawater desalination, pure and ultrapure water production, drinking and industrial water production and wastewater treatment (Amy et al. 2005).

Despite considerable research efforts undertaken by the scientific community, membrane fouling is still a major technical hurdle that needs to be addressed to enhance the cost-effectiveness of operating RO systems for wastewater reclamation. Therefore, organics in wastewater applications, even at very low concentrations, must be evaluated since they could be precursors of organic fouling (Baudequin et al. 2014; Gautam & Menkhaus 2014). Influent water with high organic matter content is the cause of organic fouling deposits. In addition, organic foulants are the precursors of biological growth, which leads to biofouling (Swietlik et al. 2004). Biofouling can be considered as a biotic form of organic fouling and has been known as a contributing factor to more than 45% of all membrane fouling problems in RO (Jin et al. 2009).

Fouling is an inherent phenomenon that reduces membrane performance, resulting in higher energy consumption, and lower removal efficiency. In particular, organic matter plays a crucial role in formation of RO
fouling, limiting the widespread use of membranes (Jarusutthirak et al. 2002; Xu et al. 2006; Jeong et al. 2013a, b). Increasing adsorption of micropollutants is an advantage of the fouling formation, producing narrower membrane pores and decreasing mass transport through the membrane (Agenson & Urase 2007). Moreover, the consequences of fouling include a decrease in water production, increased differential pressure (and energy consumption), higher cleaning frequency and a possible decrease in the effluent quality (Peña et al. 2013).

One way to find strategies to minimize the fouling is to characterize the foulants found on the membrane surface, because, as a result, it would be possible to understand how fouling could be reduced or avoided. To determine the nature of membrane fouling, several analytical techniques have been applied. Most of the major methods typically used include visual observation, loss on ignition (LOI), heterotrophic plate count (Speth et al. 1998), phospholipids, polysaccharides, TOC, pyrolysis–gas chromatography–mass spectrometry (GC–MS) for some hydrophobic organics characterization (Luo & Wang 2001; Khan et al. 2015), scanning electron microscopy, energy dispersive X-ray, Fourier transform infrared spectroscopy and GC–MS (Fernandez-Alvarez et al. 2010; Xu et al. 2010; Ding et al. 2013). Those methodologies are focused on characterizing, as a general trend, the organic fouling, identifying specific surface functional groups in RO membrane fouling. In addition, a few studies have focused on describing the types of polymers and microorganisms that are associated with membrane biofouling, analyzing also organic and biological compounds (Nuengjannong et al. 2005; Velten et al. 2007; Vrouwenvelder et al. 2008; Zhao et al. 2010; Jeong et al. 2013a, b). However, there still remains a basic lack of understanding about which specific foulants, such as microorganism cells and their fragments, NOM, extracellular polymeric substances and by-products of microbial metabolism, govern membrane organic fouling. Despite extensive studies on the relationship between membrane surface properties and membrane fouling, the role of specific surface functional groups in RO membrane fouling under different solution conditions still need further understanding (Puro et al. 2002).

The aim of the present study was to provide valuable information as well as to gain knowledge by characterizing specific organic compounds present in the fouling layer and classifying them into different families. The application of different polarity solid phase microextraction (SPME) fibers directly into the fouling has been studied for the first time.

Several extraction techniques can be used for the extraction of organic micropollutants from the organic fouling, whereas SPME has been studied for the first time, taking advantage of the facts that it can selectively extract compounds and no solvents are required (Nerin 2007; Yi et al. 2008; Buchberger 2011). SPME allows complete elimination of organic solvents in the pretreatment step and decreases the steps for sample preparation, and has become an accepted method for the determination of volatile and semi-volatile organic compounds. Therefore, in this study headspace (HS)-SPME has been used for the characterization of the organic compound families in the membrane fouling, due to its advantages. The advantage of HS techniques when volatile compounds are analyzed is that the extraction is more selective and the matrix influence becomes lower (Lambropoulou et al. 2007). To our best knowledge, no studies have evaluated the SPME preconcentration technique for organic compound extraction from RO membrane fouling.

For better characterization of the organic fouling, different organic solvent extractions of the RO membrane have been performed and analyzed by GC–MS in order to identify specific organic compound families and compare them with the SPME extraction. According to the literature (Wu et al. 2014), depending on the solvent, different compounds can be extracted, for example, the organic foulants on membranes fouled by pulp and paper mill effluent using solid–liquid extraction. In addition, complementary organic analyses, including TOC and LOI, were done on the RO membranes for better understanding the organic fouling.

MATERIALS AND METHODS

Materials and solvents

Methanol (MeOH), isopropanol (IPA), hexane (HX), dichloromethane (DCM) and acetonitrile (ACN) solvents were GC grade with purity >99.9% from Prolabo (Barcelona, Catalonia, Spain). Helium gas 99.999% was supplied by Praxair (Barcelona, Catalonia, Spain).

