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Autopsy of RO desalination membranes Part 2. Chemical characterisation

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1. Context survey

Recent advanced in membrane technologies allow a large application of this process and reverse osmosis systems show today a dazzling development in desalination, contributing to more than 50% of the world installed capacity. Despite progress realised on membrane materials, a degradation of membrane performances appears with time. This major problem is mainly due to the fouling phenomenon and depends for a large part on the physico-chemical characteristics of the used resource. Several mechanisms are responsible for this fouling. Desalination membranes have the particularity of retaining salts. Precipitation phenomena can appear at the membrane surface because of the increase in salts concentration. Antiscalants could prevent this scaling problem. Deposits could also come from colloidal particles of organic origin which will accumulate (interactions with inorganics, co-precipitation) near the membrane to form a gel layer or a cake leading to a higher flow resistance (secondary membrane). Finally, adhesion and microorganism development at membrane surface constitute another type of fouling called biofouling. This biofouling is often initiated by a primary film containing proteins and sugars (bacterial or algae exudates). Membrane fouling is a complex phenomenon including sorption and precipitation mechanisms in which microbial activity (biofouling) plays an important role in particular in the case of seawater.

Performances improvement of desalination units necessitates an optimisation of the pre-treatment conditions (before RO membranes) which depends on the feed water plant quality but also on the membrane cleaning sequence. A better structural knowledge of the deposits accumulated at the surface of RO membranes removed from desalination plants, thanks to advanced microscopic, molecular and elemental analysis, may enable to give important information for a better operation of these facilities. This work is integrated in the European project MEDINA (Membrane-Based Desalination: An Integrated Approach), co-funded by the European commission within the Sixth Framework Programme (project number: 036997).

2. Scientific approach and analytical procedures

2.1. Evaluation of the fouling state of the membranes

Membranes modules from a seawater desalination plant were removed in December 2007 and in March 2008. These modules were fed by seawater that had undergone a conventional pretreatment, i.e. a coagulation with ferric sulphate followed by a filtration on dual media. A visual examination of these membranes revealed the presence of an important brownish deposit (Fig. 2). The first step of this study was to determine the importance of this deposit in comparison to the hydraulic performances of the system. Membrane sheets were carefully cut and placed in a bench-scale reverse osmosis unit (Fig. 1). The permeability of these fouled membranes was measured using synthetic seawater and compared with the permeability of a virgin or manually cleaned membrane.

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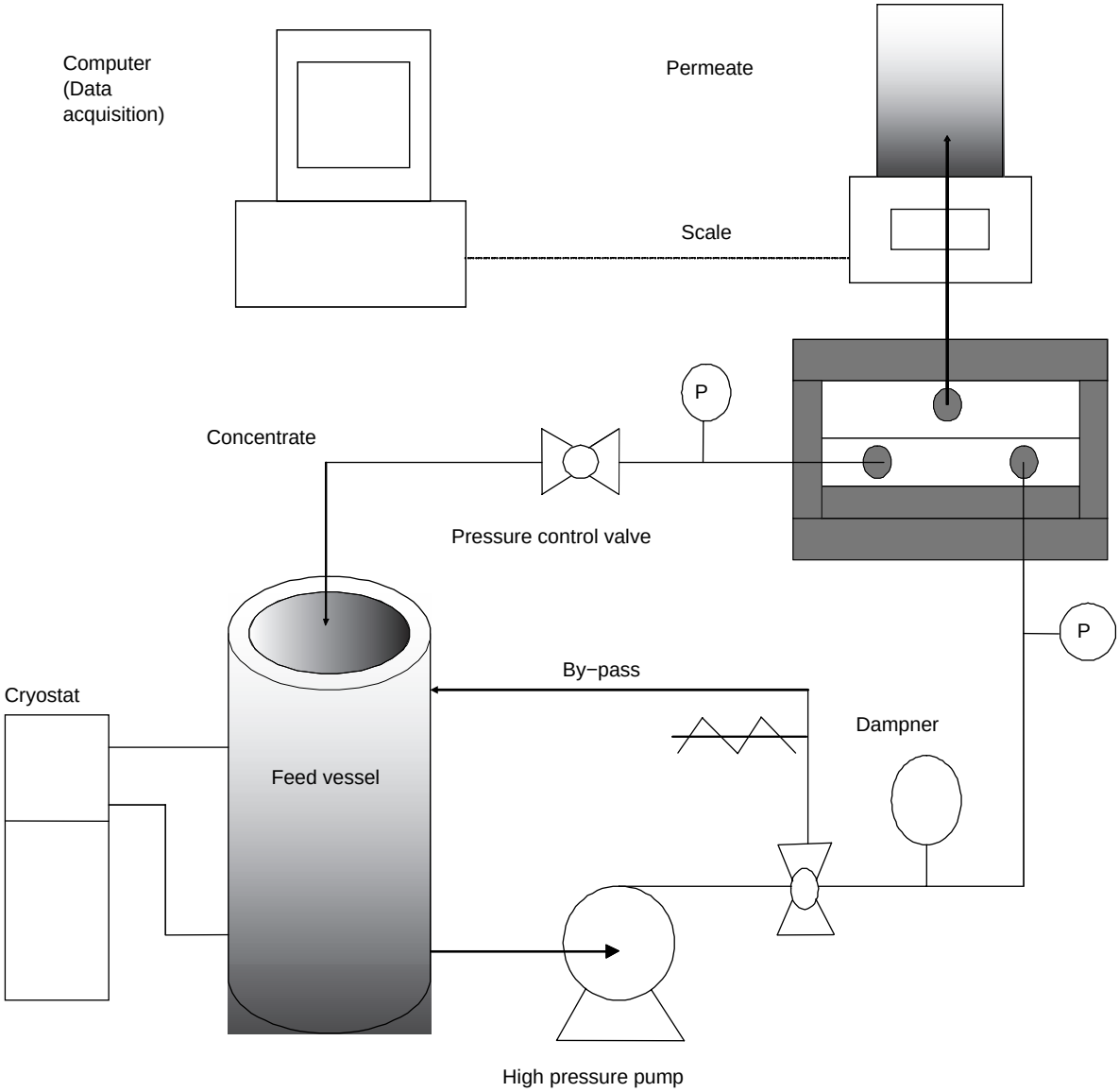

