Evaluation of Neophil™ membranes for seawater ultrafiltration

Mediterranean Sea - Palavas-les-Flots. December 2016 to July 2017

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PILOT PLANT LOCATION	Palavas Les Flots (France). IFREMER Avenue Evêché de Maguelone, 34250 Palavas-les-Flots
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1) Introduction

Today, PVDF ultrafiltration membranes are widely used worldwide for water treatment where their hydrophilic character is determinant. Nevertheless, PVDF membranes are made hydrophilic mainly thanks to hydrophilic additives, which are blended to PVDF during membrane manufacturing. Without these agents, the PVDF polymer is naturally hydrophobic and thus quickly fouled by hydrophobic compounds, contained in the seawater and mainly natural organic matter.
However, these hydrophilic agents, like polyvinylpyrrolidone (PVP), have poor chemical resistance to oxidants [1], [2], which are daily used in water treatment processes to clean the membranes. Therefore these agents are progressively degraded and released out of the membrane. Thus, during plant operation, PVDF ultrafiltration membranes lose their protective hydrophilic layer and thus become hydrophobic again and so prone to natural organic matter fouling.

Polymem, in partnership with Arkema has developed a new PVDF ultrafiltration membrane generation made from PVDF Kynar blended with a new nanostructured hydrophilic additive. This new additive is a di-block copolymer composed of a PMMA bloc, miscible into the PVDF, and an hydrophilic block with hydroxyl groups [3]. Thanks to its miscibility, the PMMA bloc is deeply and durably anchored in the PVDF backbone while the hydrophilic bloc is orientated toward the pores surface providing hydrophilicity to all the inner and outer membrane porosity. Furthermore, the two blocs having a strong resistance to oxidation this new additive remains in the membrane matrix during its entire lifetime. This membrane has been launched commercially in 2017 with the Neophil™ brand name.

Total and Polymem companies have evaluated Neophil™ performances on seawater filtration in a pilot platform, hosted by IFREMER at their Palavas-les-Flots research center on the Mediterranean coast. Neophil™ membrane had been evaluated from December 2016 to June 2017. Furthermore, a commercial polysulfone (PSU) membrane, already successfully operated in large capacity plants, has been tested in parallel to Neophil™ membrane as a comparison point.

2) Pilot platform presentation

Figure 1: pilot plant platform at Palavas-les-Flots

The pilot platform, figure 1, is located on the coast with a seawater intake located at 50m from the shore at only 2m depth. Due to this particular localization, the quality of the seawater is very poor, for instance the fouling index, measured by the Silt Density Index is out of range for SDI_{15} and between 17 to 20 for SDI_5. However, this poor quality constitutes a very good evaluation test for this new membrane. Main characteristics of the inlet seawater are listed in the tables 1 and 2.

Table 1: Raw seawater quality

Parameters	*Quality of inshore seawater entering the demonstration plant*
Temperature	5-25
pH	8-8.5
Salinity	37 500
SDI_{15}	6.0-6.7
SDI_5	17-20

Table 2

Parameters	*Accuracy*	*Quality of inshore seawater entering the demonstration plant*
Chloride (NF EN ISO 10304)	*±0.1 mg/l*	20.1 g/l
Iron (NF EN ISO 11885)	*±0.1 µg/l*	18.2 µg/l
Calcium (NF EN ISO 11885)	*±0.1 mg/l*	390 mg/l
Potassium (NF EN ISO 11885)	*±0.1 mg/l*	408 mg/l
Magnesium (NF EN ISO 11885)	*±0.1 mg/l*	1.39 g/l
Sodium (NF EN ISO 11885)	*±0.1 mg/l*	11 g/l
Sulfate (NF EN ISO 11885)	*±0.1 mg/l*	988 mg/l
COD HACH COD Reactor	*±0.5 mg/l*	53 mg/l
TOC Shimadzu TOC	*±0.5 mg/l*	7.2 mg/l

The process of the pilot plant is similar to one of the offshore platform plant. Indeed, it is composed of 6 lines or modules working in parallel, figure 2.

