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Membrane hybrid processes for pretreatment before seawater reverse osmosis desalination

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ABSTRACT

The objective of this work is to study at lab-scale the efficiency of a hybrid process coupling ultrafiltration (UF) and adsorption as a pretreatment before seawater reverse osmosis desalination (SWRO). Powdered activated carbon (PAC) and bentonite were used as adsorbents. Actual seawater from Mediterranean Sea was filtered by regenerated cellulose membrane of molecular weight cut-off 30 kDa. The PAC addition allows a decrease of UF fouling rate and an increase of the natural organic matter (NOM) removal, especially for a PAC concentration of 200 mg L^{-1}. An increase of contact time between PAC and seawater induces a reduction of fouling rate. When the contact time increases, the contribution to NOM removal due to PAC adsorption becomes more significant compared to that due to UF alone. Concerning studies with bentonite, the UF fouling rate depends on the bentonite concentration. Addition of more than 500 mg L^{-1} bentonite can decrease the fouling rate in comparison to ultrafiltration without bentonite. But no obvious improvement of the NOM retention rate was observed. Besides, precoating the membrane with 500 mg L^{-1} bentonite does not present a major interest since a considerable increase of fouling rate is obtained compared to experiments without precoating. Membrane fouling reversibility, membrane surface hydrophobicity and molecular weight distribution of solutes contained in the different permeates were also studied.

Keywords: Hybrid Process; Seawater; Ultrafiltration; Adsorption; Fouling; Natural organic matter

1. Introduction

The use of reverse osmosis (RO) for seawater desalination has developed over the past 40 years to a 44% share in world desalting production capacity and an 80% share in the total number of desalination plants according to Greenlee et al. [1]. However, the performance of RO system is significantly limited by membrane fouling. The main types of fouling mechanisms in RO membranes are scaling, colloidal fouling, biofouling and organic fouling [2]. According to Ma et al. [3], natural organic matter and algae are a principal cause of severe fouling in seawater RO membranes. Consequently, RO processes require sufficient and reliable pretreatment to limit and reduce the fouling of the membranes.

Although conventional pretreatment—i.e. coagulation, sedimentation and filtration—has been widely used for seawater RO plants, constant degradation of seawater quality and unpredictable variations in feed water can cause variations in this pretreatment effectiveness [1]. Thus low pressure membrane filtration as microfiltration (MF) and ultrafiltration (UF) has gradually developed as an efficient pretreatment to SWRO. In recent years, pilot-scale testing and installations of UF have grown up [4–7] due to the reliability of these processes for producing superior quality feed to RO regardless of raw seawater quality.

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In a 4-month experimentation on a pilot plant platform installed in Gibraltar [6], UF decreased the silt density index (SDI) of a surface seawater below a value of 1.0 while conventional pretreatment failed to decrease the SDI below 2.5. Different other cases are presented by Pearce et al. [7]. UF was used as pretreatment to RO in case studies in the Gulf of Mexico, the Red Sea and the Mediterranean. In each case, UF was demonstrated to provide excellent pretreatment to RO, with no RO membrane cleaning required in 6-month trial periods. However, if low-pressure membrane processes produce water with constant quality and low values of SDI, this membrane pretreatment is not efficient enough to remove low molecular organic substances in seawater. Remize et al. [8] demonstrated that pretreatment with MF membrane improved removal of bacteria, plankton and particle but performed a lower removal of natural organic matter (NOM) compared to conventional pretreatment. Moreover another drawback of membrane pretreatment lays in the inherent property of the membrane to retain foulants from raw water and then become fouled itself.

Therefore, the aim of this study is to develop a hybrid process based on membrane filtration to take advantage of the process performance—such as the total rejection of suspended solids—and also to overcome its drawbacks. Thus the idea is to couple ultrafiltration with an adsorption step in order to enhance organic matter removal and also to reduce the low-pressure membrane fouling.

