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Research Paper

Comparison of Seawater and Freshwater Ultrafiltration on Semi-Industrial Scale: Ballast Water Treatment Application

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Highlights

- A demonstration of ballast water treatment using ultrafiltration process at industrial scale
- Treatment of challenging water
- Complying with International Convention for the Control and Management of Ships' Ballast Water and Sediments (BWM Convention) requirements

Abstract

Non-native aquatic species can be introduced in new areas through emptying of the ballast tanks, with a high impact on health, economy and environment. This is considered by the International Maritime Organization (IMO): (i) in 2004, the IMO adopted the International Convention for the Control and Management of Ships' Ballast Water and Sediments (BMW Convention) in order to diminish the risk of introducing harmful and/or potentially invasive species through ballast water. (ii) the BWM convention entered into force on 8 September 2017 and could open a new market for ballast water treatment. The aim for industry is to operate with an acceptable fouling rate between cleaning steps. Indeed, if fouling rates are low, clean in place will be infrequent. The aim of this work is to develop a sustainable ultrafiltration system designed for ballast water treatment and the first step is to have a better understanding of membrane fouling in relation to intake water variations. The major contribution and novelty of this study is successful ballast water treatment using an ultrafiltration process at industrial scale a high technological readiness level in order to show the applicability of the ultrafiltration processes for the ballast water treatment. In this study operating conditions were determined for seawater and freshwater conditions.

1. Introduction

Ballast water is fresh, brackish or seawater taken in to stabilize the ship. With it, different species can be introduced into new areas with potentially a high impact on health, economy and the environment. It is considered by International Maritime Organization (IMO) as one of the major threats to the oceans. The International Convention for the Control and Management of Ships' Ballast Water and Sediments (BWM Convention - IMO) adopted in 2004, imposes the retention of organisms in function of size classes [1]. The discharged water has to contain concentrations less than 10 viable organisms per m^3 and mL for plankton larger than 50 µm and between 10 and 50 µm respectively. Concentrations of Vibrio cholera, Escherichia coli and

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enforced and in a following step, zero detectable living organisms for all organism size classes is scheduled to be implemented on January 1, 2030 [4]. Development of new treatments has to initiated in order to comply with future IMO and USCG standards that will be more and more stringent. When the standards are not met, all ballast water has be retained on board, and can only be discharged after a ballast water treatment approved by IMO or USCG (for a discharge in California waters), or into a reception facility when available [4].

Conventional treatments are limited by extremes in water quality. For instance, UV treatment are not efficient in case of high turbidity/low transmittance in the water [5]. Currently, 30 % of ballast water treatment systems use UV, while 45 % use a chlorine production process (e.g. electrochloration) [6]. Most systems are combinations of filters followed by oxidizing chemicals or UV radiation, but oxidative water disinfections produce by-products which may cause long-term toxicity and impact biodiversity [7-9]. After UV disinfection, irradiated phytoplankton regrowth is slow, but it may be faster when the receiving water is rich in nutrients [10]. This considerably increases the risk of phytoplankton introductions by ballast water discharges. An efficient ballast water management system is required before discharging treated water into the environment.

As membrane filtration allows to physically retain microorganisms in one step of treatment, it could be a promising alternative or complementary method (in case of treatment failure for example) to common systems to treat ballast water. This study focusses on ultrafiltration to retain all microorganisms. Fouling is the key to membrane filtration efficacy and chemical cleaning frequency has to be limited to ensure a sustainable treatment.

Contrary to tangential filtration, dead-end filtration corresponds to a pseudo steady state that induces a progressive fouling. The critical flux method corresponding to zero rate of Trans Membrane Pressure (TMP) increase (at constant flux) may never be obtained in some applications [11]. Many studies used flux-steps of a few minutes to determine the critical flux [11-13]. The extrapolation of these laboratory results to industrial scales is not straightforward, notably because of the variability of natural feed water and the short operation times used in the laboratory tests. As a low degree of fouling is inherent to dead-end filtration even at low flux, the critical flux is inappropriate for pseudo steady state systems normally used in water applications [11]. In this study, the threshold conditions in dead-end filtration will be observed and compared in ultrafiltration of natural waters to highlight the performance derivation. Irreversible fouling, defined as the residual fouling which is not removed by backwash [12, 14], is accumulated during the filtration process until chemical backwash or clean in place are initiated, in order to recover permeability. Hydraulic irreversible fouling accumulation slowly increases with flux under threshold conditions. Above these conditions, irreversible fouling increases significantly. Chemical Enhanced Backwash (CEB) and Clean-in-Place (CIP) efficiencies, that have a direct consequence on fouling rates of the following filtration step, are studied too.

The aim for industry is to operate with an acceptable fouling rate between cleaning steps since CIP will be infrequent if fouling rates are low [11, 15]. The aim of this work is to develop a sustainable ultrafiltration system designed for ballast water treatment and the first step is to have a better understanding of membrane fouling in relation to intake water variations.

The intend of this paper is to treat ballast water and the challenge of this application is to propose a process which can be used to disinfect natural water with different salinities and variable organic and biological concentrations. Membrane ultrafiltration performances was studied using 2 types of waters (as request by IMO) representing the extremes in expected salinity: seawater and freshwater, the latter one being more challenging because it contains higher particle and organic matter concentrations. The major contribution and novelty of this study is to show the applicability of ballast water treatment using an ultrafiltration process. It builds upon previous work at laboratory scale [16] by using a filtration set-up at industrial scale with a higher technological readiness level in order to investigate the viability of the ultrafiltration process for use in ballast water application in agreement with IMO approbation that requires some tests with 2 water qualities (sea and freshwater).

2. Experimental

2.1. Experimental locations

The first part of the study was conducted with seawater at the Marine Station of Sète (Thau Lagoon, Experimental Marine Ecology Center MEDIMEER UMS 3301, University of Montpellier-2, France) and the second part was conducted with freshwater at Wageningen Marine Research Ballast Water Test Facility, Den Helder (the Netherlands).

2.2. Ultrafiltration experiments

Constant flux in dead-end ultrafiltration experiments were performed in a mobile unit containing an automatic pilot plant at semi-industrial scale (Figure 1). On the basis of a literature review and a preliminary study [16], dead-end ultrafiltration mode was preferred because energy consumption is lower and low fouling rates during the preliminary tests in cross-flow mode didn't justify the additional energy costs of tangential filtration. This pilot plant is composed of 2 industrial modules in parallel with Polysulfone (PS) hollow fibers (100 kDa). The membrane surface is 84 m² and filtration flow is led from the outside to the inside of fibers. Before each run, a CIP of the ultrafiltration membrane was performed to reach a permeability equal to 90 % of the initial permeability of the membrane (150 $L.m^{-2}.h^{-1}.bar^{-1}$ corrected at 20°C). A CIP consists of a basic cleaning with NaOH (pH 12), followed by chlorine (200 ppm) recirculation (during 90 min) and a rinsing phase with tap water. When the permeability reaches a threshold of 80 $L.m^{-2}.h^{-1}.bar^{-1}$ corrected at 20°C, a Chemical Enhanced Backwash (CEB) is automatically activated to remove fouling. It consists of an automatic backwash (BW) with chlorine (20 ppm during 25 min of contact time) followed by an automatic backwash with citric acid (pH 3 during 25 min of contact time). After each automatic backwash, membranes are rinsed with permeate to remove chemicals. No automatic basic backwash is performed to avoid mineral precipitation due to the reaction of high salinity seawater and NaOH. Bubbling with air during 30 s every 100 s is applied between the hollow fibers during contact time of chemicals to increase efficiency of the cleaning procedure. In this study, the term "sequence" is defined as the time between the start of the run with clean membrane (after CIP) and the first CEB or between 2 CEB if it is necessary. During a sequence, dead-end ultrafiltration in constant flux was performed at a given filtration time. At the end of each filtration time, a backwash in compliance with supplier requirements, with permeate and air scouring, without addition of chemical is programmed and water flows from the top of the module (total backwash time: 2 min; backwash with a flux around 100 $L.m^{-2}.h^{-1}$). Filtration followed by the BW is defined as a filtration cycle.

