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Ceramic membrane as a pretreatment for reverse osmosis: interaction between marine organic matter and metal oxides

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ABSTRACT

Scaling and (bio)fouling phenomena can severely alter the performance of the reverse osmosis process during desalination of seawater. Pretreatments must be applied to efficiently remove particles, colloids, and also precursors of the organic fouling and biofouling. Ceramic membranes offer a lot of advantages for micro and ultrafiltration pretreatments because their initial properties can be recovered using more severe cleaning procedure. The study focuses on the interaction between metal oxides and marine organic matter. Experiments were performed at laboratory scale. The first series of experiments focus on the filtration of different fractions of natural organic matter and model compounds solutions on flat disk ceramic membranes (47 mm of diameter) characterized with different pore size and composition. Direct filtration experiments were conducted at 0.7 bar or 2 bars and at room temperature (20 ± 0.5°C). The efficiency of backflush and alkaline cleaning were evaluated. The second series of experiments were carried out with metal oxide particles of the same composition than the disk ceramic membranes. Isotherm adsorption and adsorption kinetics of different fractions of organic matter with different concentration and physico-chemical characteristics were studied (pH, temperature, and ionic strength). Metal oxides studied are aluminum, zirconium, and titanium oxides. Each metal oxide corresponds to a specific pore size for the disk ceramic membranes: 80, 60, and 30 nm. Different sizes of metal oxide particles are used to measure the impact of the surface area on the adsorption of the organic matter. Seawaters from the Arabian Gulf and from the Red Sea were collected during algal blooms. Cultures of algae were also performed in the laboratory and in cooperation with woods hole oceanographic institute. Solutions of algal exudates were obtained after a couple of weeks of cultivation followed by sonication. Solutions were successively filtered through GFF (0.7 μm) and 0.45 μm membrane filters before use. The dissolved organic carbon (DOC) concentration of final solution was between 1 and 4 mg/L and showed strong hydrophilic character. These various solutions were prepared with the objective to mimic the dissolved organic matter composition of seawater subjected to algal bloom. Characterization of the solutions of filtration experiments (feed water, permeate water, and backwashes) and batch experiments (raw solution and supernatant solutions) included fluorescence, UV, total organic carbon, total nitrogen, and Liquid Chromatography – Organic Carbon Detection measurements. In comparison to seawater under normal condition, seawaters collected during algal bloom and algal exudates solutions led to very severe fouling of all ceramic membranes (with some DOC removal of 10–20%). It is important to indicate that algal exudate permeates still exert fouling properties when filtered through similar new (virgin)

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membrane. These results indicate that both size exclusion and adsorption phenomena occur (on surface, inside pores). In all cases, the backflush (performed with MilliQ [MQ]) showed minor or no effect and the cleaning backwash was not able to recover the initial flux (30–60%). Analyses performed on the backflush solution (performed with MQ) and on the alkaline cleaning solution revealed the retention of both high and low molecular organics on the different metal oxides. Unfortunately, analyses of membrane surface using imaging various tools are not providing informative results in term of foulant/adsorbed material composition.

Keywords: Ceramic membrane; Marine organic matter; Metal oxide; Adsorption

1. Introduction

Throughout the world, there is a trend to intensify use of desalination as a mean to reduce current or future water scarcity. Water scarcity occurs in arid regions but not exclusively. Pollution and over exploitation of fresh waters (groundwater aquifers and surface waters) have significantly diminished the water quantity available for conventional treatment. At the same time, population, industrial activities, and agriculture exploitations are growing fast, leading to higher water demand and higher water consumption. Alternative water resources are needed. Membrane desalination provides such an alternative source, offering water otherwise not accessible for industrial and municipal use. Reverse osmosis (RO) is the most common membrane-based desalination option for seawater and brackish water. The water passes through the membrane while salts are almost completely retained. This technique presents an extremely good removal of colloids, dissolved organic matter, and salts.

In RO technology, fouling control is important as fouling results in increased energy consumption, decreased salts rejections, and higher cleaning frequency, which shorten the lifetime of the membrane. Fouling concerns colloidal, organic fouling, and biofouling. To minimize RO fouling, pretreatment must be applied to efficiently remove particles, colloids, and also precursors of the organic fouling and biofouling. Conventional pretreatments such as dual media filtration (with coagulation) or microfiltration/ultrafiltration are usually performed. Both membrane types have proven their efficiency against particles (including bacteria) and colloidal material. Ceramic membranes (porous media composed by optional porous layers of metal oxides) offer several advantages for micro and ultrafiltration pretreatments because their initial properties can be recovered using more severe cleaning procedure (strong acids and bases, oxidants, and high backflush capacity) as compared to polymeric membranes. Furthermore, ceramic membranes offer other advantages such as mechanical stability under large pressure gradients (noncompressible and no creep); long lifetime; (electro) catalytic and electrochemical activity easily realizable; high throughput volume; and good control of pore dimension and pore distribution [1].

