Ultrafiltration as direct pre-treatment of seawater – a case study

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Abstract

Reverse osmosis (RO) and nanofiltration (NF) processes gain more and more interest in the desalination market. Recently seawater reverse osmosis (SWRO) has become more widespread, using relatively large plants, whilst NF is being applied before thermal desalination, as an advanced treatment for increased efficiency of thermal processes. A proper and reliable seawater treatment before RO and NF, capable to retain suspended solids that cause fast fouling and plugging of sensitive spiral wound membrane modules, is a key to success of desalination processes. Reliability, high and constant quality of permeate, regardless of changes in seawater characteristics, are major advantages of microfiltration/ultrafiltration (MF/UF) over conventional pre-treatment, allowing a stable and high performance of RO and NF processes. This experimental work evaluates performance of two different UF, hollow-fibre membrane modules, when fed directly with raw seawater taken from the industrial harbour of Genoa. The study reports the performance of nanofiltration process fed with UF permeate versus the performance of NF fed with raw seawater.

Keywords: MF/UF seawater pre-treatment; harbour seawater; hollow fibre membranes; dead-end operation; fouling control.

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1. Introduction

Seawater pre-treatment is one of the major factors determining the success or failure of a desalination plant. This is particularly true for RO, but for distillation process is also highly important [1]. Spiral wound modules used in RO/NF processes require an enhanced pre-treatment of seawater for eliminating suspended solids that may cause membrane fouling or plugging feed channels and spacers. Conventional pre-treatment of seawater, even if well designed, maintained and operated, does not provide a proper solids removal from seawater in the case of upsets in the process. This fact leads to a decrease in RO/NF efficiency and an increase in frequency of cleanings, resulting in the use of chemicals and sanitizers and shorter membrane lifetime [2]. Recently, MF/UF processes have been considered an alternative to conventional seawater pre-treatment for a reliable supply of constant and high-quality feed to desalination process. UF has been reported to be especially successful in treating difficult water from surface intake [3].

In particular, UF is capable to retain colloidal contaminants, smaller bacteria and viruses, thus allowing total removal of turbidity and a considerable reduction of Silt Density Index (SDI), assuring a stable operation of RO and NF processes. Although the capital costs of membrane pre-treatment exceeds that of conventional pre-treatment by 20-50%, the improved quality of treated water can reduce the size of the RO plant by allowing a higher RO flux to be used. Further savings are due to reduced replacement rate and cleaning frequency of RO/NF membrane modules. Space savings, because of a high compactness of membrane installations, are an additional advantage of MF/UF pre-treatment over the conventional processes [4]. In this work the authors focused on the application of hollow fibre UF modules to seawater pre-treatment before NF process. Performance of two different hollow fibre ultrafiltration membranes on pilot plant scale is presented and the positive influence of UF pre-treatment on the performance of NF process is demonstrated.

2. Experimental

2.1 UF membranes and pilot plant

Technical specifications on membrane modules, used for continuous seawater ultrafiltration in Genoa’s harbour, are provided in Table 1. The elements are simply named with letters (A and B) because of a secrecy agreement between the authors and the manufacturers. The plant was fed with raw seawater from the industrial harbour of Genoa after pre-screening with

150μm filters. The plant operated at constant permeate flow rate (Qp), while transmembrane pressure (TMP) varied. Membrane performance was studied at various permeate flow rates (60, 80 and 100 L/m^2h). Process parameters (TMP, Qp, temperature, feed and permeate turbidity) were registered in 10 seconds intervals. In addition, SDI was measured manually on the permeate line. Feed and permeate samples were analysed for total organic carbon (TOC), total suspended solids (TSS) and bacteria presence once a week, while analysis of seawater were carried out monthly. Periodic backwashing was performed with the UF permeate. Various parameters of the backwash process (BW) like frequency, duration (t_{BW}) and flow rate (Q_{BW}) were analysed. Chemically enhanced backwash (CEB) with sodium hypochlorite (20-100 ppm of free chlorine), carried out every 4 hours for 2 minutes contact time, was investigated only with module A. Cleanings using sodium hypochlorite solution (200 ppm of free chlorine), usually followed by sodium hydroxide solution (optionally hydrochloric acid), were carried out when TMP reached 0,8 bar. Further details on the process conditions adopted for UF experiments are given in Table 2.