The combining of powdered activated carbon (PAC) adsorption with ultrafiltration has been developed in the beginning of the 90's for drinking water production from fresh water [2]. PAC addition to UF can increase the efficiency of the membrane process. Laîné et al. [9] found that the addition of 250 mg L^{-1} of PAC to a lake water could decrease irreversible fouling of several UF membranes. Tomaszewska and Mozia [10] performed the filtration of a mixture of humic acids and phenol. The application of PAC/UF system was found very effective in the removal of organic substances having both low and high molecular weights. Humic acids were removed in about 90% and phenol was removed totally for the same PAC concentration of 100 mg L^{-1}. Haberkamp et al. [11] suggested that activated carbon adsorbed organic compounds of a wide range of molecular weights, with differences in the removal efficiencies depending on the type of applied activated carbons.

Some studies involved the combining of UF and adsorption by natural bentonite for fresh water treatment. N. Al-Bastaki et al. [12] found that the addition of bentonite in UF process significantly increased the rejection coefficient of methylene blue (MB) dye, a model textile wastewater, but decreased the permeate flux. Bentonite concentration varied between 200 and 800 mg L^{-1} but a dose of 600 mg L^{-1} was sufficient to reach 97% dye rejection. Lin et al. [13] studied a hybrid process of clay adsorption and UF for phenol and o-cresol removal. Kaolin and montmorillonite were compared. The removal of phenol reached 80% for some conditions of pH and clay doses.

Most of the studies concerning the combining of ultrafiltration and adsorption concern fresh water treatment. Very few studies were carried out on this hybrid process with seawater that is to say a low organic concentration source in highly salty environment. Therefore, the aim of this work is to study at lab-scale the efficiency of a hybrid process (adsorption-UF) for NOM removal from actual seawater. Two types of adsorbents will be studied: PAC and bentonite and their efficiency on the UF performance will be compared in term of membrane fouling rate and NOM retention rate.

2. Materials and methods

2.1. Feed water, membrane and adsorbents

All experiments were carried out with actual seawater (SW) from Mediterranean Sea with average TOC about 1.3 mg L^{-1} and a salinity of 39 g L^{-1}. Table 1 presents the characteristics of seawater used in experiments.

The UF membranes were regenerated cellulose membrane (YM30, Millipore, France), with a molecular weight cut-off (MWCO) 30 kDa. Characteristics of the membrane are shown in table 2. Contact angle measurements were realised with a goniometer (GBX, Digidrop) and confirmed that the membrane is hydrophilic. Bentonite used

Table 1
Characteristics of seawater.

Properties	Minimum	Maximum	Average
Temperature (°C)	12.7	27.5	17.7
pH	7.74	8.40	8.12
Turbidity (NTU)	0.11	1.81	0.45
Conductivity (mS cm^{-1})	54.1	58.9	56.8
UV 254 (m^{-1})	0.42	2.12	1.03
TOC (mgL^{-1})	0.96	3.30	1.30
DOC (mgL^{-1})	0.71	1.42	1.15

Table 2
Characteristics of the UF membranes.

Characteristics	Values
Water permeability (L/h/m^2/bar) at 20°C	220–250
Membrane resistance (m^{-1})	$1.44 \times 10^{12} - 1.63 \times 10^{12}$
Contact angle of new membrane (°)	15.9
Zeta potential at pH 7 (mV) [14]	–2

is in dry powdered form (SÜD-CHEMIE) with mean diameter of 5–6 µm and specific surface of 3.5×10^6 m^2 m^{-3}. A microporous PAC was supplied by the company PICA. The BET surface area of PAC is approximately 800 m^2 g^{-1} and the mean particle diameter is 15–35 µm.

2.2. Ultrafiltration unit

Ultrafiltration was performed in a dead-end stirred cell (Amicon 8400, Millipore, France) at constant transmembrane pressure (TMP). The membrane surface was 39.6 cm^2 and maximum cell capacity 400 mL. A 5L solution reservoir was connected to a circuit of compressed air allowing TMP between 0.4–2.4 bars (Fig. 1). Measurement of permeate mass was performed during experiment by an electronic balance connected with a personal computer.