Fig. 1. Reverse osmosis unit used in the laboratory.

The experimental device is composed of a Sepa CF II cell (Osmonics) fed by a high pressure pump (Wanner G13, Axflow) linked to a 50L vessel. The double envelop of the tank is connected to a cryostat equipped with an external probe immersed in the tank controlling the temperature to 20 ± 0.5°C. Experiments were carried out at a constant cross-flow velocity of 0.2 m/s, corresponding to a concentrate flow of about 1 L/min for the considered system. Pressure was set at 60 bars. Active filtration surface is 140 cm². The evolution of the flow with time was monitored using a flowmeter (Analyt-MTC). Membranes were provided as a flat sheet and were cut to the cell size to conduct these experiments.

2.2. Membrane surfaces characterisation

Surface analyses were conducted on membrane sheets to characterise the foulant deposit accumulated as well as its organisation. Infrared spectroscopy type FT-IR equipped with an ATR accessory was used to give information on the deposit composition. Electronic microscopy (SEM-EDX) was carried out to understand the organisation of the deposit and the elements which could be on the surface.

2.3. Characterisation of the foulant scrapped on membrane surfaces

The deposit accumulated at membrane surfaces was carefully scrapped with a spatula and lyophilised.

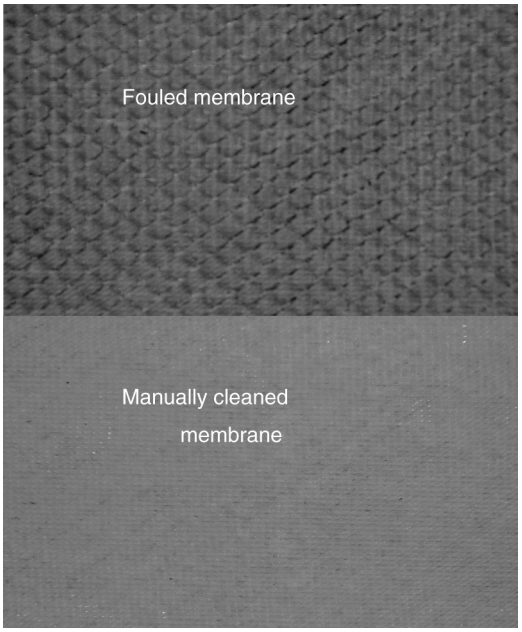

Fig. 2. Reverse osmosis membranes.

Several analyses were conducted on the different deposits recovered (Table 1).

3. Results

3.1. Evaluation of the fouled state of the membranes

Permeability measurements were conducted on the lab scale unit to confirm that the deposit accumulated on the surface was responsible for a permeability drop.

The tests were carried out on membranes recovered in December 2007 and March 2008 from the 1st module of the 1st stage of the RO unit. A complementary test was conducted on the 1st module/1st stage membrane of December 2007 on which the deposit was removed with a sponge and ultrapure water. Lastly, a permeability measurement was also performed on a membrane sheet coming from the last module of the pressure vessel/1st stage of December 2007, this membrane did not show any apparent fouling.

Fig. 3 shows that the 1st module/1st stage membrane of December 2007 has a lower permeate flux than the last

Table 1
Analytical techniques used to characterise the foulant material.