In this study, 8 different operating conditions are tested and 6 are described with the same conditions of BW, CEB and CIP:

- for seawater runs: 59.5, 47.6 and 35.7 $L.m^{-2}.h^{-1}$ and filtration cycle times of 45, 30 and 20 min (3, 4 and 5 $m^3.h^{-1}$ for 84 m² of membrane surface)
- for freshwater runs: 35.7, 23.8 and 11.9 $L.m^{-2}.h^{-1}$ and filtration cycle times of 45, 30 and 15 min (1, 2 and 3 $m^3.h^{-1}$ for 84 m² of membrane surface).

The ranges of fluxes and cycle times are not the same for both freshwater and sea water tests because, TOC and turbidity were higher in freshwater than in seawater and it was not possible to filter both waters in the same conditions while keeping reversible fouling conditions. Transmembrane pressure, permeate flux and in-line analyses are recorded versus time. Feed water pipes were placed at 1 and 2 meters deep. Feed waters were pre-filtered with a disc filter (140 µm) before ultrafiltration. The minimal run times were 60 h and 500 h for seawater (essays on short and long time) and 20 h for freshwater ultrafiltration. This difference will be explained in the result part. Irreversible fouling rate corresponds to the slope of the curve of the TMP in function of the time for each sequence. CEB efficiency ($E_{irr\text{-}CEB}$) is calculated using equation 1.

$$E_{irr-CEB} = \frac{(R_{irr})_{s-1,n} - (R_{irr})_{s,1}}{(R_{irr})_{s-1,n}} \quad (1)$$

where $(R_{irr})_{s-1,n}$ and $(R_{irr})_{s,1}$ are the irreversible fouling resistance (m^{-1}) of the last filtration cycle (n) of the sequence "s-1" (i.e. just before the CEB) and the irreversible fouling resistance of the first filtration cycle of the sequence "s" (i.e. just after the CEB), respectively. It corresponds to fouling removal efficiency of each sequence independently from the others to highlight the impact of the water quality variations.

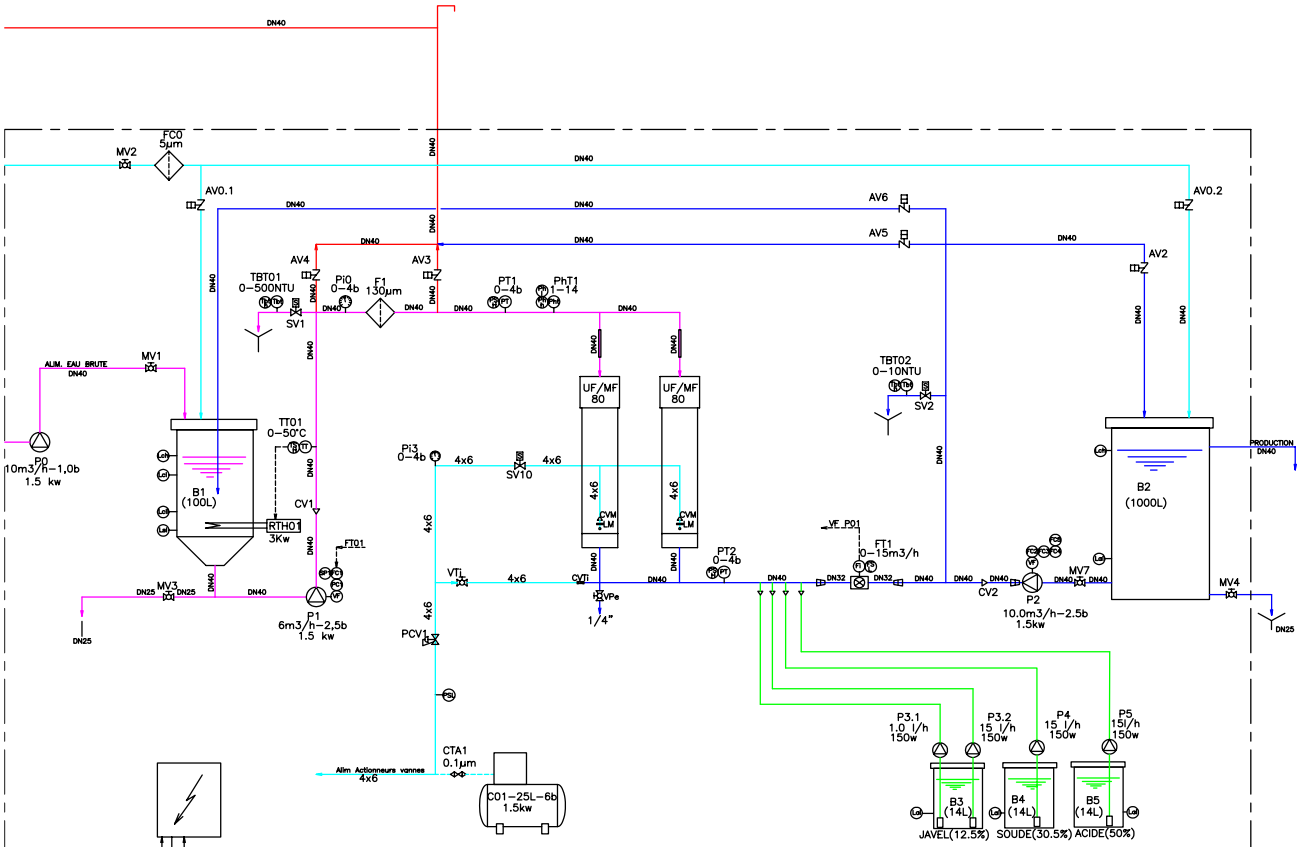


Fig. 1. UF pilot plan.

2.3. Analyses: water characterization

In the mobile membrane filtration unit, in-line analyses of turbidity, temperature, and pH (Syclope probes) were recorded every 10 seconds. Chlorophyll-a concentration (Wetlabs Ecopuck probe for seawater) and conductivity (Wetlabs Ecopuck probe) were automatically recorded every hour. Every day or twice a day in function of the run time, feed water, permeate at the beginning and at the end of a filtration cycle were sampled and directly analyzed. Flow cytometry analyses (Becton Dickinson) allows to follow the picoplankton and nanoplankton with natural autofluorescence and total bacteria flora with sybr-green stain. Culture for 24h at 37°C on selective media as Thiosulfate Citrate Bile Saccharose (TCBS), Enterococcus selective agar (ESA) and Tergitol7-TTC with membrane method [17, 18] allowed to highlight the retention of *Vibrio sp*, *Enterococcus sp* and coliforms in the permeate. Coliforms and Enterococci in freshwater were also analyzed by bacterial enumeration, using the: Colilert® and Enterolert® IDEXX kits that apply a most probable number method. Total and dissolved organic carbon analyses (TOC and DOC) were performed using a TOC-L Shimadzu [19] on permeate and feed water samples. TOC and DOC analyses were considered valid if the coefficient of variation (CV) was less than 2 %. As the high DOC concentrations in freshwater induced perturbation of the signal, chlorophyll-a concentrations in freshwater were analyzed for each sample with a spectrofluorimeter (BBE Moldaenke AlgaeLabAnalyser).

3. Results and discussion

Seawater ultrafiltration results are presented in this first part.