2.2 Seawater characteristics

During the experimental period from October 2007 to April 2008, harbour water had rather low turbidity varying from 0,5 to 2,0 NTU, with an average value around 0,8 NTU. High picks of turbidity appeared temporary, when large ferries docked in the harbour. Temperature of seawater was gradually decreasing from 19°C at the beginning of October, with the minimum of 12°C in January. Main characteristics of seawater during the experimental period are provided in Table 3.

3. **Results and discussion**

3.1 Permeate flux vs. TMP behaviour

Changes in TMP vs. experimental time at different permeate flow rates are reported in Fig.1.
During this experimental phase no CEB was performed. Due to changes in seawater temperature during the whole experimental period, the reported results are normalized to a reference temperature of 15°C. For any given flow rate, the TMP increases with operating time. The rate of TMP increase depends on the flow rate and varies from module to module.
Figure 2 shows the trend of membrane permeability as the function of the experimental time for different permeate flow rates. Comparison of the results shows that module B at the

beginning of each experiment presents a higher permeability (ca. 30%) than module A. However, because of its higher fouling tendency, module B loses its permeability much faster than module A. For instance, after 42 hours of operation at 80 L/m^2h permeate flow rate, the permeability of the two modules becomes similar, moreover, a further decrease in permeability below 100 L/m^2h bar is observed for module B in less than 72 h, while the permeability of the module A is still above 120 L/m^2h bar. As a result of such different behaviour, module A could operate longer between chemical cleanings, than module B.

Possible run time of both modules A and B can be easily determined using the estimated daily increase in TMP given in Table 4, calculated using a linear regression of experimental data. The use of a linear function is a good approximation only at relatively low TMP values, because at higher TMP the increase of TMP is much faster and data can be better fitted with an exponential function. To minimise errors resulting from nonlinear TMP behaviour at higher pressure, only measurements from the same TMP range (0,25 to 0,8 bar) were used for calculations. The change of TMP slope with increasing process pressure can be explained by a lower effectiveness of backwash operation at higher pressure. In fact, at a higher pressure, the cake deposited on the membrane surface becomes more compact, and, consequently more difficult to remove by backwashing. A relatively short operation time between chemical cleanings can be justified by harsh conditions in which modules were tested in the harbour. Seawater was fed to UF unit without any pre-treatment while numerous studies introduced coagulation of seawater for a better UF performance [3,5].

3.2 Influence of backwash conditions on TMP

Efficiency of backwash operation, serving in a dead-end configuration of ultrafiltration as a mechanical cleaning of a membrane surface from deposits, has a key meaning for process stability. For module A, backwash at the flow rate two times higher than the filtration flow was initially carried out every 30 min for 30s time. Later, backwash time was extended to 70s, but no improvement in TMP trend was noticed. Further, backwash conditions were thoroughly studied with module B. For this module more frequent and longer backwash resulted in a significant reduction of TMP slope. Table 5 shows an improvement in TMP behaviour at specific flow rate of 60 L/m^2h, when using different backwash conditions. A linear function was used for estimation of TMP slope for TMP measurements from the range 0,2 to 0,4 bar. The improvement in TMP stability when more frequent and longer backwash was used, was however followed by a significant increase in permeate turbidity.

3.3 Influence of chemically enhanced backwash on TMP

Chemically enhanced backwash (CEB) with sodium hypochlorite is a common practice for UF seawater pre-treatment. In our study, CEB carried out only on module A was set was set every 4 hours of ultrafiltration for 2 min contact time. The use of a relatively high concentration of chlorine (~100 ppm) resulted in about two times slower TMP increase than during trials without CEB. However, a low chlorine concentration (~20 ppm) resulted in only very slight improvement in TMP slope. Halpern at al. [5] reported stabilisation of TMP, when three times a day CEB with 30 ppm free Cl was introduced. The low efficiency of CEB in our study can be due to too short contact time; this parameter will be optimised during further trials.

3.4 Permeate quality

On-line turbidity measurements showed that module A was able to produce permeate of turbidity continually below 0,05 NTU regardless of changes in seawater turbidity. Only after chemical cleanings permeate turbidity increased temporary. Permeate of module B showed variable quality and was not always below 0,1 NTU, as guaranteed by the manufacturer. Product turbidity was not dependent on seawater turbidity, as for module A; however, chemical cleanings and frequency of backwashing had a strong influence on permeate turbidity during most of the experimental time with module B. In particular, a significant, irreversible increase in permeate turbidity after the first chemical cleaning was observed. “Virgin” module B gave low permeate turbidity: from 0,02 to 0,04 NTU, while after the first chemical cleaning values constantly above 0,05 NTU were measured. A high turbidity (above 0,1 NTU) was registered for a period of 48 hours up to 4 days after a chemical cleaning with module B, while with module A for maximum 12 hours. A comparison of permeate turbidity for both modules A and B during selected trials, each started after a chemical cleaning, is given, as an example, in Fig. 3.