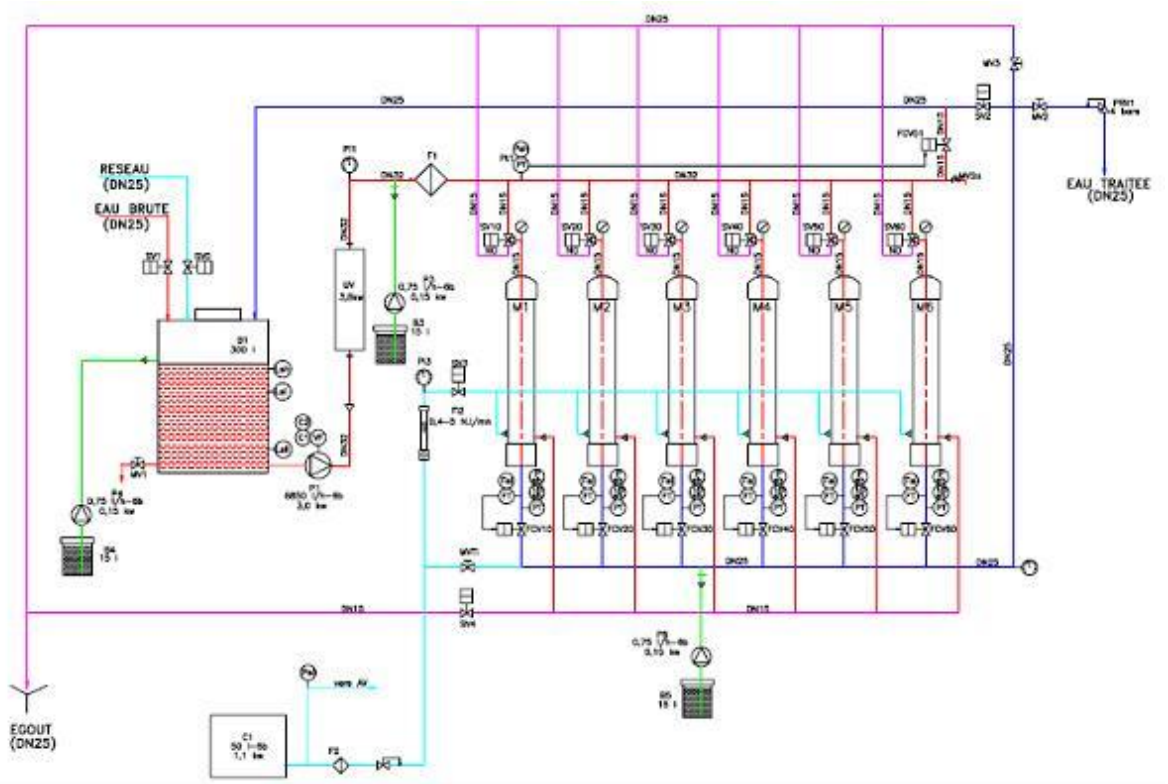

Figure 2: pilot plant flowsheet

Raw seawater feed the tank B1. The pump P1 feeds the 6 lines or modules at a relative high pressure of 5 bars. With a filtration transmembrane pressure (TMP) varying from 0.3 to a maximum of 1.2 bar the available permeate pressure is always higher than 3.8 bar. Periodically, the permeate produced by 5 lines is thus used to backwash (BW) one line. This allows removing the need of a huge permeate tank and thus saving space and weight on the offshore platforms.

In each module there is one bundle of several thousand of hollow fibers. Each bundle develops 10.5 m² of membrane filtration. The filtration flux is typically between 50 and 75 L/h.m² at 20°C. The hollow fibers work in outside/in mode, the permeate being in the lumen of the fibers. The permeate

is collected at the bottom of the modules. 6 pneumatic valves, controlled by the PLC, regulate the flows at a constant value. Since TMP is between 0.3 and 1.5 bar the remaining pressure at the outlet is always higher than 3.5 bar and sufficient to backwash the lines. The backwash cycle, lasting one minute, is described in the table 3:

Table 3 : Steps BW

	Flow L/h.m².bar@20°C	**Duration s**
Low flow	100	10
Low flow + air scouring	100	10
High flow + chlorine 10 ppm	130	20
High flow	130	20

To assist the backwash, a maintenance cleaning MC is done every 48 hours with a higher concentration of chlorine and soaking period of 30 minutes. The sequence of the MC is detailed in table 4:

Table 4 : Steps MC

Table 4 : Steps MC	**Flow L/h.m².bar@20°C**	**Duration min**
BW	Same as table 3	1
Chlorine injection 200 ppm through in the permeate during very low flow BW	20	3
Soaking time with air scouring 3s/min	0	30 min
BW	Same as table 3	1
Rinsing	50 LMH	5

Finally, when the TMP reaches 1.25 to 1.5 bar an intensive chemical cleaning or cleaning in place (CIP) is carried out. This CIP is performed using fresh tap water and is composed of 2 main steps, one cleaning with a blend of caustic and chlorine and a second cleaning with acid. The sequences of the CIP are detailed in the table 5 :

Table 5 : Steps CIP

	Detail	**Duration (min)**
Module drain		2
Potable water rinsing		5
Module drain		2
Caustic + chlorine injection	4g/l + 200 ppm	3
Soaking with intermittent air scouring	Aeration = 3s/min	30
Module drain		2
Acid injection for neutralisation		3
Soaking with intermittent air scouring	Aeration = 3s/min	5
Module drain		2
Acid injection		3
Soaking with intermittent air scouring	Aeration = 3s/min	5
Module drain		2
Potable water rinsing		5

3) Results

Neophil™ hydraulic performances

The trial campaign last 7 months from December 2016 to June 2017. Several fluxes have been tested corresponding to 4 different periods of trials. Each period lasts at least 1.5 months. The figures 3, 4 and 5 plot data of flux, TMP and permeability normalized at 20°C as a function of time for these periods.