3.1. Seawater quality and retentions

Seawater sampled in Thau Lagoon from September to June 2014 has a salinity between 35 and 40 $g.L^{-1}$, with a low average turbidity of 1 NTU, but with significant TOC and bacterial concentrations (Table 1a). TOC concentrations varied between 1.5 and 2.9 $mg.L^{-1}$ (average: 2.2 $mg.L^{-1}$) and the average concentration of total flora was equal to $5.2x10^{8}$ $cells.100mL^{-1}$. Dissolved organic carbon concentration generally corresponded to a minimum of 90 % of the TOC. With a maximum concentration of $1.7x10^{5}$ $CFU.100mL^{-1}$, *Vibrio sp* was the dominant the bacteria family compared to coliforms and enterococci. Flow cytometry highlighted that cyanobacteria and picoplankton with a size less than 1 µm form the majority of the plankton in seawater during the runs. Flow cytometry analysis and bacterial analysis highlight the successful retention of the phytoplankton and target bacteria (coliforms, enterococci and vibrio) in seawater by 100 kDa PS membrane for all the experimental conditions tested. For all the runs in seawater, turbidity in permeate was < 0.2 NTU and the average TOC retention was only 10 % excepted for the runs at 47.6 $L.m^{-2}.h^{-1}$, 45 min where the retention increased to 49% in the middle of the run. Seawater is mainly composed of organic carbon with low molecular weight. Indeed, 1-10 kDa organic carbon (1-3 nm) represent around 60 to 80 % of the TOC in average [20]. On the whole, organic carbon retention by the membrane was low.

3.2. Hydrodynamic and fouling mechanisms

3.2.1. TMP variation as function of seawater quality

In the beginning of each test, initial TMP was 0.24; 0.33 and 0.40 bar for 35.7, 47.6 and 59.5 $L.m^{-2}.h^{-1}$ runs, respectively (Figure 2a).

Initially TMP at the beginning (TMP_i^n) and at the end (TMP_f^n) of each filtration cycle increased more or less linearly with time during each sequence and for each condition. For the ultrafiltration runs at 35.7 $L.m^{-2}.h^{-1}$ 20, 30, 45 min and 47.6 $L.m^{-2}.h^{-1}$ 20 min, the initial and final TMP curves are superimposed indicating that backwashes without chemical addition were not efficient to remove fouling ($TMP_f^n = TMP_i^n$). This low fouling is also considered as irreversible. For these runs, turbidity remained stable around 1 NTU and TOC concentration varied around 2 $mg.L^{-1}$. For the run at 47.6 $L.m^{-2}.h^{-1}$ 30 min with stable concentrations of TOC and turbidity, the distance between TMP curves appears at the 20th hours of filtration and remained constant. For the other runs 47.6 $L.m^{-2}.h^{-1}$ 45 min and 59.5 $L.m^{-2}.h^{-1}$ 20, 30 min, TMP curves were parallel with a constant and higher gap. This show the presence of reversible resistance at the end of each filtration cycle. In these last runs, turbidity varies (e.g. between 1 and 4 NTU for 47.6 $L.m^{-2}.h^{-1}$ 45 min) and backwashes without chemical additions were able to remove a part of the fouling.

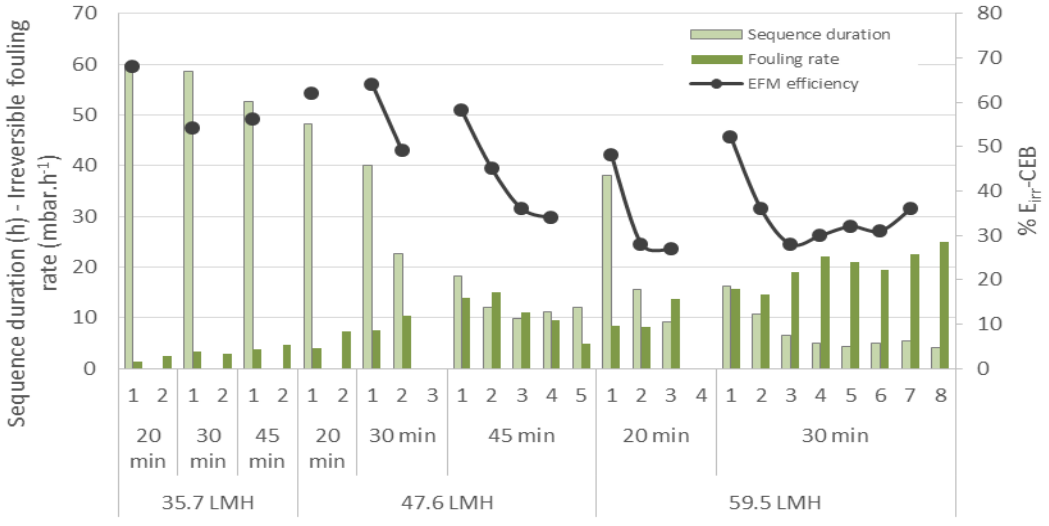
Table 1
Seawater (a) and fresh water (b) analyses.

(a)

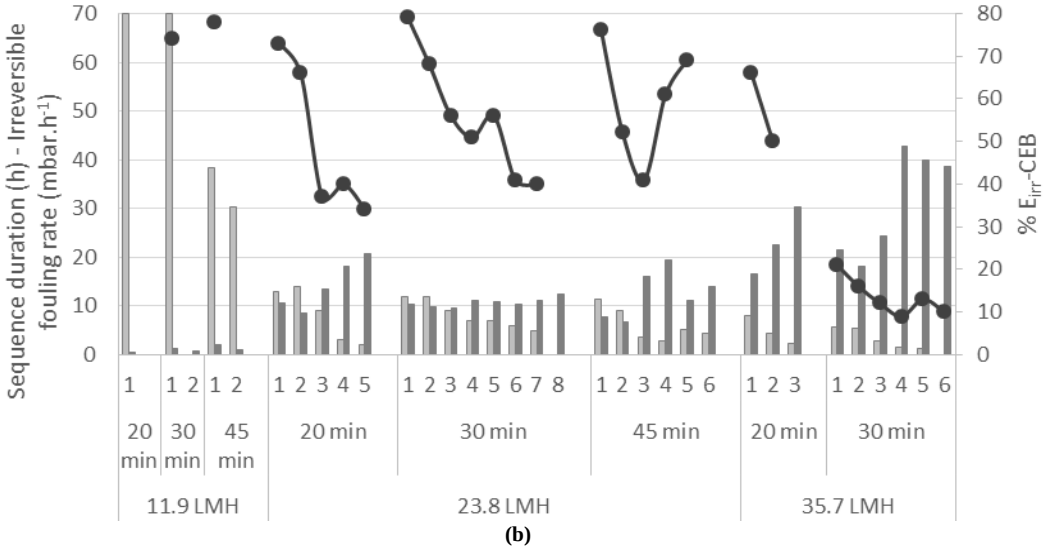
June to September 2014 - Sète	Temperature (°C)	Salinity ($g.L^{-1}$)	Phytoplankton concentration ($cells.mL^{-1}$) Total (cytometry)	Chlorophyll-a ($\mu g.L^{-1}$)	Total flora ($cells.mL^{-1}$)	TOC ($mg.L^{-1}$)	Turbidity (NTU)
Average	22.5	37.6	$2.8\ 10^4$	0.9	$5.5.10^6$	2.2	1.00
Standard deviation	1.5	1.5	$1.6\ 10^4$	0.6	$1.2.10^6$	0.3	0.69
Min. value	18.5	35.0	$7.0.10^3$	0.2	$3.3.10^6$	1.5	0.23
Max. value	28.5	40.2	$6.7.10^4$	3.7	$8.6.10^6$	2.9	4.03

(b)

UF June-July 2015 - Den Helder	Temperature (°C)	Salinity ($g.L^{-1}$)	Phytoplankton concentration ($cells.mL^{-1}$)		Chlorophyll-a ($\mu g.L^{-1}$)	Total flora ($cells.mL^{-1}$)	TOC ($mg.L^{-1}$)	DOC ($mg.L^{-1}$)	Turbidity (NTU)
			10-50 µm (microscopy)	Total (cytometry)					
Average	16.9	1.4	4217	$1.2.10^5$	24.1	$1.2.10^7$	21.5	19.5	6.0
Standard deviation	0.7	0.1	2265	$6.3.10^4$	9.7	$3.3.10^6$	0.8	0.5	1.4
Min. value	13.9	0.2	1100	$5.4.10^4$	6.5	$6.8.10^6$	19.4	18.8	2.1
Max. value	23.0	2.2	11200	$3.0.10^5$	48.3	$1.9.10^7$	23.2	20.8	17.0



(a)



(b)

Fig. 2. Sequence duration, irreversible fouling rates and CEB efficiency for irreversible fouling removal at each run with seawater (a) and with fresh water (b); The absence of histogram value for the last sequence means that the sequence was not finished when the run had been stopped – LMH: $L.m^{-2}.h^{-1}$.