Several works have been developed on the performance (pressure filtration, backwash frequency and backwash pressure, and pore size) of ceramic membrane filtration [2–6]. Only few studies are considering the interaction of NOM with metal oxides in the ceramic filtration process. A few projects can be found, focusing on the interactions between natural metal oxides (such as goethite, iron oxides) with fresh water NOM under real conditions [7–16]. NOM adsorption on mineral surface seems to depend both on the NOM origin and on the type of mineral. NOM is a heterogeneous mixture of different organic molecules that may have different adsorption affinities for the mineral surface. These different organic compounds compete for adsorption when the surface adsorption sites are limited. In the majority of the studies, the NOM is usually treated as a single organic component representative such as humic substances (HS) or more precisely humic or fulvic Acids (respectively, HA and FA). Different studies have been done on natural minerals present in solution, such as iron oxide, goethite, and alumina oxides. It has been observed that the fraction of organic matter that fouled the most was the high molecular weight fraction with high aromatic moieties [7,9–13,15,16]. The influence of the pH has been observed in all the studies: sorption decreases with increasing pH. For pH below the mineral pH_{pzc}, anion exchange reaction cannot be excluded of the whole process but is very insignificant at high pH. Results on the ionic strength dependence are more debatable. Gu et al. [12] demonstrated that the ionic strength does not have real impact on the adsorption of NOM on iron oxide. This means that the electrostatic interactions are a minor mechanism. However, Weng et al. [10] found that an increase in ionic strength leads to a decrease in size of the HA structures. Thus, the HA moieties get closer to the surface, which leads to a stronger competition with the anions that are adsorbed as ion pairs on the surface. The FA molecules are by nature smaller, so the conformational change is less important and their sorption is less ionic strength-dependent. Ghosh et al. [8] and Chen et al. [11] also showed that in the presence of cations such as Ca^{2+} and Na^+, the aggregation between HA and nano-alumina oxides is more important.

The quality and composition of the feed water has a great importance on the performance of high pressure membrane filtration. Algal bloom events are of particular importance for RO desalination process because of the release of significant amount of organic matter that leads to membrane fouling. RO desalination plants had to be shut down during major algal bloom event in the Middle East region during the past few years.

Our study focuses on the fouling of ultrafiltration ceramic membrane by marine organic matter. Special attention is given to algal exudates with the objective to simulate RO pretreatment during algal bloom event occurring in seawater.

2. Materials and methods

2.1. Sample description

The first part of the study focuses on two different natural seawaters collected at different times of the year.

The first seawater was collected at the inlet of a seawater RO plant located in Jubail, Saudi Arabia on the Arabian Sea. Water samples were obtained during the summer season, on July 2011. It shows a dissolved organic carbon (DOC) of 1.70 mg/L with a conductivity of 62.5 mS/cm (at 20.5°C) and a pH of 8.2.

The second seawater was collected 3 km offshore of Thuwal (Saudi Arabia) in the Red Sea on October 2011 and January 2012. The two samples showed similar DOC around 0.8 mg/L. The conductivity of the Red Sea is 59.3 mS/cm (at 20.5°C) and a pH of 8.2.

The second part of the study was to focus on the influence of marine organic matter on the ultrafiltration. Algal exudates from *Chlorella vulgaris* species were studied. *C. vulgaris* is a microalgae, living in all aqueous habitats—essentially cosmopolitan in both freshwater and marine habitats. It is known to be responsible for unharmful algal bloom. This study focuses on the high molecular weight (HMW) compounds of *Chlorella* exudates isolated from dialysis (3.5 KDa) against MilliQ (MQ) water. Red Seawater, collected on October 2011, was enriched with the *Chlorella* HMW compounds. The final conductivity was 45 mS/cm (at 20.5°C) and the pH was 8.2.

2.2. Filtration experiment

Dead-end filtration experiments were conducted at room temperature (20.5°C ± 0.5) and constant pressure (0.7 bar).