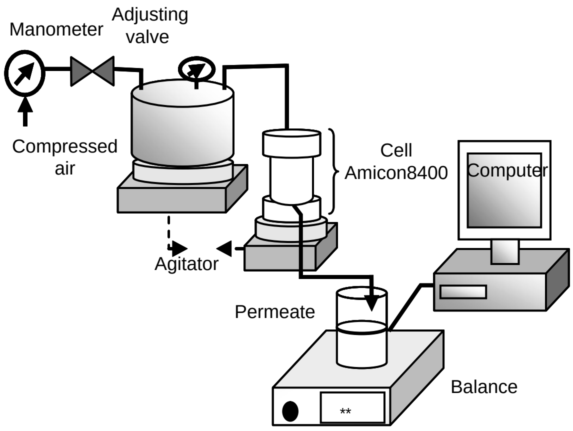

Fig. 1. Diagram of experimental set-up used in filtration experiments.

2.3. Filtration methods

Experiments were performed by the pressure step method. This method consists in filtering feed water with constant TMP during the production of a fixed permeate volume and then increasing the TMP to another value. Each constant TMP was applied for a 100 mL permeate volume, which corresponds to duration between 5 and 15 min. The TMP step was equal to 0.4 bar. The range of studied TMP was between 0.4 and 2.4 bars. According to the filtration model, for each constant TMP, a decrease of permeation flux versus time is observed due to membrane fouling (see Fig. 2). This flux decline can be described as an increase of fouling resistance versus time.

$$J_{(20^\circ\mathrm{C})} = \frac{\Delta P}{\mu_{(20^\circ c)}(R_m + R_f)} \qquad (1)$$

where $J_{(20^\circ C)}$ is the flux, ΔP is the TMP, $\mu_{(20^\circ C)}$ is the viscosity of the permeate and R_m and R_f are the resistance of the membrane and fouling, respectively.

Thus, the fouling rate (dR_f/dt) is the slope from the graph of fouling resistance versus time at each constant TMP (see Fig. 2) and is calculated by:

$$\frac{dR_f}{dt} = \frac{R_{f2} - R_{f1}}{t_2 - t_1} \qquad (2)$$

2.4. Analytical methods

The total organic carbon (TOC) concentration was measured by TOC-meter (TOC-Vcsh, Shimadzu, France). The non-purgeable organic carbon (NPOC) method was used. The detection of TOC-meter is limited to 0.1 mg L^{-1} TOC in presence of high salt concentration as in the case of seawater.

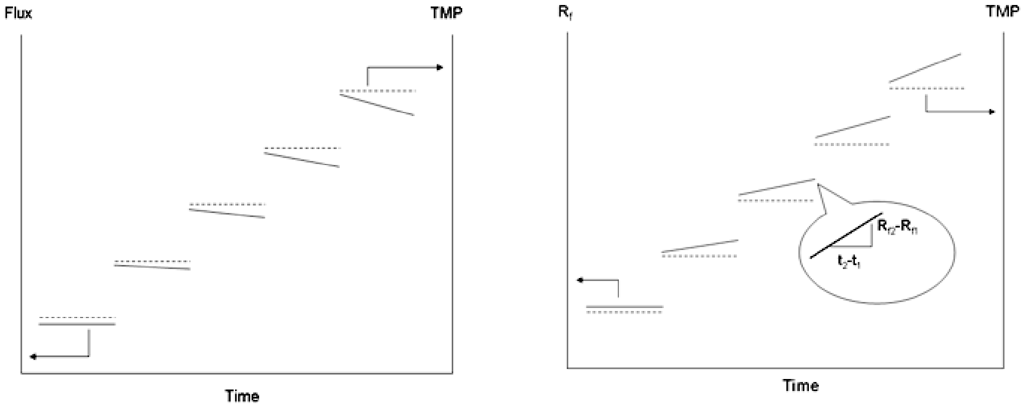

Fig. 2. Pressure step method illustration.

Molecular weight (MW) distributions of different samples were determined by high-pressure size exclusion chromatography (HP-SEC, AKTA) method with a fluorescence detector at 350–445 nm. SEC column used in this study can measure MW in range of 10–100 kDa.

The apparent retention rate (R) of NOM is defined by

$$R = \left(1 - \frac{C_{permeate}}{C_{feed}}\right) \times 100 \qquad (3)$$

where $C_{permeate}$ and C_{feed} are TOC concentration in permeate and feed water, respectively.