Analytical techniques	Implementation	Objective
Mass of deposit	Weighing of a balloon before and after lyophilisation	Determine the mass of deposit per surface unit
Organic/inorganic content	Weighing of a cupel before and after combustion at 550°C (APHA, 1992)	Determine the proportion of organic matter in the deposit
Elemental analysis	Sample combustion	Determine the proportion of C, H, N, O, and S
ICP-OES	Acidic mineralisation of the deposit before ICP-OES analysis	Determine content in major and trace elements (Ca, Mg, Fe, Cr…)
FT-IR ATR	Infrared spectrometer in mode attenuated total reflexion or internal reflexion	Identify absorption bands of functional groups present
Flash Pyrolysis GC/MS	Pyrolysis of the deposit at 650°C, compound separation in GC and identification in MS (Bruchet et al., 1990)	Identify organic compound classes (proteins, polysaccharides, aminosugars…)
Thermochemolysis TMAH GC/MS	Pyrolysis of the deposit at 400°C after hydrolysis and methylation, compound separation in GC and identification in MS (Saiz-Jimenez, 1994)	Identify fatty acids and aromatic compounds presents
Phospholipids content	Extraction, purification and esterification of phospholipids (methyl esters) separation in GC and identification in MS (Keinanen et al., 2003)	Quantify phospholipids presents
Sugars content	Hydrolysis, derivation and acetylation of polysaccharides (alditols acetates) separation in GC and identification in MS (Rumpel and Dignac, 2006)	Quantify polysaccharides presents

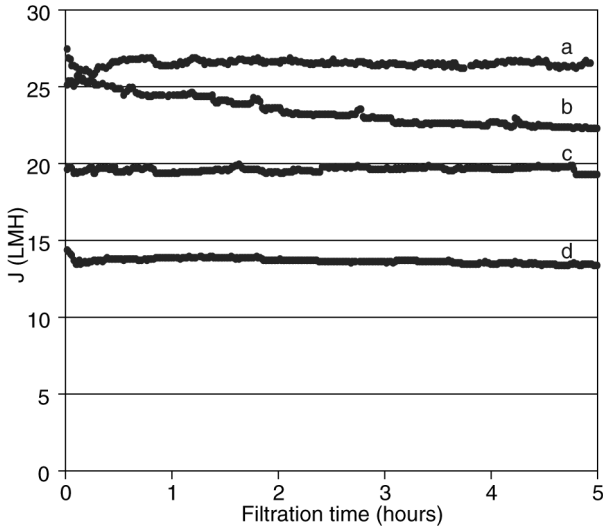

Fig. 3. Permeability tests conducted with synthetic seawater on different membranes. (**a**: last module/1st stage December 2007; **b**: membrane, manually cleaned December 2007; **c** and **d**: 1st module/1st stage March 2008 and December 2007, respectively)

module/1st stage membrane. The flux loss observed was around 50%. In comparison, the 1st module/1st stage membrane of March 2008 seems to be less fouled. The manual cleaning of the December 2007 membrane allows to restore about 85% of the flux (calculated from the flux of the last module/1st stage membrane considered not fouled).

This result suggests that a chemical cleaning is probably necessary to obtain a full recovery of the permeability.

3.2. Membrane surfaces characterisation

The composition and organisation of the deposit at the membrane surface was studied using spectroscopic and microscopic tools. Infrared spectroscopy (FTIR ATR) allows to identify the functional groups characteristic of the foulant matrix constituents. In comparison with the spectra of the virgin membrane as a reference, the spectra of fouled membranes show an accumulation of structures of polysaccharides type (1040 cm^{-1}) and proteins characterised by amid bands I and II (1550 cm^{-1} and 1650 cm^{-1}) (Fig. 4).

The observations with SEM-EDX underline the presence of a fouling layer on the whole membrane surface showing (clearly visible for December 2007) a honey combe characteristic structure (lighter deposit) in which a darker matrix is accumulated. Locally organic structures (diatom, unexpected observation considering the 5 µm prefiltration) and inorganic structures appear at the surface of this layer (Fig. 5). Elemental analysis with a X rays microprobe revealed that these inorganic structures are mainly composed of Fe but also of Ca, Si and Cr (phenomenon may be linked to a specific microbial activity).

3.3. Characterisation of the foulant scrapped on membrane surfaces

Deposits recovered from the surfaces of the different membranes and lyophilised were weighed before proceeding to a detailed characterisation. The deposit recovery was sometimes performed on a compartmented module to distinguish three areas: the feed area, the area at the rear of the module (brine area) and the intermediate area. Fig. 6 gives deposit quantities recovered on the different areas of the December 2007 and March 2008 membranes.

The quantities of deposit were similar for the two considered period, and they were close to those found on NF or RO membranes fed with pretreated river water (Speth et al., 1999 ; Croué et al., 2003) but it decreased