It must be noted that, generally, modules A and B were operated in the same way and no high pressure, which might result in fibres breakage, was registered during experimental period. Chlorine concentration, temperature and pH during chemical cleanings were carefully checked and never exceeded allowed levels.

Permeate quality was monitored also by measuring SDI_{15} and a plugging rate of 5µm cartridge filters downstream the UF unit (pre-screening of NF process). A much slower increase in pressure drop on cartridge filters was observed for permeate from module A.

SDI_{15} was measured only for the permeate from module B. Measured values varied from 2,85 to 3,18, with the tendency to increase with increasing frequency and duration of backwashing.
Bacteria rejection was very high for both tested modules, even during increased permeate turbidity periods observed with module B. Analysis of permeate samples collected during 10 weeks of experiments with the module A showed a very good reduction of bacterial load. Usually permeate was characterised by 0 to 4 colony-forming units in 1 mL (CFU/1mL), while in seawater even up to 500 CFU/1mL were found. Similar results were obtained with permeate samples from the module B. Since organisms can grow on the permeate side of the installation, the presence of a single bacterium does not necessarily indicate fibres breakage or imperfections in skin layer of ultrafiltration membrane.

Performance of the NF process downstream the UF unit was used as a main quality indicator of UF permeate. Any changes in pressure drop on NF spiral wound elements or in process pressure were carefully analysed. Results shown in Fig. 4 indicate that the integration of ultrafiltration and nanofiltration processes results in a very stable NF performance even at the single element permeate recovery of 15 %. On the contrary, NF process fed directly without any pre-treatment shows a significant increase in process pressure, as well as in a pressure drop.

4. Conclusions

Investigated ultrafiltration modules proved to be perfectly applicable to seawater pre-treatment prior to RO/NF processes. Both tested membrane modules were capable to deliver low turbidity permeate, regardless of changes in seawater turbidity. Nanofiltration process exhibited a stable performance when fed with permeates produced with both ultrafiltration modules.

During field experiments, module A was characterised by a higher stability of TMP and a lower permeate turbidity than module B. TMP increased slower for module A, although for module B stronger and longer backwashing was used. Though slightly higher starting permeability of module B, module A showed better features for the application to seawater pre-treatment due to lower flux decline with time.

It must be stressed that ultrafiltration membranes worked in harsh, harbour conditions, fed with surface intake seawater, without any pre-treatment. Thus, reported in here TMP increase versus filtration time and rather short run time between chemical cleanings, should not be directly compared with results of other studies using seawater after coagulation or from deep well intakes. Further experiments, based on the experience reported in this article, will be carried out with the focus on optimisation of process performance.

Acknowledgments

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Table 1 Technical specification of membrane modules used for UF experiments

Parameter	**Module A**	**Module B**
Membrane material	PES based	PES based
Fibres ID [mm]	0,9	0,8
Membrane area [m^2]	30	40
Operating mode	In-out; dead-end	In-out; dead-end
Application data (during cleaning)	P = 5 bar T = 40°C pH = 3-10 (1-13)	P = 8 bar T = 80°C pH = 2-12 (1-13)

Table 2 Process parameters used for UF experiments

Parameter	**Module A**	**Module B**
Specific permeate flow Q_p (L/m^2h)	60; 80; 100	60; 80
Backwash flow rate Q_{BW} (m^3/h)	3,6; 4,8; 6,0	6,0; 8,0
Transmembrane pressure TMP (bar)	0,2 - 0,8	0,2 - 0,8
Filtration time t_f (min)	30	20; 30
Time backwash from the top t_{BWT} (s)	30; 70	30
Time backwash from the bottom t_{BWB} (s)	NO	20; 40
Chemically enhanced backwash CEB (ppm)	20-100 Cl_2	NO
Chemicals dosage for cleaning	200 ppm Cl (after NaOH or HCl)	200 ppm Cl (after NaOH)