Two different ceramic membranes (47 mm diameter planar disk and effective filtration area: 12 cm^2) are used. Both of them are made with a silica support coated with alumina or titanium oxide for nominal pore size of 80 and 30 nm, respectively. The pure water permeability determined at room temperature (20°C ± 1) with MQ water is $1{,}000 \pm 50\ L/m^2\,h\,bar$ and $680 \pm 50\ L/m^2\,h\,bar$ for the alumina and titanium membrane, respectively.

The permeate flux was recorded with a balance connected to a computer.

Three filtrations in series are performed at 0.7 bar separated by backflush with MQ water at 2 bars and a final chemical cleaning using NaOH (0.1 M) at 2 bars.

The pure water permeability of the membrane was determined before and after all fouling tests.

UV, fluorescence, DOC, and Liquid Chromatography – Organic Carbon Detection (LC–OCD) analyses were conducted on the permeate solutions, the backflush solutions, and the cleaning solutions.

2.3. Unified membrane fouling index

Fouling can be quantified using a resistance-in-series approach. For low-pressure membrane, the flux (J, $L/m^2\,h$) can be described as:

$$J = \frac{\Delta P}{\mu R}$$

where ΔP is the transmembrane pressure, R is the resistance to flow through the membrane, and μ is the water viscosity.

R is the total resistance. It sums the resistance of the clean membrane (R_{memb}) and the resistance due to the fouling the membrane (R_{foul}):

$$R = R_{\mathrm{memb}} + R_{\mathrm{foul}}$$

The resistance of the fouling increases linearly with the volume of solution filtered. Thus, we can express R_{foul} as: $R_{\mathrm{foul}} = r_{\mathrm{foul}} \cdot V$, where r_{foul} is a rate constant for the increase in the resistance and V is the specific volume (L/m^2).

Combining the three equations, we obtain:

$$\mathrm{Js} = \frac{J}{\Delta P} = \frac{1}{\mu(R_{\mathrm{memb}} + r_{\mathrm{foul}}.V)}$$

For a new membrane, $Js_0 = \frac{1}{\mu R_{\mathrm{memb}}}$ We can normalize the specific flux (Js) by dividing Js by Js_0. The equation obtained is the following:

$$J's = \frac{Js}{Js_0} = \frac{1}{1 + \frac{r_{\text{foul}}.V}{R_{\text{memb}}}}$$

And:

$$\frac{1}{J's} = 1 + \text{UMFI}.V$$

where Unified membrane fouling index (UMFI) = $\frac{r_{\text{foul}}}{R_{\text{memb}}}$.

Fouling can then be expressed by drawing the graph $\frac{1}{J's} = f(V)$. The slope of the curve will be the UMFI.

3. Results and discussion

3.1. Natural seawaters

The two seawaters are significantly different in term of DOC concentration. The Arabian Sea water presents a DOC that is almost double the DOC of the Red Sea water (1.70 and 0.74 mg/L). However, the DOC composition is qualitatively comparable. Fig. 1 gives the LC–OCD chromatogram of the two seawaters (bottom: Arabian Sea, July 2011 and top: Red Sea, October 2011). Table 1 summarizes the concentration of the different components of the marine organic matter and their relative abundance.

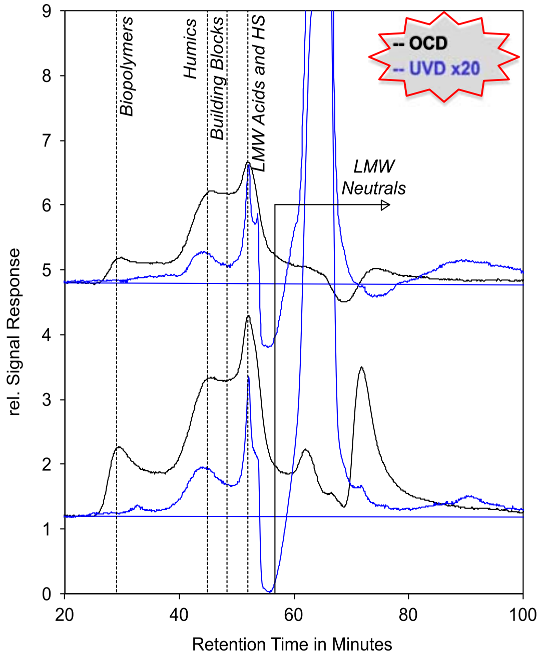


Fig. 1. LC–OCD chromatogram of natural seawaters (bottom: Arabian Sea, July 2011 and top: Red Sea, October 2011).