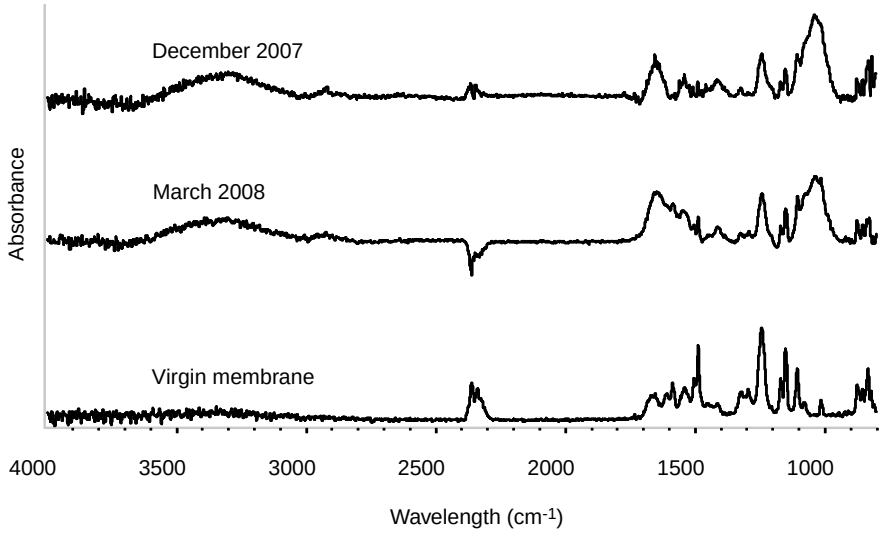

Fig. 4. Infrared spectra (FT-IR ATR) of a virgin membrane and fouled membranes of December 2007 and March 2008.

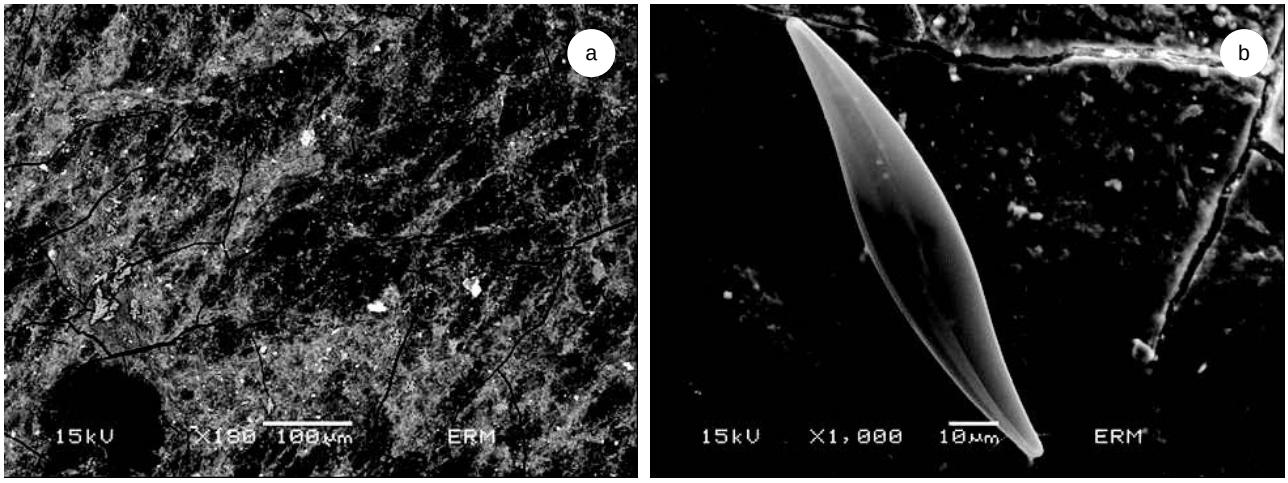

Fig. 5. SEM images of the deposit structure (**a**) and a diatom (**b**) observed on the surface of a fouled membrane of March 2008.

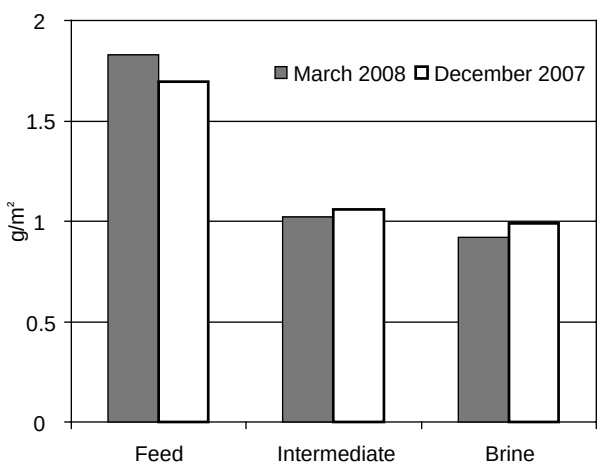

Fig. 6. Mass of dried deposit recovered on the surface of the desalination membranes.