3. Results and discussion

3.1. Effect of bentonite addition on UF performance

The effect of bentonite addition on fouling rate as well as NOM retention rate was determined for different bentonite concentrations. Fig. 3 shows the variation of the fouling rate (a) and the retention rate (b) at bentonite concentrations of 200, 500 and 1000 mg L^{-1}. Average values of retention rate are presented for each dose of bentonite since this rate remains constant during the experiment, for all the experiments. As shown in the figure, the fouling rate increases with TMP for all bentonite doses. An addition of bentonite with a concentration between 200 and 500 mg L^{-1} seems to have no effect on the fouling rate which is very similar to that of test done without bentonite. However, the addition of 1000 mg L^{-1} bentonite allows a slightly lower increase of the fouling rate. In that case of highly concentrated bentonite, more adsorption sites are available to fix organic matter. It can be assumed that the membrane is less adsorbed and thus less fouled by NOM, what is traduced by a lower fouling rate. Fig. 3(b) presents values of average retention rate for the different doses of bentonite. This retention rate of seawater by UF alone is approximately 5%. The addition of bentonite at different doses can not improve significantly the retention rate that stays between 3 and 10%. Consequently, the hybrid process coupling bentonite adsorption and UF is not efficient enough to remove the NOM in seawater.

The effect of precoating membrane by bentonite particles was also studied (Fig. 4). The idea of these experiments was that the bentonite particles precoated on membrane surface might improve the NOM retention by trapping organic molecules in their cake deepness. To carry out this experiment, 500 mg L^{-1} of bentonite suspension was filtered for 1 hour at constant pressure of 2 bar. The mass of deposited bentonite on membrane surface is approximately 40 g m^{-2}. Then seawater without bentonite was filtered by pressure step method. The results show a considerable increase of fouling rate compared to experiments performed with no precoated membranes (Fig. 4(a)). A contrary result was obtained for a dynamic MF membrane precoated by mineral bentonite in the case of a membrane bioreactor for wastewater treatment [15]. The authors showed that precoating membrane presents many advantages including stable permeate flow rate. Of course, the characteristics of the feed solution were very different in their study. Moreover the particle size distribution of the bentonite that precoats the membrane plays an important role in structuring the deposit. The size distribution of bentonite particles used in our experiments may be too small (5–6 µm); therefore, this bentonite deposit is too dense and compact and cause pore blocking on membrane surface. Fig. 4(b) shows that the retention rate of membrane precoated by bentonite is nearly similar to that of filtering suspended bentonite through the membrane. So, there is

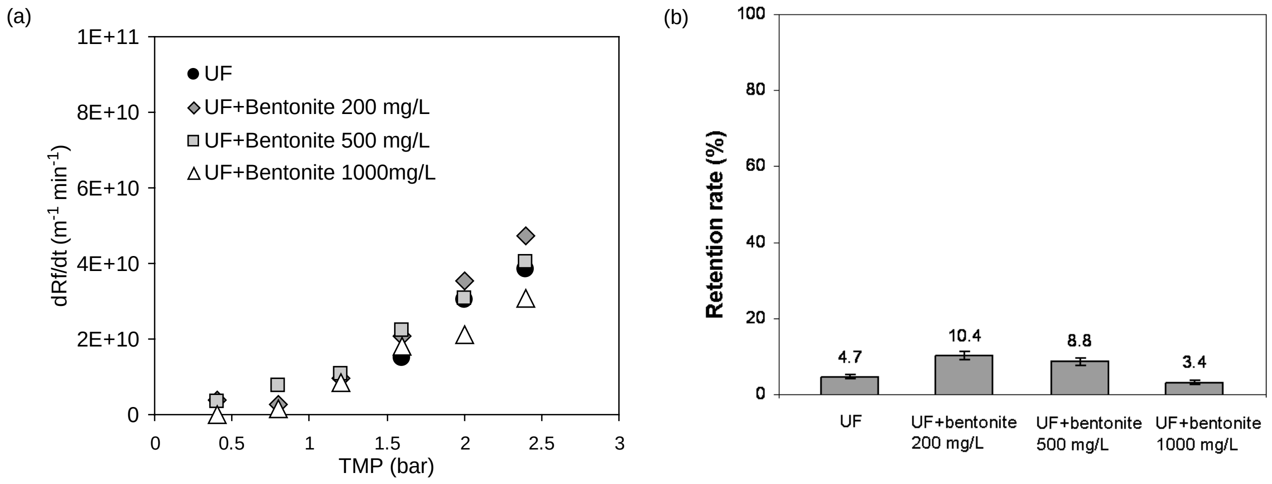

Fig. 3. Effect of bentonite concentration on (a) the fouling rate and (b) the TOC retention rate.