Table 1
Distribution of the DOC of the Arabian Sea and Red Sea

	DOC (mg/L)	Biopolymers (mg/L)	Humics (mg/L)	Building blocks (mg/L)
Red Sea water	0.76 ± 0.05	0.089 (11.7%)	0.389 (51.2%)	0.156 (20.5%)
Arabian Sea water	1.70 ± 0.05	0.214 (12.6%)	0.671 (39.4%)	0.236 (13.8%)

Results indicate that the biopolymers represent around 12% of the DOC of the two seawaters, however the Arabian Sea water is much more enriched than the Red Sea water in this fraction. The humics and building blocks are also twice as high in the Arabian Sea water, than in the Red Sea, but their relative contribution is lower. One can notice the presence of a significant low molecular weight neutrals peak, at around 75 min for the Arabian Sea water. The UV signal of the chromatogram has been magnified by 20. HS from marine water are known to exert low arolatic signature.

In this study, seawater samples are filtered through a 80 nm alumina membrane. The relative permeate flux decline curves, recorded during the filtration of the Arabian Sea and Red Sea waters, are shown in Fig. 2.

The permeate flux of the Arabian Sea water declines very rapidly. After only 6 min, the flux has already been reduced by 20% for the Arabian Sea and only 7% for the Red Sea water. In both cases, the different backflushes showed only minor effect in recovering the initial flux. Similar observation can be made

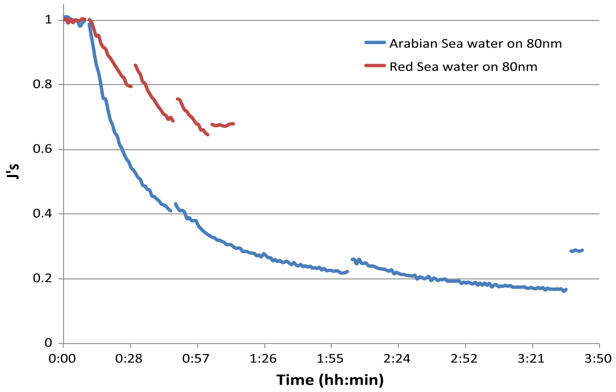
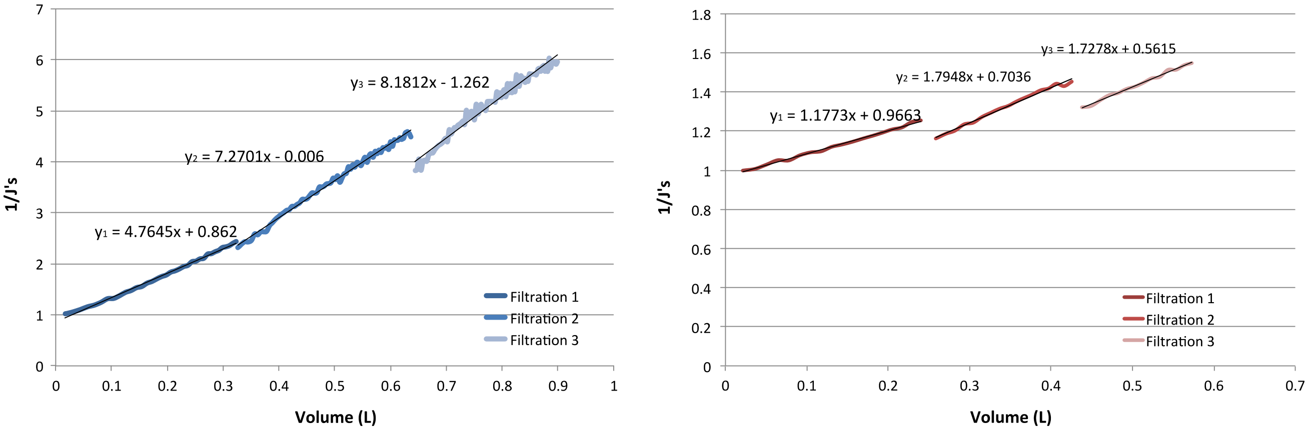


Fig. 2. Permeate flux decline during the filtration of the Arabian Sea and Red Sea waters through a 80 nm alumina ceramic membrane.