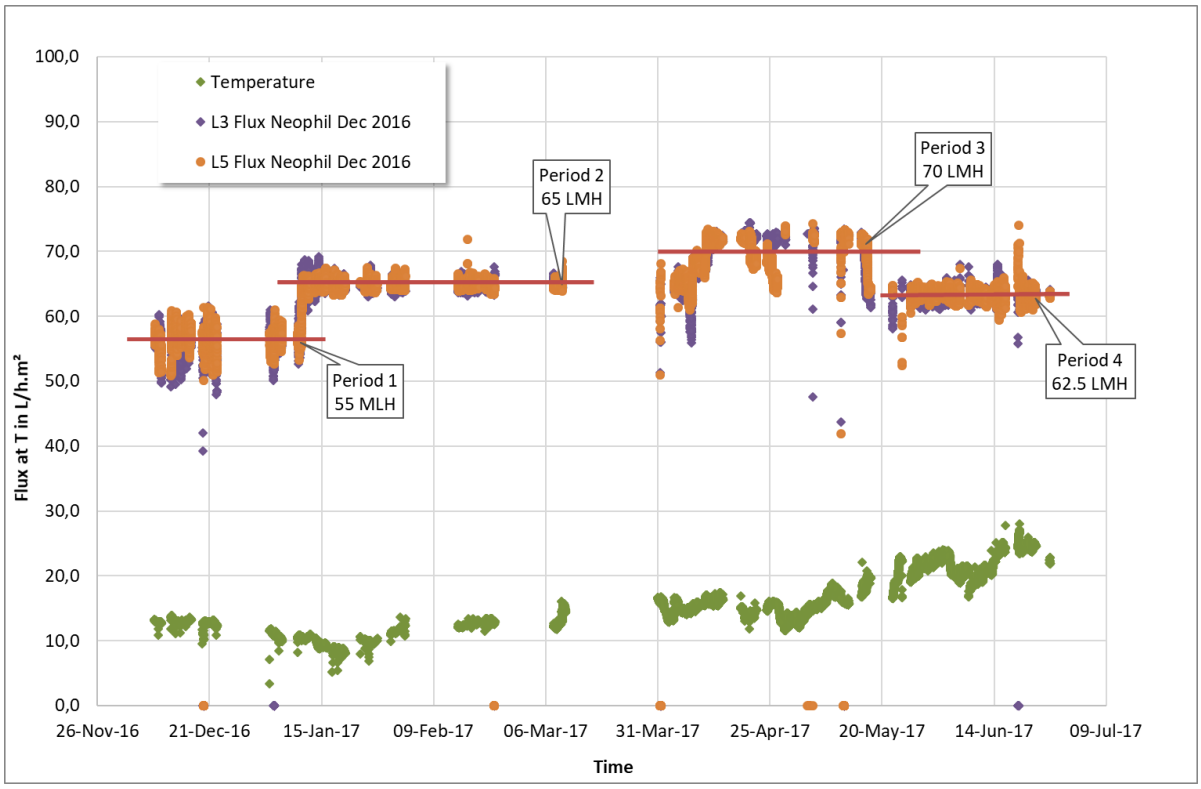

Figure 3: Fluxes @T°C and temperature evolution versus trial time

The fluxes are maintained constant by the PLC during the period.
The range of operating conditions of the Neophil™ membrane was 55 to 70 L/h.m² from 8°C to 28°C.

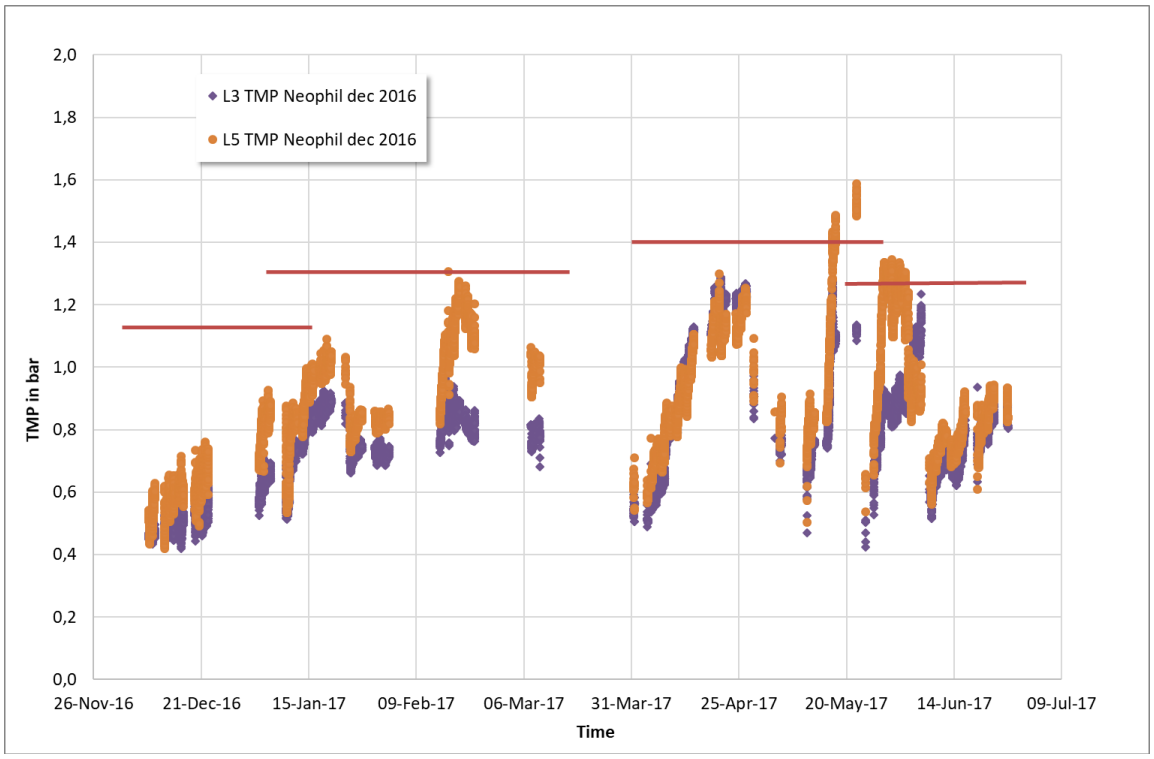

Figure 4: TMP versus trial time

The two Neophil™ membranes have the same behavior most of the time. However, at the beginning of February and May 2017, TMP of the line number 5 increased surprisingly faster because of a failure in the chemical injection during maintenance cleaning. CIP performed in March, April and May were really efficient to recover initial Neophil™ permeability. It has to be noticed that during the beginning of period 3, March 2017, the quality of inlet water was extremely poor and the membrane fouling increased quickly. In April, the quality became better again and the TMP decreased simply with the BW and MC effects.