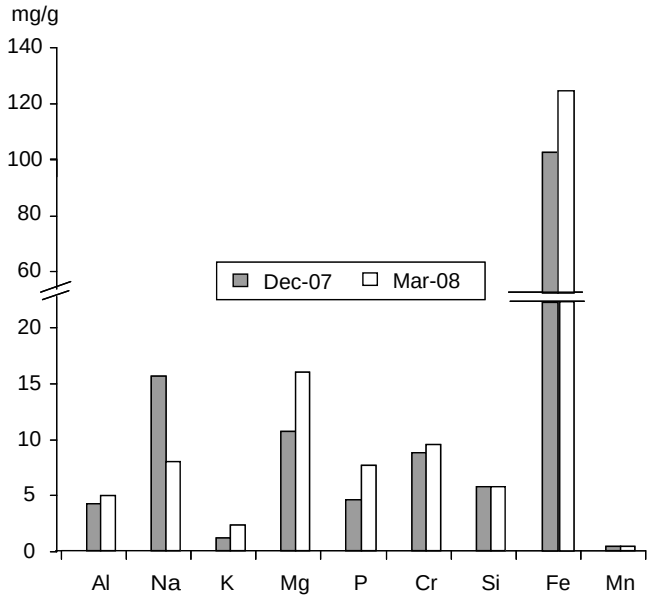

Fig. 7. ICP-OES analysis of the deposit accumulated at the surface of the desalination membranes.

significantly from the feed area to the brine area. Therefore, the mass of deposit is not quantitatively homogenous on the whole membrane surface.

Elemental analysis: Elemental analysis showed that the deposits were predominantly organic in nature, the residue after combustion (inorganics) represents an average of 20 to 25% in mass of the deposit. The deposit composition is around 30 % in C, 5 % in H, 4 % in N, 1 % in S and 0,7 % in P. ICP-OES analysis (Fig. 7) enabled to show that the deposits contain a high quantity of iron which is probably a residual of the coagulant used in the pretreatment step.

Pyrolysis and thermochemolysis GC/MS: The heat degradation of natural biopolymers leading to the production of specific molecules enables the identification of the nature and the chemical composition of a complex matrix. The combination Pyrolysis/gaz chromatography-mass spectrometry or Pyrolysis-GC/MS is adapted to the study of polymeric substances and presents an interest particularly for the analysis of foulant matrices. This technique was widely used for studies conducted on the characterisation of NOM extracted from soils and aquatic environment but also for the characterisation of foulant material recovered from surfaces of reverse osmosis membranes (Septh et al., 1998; Croué et al., 2003), ultrafiltration membranes (Mallevialle et al., 1989), or hollow fiber membranes (Kaiya et al., 2000). This method is based on the identification of by-products coming from the heat degradation of organic structures. The by-products of the NOM Pyrolysis find their origin in four major classes of organic structures, that is to say sugars, amino sugars, proteins and polyhydroxyaromatic type structures originated from lignins (Bruchet, 1985). Each of these major biopolymers classes releases during Pyrolysis a wide variety of

molecules some of which are specific to a major class. The surface of chromatographic peaks of many specific fragments can be used to determine the relative proportion (semi-quantitative approach) of the main biopolymers in comparison to the whole organic matter (Bruchet et al., 1990). Proteins and especially polysaccharides exert higher pyrolysis efficiency than polyhydroxyaromatic type structures, characteristic that can lead to an overestimation of the first biopolymers in the global matrix (Van de Meent, quoted by Biber et al., 1996). Fingerprints (relative distribution of the biopolymers) obtained by Pyrolysis might be sensibly distorted from reality by overestimating sugars for example.

Fig. 8 shows the pyrochromatogram obtained with March 2008 deposit whose profile and relative distribution of identified peaks are comparable to those of December 2007 deposit. This fingerprint is characteristic of the membrane deposits (Mallevialle et al., 1989 ; Croué et al., 2003 ; Habarou et al., 2006) underlining the strong abundance of sugars and amino sugars type structures, characteristic of biofilms and organic colloids isolated from natural waters (microbial residues). The signature of this biofilm is also confirmed by the presence of proteins. However, it can be noted that the relative proportion in polyhydroxyaromatic structures (phenol derivated) is unusually high for that kind of deposit. The origin of this kind of aromatic structures is commonly attributed to humic like substances which are present in seawaters (i.e. marine humic substances) and are almost not eliminated by direct filtration in desalination pretreatments (very low COT removal, Leparc et al., 2007). The possible contribution of the algae material should however be considered.

Thermochemolysis TMAH (tetramethyl ammonium hydroxyde) GC/MS is a complementary technique which promotes by hydrolysis and methylation the analysis of carboxylic acids (limitation of the decarboxylation reaction by methylation) especially fatty acids but enable also to better identified lignin markers (alkyl phenol, phenolic acids) (Saiz Jiminez, 1984). Figs. 9 and 10 present the fragmentograms m/z 74 and m/z 77 of the analyses by thermochemolysis GC/MS of the March 2008 deposit.

The m/z 74 fragmentogram puts into evidence the fatty acids fingerprint. Fatty acids from biological origin characterised by short carbon chains (C12 to C20) are predominant. The bacterial origin of this deposit is also confirmed with a C16 as a dominant peak and C15 iso and anteiso fatty acids. The unsaturated C18 present in the March 2008 deposit but absent in the December 2007 analysis revealed the presence of a more recent biological material (higher biological activity) in the March 2008 biofilm. Fatty acids with long carbon chains (C22 to C26) could be related to upper vegetables (terrestrial origin) or to algae. Fatty acids abundance is low in our deposits. Semi quantitative analysis of these chromatographic fingerprints allow us to deduce relative contents in short fatty acids (area sum C12 to C20/ area sum C12 to C26) and in long fatty acids (area sum C16 to C26/ area sum C12 to C26). Table 2 shows that March deposit seems to present a bacterial origin stronger than December 2007 deposit.