A: Filtration of Arabian Sea water - UMFI

B: Filtration of Red Sea water - UMFI

Fig. 3. UMFI of the filtration of Arabian Sea (A) and Red Sea (B) waters.

after chemical cleaning with NaOH, at 2 bars, indicating that the severe irreversible fouling occurred.

The UMFI for the first filtration (UMFI 1) is 4.76 L^{-1} for the Arabian Sea and only 1.18 L^{-1} for the Red Sea. After backflush, in the successive filtrations, the UMFI continues to rise (see Fig. 3).

From a qualitative point of view, the filtration on 80 nm slightly reduced the DOC concentration for the Arabian Sea water (almost 20%), but no significant change was observed for the Red Sea water. Table 2 shows the concentrations of feed and permeate for each experiment.

In terms of distribution of the DOC (Fig. 4), a reduction of the biopolymers can be observed in the filtration of the two different seawater samples. The filtration on 80 nm shows a reduction in biopolymers of 30% for the Arabian Sea water and 20% for the Red Sea water. No particular trends can be found regarding humics and building blocks.

Table 2
Natural seawaters filtration: DOC concentrations of feed and permeate

	DOC (mg/L)	
	Feed water	80 nm permeate
Red Sea water (KAUST)	0.76 ± 0.05	0.79 ± 0.05
Arabian Sea water (Jubail)	1.70 ± 0.05	1.38 ± 0.05

3.2. *Algae exudates*

To understand the role of HMW compounds on the filtration of seawaters, the Red Sea water (collected on October 2011) was enriched with HMW exudates isolated from a *Chlorella* cultures using 3.5 kDa dialysis bag.

Fig. 5 shows the LC–OCD chromatogram of the algae exudates before (A) and after (B) dialysis.

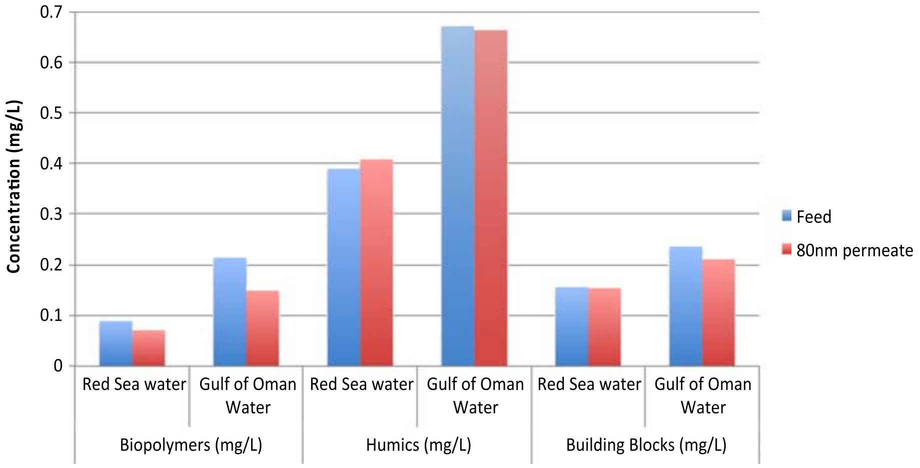
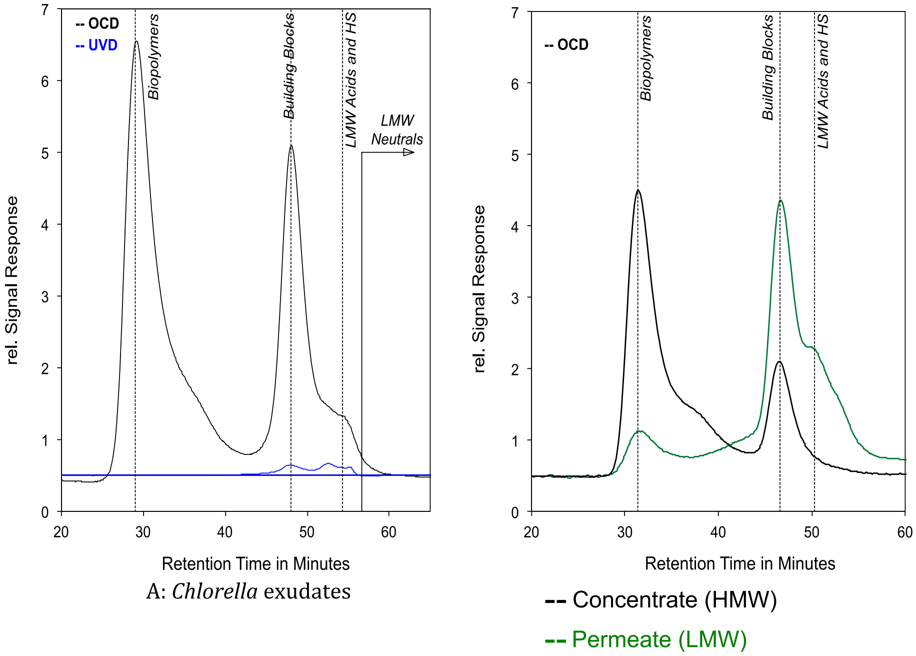