CEB frequency allows defining the sequence durations and induces a decrease of net productivity. The more the filtration time per cycle, the number of sequence and the flux increase, the more sequence duration and the CEB efficiency for irreversible fouling removal decrease. Sequence duration and the CEB efficiency, however, seem to be stabilized around 10 h for 47.6 $L.m^{-2}.h^{-1}$ 45 min and 5 h for 59.5 $L.m^{-2}.h^{-1}$ 30 min and between 30 and 40 %, respectively (Figure 2).

3.2.2. Development of fouling and impact of chemical backwashes (CEB)

In low fouling conditions, for runs 35.7 and 47.6 $L.m^{-2}.h^{-1}$ 20 min, CEB was triggered manually to highlight the impact on fouling rate evolution and CEB efficiency. Low fouling rates of 1.4 and 3.4 $mbar.h^{-1}$ respectively are observed on the first sequences. Microorganisms and organic matter are gently deposited on the membrane surface in multilayer. Injections of chlorine followed by acid during automatic backwashes cause a destabilization of the deposited layers leading to production of dissolved organic matter and smaller cellular fragments by cell lysis. This induces higher fouling rates in the following test sequences of 2.5 and 7.2 $mbar.h^{-1}$ respectively. Thus, fouling properties change after the first CEB as irreversible fouling rates increase.

For the other runs, automatic chemical backwashes started when the permeability reached the threshold value of 80 $L.m^{-2}.h^{-1}.bar^{-1}$. With a similar seawater quality (Turbidity ≈ 1 NTU, chlorophyll-a concentration < 1 $\mu g.L^{-1}$, TOC ≈ 2.3 $mg.L^{-1}$), CEB was triggered at 60 and 50 h for 35.7 $L.m^{-2}.h^{-1}$ 30 and 45 min respectively and 40 h for 47.6 $L.m^{-2}.h^{-1}$ 30 min. So, an increase of 15 min of filtration per cycle for 35.7 $L.m^{-2}.h^{-1}$ induces a decrease of 10 h of the first sequence duration. The flux increases from 35.7 to 47.6 $L.m^{-2}.h^{-1}$ (30 min) causes a reduction of 20 h of the first sequence duration. The same tendency is observed with irreversible fouling rate values. Consequently, reduction of the flux and/or filtration time per cycle induced a decrease of sequence durations caused by increase of irreversible fouling rates in the first sequence. For 47.6 $L.m^{-2}.h^{-1}$ 45 min and 59.5 $L.m^{-2}.h^{-1}$ 20 and 30 min (Figure 3), the CEB frequencies vary with Volume Reduction Factor (VRF). Indeed, 4 and 3 CEB are observed for runs 47.6 $L.m^{-2}.h^{-1}$ 45 min (VRF = 69) and 59.5 $L.m^{-2}.h^{-1}$ 20 min (VRF = 39) respectively. But with a VRF equal to 58 for the run 59.5 $L.m^{-2}.h^{-1}$ 30 min, CEB were almost 2 times more frequent than during 47.6 $L.m^{-2}.h^{-1}$ 45 min run (VRF = 69). This phenomenon was induced by seawater quality during the run 59.5 $L.m^{-2}.h^{-1}$ 30 min. In the first minutes of run, turbidity and TOC were stable around 0.5 NTU and 2.3 $mg.L^{-1}$, even though chlorophyll-a concentration reached a peak at 3.7 $\mu g.L^{-1}$ during the 2nd sequence (23rd hours of run). Then, the chlorophyll-a concentration decreased to a value < 2 $\mu g.L^{-1}$. The sequence duration, fouling rate and CEB efficiency (albeit oscillating) remain stable after the 3rd sequence. Consequently, temporary high phytoplankton fouling irreversibly modified the membrane fouling and performances even though seawater quality became less challenging afterwards. During the 4th sequence, the concentration of *Vibrio sp* in the inlet reached a peak concentration of $9.3x10^3$ $UFC.100mL^{-1}$. Phytoplankton declined after blooming induced first a chlorophyll-a decrease and then a production of fragments and dissolved organic matter from cell lysis. These products such as exo-polysaccharides are used by bacteria [21, 22]. Bacteria concentration increase was stimulated by high temperature during runs (25°C). With high VRF (58), bacterial and phytoplankton accumulation rapidly resulted in a biofilm on the membrane surface. Biofilm layer destabilization by chemical attack during CEB leads to cells fractionating and increases the accumulation of irreversible fouling rate.

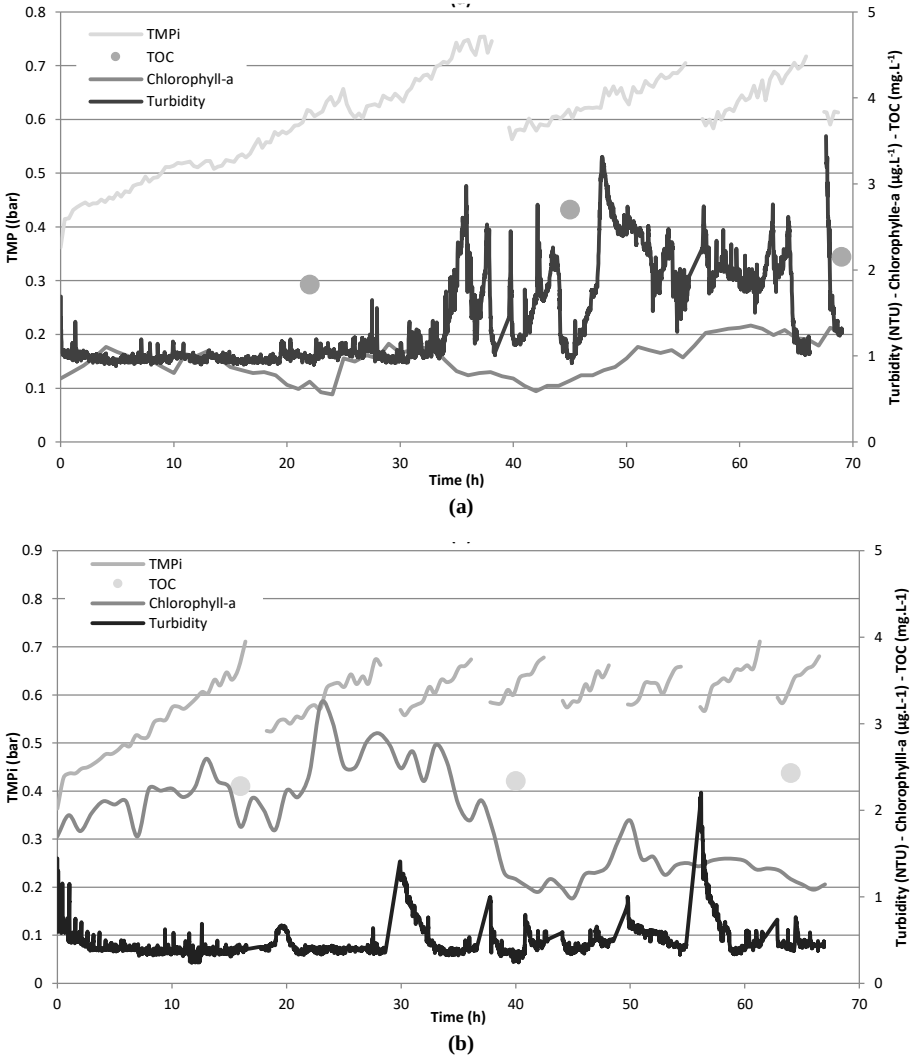


Fig. 3. Initial TMP evolution in function of time and seawater quality for the run 59.5 $L.m^{-2}.h^{-1}$ 20 (a) and 30 min (b).