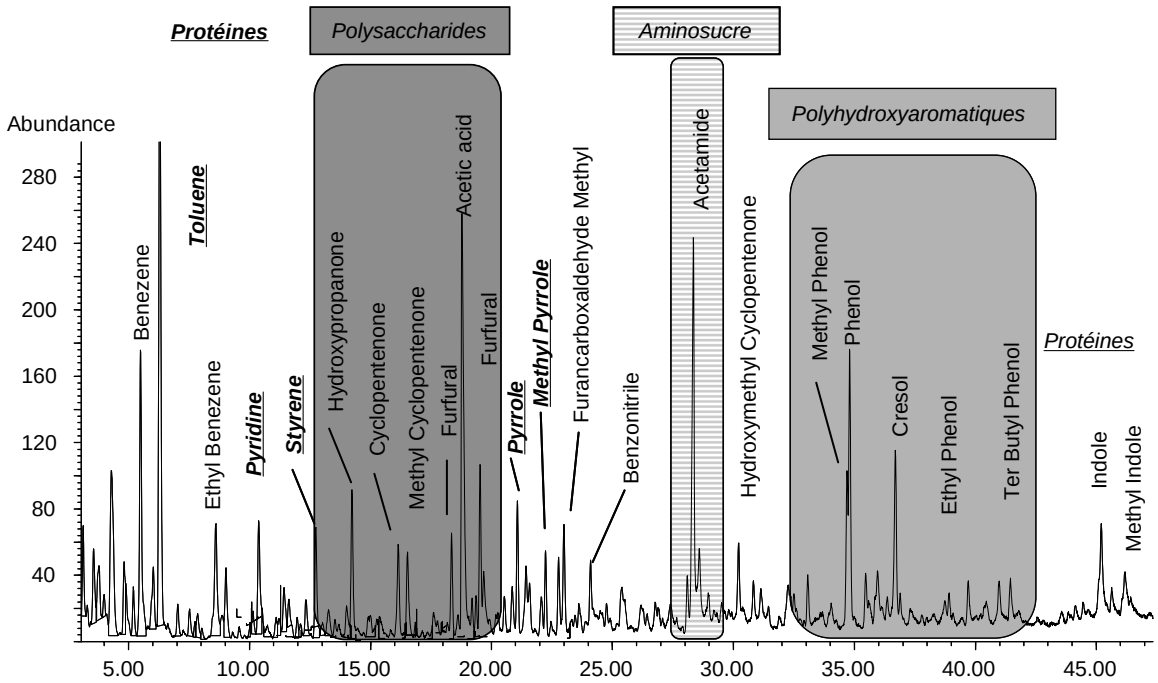

Fig. 8. Profil in pyrolysis GC/MS of the deposit of March 2008.

The m/z 77 fragmentogram presents the fingerprint of aromatic derivatives, structures generally attributed to humic like structures. If the origin of methoxybenzen, methoxybenzoate and benzoate (probable methylation of the acid groups and OH-phenolic by TMAH) is not certain in our case (algae origin to consider), the origin of the phenyl propenoic derivative could be attributed to lignocellulosic structures, which would corroborate the contribution of organic matter from terrestrial origin in these deposits. However, Pyrolysis TMAH of sugar monomers and cellobiose was found to produce similar aromatic derivatives. The use of different alkylated agent

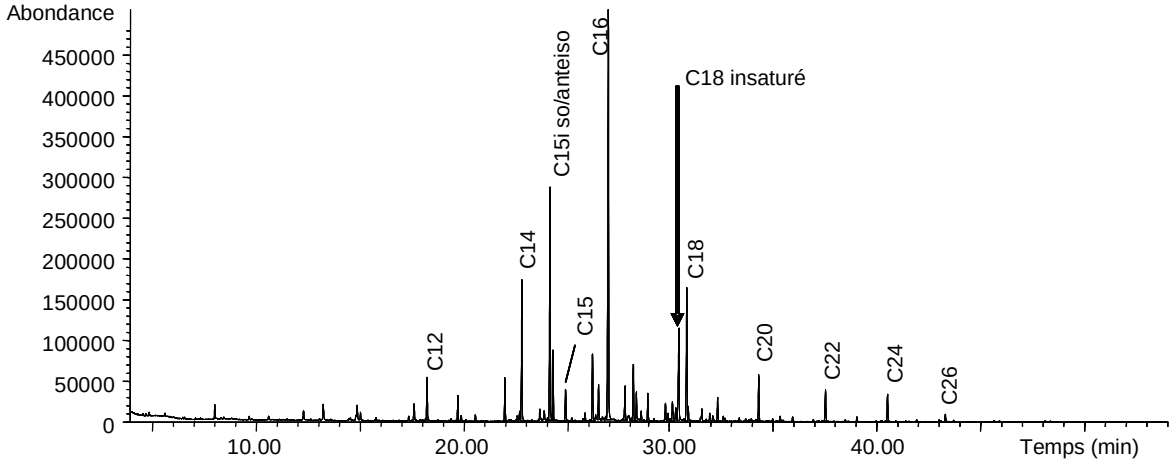

Fig. 9. Fragmentogram m/z 74 (fatty acids) in thermochemolysis GC/MS of the March 2008 deposit.