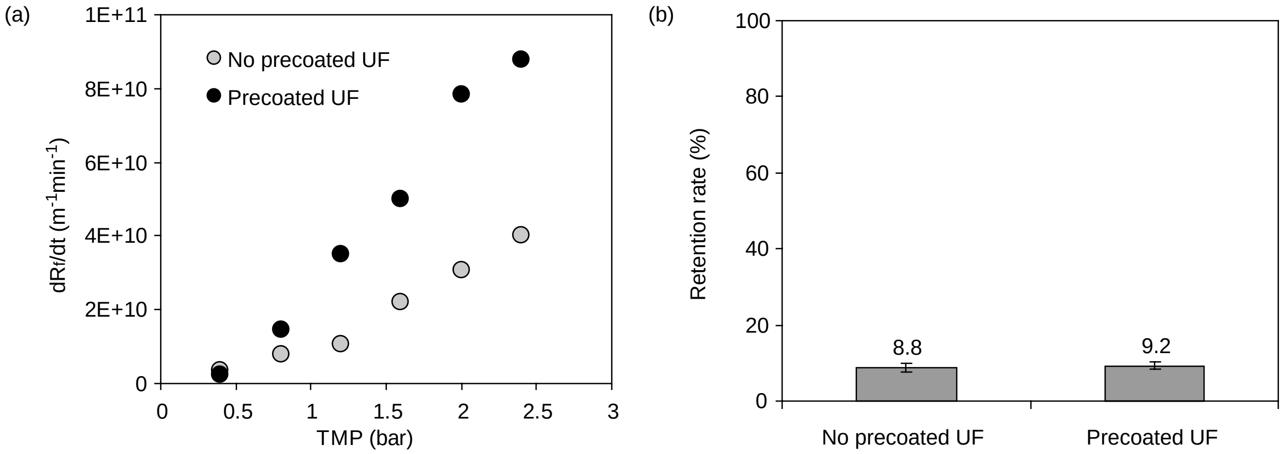

Fig. 4. Effect of membrane precoated by bentonite (40 g m^{-2}) on (a) fouling rate and (b) NOM retention rate.

no interest of precoating this membrane with that kind of particles.

3.2. *Effect of PAC addition on UF performance*

The effect of PAC concentration on fouling rate and retention rate was investigated at three concentration values: 50, 100 and 200 mg L^{-1}. The results obtained are shown in Fig. 5.

The fouling rate seems to be reduced for a PAC concentration of 200 mg L^{-1}. The decrease of fouling rate when increasing PAC dose can be explained as previously by an increase of available adsorption sites that fix NOM. Fig. 5(b) presents the average NOM retention rate for different PAC doses. The results show that PAC can extremely enhance the NOM removal from approximately 10% without PAC to 40–45% for tests carried out with a PAC concentration of 200 mg L^{-1}. This retention rate seems to increase with PAC concentration.

Different contact times between PAC and seawater were applied. The seawater was mixed and stirred with 100 mg L^{-1} of PAC during 40 and 100 min, and then the mixture of PAC and seawater was fed to UF. The fouling rate appears to decrease when the contact time increases, but the contact time has no significant effect on total removal efficiency (R_{total}) and it is about 30–45% for all contact times (Fig. 6).