Table 3 Main seawater characteristics of industrial harbour of Genoa

Parameter	**Range**	**Average**
Conductivity, 25°C (mS/cm)	53,1-56,0	54,5
pH	8,0-8,1	8,1
TSS (mg/L)	<5	<5
TDS (mg/L)	39300-40900	39970
TOC (mg/L)	<1	<1
Chlorophyll-a (μg/L)	<0,2	<0,2
Total bacterial count, 22°C (UFC/1mL)	27-450	200
Total bacterial count, 36°C (UFC/1mL)	5-500	150

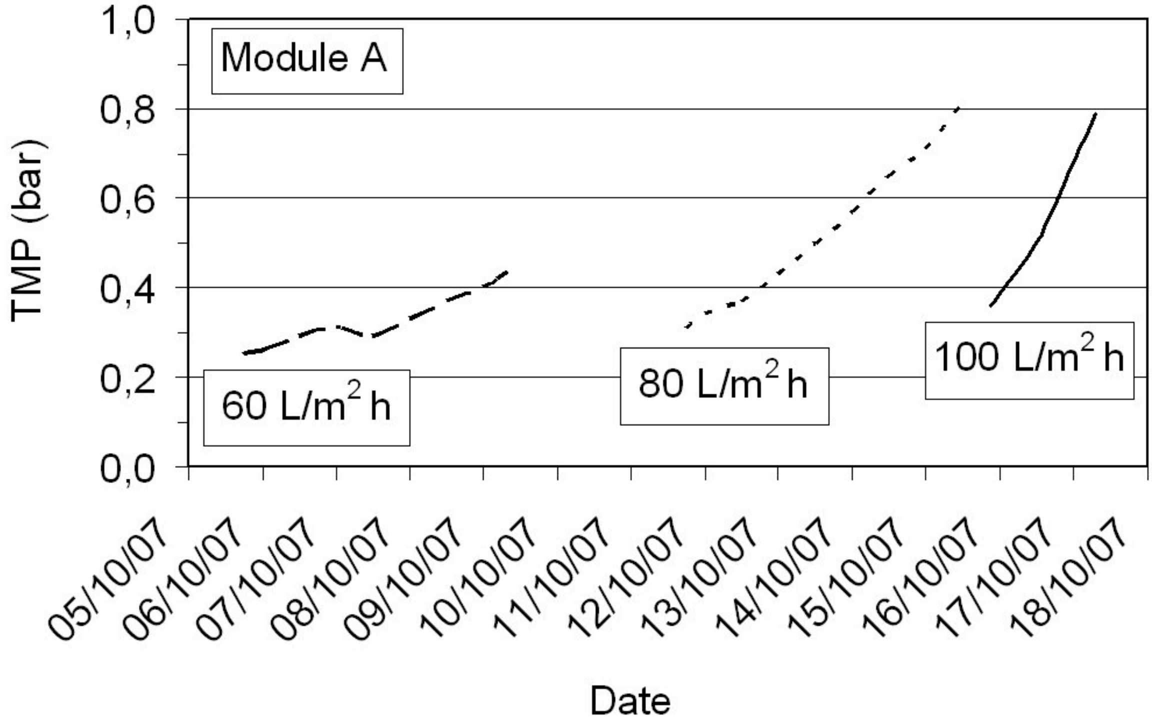
Table 4 Linear estimation of an increase in TMP for modules A and B at various permeate flow rates

Specific permeate flow rate (L/m^2 h)	**Estimated increase in TMP [bar/day]**	
	MODULE A	MODULE B
60	0,050*	0,110
80	0,130	0,200

* TMP measurements from the range 0,25 – 0,45 bar

Table 5 Influence of backwash conditions on TMP increase for module B at 60 L/m^2 h permeate flow rate

Backwashing conditions	**TMP increase (bar/day)**
frequency=30min; t_{BW}=50s; Q_{BW}=6,0m^3/h (2,5xQ_f)	0,095
frequency =20min; t_{BW}=50s; Q_{BW}=6,0m^3/h (2,5xQ_f)	0,047
frequency =20min; t_{BW}=70s; Q_{BW}=6,0m^3/h (2,5xQ_f)	0,037