Four commercial extraction fibers, 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, Community of Madrid, Spain).

Wastewater treatment plant setup

The urban wastewater conventional treatment plant located in the north-east of Spain has a first stage consisting of a
primary treatment and a secondary biological treatment designed to treat 15,000 m³ d⁻¹ of water during winter time and 47,500 m³ d⁻¹ during summer time. The study was carried out in a research unit, which consisted of RO membranes with a UF system used as a pretreatment. The research unit was operated using the secondary clarified water coming from the conventional wastewater treatment plant (WWTP).

The tested RO membranes were Dow Filmtec™ XLE – 4040. They are extra low energy RO elements designed to deliver high quality water at low operating costs for urban and industrial water applications. The RO elements tested were operated for 2 months to investigate the organic and biofouling resistance, as well as the removal of organic compounds present in the water from the secondary effluent of the WWTP.

Membrane autopsy and general parameters

The RO membrane elements were autopsied to determine foulant accumulation onto the membrane surface. They were packed in plastic bags and stored at 4 °C until the autopsy, which was performed within 24 h after their removal from the installation. RO membrane elements were opened lengthwise to take a representative amount of membrane sample.

To analyze the LOI, approximately 10 g of fouling was removed with a small flexible rubber spatula from one side of a single membrane leaf. After drying the samples at 110 °C, they were then ignited at 550 °C and weighed again to identify inorganic and organic portions of foulant materials. The loss of weight after ignition was taken as the organic portion of the foulant and the residual as the inorganic portion, following the standard method (ASTM 2013).

For the analysis of the organic carbon on the membrane surface, a previous extraction is required. A section of 4 cm² over the length of the membrane element was cut and placed in a 40 mL sealed vial. The sample included the feed spacer and the membrane. Then, 20 mL of ultrapure water was added and the vial was placed in an ultrasonic cleaning bath from Fisher Scientific (Massachusetts, USA). The ultrasonic treatment (2 min) followed by mixing of the vial manually for a few seconds was repeated three times. Next, 20 mL of water was collected from the vial to measure the TOC (Shimadzu TOC-L equipment), measuring only the dissolved organic carbon part (Standard Methods for the Examination of Water and Wastewater 2005).

Organic fouling characterization by GC–MS

For the organic fouling characterization, the potential of the SPME was evaluated and a comparison with liquid extraction using different organic solvents was performed.

Regarding the SPME procedure, the fouling was removed with a small flexible rubber spatula from one side of a single membrane leaf. Then 0.5 g of fouling was analyzed by extracting the organic compounds with HS-SPME, using four different polarity fibers, followed by GC–MS determination. The fouling was introduced into a 20 mL vial, which was closed and put in a water thermostatic bath at 50 °C without agitation. The extraction time was 30 min and the SPME fiber was exposed to the HS. After 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.

Five different solvents were tested for the organic solvent membrane extraction: MeOH, IPA, HX, DCM and ACN (internal procedure of Dow Chemical). The organic solvents used had different chemical properties, which were closely associated with the results from characterizing the extracted organic fouling. HX was classified as a non-polar solvent with a polarity (given as the dielectric constant) of 1.88. IPA and MeOH were classified as protic solvents with a dielectric constant of 18 and 33, respectively. ACN and DCM were classified as polar aprotic solvents with a dielectric constant of 37.5 and 9.1, respectively.

Four sections of 20 × 30 cm² over the length of the membrane element were cut. First, the membrane sections were dried in an incubator at 35 °C overnight. Membrane samples were cut into small pieces for easy extraction. Then, the membrane pieces (approximately of 1 cm²) were placed into a 100 mL glass bottle. Fifty milliliters of solvent was added to ensure all the membrane pieces were covered. The bottle was placed in the ultrasonic bath and the extraction was carried out applying temperature, 10 °C less than the boiling point of each solvent, for 1 h. After the extraction, the extract was filtered using a syringe filter of 0.45 μm. The filtrate was placed in a round-bottom flask and evaporated to dryness in a rotary evaporator. Finally, it was re-dissolved in 1 mL of the tested solvent, and 1 μL was injected in the injection port of the GC. New membranes were also evaluated and therefore extracted and analyzed in order to eliminate the organic compounds, which could be extracted from the membrane, being first immersed in distilled water overnight to remove excess compounds from the manufacturing process.
Gas chromatographic analysis of both extracts was 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 a TRB-5MS column (60 m × 0.32 mm i.d., 1 μm film thickness) from Tecknokroma (Barcelona, Spain). The split/splitless injection port was equipped with a 0.75 mm i.d. liner from Supelco, and operated at 280 °C, allowing direct injection of SPME fiber. The oven temperature program 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 run was 42 min. The MS analyses were conducted in full-scan mode with a single quadrupole and monitored masses 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.