Fig. 4. Distribution of the DOC in the feed and permeate of the filtration of natural seawaters on 80 nm.



A: *Chlorella* exudates

B: Concentrate and permeate of the 3.5kDa dialysis

Fig. 5. LC–OCD chromatogram of the *Chlorella* exudates dialysis: feed, concentrate, and permeate.

Fig. 6 presents the LC-OCD profiles of the raw Red Sea water (bottom) and the enriched one with *Chlorella* HMW compounds (top). Table 3 summarizes the concentration of the different components of the marine organic matter and their relative abundance.

The DOC remains in the same range of concentration after the water was spiked with HMW exudates (9% increase i.e. 0.08 mg/L). The different fractions of DOC remain in the same range of concentration except the biopolymer content that was doubled for the Red Sea water enriched with *Chlorella* HMW compounds in comparison to the raw Red Sea water. Thus, the two seawater samples mainly differ on the concentration of the biopolymers.

The relative permeate flux decline recorded during the filtration of the raw and the enriched in HMW exudates Red Sea water is displayed on Fig. 7.

The permeate flux of the Red Sea water enriched with *Chlorella* HMW compounds declines very rapidly. After 6 min, the flux has already been reduced by 15%. A decrease in the flux of only 7% is observed for the raw Red Sea water. Again, the efficiency of the backflushes is limited. After chemical cleaning with NaOH, at 2 bars, the initial flux is not recovered. Table 4 shows the DOC concentration and the DOC distribution of the feed and the permeate for each Red Sea water experiment and the UMFI of the first filtration cycle.

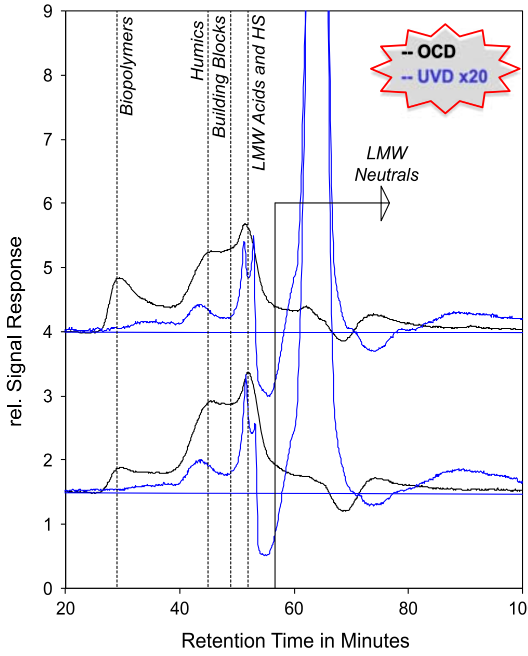


Fig. 6. LC–OCD chromatogram of the Red Sea water (bottom) and the Red Sea water enriched with *Chlorella* HMW compounds (top).

UMFI 1 for the Red Sea water enriched with *Chlorella* HMW compounds is more than twice the UMFI 1

Table 3
Distribution of the DOC of the Red Sea water and the Red Sea water enriched with HMW compounds

	DOC (mg/L)	Biopolymers (mg/L)	Humics (mg/L)	Building blocks (mg/L)
Red Sea water enriched with Chlorella HMW compounds	0.84 ± 0.05	0.170 (20.2%)	0.364 (43.1%)	0.122 (14.5%)
Red Sea water	0.76 ± 0.05	0.089 (11.7%)	0.389 (51.2%)	0.156 (20.5%)