According to the results in Fig. 6(b), the NOM removal efficiency by PAC adsorption (R_{PAC}) was calculated separately from that by UF by:

$$R_{PAC} = \left(1 - \frac{Ct}{C_0}\right) \times 100 \tag{4}$$

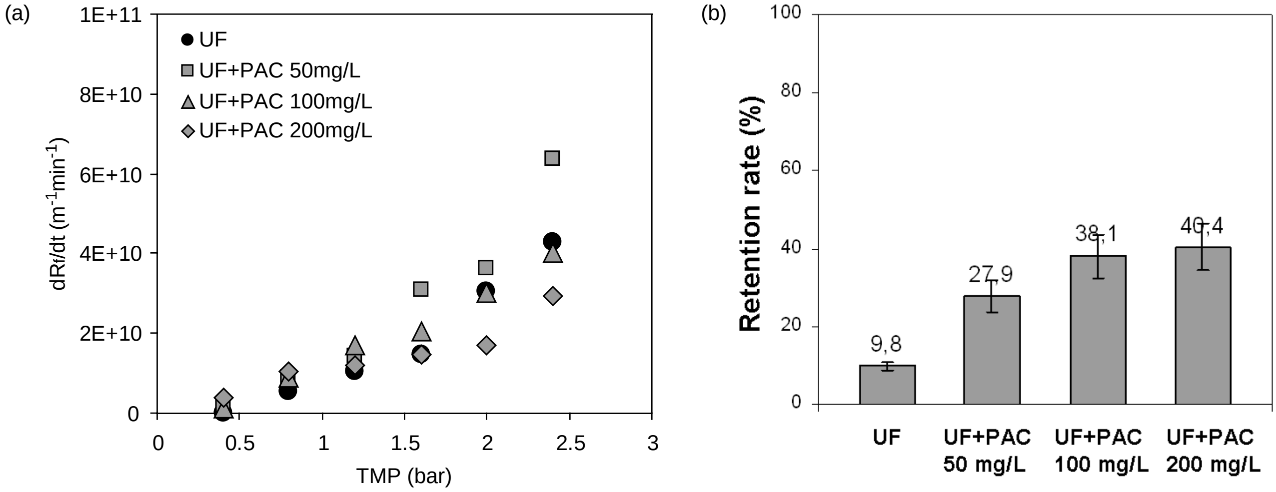

Fig. 5. Effect of PAC concentration on (a) fouling rate and (b) NOM retention rate (Contact time = 0 min).

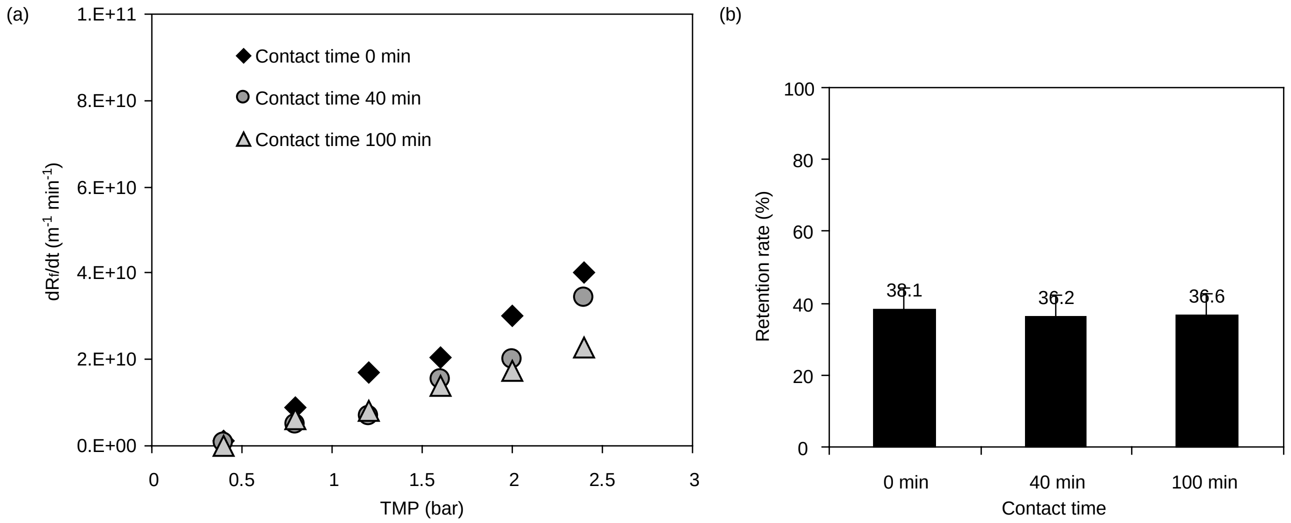

Fig. 6. Effect of contact time between PAC and seawater on (a) fouling rate and (b) NOM retention rate (PAC = 100 mg L^{-1}).

where C_t is TOC concentration after mixing of feed and PAC at time = t before UF and C_0 is the initial TOC in feed solution.