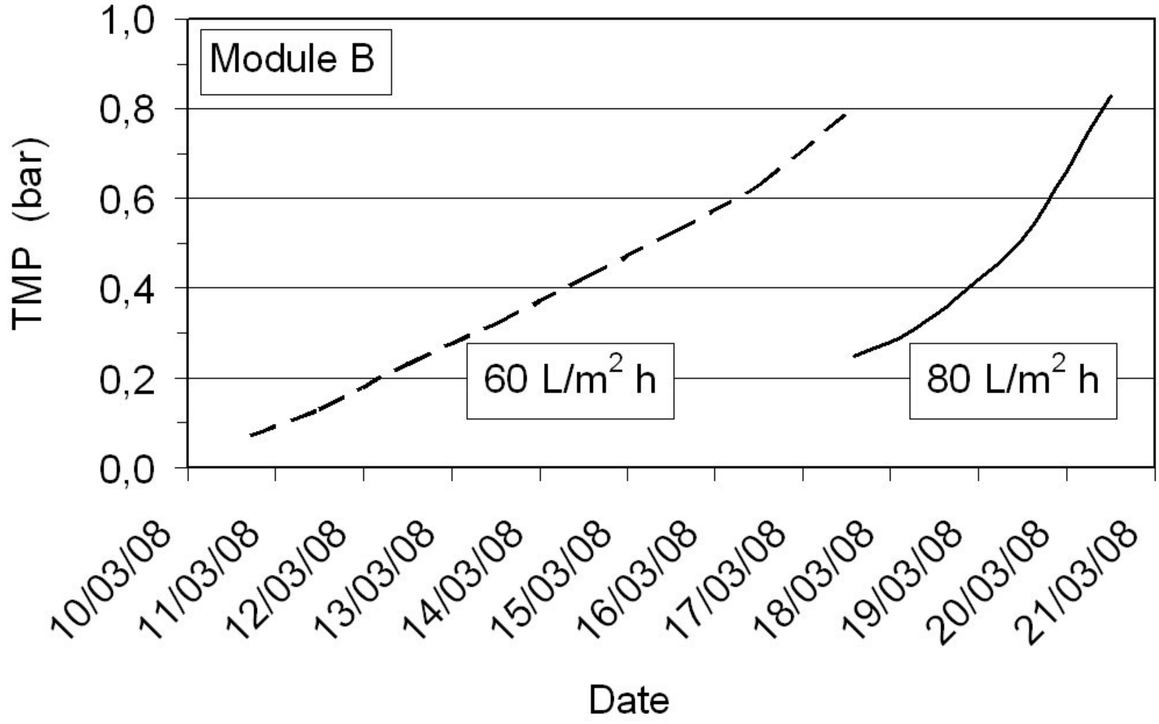
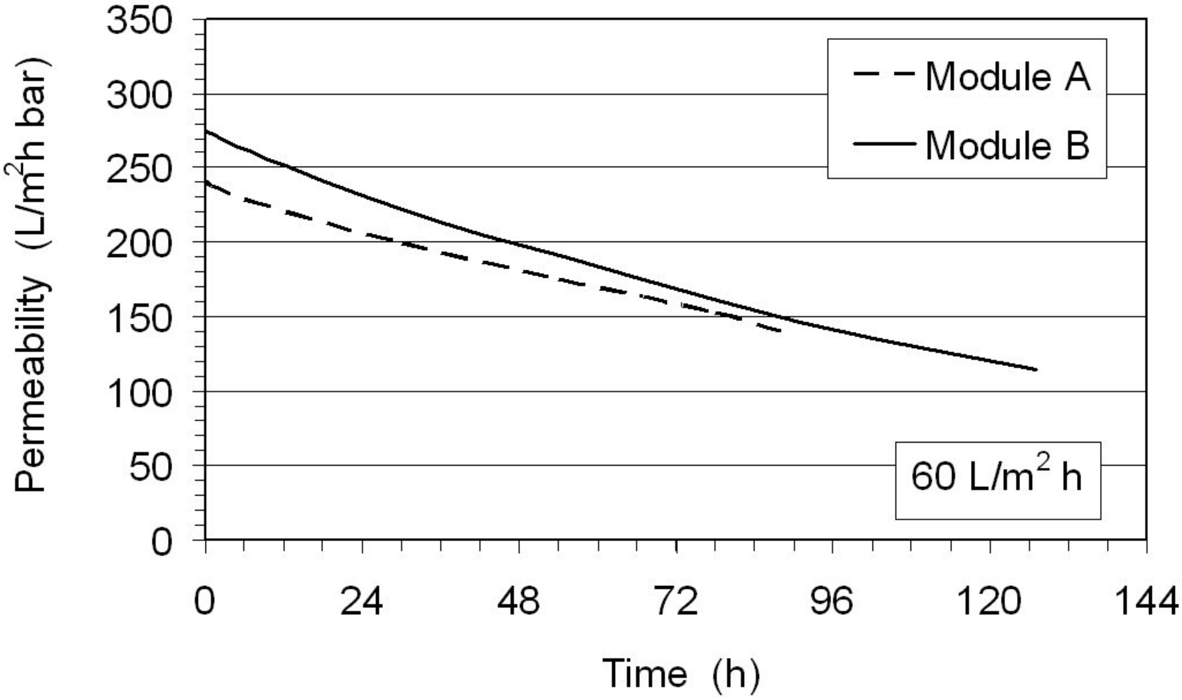