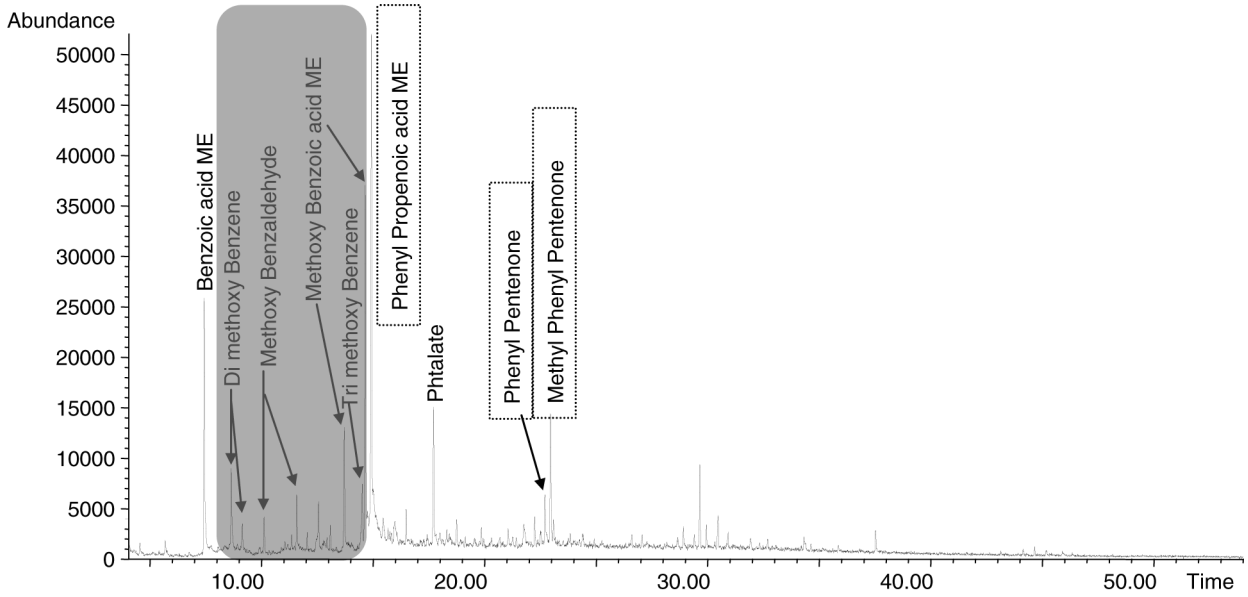

Fig. 10. Fragmentogram m/z 77 (aromatics) in thermochemolysis GC/MS of the March 2008 deposit.

Table 3
Fatty acids proportions in the deposits.

		Relative contents (%)	
Fatty acids	Origin	December 2007	March 2008
Short (C14 to C20)	Bacterial	82.4	90.6
Long (C22 to C26)	Algae and/or Terrestrial	17.6	9.6

i.e. TEAH would probably help to discriminate the two possible origins (sugar vs. lignin derivatives).

Phospholipids and sugars content: Chromatograms of specific analyses of phospholids and sugars extracted from the deposits are presented on Figs. 11 and 12. Quantitative analyses results (C16 predominance in accordance with thermochemolysis GC/MS) give a phospholipid content (microbial origin) significantly higher in the March deposit compared with the December deposit; 9.5 and 13 µg/mg of dried lyophilised deposit, respectively. This result confirms again a stronger microbial presence in the March 2008 deposit. Sugars analysis indicates a higher content in proportion in C6 derivatives (bacterial origin) than in C5 derivatives (terrestrial-upper vegetable origin) for the two deposits; these results are expected for a biofilm. However, quantitative analysis did not put into evidence significant differences between the two deposits (around 10 µg/mg of dried lyophilised deposit).