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

RESULTS AND DISCUSSION

Loss on ignition and organic carbon determination

LOI was determined by drying and weighing isolated foulant material at 110 °C. The samples were then ignited at 550 °C and weighed again to identify inorganic and organic portions of foulant materials. The loss of weight after ignition was taken as the organic portion of the foulant and the residual as the inorganic portion of the foulant.

Fouling distribution was also calculated by the LOI test, which also differentiates between the inorganic and the organic fouling distribution. The membrane fouling distribution was 1.02 g m⁻² of membrane, being 3% dry substance and 97% water. Therefore, there was approximately 30 mg m⁻² of fouling in the membrane surface (3% of 1.02 g m⁻²). Moreover, the percent contribution of inorganic and organic fouling was estimated. The contributions of organic and inorganic fouling were 91% and 9%, respectively, being a total of 27 mg m⁻² of organic fouling in the membrane surface. The results indicated that there was a considerable presence of organic fouling in the membrane surface.

Organic carbon concentration on the RO membrane surface was 47 mg m⁻², quantified as the soluble organic carbon part in the water extract. Visual observations and analysis of the biomass parameters LOI and organic carbon supported the findings from the pressure drop and flow-rate loss operational measurements observed.

Organic fouling characterization

HS-SPME followed by GC–MS analysis was performed for characterizing the presence of organic species in the RO membrane fouling. The tested fibers were PDMS for low polarity, PDMS/DVB and PDMS/DVB/CAR for intermediate polarity and PA for high polarity. The aim of this analysis was to compare the organic fouling extraction performed by different SPME fibers, comparing the chromatograms, analyzing the compounds individually and classifying them into different families, which would be prominent signals of biofouling and microbial activity occurring on all the membranes (Khan et al. 2013). As an example, acetamide could be a mass fragment of aminosugars, while other families such as proteins detected were composed of phenylalanine, tyrosine and tryptophan, with mass fragments of tolucene, phenol and indole.

Chromatograms of the membrane fouling extracted by the different SPME fibers are depicted in Figure 1.

It could be observed that PDMS/DVB/CAR extracted more compounds than the other fibers, due to its intermediate polarity, which could extract polar and less polar compounds. In addition, the organic compounds detected after the first 25 min of the GC analysis were only extracted by the PDMS/DVB/CAR and PA fibers, the first one having best response area. PA fiber was not able to extract those compounds eluted at the beginning of the chromatogram, which were extracted by the PDMS/DVB/CAR fiber, such as ketones (2-nonanone), sulfur-containing compounds (dimethyl trisulfide) and amides (4-ethylbenzamide). As mentioned before, all of these compounds families and mass fragments provided evidence of the presence of material originating from microbial cells.

The families of compounds extracted for each type of fiber are also presented in Figure 2. The families were represented as the percentage of the total compounds found by each fiber.

For example, in the PDMS/DVB/CAR extraction, 6% of the organic compounds extracted were hydrocarbons (i.e. dodecane and tetramethyloctane), 6% ketones (i.e. 2-nonanone), 15% acids, 13% sulfur-containing compounds (i.e. dimethyl trisulfide), 6% alcohols (i.e. 1-hexanol, 2-ethyl),
6% fragrance allergens (i.e. tonalid), 13% aromatic hydrocarbons (i.e. benzene, 1-methyl-2-(1-methylethyl)-), 6% amides (i.e. 4-ethylbenzamide), 19% fatty acids (i.e. octadecanoic acid, ethenyl ester and benzoic acid, 5-acetyl-2-methoxy-, methyl ester) and 13% sugars (i.e. D-arabino-hex-1-enitol, 1,5-anhydro-2-deoxy-). Hydrocarbons (71%) and alcohols (29%) are the families of compounds extracted with the PDMS fiber, while the PA fiber extracted hydrocarbons (46%), alcohols (23%), fatty acids (15%) and halogenated hydrocarbons (15%). PDMS/DVB fiber extracted more families of compounds than PDMS and PA. However, the PDMS/DVB/CAR fiber extracted more families than PDMS/DVB, and thus was the best fiber tested in terms of compound families extracted.
RO processes can either directly or indirectly remove NOM from water, depending on their operational conditions and the specific characteristics of the NOM such as its molecular weight, carboxylic acidity and humic substances content (Collins et al. 1985; Owen et al. 1995). However, more recent studies have shown that low molecular weight NOM compounds, such as those found in the present study, are considered the most difficult to remove by conventional coagulation (Sharp et al. 2006; Fabris et al. 2008). In addition, some investigations have found that hydrophilic NOM (non-humic acids, including fatty acids) might be a significant membrane fouling compound.

Regarding the organic solvent extraction, different polarity solvents were tested (ACN, IPA, HX, MeOH and DCM), whose GC–MS chromatograms are shown in Figure 3.