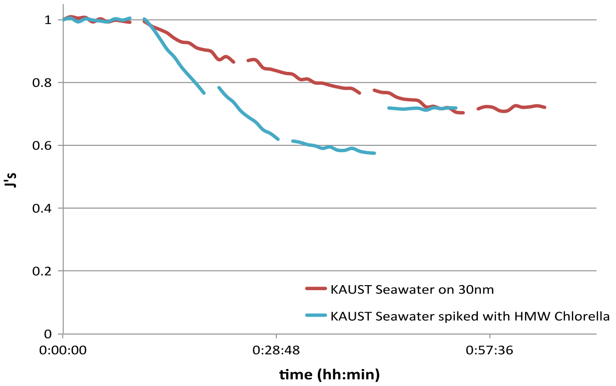


Fig. 7. Permeate flux decline during the filtration of the Red Sea water and the Red Sea water enriched with *Chlorella* HMW compounds.

for the raw Red Sea. The increase of the UMFI 1 relates to the increase in the biopolymers content. Fig. 8 shows the composition of the feed and permeate of the two filtration experiments.

Biopolymers are the group of compounds that are the most affected by the filtration on 30 nm. The 40% of the biopolymers are removed from the raw Red Sea water and up to 60% for the Red Sea water enriched with HMW compounds. Thus, we can clearly conclude that the HMW compounds play a major role on the fouling of the ceramic membranes.

Table 4
Distribution of DOC in the raw and enriched with *Chlorella* HMW compounds Red Sea water

	DOC (mg/L)		UMFI 1 (L^{-1})
	Feed water	30 nm permeate	30 nm
Red Sea water	0.76 ± 0.05	0.8 ± 0.05	1.58
Red Sea water enriched with HMW *Chlorella*	0.84 ± 0.05	0.8 ± 0.05	4.09

The 30 nm permeate was then filtered on a new 30 nm membrane. Fig. 9 displays the relative permeate flux decline recorded during the filtration of the 30 nm permeates of the two waters filtered through 30 nm.

A decline of the permeate flux is still observed during the repeated filtration of the Red Sea waters on 30 nm. These results clearly indicate that size exclusion is not the only mechanism involved on the fouling phenomena of ceramic membranes with marine organic matter. Adsorption of low molecular weight molecules also occurs.

To understand the strong affinity of the HMW compounds with the membrane (no significant impact

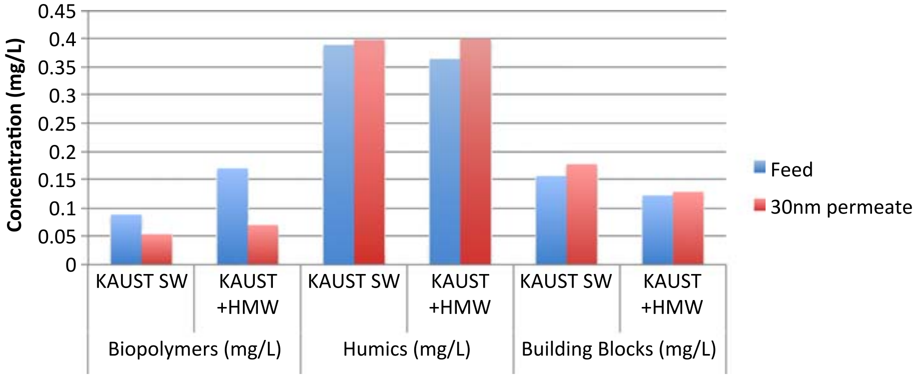


Fig. 8. Distribution of DOC on the feed and permeate water for the filtration of raw and Red Sea water enriched with *Chlorella* HMW compounds.

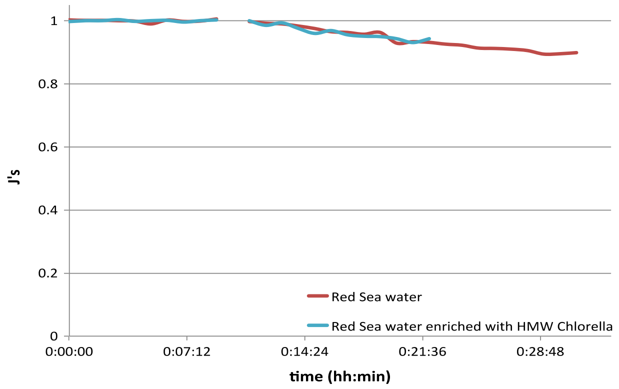


Fig. 9. Permeate flux decline during filtration of the 30 nm permeate of the raw and enriched with *Chlorella* HMW compounds Red Seawater on a virgin 30 nm membrane.