4. Conclusion

The whole analyses performed showed that the deposits collected at the surfaces of reverse osmosis membranes used in seawater desalination are linked to the development and the accumulation of a biofilm (biofouling). The high relative proportions in amino sugars and sugars are associated with those of proteins which

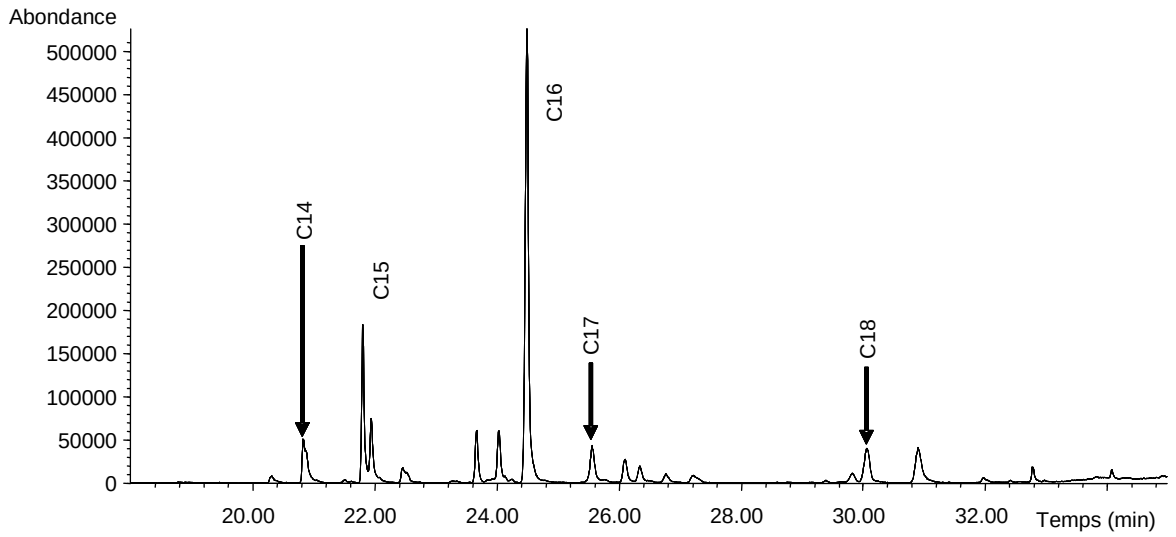

Fig. 11. Chromatogram of phospholipids analysis – March 2008 deposit.

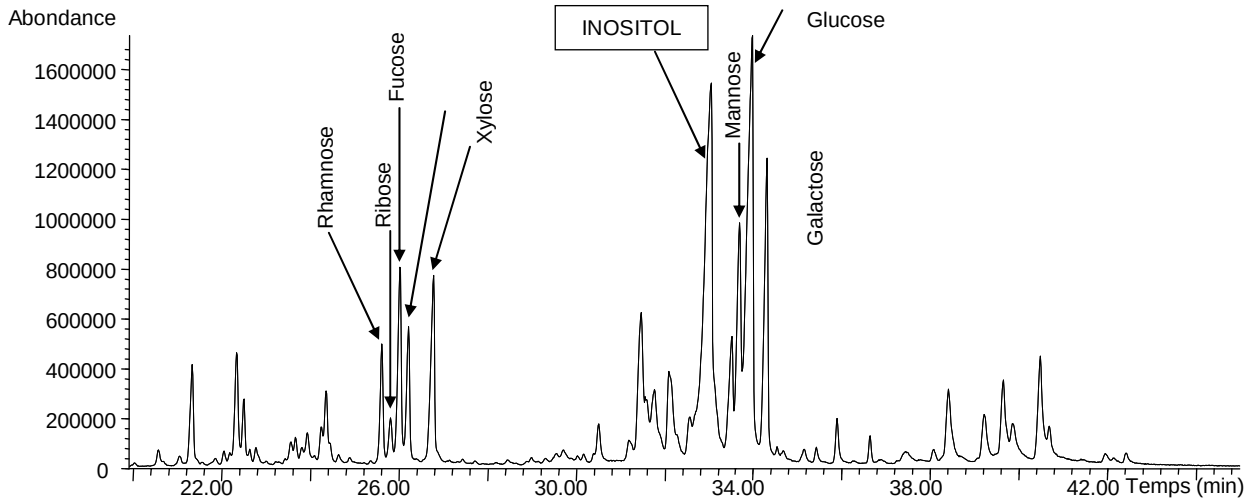

Fig. 12. Chromatogram of sugars analysis – March 2008 deposit.

are the base structure of the foulant material (microbial residues i.e. peptidoglycane + exopolysaccharides). The presence of phospholipids and specific fatty acids (C15 iso and antéiso) confirms a significant bacterial presence. These deposits also incorporate unusual high proportions in polyhydroxyaromatic type structures generally attributed to humic substances, structures incorporated into the organic matrix of seawater. In deposits, the contribution of a terrestrial organic matrix on the coastal border is possible, the presence of phenolic derivatives from algae origin also. It is important to underline that pretreatments applied in desalination do not have any real effect on dissolved organic carbon (around 1 mg/L DOC in seawaters) removal, this inefficiency can justify the accumulation of humic like structures on reverse osmosis membranes. The foulant deposits analysed showed an organic dominant character with a content of inorganic compounds between 25 to 30%. Iron (10 to 15% in mass) appeared to be a major element that more probably come from the use of iron coagulant for pretreatment, silica and calcite were also identified at lower concentrations. The different analyses performed (semi quantitative and quantitative) showed that the composition of these biofilms changed with the sampling date, the biological contribution was higher for the March 2008 membranes compared to the December 2007 membranes. This result is probably linked to a change in the water quality of the resource.

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