Fig.1 TMP at various permeate flow rates for membrane modules A and B



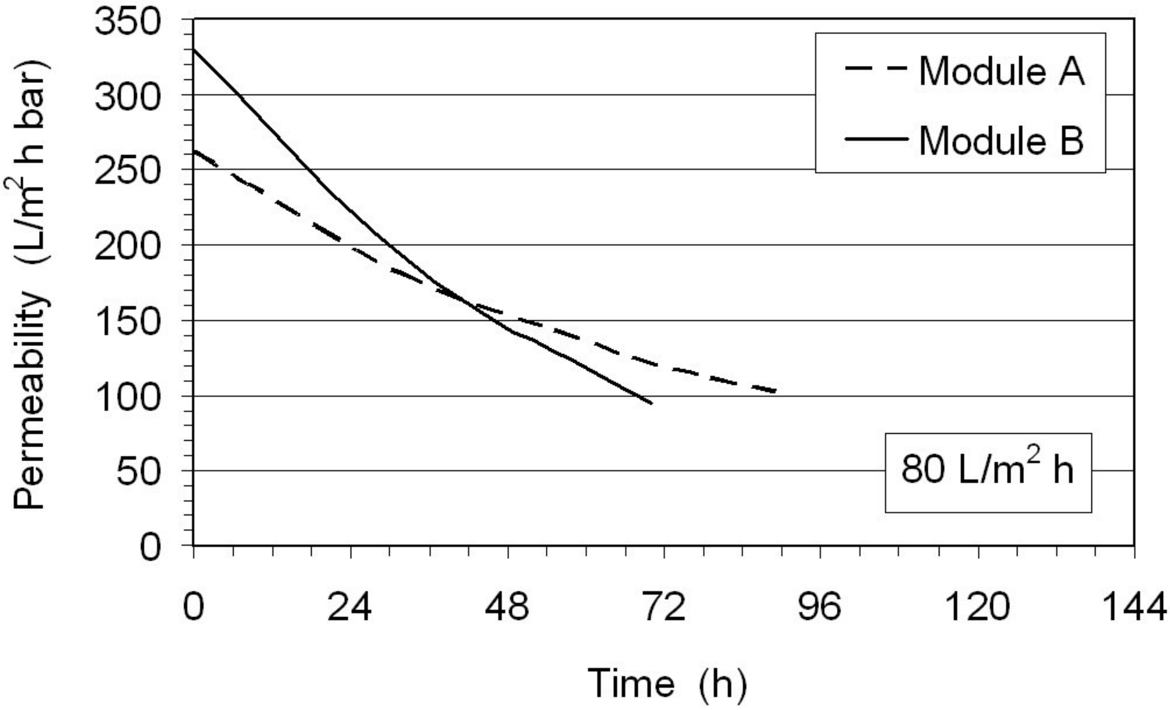


Fig.2 Permeability of modules A and B at permeate flow rates of 60 and 80 L/m^2h.