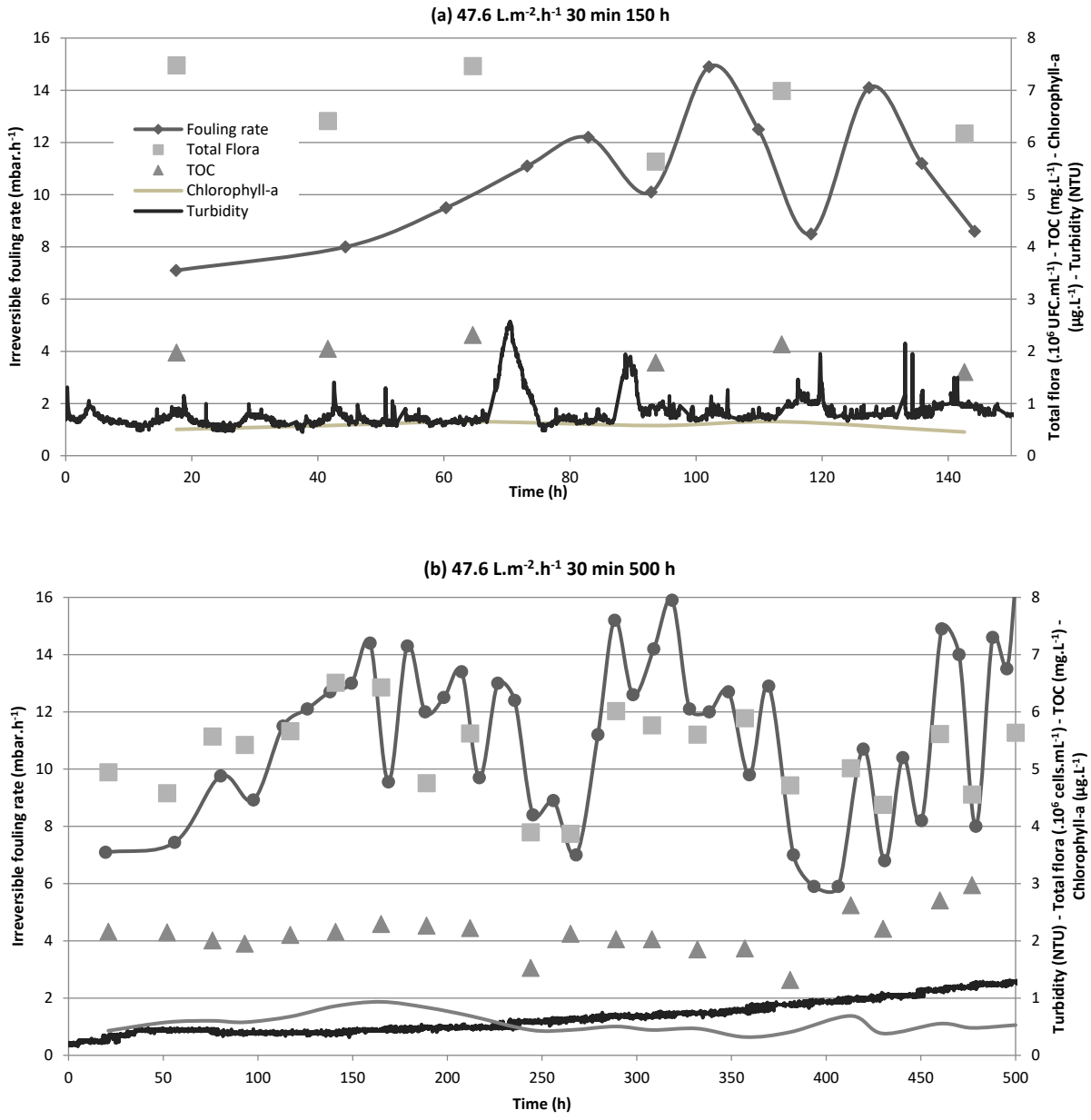


Fig. 4. Evolution of irreversible fouling rate for 47.6 L.m^{-2}.h^{-1} 30 min during 150 h (a) and 500 h (b) of run in function of seawater quality.

3.2.3. CIP efficiencies

The CEB allowed to recover between 53 % (threshold permeability for CEB) and 75 % of the initial permeability in function of the filtration conditions. Chlorine and acid backwashes were not efficient enough to remove all fouling matter from membrane surface (Figure 2). These strong foulings were removed by one basic CIP to recover 90 % of the initial permeability.

3.2.4 Seawater ultrafiltration run on long time filtration

Runs with extended duration periods were performed at: 47.6 L.m^{-2}.h^{-1} 30 min during 150 and 500 h. Irreversible fouling rates increased from 7.1 to 12.2 mbar.h^{-1} in 5 sequences and oscillated from 8.5 to 14.9 mbar.h^{-1} during the remaining 7 sequences of 150 h running period (Figure 4a). During the 500h run, the irreversible fouling rate increased from 7.1 to 14.4 mbar.h^{-1} in the first 165 h of running and oscillated between 5.9 and 15.9 mbar.h^{-1} during the remainder of the run (Figure 4b). For 47.6 L.m^{-2}.h^{-1} 30 min 150 h, the total flora concentration in the first 60 h of filtration were around 7.5x10^{6} Cells.mL^{-1} against 5x10^{6} cells.mL^{-1} for 500 h run (x1.5). For 500 h run, a rise of chlorophyll-a concentration to 1 µg.L^{-1} was observed. Up to 90 % of the phytoplankton consisted of picoplankton smaller than 1 µm (5.8x10^{4} cells.mL^{-1}). During the 150 h run, the chlorophyll-a concentration was lower than at 500 h run (< 1µg.L^{-1}). The phytoplankton concentration reached 6x10^{4} cells.L^{-1} in the beginning and decreased slowly to 3-4.2x10^{4} cells.L^{-1}. Approx. 45 to 57 % of the phytoplankton consisted of cyanobacteria. Although turbidity and TOC were stable around 1 NTU and 2 mg.L^{-1} respectively in the first 150 h for both experiments, the bacterial concentration varied and seems to be the cause of the irreversible fouling rate variation.

From the 400th to the 500th hour of filtration, the TOC increase to 2.7 mg.L^{-1}. This was probably due to rainfall. With the same bacterial concentration (≈5.6x10^{6} cells.L^{-1}), the irreversible fouling rate was 23% higher at 460h than at 332h, with 2.7 and 1.85 mg.L^{-1} of TOC, respectively. Organic matter is transported into the Thau lagoon by rain. This nutrients supply may induce an increase of bacterial concentrations in seawater, but also feeds the biofilm on the membrane that induces the irreversible fouling increase.

Freshwater ultrafiltration is described in this second part.