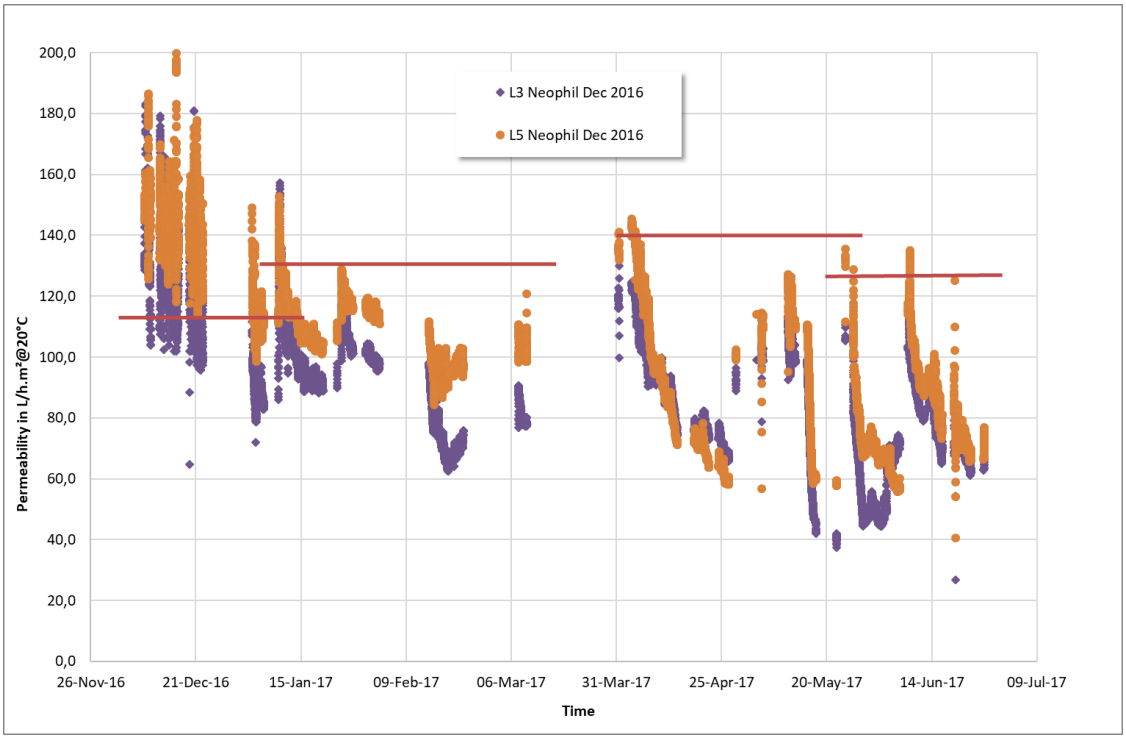

Figure 5: Normalized permeability versus trial time

The behavior of the Neophil™ membrane expressed in normalized permeability leads to the same conclusions. The normalized permeability goes from 140 L/h.m².bar@20°C when the membrane is clean to 40 when the membrane is fouled. CIPs performed in early April 17, at the end of May and in early June, allow to recover close to 100% of the initial permeability.

Neophil™ compared to commercial PSU membranes

During the same periods, PSU membranes have been operated in parallel to Neophil™ ones. In January 2017, a new PSU membrane had been installed and operated at a flux of 50-55 LMH, which is the recommended operating conditions of these membranes, already evaluated during previous trials. Figure 6 and 7 plot the flux and permeability evolution of PSU and Neophil™ during the trial time. Only data for one line of Neophil™ have been plotted to simplify the chart.