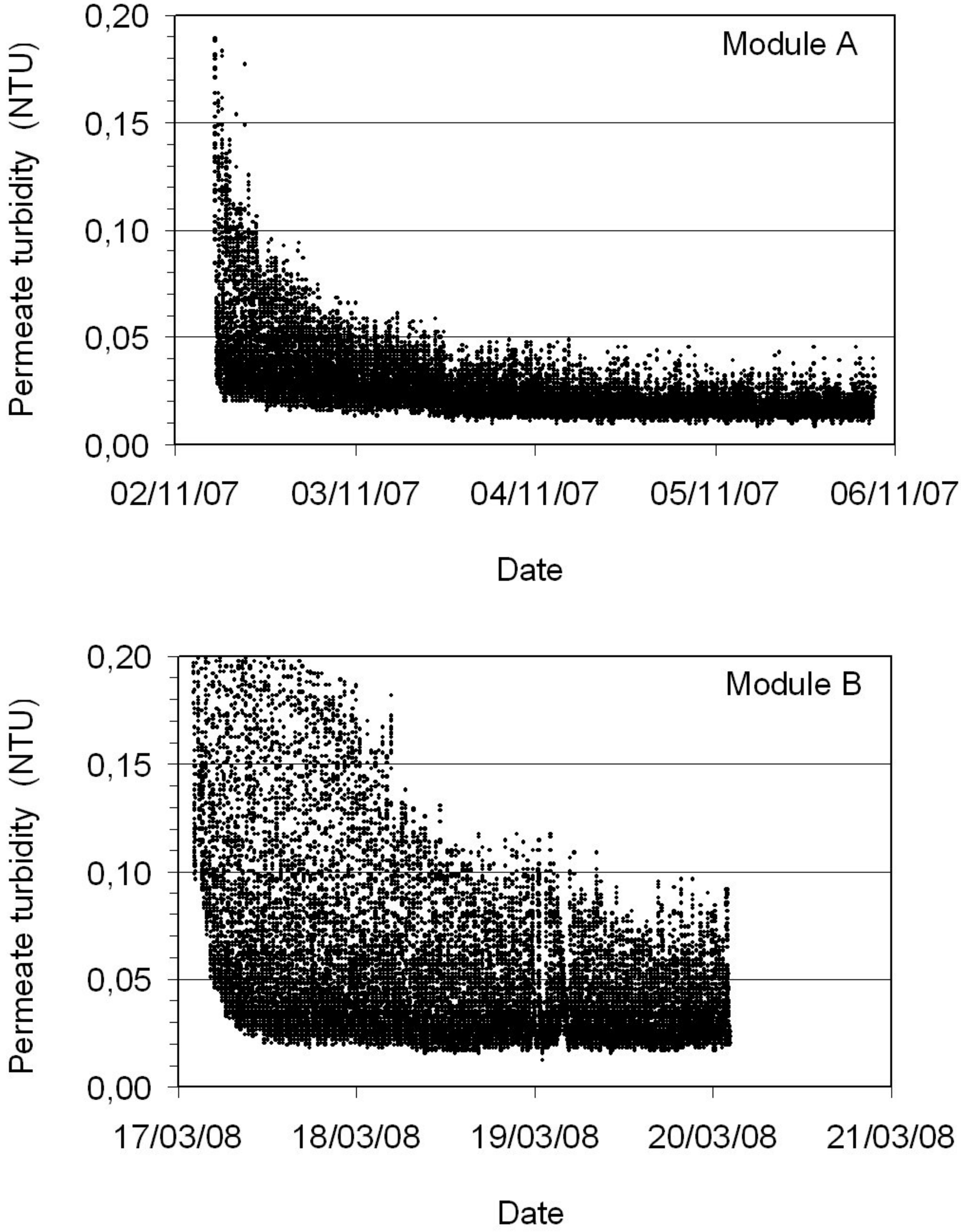
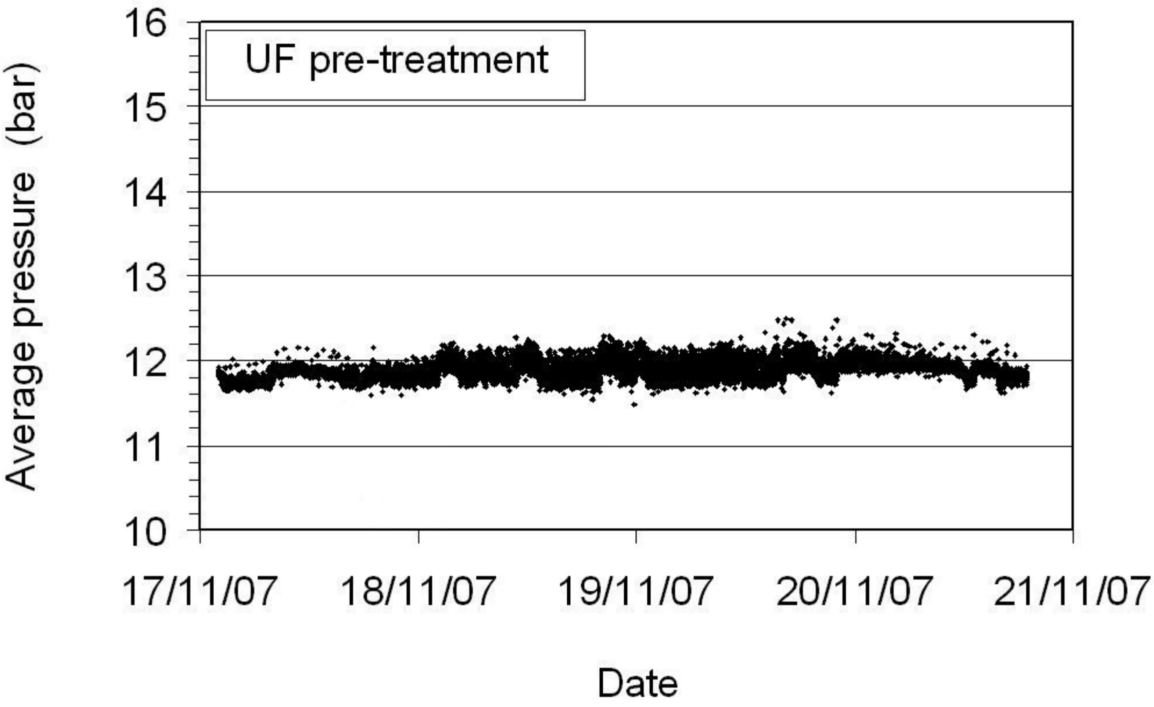