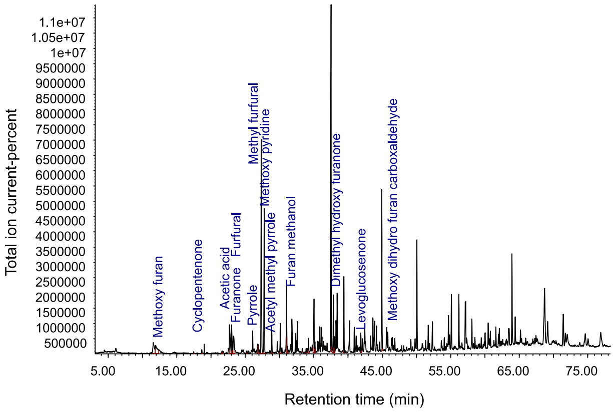


Fig. 10. GC–MS pyrochromatogram of the HMW compounds.

of the backflushes), HMW compounds have been lyophilized and characterized using pyrolysis-GC-MS analysis and FTIR analysis.

The pyrochromatogram (Fig. 10) is processed by assigning the pyrolysis products to one of the following four categories: polysaccharides, proteins, N-acetylamino sugars, and polyphenolic material [17]. The pyrochromatogram obtained for the HMW compounds shows that most of the pyrolysis by-products are furan derivatives and cyclic ketones such as Methoxy furan (12.7 min), Cyclopentenone (19 min), Furfural (22 min), Furanone (22.5 min), Methyl Furfural (27.5 min), Furan methanol (31 min), Dimethyl hydroxyl furanone (37.9 min), and Methoxy furan carboxaldehyde (45 min). These compounds are known to originate from the pyrolysis of polysaccharides. Proteins are also present at a lower extent in the sample. The estimate of the proteins is based on the pyrrole derivatives such as pyrrole (26 min) and acetyl methyl pyrrole (31 min).

The infrared spectrum of the algal HMW compounds (Fig. 11) shows distinct C–O vibration between 1,100 and 1,000 cm^{-1}. These peaks can be assigned to polysaccharides. amide 1, amide 2, and CH_3 peaks located at 1,631, 1,544, and 1,408 cm^{-1}, respectively, are diagnostics of N-acetylamino sugars. Both characterization techniques indicate that HMW compounds are mainly composed by polysaccharides with a lower amount of proteins. The biopolymer composition can explain the lack of efficiency of the sodium hydroxide cleaning. Alkaline solutions do not strongly interact with polysaccharides.

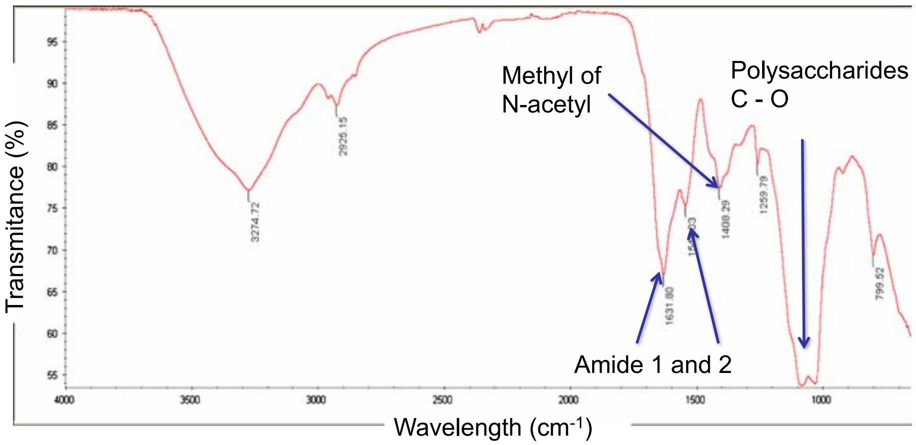


Fig. 11. FTIR analysis: transmittance profile of HMW compounds.

4. Conclusion

Fouling property of marine organics especially algal exudates is very important in ceramic membrane filtration. The severe and irreversible fouling of algal exudates is mainly due to the biopolymers content. Algal biopolymers are essentially composed of polysaccharides. It is thus difficult to chemically clean the membrane using alkaline solutions such as sodium hydroxide. Additional work will be done on the characterization of those polysaccharides for different algae species, at different ages, and under different stress conditions to understand their origin. Different pretreatments will be studied, such as coagulation, dual media filter, or flotation, to remove and minimize the biopolymers impact on the filtration.

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