The most polar solvent was MeOH, followed by ACN, IPA and DCM, with intermediate polarity. And finally, HX was the least polar organic solvent. It could be observed that the best solvent for the extraction was the HX, since it could extract the apolar compounds, such as some hydrocarbons (including eicosane, pentadecane and nonadecane), as well as some polar compounds, which appeared at the beginning of the GC chromatogram, such as fatty acids (docosanoic acid, docosyl ester), alcohols (tetradecadien-1-ol) and ketones (benzophenone). In addition, it could be observed that, with HX, the extraction was more sensitive than with the other solvents obtaining high responses. Figure 4 shows the different solvents tested and the families of compounds found for each solvent. Linear hydrocarbons (including eicosane, dodecane, 2-methyl-6-propyl-, nonadecane, tricosane, hexacosane, heptadecane- tetramethyl- and octadecane, 2-methyl-) are the family of compounds most extracted, all of them with match spectra higher than 95%. In the case of IPA, DCM and HX extractions, the hydrocarbons represented more than 58% of organic compounds extracted.

However, in the ACN and methanol extractions, more families of compounds were extracted such as aromatic hydrocarbons (benzene, 1,3-trichloro and indole, 3-methyl-), alcohols (9-decen-2-ol, hexadecen-1-ol, trans-9- and tridecan-1-ol), acids (phthalamic acid), nitro-containing compounds (benzonitrile, 4-(4-butyl-1-cyclohexen-1-yl)-) and sulfur-containing compounds, all of them being identified with match spectra higher than 90%.

When comparing both extraction methodologies, SPME and organic solvent extraction, it has been demonstrated...
that similar families of compounds were found. As mentioned before, membrane studies have highlighted that NOM rejection is controlled by size exclusion and physicochemical influent water conditions as well as interactions between the organic foulant and the membrane properties. This is particularly important as the hydrophobic membranes have been deemed to be more susceptible to fouling adsorption than hydrophilic membranes (Hong & Elimelech 1997; Fan et al. 2001; Khayet et al. 2004). It has actually been demonstrated that humic compounds adsorbed more favorably onto hydrophobic membranes (Jucker & Clark 1994). The RO membrane studied in this paper has more hydrophilic behavior than other membranes in the literature. Therefore, the families of compounds found in the membrane fouling were of less humic character.

Furthermore, SPME is a fast method which requires a total of 30 min for the extraction and allows complete elimination of organic solvents in the pretreatment step, decreasing the steps for sample preparation, while the organic solvent extraction needs more time and consumes more solvents. In addition, a higher number of compound families has been found with the new tested SPME technique than with the organic solvent extraction, providing valuable information of organic fouling.

Currently, the SPME technique has been used for the determination of the organic compounds from the RO influent water. Therefore, the organic compounds commonly found in the influent water as well as in the membrane fouling are presented in Table 1. All of them were identified by the mass spectrum library with a match higher than the 95%.

The results indicated that there were several common families of compounds found in the influent water and on the membrane surface fouling: fatty acids (i.e. benzoic acid, 5-acetyl-2-methoxy-, methyl ester), amines (i.e. 3,6-bis...
(N-dimethylamino)-9-ethylcarbazole), alcohols (i.e. 1-hexanol, 2-ethyl), aromatic hydrocarbons and fragrance allergens. Those families of organic compounds found are characteristic carboxylic acids (e.g. the derivate compounds of the octadecanoic acid and 1-[(tetradeoxy)carbonyl]pentadecyl ester), amino acids, proteins and carbohydrates, and they could promote bacterial growth in the aquatic environment and biofilm growth causing operational problems in the RO system (i.e. clogging of the influent channel at very low concentrations) due to the biofouling layer formation [Nguyen et al. 2012]. The fragrance allergens (such as tonalide) are organic compounds coming from anthropogenic sources [Einsle et al. 2006]. All these organic fouling compounds could be absorbed by the RO membrane, leading to flow-rate loss. The adsorbed organic foulants could change the membrane surface characteristics, which could result in severe flux decline and affect the rejection.

CONCLUSIONS

In the present study, the SPME technique has been tested for the first time, to provide valuable information regarding the organic fouling. It has been demonstrated that similar families of compounds were found also by organic solvent extraction. In addition, SPME has the advantage of being a solvent-free technique, robust and fast. A detailed analysis of the organic membrane fouling has been done by analyzing the specific organic compounds by GC–MS, as well as the LOI and the organic carbon on the membrane surface.

PDMS/DVB/CAR was the best fiber selected, which provided more information regarding the organic compounds extracted. In the case of the organic solvents, HX gave more information regarding the organic fouling than the other solvents.

Furthermore, some compounds were commonly found in the fouling and on the membrane surface, as well as in the influent water. They probably could lead to RO membrane organic fouling and consequently membrane flux rate loss.

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