Then the NOM removal efficiency by UF (R_{UF}) was calculated by:

$$R_{UF} = R_{total} - R_{PAC} \qquad (5)$$

The results are presented in table 3. The total efficiency of NOM removal obtained for the three contact times demonstrates almost the same values i.e. about 36–37%. For two contact times, 40 and 100 min, the removal efficiency by PAC adsorption is greater than that by UF (24% against 12% for 40 min and 29% against 8% for 100 min). It was also observed that when the contact time increases from 40 to 100 min, the removal efficiency by PAC slightly increases from 24% to 29%. This proves that the more the contact time is long, the more PAC adsorption is involved in the NOM retention.

In conclusion, when the contact time increases, the contribution to NOM removal due to PAC adsorption becomes more significant compared to that due to UF alone.

Table 3
Removal efficiency by PAC adsorption and by UF at different contact times.

Contact time (min)	Removal efficiency (%)		
	by PAC adsorption	by UF	Total removal by PAC/UF
0		36	36
40	24	12	36
100	29	8	37

3.3. Characterisation of UF membrane fouling

The measurement of membrane permeability with osmosed water was performed before and after filtration tests in order to evaluate the fouling reversibility. The permeability was measured immediately before filtration. After filtration, the membrane surface was scrubbed softly by hand, and then the permeability measurement was performed. Three types of results are presented: for experiments of ultrafiltration without adsorbent, of UF coupled with bentonite and of UF coupled with PAC adsorption. A slight difference of water permeability before and after tests was observed as shown in table 4. For the three experiments the reduction of the permeability is about 3–4%. This reduction is quite low, and could let assume that the membrane fouling occurring during seawater filtration for short-term filtration is only deposit formation on membrane surface and is totally reversible. Nevertheless, it must be noted that the total duration of an experiment is quite short (about 40 min) so a less reversible fouling could occur for longer experiments.

Table 4
Evolution of water permeability for different pretreatments.

	Water permeability (L/h/m^2/bar)		
	Before UF	After UF	Reduction (%)
UF alone	230	222	3.5
UF + Bentonite (200 mg L^{-1})	242	232	4.1
UF + PAC (100 mg L^{-1})	231	224	3.0

Table 5 shows the contact angles of membrane fouled during the different experiments: UF alone, UF + bentonite and UF + PAC. It is observed that the contact angle increases from 15.9° for a new membrane to 89° for the membrane fouled during UF performed without adsorbent. This is due to the hydrophobic property of organic matter in seawater resulting in an increase of the membrane surface hydrophobicity. For a membrane fouled during experiment with bentonite, the contact angle is of the same value as without adsorbent: 88.9°. This result confirms previous observations concerning bentonite i.e. its very low adsorption capacity of NOM contained in seawater. On the contrary the reduction of contact angle from 89° for membrane fouled by seawater to 40° when PAC was added also confirms that organics were adsorbed on PAC particles and changed surface charge and hydrophobicity of PAC [16]. In addition, because of the hydrophobicity property of PAC, it preferably adsorbs organic compounds that mainly are hydrophobic. That is why PAC can adsorb more organic matter than bentonite that is rather hydrophilic [17]. These results point out a potential interest of PAC addition which allows reducing surface membrane modification. These phenomena have no measurable effects on membrane permeability for short term experiments (table 4) but are visible on fouling rate (when the contact time is high enough); they might induce permeability modification (and thus irreversible fouling) for long term filtration experiments.

Table 5
Contact angle measurement of membrane fouled by different adsorbents.