3.3. Freshwater quality and retentions

Table 1b presents the freshwater characteristics. The average temperature in freshwater was 16.9°C compared to 22.5°C during the seawater runs. The average chlorophyll-a concentrations analyzed by spectrofluorimeter (BBE Moldaenke AlgaeLabAnalyser) were 24.1 µg.L^{-1} increasing to 48.3 µg.L^{-1} during phytoplankton blooms. As the chlorophyll-a concentration during blooms reached only 3.7 µg.L^{-1} in seawater, a log difference is observed between both sites for this parameter. Compared to seawater, the average

concentration of picoplankton (< 1µm and between 1-2 µm) was ten times higher in freshwater and the average total phytoplankton concentration was 5 times higher in freshwater. In freshwater, the majority of phytoplankton was represented by picoplankton (size class < 1µm). The average bacteria number analyzed by flow cytometry was around 2.5 times higher in freshwater compared to seawater ($1.2x10^7$ vs $5.5x10^6$ cells.mL^{-1} respectively). The average TOC in freshwater was 21.5 mg.L^{-1} and average DOC was 19.5 mg.L^{-1}, being 90 % of TOC. In-line turbidity measurements yielded an average concentration of 6 NTU with peak turbidity reaching 17 NTU. The average transmittance for this water was 21.5 % (at 254 nm) and was stable during runs. This value is well under the acceptable limit for UV efficiency (Hijnen *et al.* 2006). Moreover, particles partition size showed that 80 % of the particles (in number) had a size < 6 µm, which means that a prefiltration step prior to UV treatment with a mesh size larger than 6 µm will have little impact on turbidity, no impact on transmittance and consequently will not improve UV efficiency. As expected, with this freshwater quality, the conditions are more challenging than with seawater for the same ballast waste treatment application.

Permeate samples were analyzed to highlight the retention of phytoplankton and bacteria. CMFDA vital staining was used to assess the number of living cells with epifluorescence microscopy. Flow cytometry analyses were performed on permeate samples to check the total phytoplankton retention. The results give a good retention whatever the filtration conditions. Results of bacteria analyses are negative with Petri dishes (until 300 mL of analyzed permeate volume per sample) and with IDEXX kits: no target bacteria were detected in the permeate. The average retention rate for TOC was 19 % (+/-5 %) during runs. The turbidity was < 0.2 NTU in permeate for all runs.

3.4. Hydrodynamic and fouling mechanisms

3.4.1. Sequence duration and TMP development as function of freshwater quality

Permeate flows of 11.9; 23.8 and 35.7 L.m^{-2}.h^{-1} were tested with filtration cycles of 20, 30 and 45 min (Figure 2b). As freshwater quality appeared more fouling than seawater, the threshold permeability (80 L.m^{-2}.h^{-1}.bar^{-1}) inducing an automatic backwash was reached quicker compared to seawater runs. As short sequence duration induces a low net production which is not desirable from a techno-economical point of view., The freshwater was, therefore considered as very challenging for the development of ballast water treatment applications. In contrast to the results obtained with seawater, the curves of initial and final TMP in function of time are not similar (except for the 11.9 L.m^{-2}.h^{-1} 20 min run). It reveals the presence of reversible resistance accumulation during the filtration cycle and the backwash efficiency to remove a part of fouling at the end of each filtration cycle. At 11.9 L.m^{-2}.h^{-1}, the first sequence durations are longer than 60 h notwithstanding high turbidity (up to 15 NTU) and phytoplankton fluorescence (36.8 µg.L^{-1}) with 20 and 30 min duration cycles respectively. With 45 min. per filtration cycle, the sequence duration decreased to 38 h and then to 30 h. This phenomenon is probably due to an increase of bacteria and phytoplankton (total flora: 0.9 to $1.5x10^7$ cells.L^{-1}; chlorophyll-a: 22 to 29 µg.L^{-1}) and/or turbidity variation (from 2 to 23 NTU). The reversible resistance removed by backwash was relatively low (< $2.8x10^{11}$ m^{-1}) and increased with the filtration time per cycle. With a flux of 23.8 L.m^{-2}.h^{-1}, the sequence durations decreased to less than 10 h in the 2nd or 3rd sequence. During the 20 min of filtration cycle, TOC was relatively stable around 21 mg.L^{-1}, although bacteria and phytoplankton concentrations decreased with time (total flora: from 1.9 to $1.4x10^7$ cells.mL^{-1} and chlorophyll-a concentration: from 27.6 to 19.6 µg.L^{-1}) (Figure 5a). During the run at 30 min of filtration per cycle, TOC was the same but chlorophyll-a concentration and total flora were lower compared to the previous analyses on freshwater (chlorophyll-a < 12 µg.L^{-1} and total flora < $0.8x10^7$ cells.mL^{-1}). On first approach, this sequence duration decrease may be explained by the turbidity variations from 2.4 to 9.2 NTU. The average reversible resistance was stable and equal to $3.4x10^{11}$ ($\pm 1.2x10^{11}$) m^{-1}. As reversible resistance removal was constant, this means that particles responsible for high turbidity are strongly attached to membrane or previous fouling layers and constitute an irreversible fouling.

In the beginning of the 23.8 L.m^{-2}.h^{-1} 45 min run, chlorophyll-a (32.6 µg.L^{-1}) and turbidity (15 NTU) reached high values that induced a sequence duration decrease during the 3 first sequences (Figure 5b). The same tendency was observed with the variations of water quality during the run. For the 3rd and 6th sequence, the average reversible resistances removed at each cycle were equal to $9.8x10^{11}$ m^{-1} and $9.12x10^{11}$ m^{-1}, respectively (instead of 7-$8x10^{11}$ m^{-1} for the other sequences) corresponding to algal bloom (chlorophyll-a: 32.6 and 29.0 µg.L^{-1}). Reversible fouling resistance varied with phytoplankton concentration (average: $7.3x10^{11}$ ($\pm 1.9x10^{11}$) m^{-1}), which means that a part of phytoplankton was removed by backwashes during the bloom.

At 35.7 L.m^{-2}.h^{-1} sequence durations were less than 8 h. A planktonic bloom (chlorophyll-a: 48.3 µg.L^{-1}) was observed during the first hour of 35.7 L.m^{-2}.h^{-1} 20 min run that could explain the rapid decrease of sequence duration (until 2 h for the 3rd sequence).

3.4.2. Development of fouling rate and impact of chemical backwashes (CEB)

The irreversible fouling rate increased with flux from 0.8 to 2 mbar.h^{-1}, 7 to 21 mbar.h^{-1} and 17 to 43 mbar.h^{-1} for the runs at 11.9, 23.8 and 35.7 L.m^{-2}.h^{-1}, respectively (Figure 2b).

During the 11.9 L.m^{-2}.h^{-1} runs, irreversible fouling rates were less than 2 mbar.h^{-1} and during 23.8 L.m^{-2}.h^{-1} 30 min, it remained stable around 10 mbar.h^{-1}. In both runs, 74 and 79 % of irreversible fouling was removed by CEB at the end of the first sequence. The CEB efficiency decreased to 40 % at the end of the last sequence of 23.8 L.m^{-2}.h^{-1} 30 min. For the other conditions, irreversible fouling rates increased with time during the first sequences and seemed to oscillate after the 4th sequence for 23.8 L.m^{-2}.h^{-1} 45 min and 35.7 L.m^{-2}.h^{-1} 30 min.

A picoplankton (1-2 µm) bloom was observed during the second sequence of 23.8 L.m^{-2}.h^{-1} 45 min ($2.4x10^4$ cells.mL^{-1}; 32.6 $\mu g_{chl\text{-}a}$.L^{-1}) resulting in an increase of TOC (23 mg.L^{-1}) and turbidity (15 NTU). In the first sample after the bloom, bacteria reached a high concentration of $1.4x10^7$ cells.L^{-1}, probably a result of bloom decline. This phenomenon induced a fouling rate increase in the 3rd and 4th sequence of filtration, as was also seen by Merle *et al.* [24]. During the 5th sequence, the fouling rate abruptly decreased from 19.5 to 11.7 mbar.h^{-1} because CEB was more efficient between the 4th and the 5th sequence (61 %) compared to between 3rd and 4th sequence (41 %). This can also be explained by the freshwater quality variations.