Fig.3 Permeate turbidity for modules A and B during 80 L/m^2h trial following chemical cleaning. BW every 30 min: module A at flow rate 2 times higher than filtration flow for 30 s; module B at flow rate 2,5 times higher than filtration flow for 50 s.



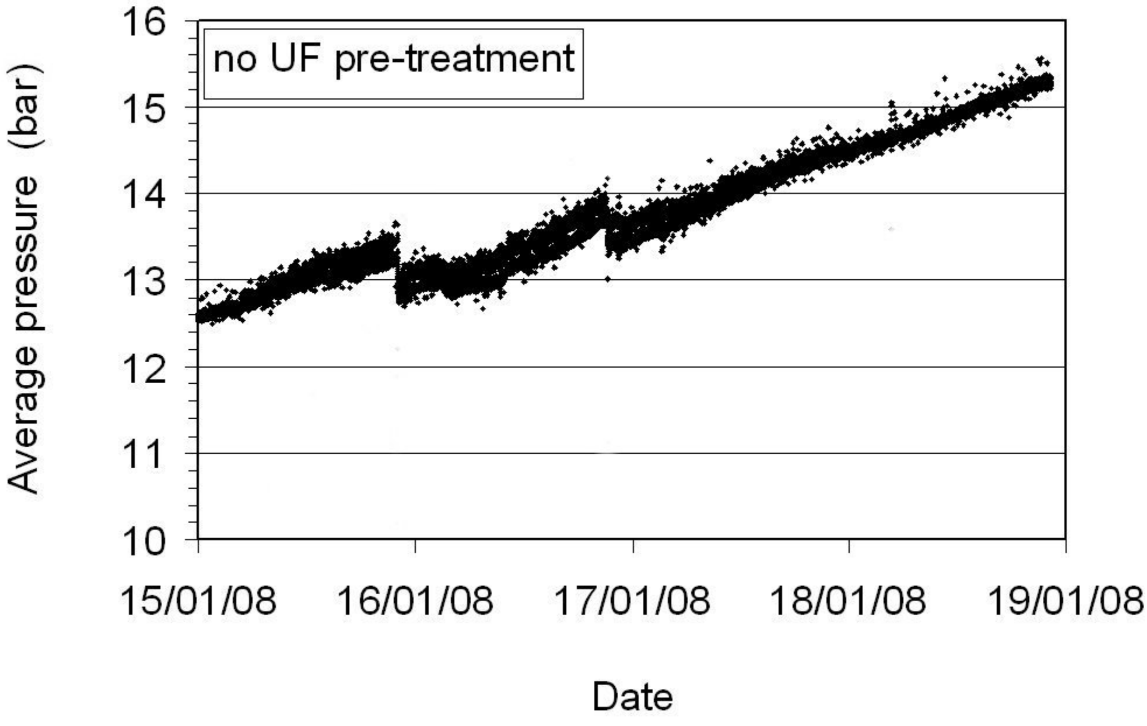


Fig.4 Average pressure in NF process with UF permeate and raw seawater