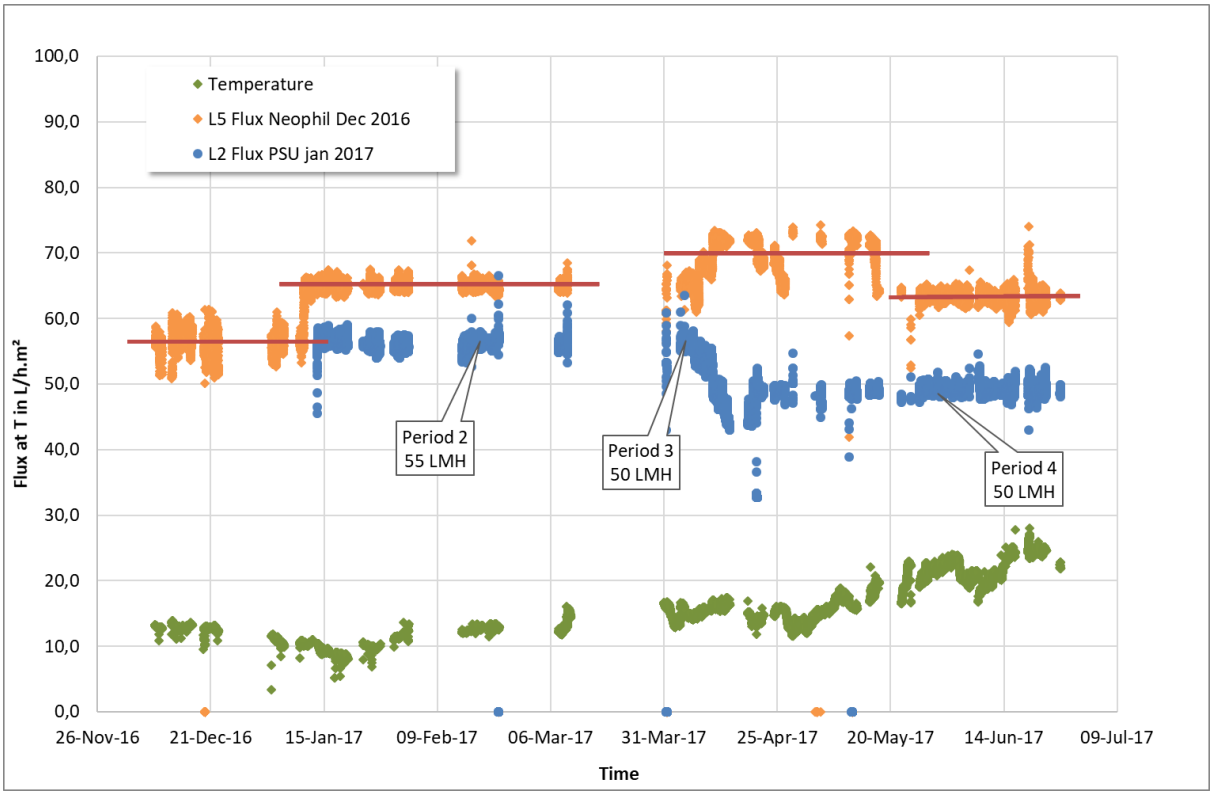

Figure 6: Neophil™ and PSU fluxes versus time

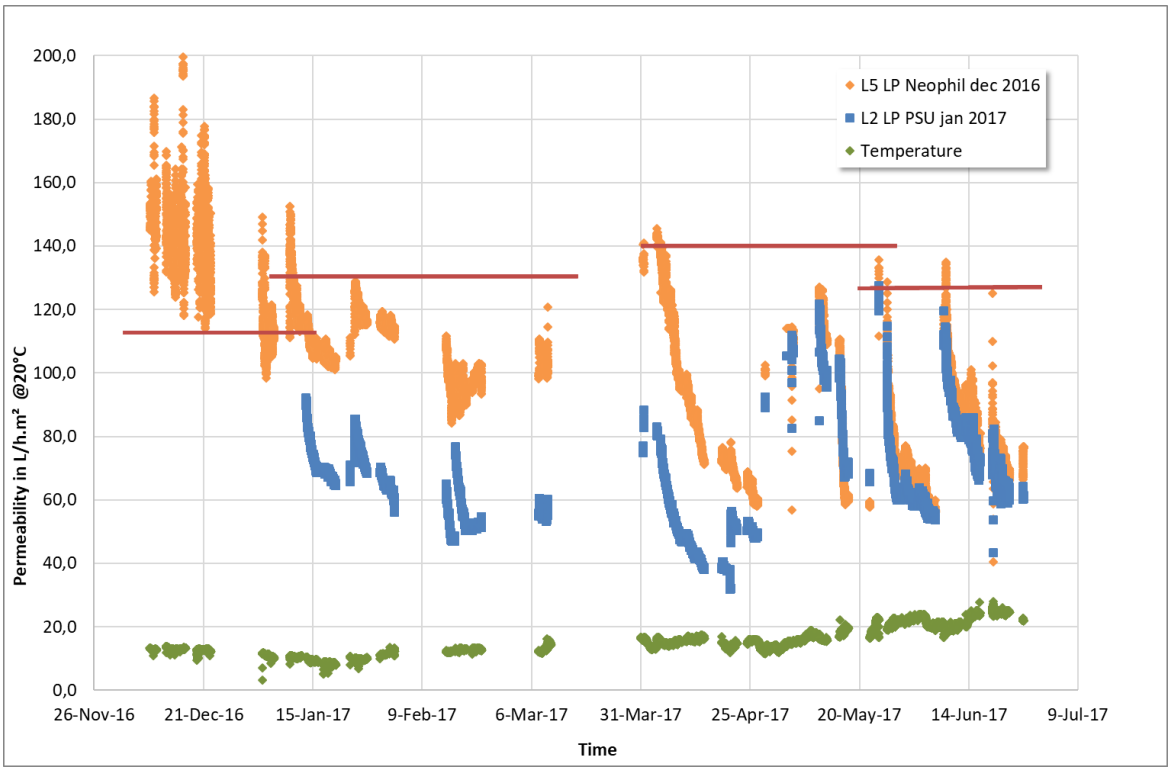

Figure 7: Neophil and PSU permeabilities versus time

Neophil™ membranes permeability remains much higher than PSU's one, whatever the operating fluxes. In the best case, Neophil™ was operated at a flux 40% higher than PSU (70 LMH for Neophil™ vs 50 LMH for PSU) but nevertheless, the Neophil™ permeability was higher than PSU's.

Neophil™ SDI removal performances

As ultrafiltration is mainly used as pretreatment of seawater before nanofiltration or reverse osmosis, the main parameter followed during this campaign was the fouling index i.e. the Silt Density Index (SDI) following standard ASTMD4189-07 recommendations. The figure 8 plots the SDI values of the raw seawater entering the ultrafiltration pilot plant. Following ASTM recommendation, filtration time which is normally of 15 minutes for SDI_{15} was sometimes reduced to 10 or 5 minutes due to severe fouling tendencies of the inlet seawater.