The last irreversible fouling rate for 35.7 L.m^{-2}.h^{-1} 20 min was around 10 mbar.h^{-1} lower than for 35.7 L.m^{-2}.h^{-1} 30 min. A phytoplankton bloom was observed in the inlet freshwater in the beginning of the 20 min run and turbidity varied from 5 to 10 NTU during this run compared to 3-5 NTU during the 30 min run. Consequently, fouling layers onto the membrane have different properties that impact fouling rates.

3.4.3. CIP efficiencies

CEB were not efficient enough to recover the initial permeability. At the end of each run, 2 CIP were required to recover at least 90 % of initial permeability. This means that fouling material in freshwater strongly interacts with the membrane.

4. Discussion

Picoplankton, cyanobacteria and bacteria form the main part of planktonic life in seawater and freshwater but were observed in higher concentrations in freshwater compared to seawater. This support the use of ultra-filtration (UF) and not micro-filtration (MF), because these microorganisms have a size close to the MF membrane pore, thereby increasing irreversible fouling. Separate runs with a 0.2 µm PS MF-membrane conducted with the same seawater (not reported), show an irreversible fouling rate 6 to 10 times higher than with UF membrane (PS 100kDa) and a permanent decrease of membrane permeability (38 % of initial permeability was not recovered after 4 runs) in spite of chemical cleanings. The particle size distribution and salinity for estuarine waters are linked. Particles size decreases when salinity increases because of natural flocculation when salt water and freshwater are mixed. Whatever the source of challenge water (sea or freshwater), all target microorganisms were retained by the membrane. In freshwater, turbidity was 4 times higher, chlorophyll-a approx. 27 times and TOC concentrations around 10 times higher compared to seawater. The transmittance in freshwater was equal to 21.5 % in average. Consequently, for this example of freshwater from the ballast water test facility, limiting conditions for UV treatment are obviously reached, so the objective to test UF with more challenging water is validated. With the same conditions of filtration: 35.7 L.m^{-2}.h^{-1} 20 and 30 min, fouling rates were between 1.4 and 3.4 mbar.h^{-1} for seawater (1 NTU) and between 17 and 43 mbar.h^{-1} for freshwater (3-8 NTU). With a 3-8 times higher turbidity, fouling rates in freshwater were 5 to 30 times higher than those observed in seawater (Figure 6).

Generally, the threshold flux is described as the flux for which the irreversible fouling abruptly increases. It corresponds to the transition from the polarization concentration to the gel formation in case of colloids filtration (Bacchin *et al.* 2006). The threshold flux concept is based upon the observation of significant increase of irreversible fouling in the beginning of one filtration cycle without taking into account the totality of UF operation at

industrial scale, including backwashes and CEB on long duration. On this base, the fouling rates in first sequences with seawater will not be observed with these filtration conditions. Nevertheless, fouling drastically reduces the sequence durations. Threshold flux is a first step and has to be completed on long duration considering the intermediate cleaning efficiency of backwashes and CEB, in order to scale up to understand fouling mechanisms. For the freshwater run at 35.7 $L.m^{-2}.h^{-1}$ 30 min, CEB efficiency was clearly lower and the fouling rates higher than those observed with other conditions. Therefore, the sequence duration is very low and becomes quickly less than 3 h, which, obviously, is not a sustainable condition for filtration. Sequences succession overall induces the sequence duration and CEB efficiency to decrease and the fouling rate to increase until a pseudo steady state, depending on feed water quality. After some CEB, the irreversible fouling is too strongly attached to be removed by CEB and filtration conditions reach a new threshold that induces the need of basic CIP.

Synergistic effects of different species or foulants occur. Backwash efficiency is limited, especially in freshwater ultrafiltration, because it contains more organic matter (in the tests with more than 80 % of humic substances) and probably more multivalent cations than in seawater. As complexation of multivalent cations (Ca^{2+}) to humic acids induces a bridge construction between the membrane and negatively charged organic matter, it plays an important role in efficiency of fouling removal by backwash [25, 26]. Microorganism's attachment to previously adsorbed macromolecules on the membrane (proteins, humic acids, polysaccharides or extrapolymeric substances [27] produces the biological fouling or biofilm, which can be organized in multilayers with different species. Multilayers are destabilized by CEB chemical attack, phytoplankton and bacteriological stress. These, however, induce polysaccharides excretion and smaller particles or macromolecules from cells lyses that can themselves be new starters to biofilm development [28]. Particles, debris or macromolecules, are strongly attached to the membrane or fouling layer and change the chemical bonding and electrostatic attraction forces. So, the consecutive acid and chlorine CEB become less efficient with time. Compared to seawater UF, the higher bacterial intake onto membrane surface as seen in freshwater UF runs, markedly decreases the membrane performances and cleaning efficacy. This could be induced by higher biofilm production [29]. These organic foulants are successfully removed by a single basic CIP (NaOH and chlorine cleaning). NaOH hydrolyses proteins and polysaccharides into small amides and sugars, neutralize organic acids and disperse colloids which are responsible for the organic fouling [26, 30]. NaOCl is an oxidant used for disinfection and to reduce biofilm growth, but it can induce formation of by-products of natural organic matter chlorination that cause damage on environment and health [26]. Currently, industry is looking for alternatives to reduce the NaOCl use [31, 32].