	Contact angle (°)
New membrane	15.9
Membrane fouled during UF without adsorbent	89.0
Membrane fouled during UF + bentonite	88.9
Membrane fouled during UF + PAC	40.0

The permeates from different combining of adsorption/UF were collected to measure molecular weight distribution by HP-SEC as shown in Fig. 7. These comparative analysis confirm the results obtained previously i.e. UF alone can only slightly remove organics with MW of 13000 g mol^{-1} from seawater, considering the area under the graph by integrating method. It only decreases from 31.2 mV mL^{-1} for test with seawater alone to 30.6 mV/mL^{-1} for permeate of UF membrane. The PAC and bentonite adding can better remove organics, especially in case of PAC (the area under the graph is 24.6 and 1.1 for bentonite and PAC addition, respectively).

4. Conclusions

This study aimed to evaluate the coupling of ultrafiltration and adsorption for seawater pretreatment before RO. Experiments were performed with actual seawater sampled from Mediterranean Sea. The addition of PAC in UF process is able to enhance UF performance: the

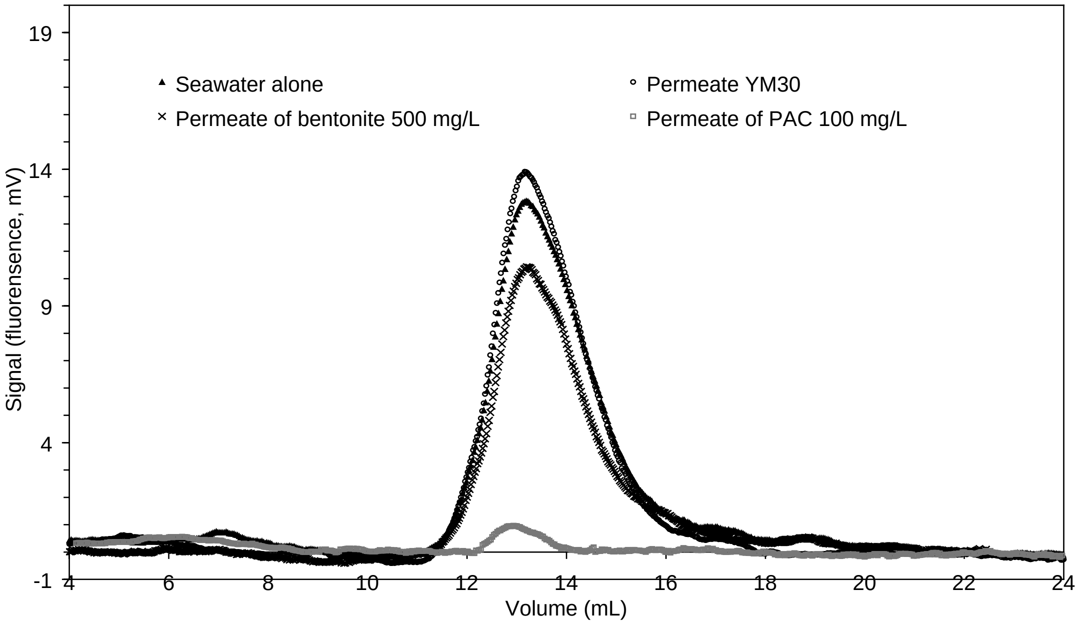

Fig. 7. Molecular weight distribution of solutes contained in permeates from different pretreatments.

UF fouling rate is reduced and the NOM retention rate increases from about 10% without PAC to 45% with PAC, for a concentration of 200 mg L^{-1}. An increase of contact time between PAC and seawater induces a reduction of fouling rate. When the contact time increases, the contribution to NOM removal due to PAC adsorption becomes more significant compared to that due to UF alone. This contact time will have to be optimised.

Because of its low cost and availability in many countries, bentonite was also envisaged as adsorbent. Results showed that addition of 5 µm bentonite to UF has no significant effect on UF performance. The effect of precoating membrane by bentonite was also studied. The precoated membrane provides an important increase of fouling rate compared to test carried out with suspended bentonite. This may be explained by the fact that the diameter of bentonite particles used in the experiments is too small; therefore, they cause blocking of pore surface.

Concerning fouling mechanisms, the results showed that the fouling occurring during ultrafiltration is only deposit formation on membrane surface and it is totally reversible for short term experiments even when PAC and bentonite are added.

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