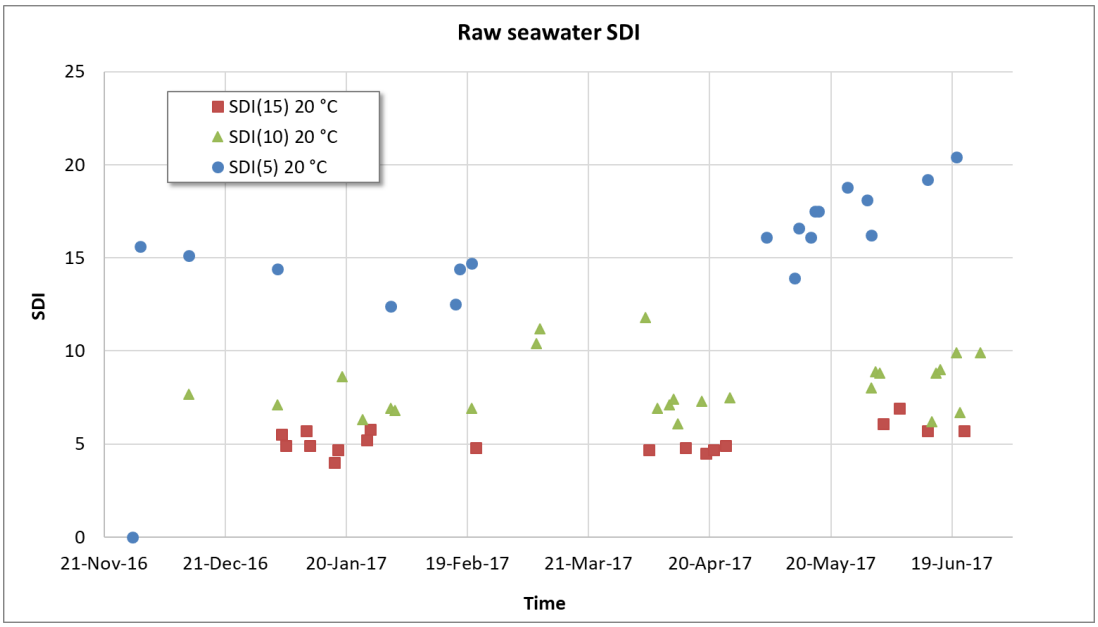

Figure 8: raw seawater SDI entering ultrafiltration pilot plant

As shown in figure 8, the SDI of the Palavas seawater is, most of the time, very high and really much high than SDI encountered in off-shore exploitation (between 3 and 5). Nevertheless, this high SDI of Palavas seawater is very challenging and constitutes a reveal trial to evaluate and compare ultrafiltration membranes. Then, the SDI_{15} of the PVDFs and PSUs permeates lines were measured and plotted on the figure 9.

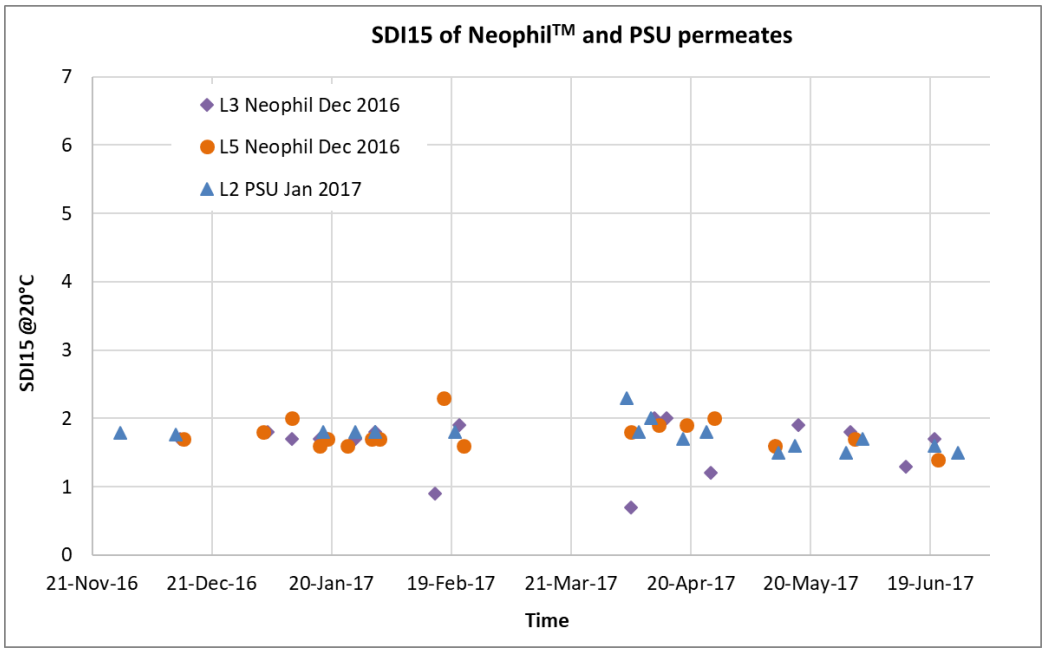

Figure 9: SDI_{15} of the Neophil™ and PSU permeates

As expected, the SDI_{15} of the permeates were very low (lower than 3 following NF and RO pretreatment requirements) whatever the quality of the raw seawater. No difference was seen between commercial PSU and Neophil™, which demonstrates furthermore the very good treatment quality of this new PVDF membrane.

4) Conclusions

Neophill™ membrane had been evaluated to filtrate seawater in a pilot platform from December 2016 to July 2017. The quality of the inlet seawater being quite poor, these trials constitutes a very good test for this new membrane. Also, Neophill™ was compared to a polysulfone membrane in parallel already installed in several offshore platforms.

Neophil™ performances were remarkable. For operating flux going from 55 to 70 LMH@20°C, Neophil™ had been operated sustainably during more than 6 months. Membrane cleaning had been achieved only using one backwash every 42 minutes, one maintenance cleaning with chlorine every 48 hours and one CIP with chlorine and caustic followed by acid every 2 months.

SDI_{15} of Neophil™ ultrafiltrated seawaters were always lower than 2 whatever the quality of the inlet raw seawaters. This filtration quality fulfil perfectly the NF and RO process requirements.

Comparison with well-established membranes in seawater filtration field shows superior performances of Neophil™ membranes.

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