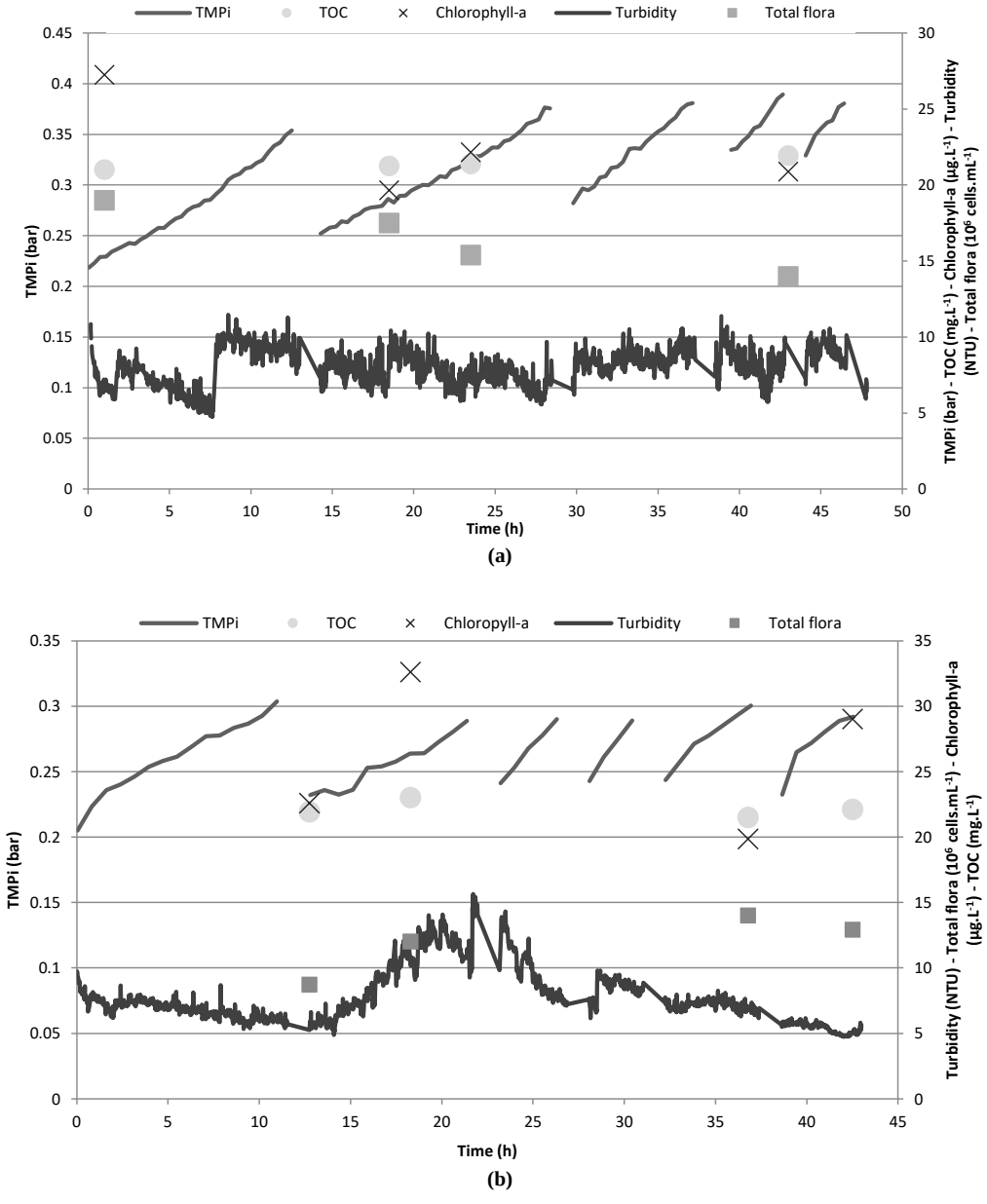


Fig. 5. Initial TMP evolution in function of time and seawater quality for the run 23.8 $L.m^{-2}.h^{-1}$ 20 min (a) and 45 min (b).

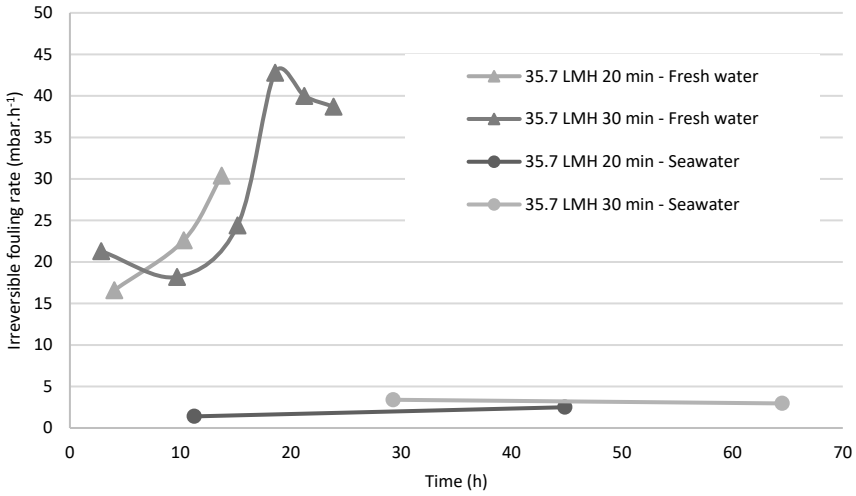


Fig. 6. Irreversible fouling rates comparison between runs with seawater and fresh water with the same experimental conditions (LMH: $L.m^{-2}.h^{-1}$).

For ballast water treatment application, UF can remove all target microorganisms from sea or freshwater in one filtration step without modifying the chemical characteristics of the water. The purification by UF is obtained in one step, whatever the transmittance of the treated water, which represents a major advantage to a UV treatment. Due to the high purity, the UF permeate can be rejected in the natural environment and the retentate will be dealing outside with an additional cost. With conventional treatments (such as UV), ballast tanks have to be cleaned regularly to remove accumulated sediments at the bottom of tank. This maintenance causes additional costs that has to be taking into account for the choice of ballast treatment. If UF is realized during the water intake, the input of sediments will be avoided, and cleaning of the ballast tanks should not be required. Based on the experimental results in seawater and freshwater, 456 m² surface membranes are estimated for ballast rate of 300 $m^3.h^{-1}$ during 10 h per ballast intake with freshwater (estimated with 2 $m^3.h^{-1}$ 30 min conditions). Therefore, the membrane surface needed is not compatible with compactness demands for ballast water treatment on board of a ship. Indeed, UF installation footprint has been estimated to be 143 m² on the basis of seawater results, which is 3 times higher than for conventional filtration followed by UV treatment. These results show that UF treatment on board is not economically and technically sustainable. However, UF treatment on a barge can be proposed as back-up facility by ports when conventional treatment is not able to treat ships' ballast waters (because of ballast treatment failure). Currently, if the ballast quality does not comply with the IMO D2 standard, ships have to pay a financial sanction to the state or country and proceed to ballast water exchange (D1) for example. UF treatment on barge could be also considered as a new sort of facilities to avoid introduction of invasive organisms or to anticipate the treatment of ballasted waters with a challenging quality for conventional treatment (i.e. low transmittance for UV). With 2 ballast loadings of 10 h (permeate rate: 300 $m^3.h^{-1}$) per day, UF membrane surface is estimated to 14,147 m² and 5,659 m² for fresh and seawater respectively. With 2 UF treatments per day during discharge (feed rate: 300 $m^3.h^{-1}$), UF membrane surface is estimated to 17,797 m² and 6,165 m². Estimated membrane surfaces for UF installations are lower for seawater, because the fouling rate is lower than for those obtained with freshwater which induces lower CEB frequency and higher sustainable permeate flux. Estimated membrane surfaces are higher in case of UF during loading than those estimated during discharging because the feed rate of UF installation during ballast loading should be higher than for discharge (300 $m^3.h^{-1}$).

5. Conclusions

A correlation between sequence duration, fouling rates, CEB efficiency and the variation of concentrations of microorganisms smaller than 1 µm (picoplankton and bacteria) is observed. Microorganism (< 1 µm) concentration increase induces a decrease of sequence duration and an increase of irreversible fouling rate which seems to be more or less temporary impacted. Indeed, fouling rates decrease with microorganisms concentrations. Bacterial concentrations are impacted by DOC variations, which themselves may be induced by rainfall and leaching of soil and/or be produced by microorganisms during the decline phase of phytoplankton bloom. A high concentration of microorganisms can accumulate on the membrane and build strongly attached multilayers that are probably induced by soluble exopolymeric substances produced by microorganisms. Chemical backwashes cause cell lyses or microorganism stress that can modify the membrane surface properties by production of smallest particles that induce an increase of fouling rate and a decrease of CEB efficiency.

During the seawater runs, the conditions did not reach threshold conditions in the first sequences of filtration at 5 $m^3.h^{-1}$ (59.5 $L.m^{-2}.h^{-1}$) 30 min in spite of seawater quality variation.

Contrary to seawater runs, critical conditions of filtration seem to appear with freshwater for 3 $m^3.h^{-1}$ (35.7 $L.m^{-2}.h^{-1}$) runs.

If CEB have a high frequency, a multiplication of modules number in the installation design has to be anticipated to compensate the net productivity lost. Therefore, runs with short sequence durations should be considered as unsustainable conditions for filtration. A holistic sustainability assessment also needs to take into account factors as chemical hazards and energy consumption, etc.

This paper emphasizes the challenges of the application: ballast water treatment has to retain all microorganisms whatever water quality at the same time being compact and cheap. This first study highlights the high potential of UF for microorganisms retentions compared to UV treatment. To provide recommendations of the future research in ballast water treatment, an economic study of a sustainable flux methodology, to define the viability of ultrafiltration for ballast water treatment will be the subject of a forthcoming paper.

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