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Monitoring particulate fouling of North Sea water with SDI and new ASTM $MFI_{0.45}$ test

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ABSTRACT

For assessing the particulate fouling of water, the modified fouling index ($MFI_{0.45}$) is a superior test to the silt density index (SDI). There is a need to compare both tests in terms of sensitivity, how they are affected by the filter material and the type of support plate and also illustrate their use for monitoring of seawater quality over time. In this work, we studied seven different filter holders with different filter support plates and three different 0.45 μm filter materials, and we applied the tests for monitoring of North Sea water quality. The results illustrated that the type of support plate of the filter holder greatly influences the measured $MFI_{0.45}$ values and thus, a correction for the effective membrane area may be needed when carrying out an $MFI_{0.45}$ test. An attempt to normalize differences in $MFI_{0.45}$ due to filter material with a Formazin solution was tested but proven not successful. When monitoring the seawater, the $MFI_{0.45}$ was much more sensitive than SDI to water quality variations in particular during algal growth. As the SDI and $MFI_{0.45}$ tests can be measured with help of the same equipment, more alignment in the ASTM protocols for both methods is recommended.

1. Introduction

The world's seawater desalination current capacity is about 57.2 million cubic meters per day of which about 55% is produced by reverse osmosis membranes and the rest by thermal processes. Two thirds of this water is desalinated in the Middle East and North Africa [1]. Moreover, the membrane fouling (particulate) due to the presence of suspended and colloidal matter hinders the smooth operation of membrane systems. Membrane fouling results in an increase in resistance and as a result a higher feed water pressure is required to maintain the capacity of the plant.

Assessment of particulate fouling in membrane-based desalination systems is performed worldwide by measuring the silt density index (SDI) and the modified fouling index ($MFI_{0.45}$). The SDI (code D4189-14, [2]) has for many years been an ASTM method while the $MFI_{0.45}$ (code D88002-15, [3]) although proposed in 1980 by Schippers et al. [4] was only approved by the ASTM in 2015 as standard method. SDI is an important test for assessing pre-treatment, as manufacturers of reverse osmosis (RO) keep the guarantee of their membranes based on the measured SDI values of RO feed water.

SDI is used to define the need of prefiltration (screening) and also to estimate the range of operating fluxes [5]. For instance, if the feed water has a SDI less than approximately 5%/min, cartridge filters with ratings ranging from about 5 to 20 μm are commonly used for RO prefiltration. However, if the SDI of feed water exceeds the value of 5%/min, a more rigorous method of particulate removal, such as conventional treatment (including media filtration) or MF/UF membranes, is recommended as pretreatment for RO. As a general rule of thumb, spiral-wound RO modules are not effective for treating water with a SDI of 5%/min or greater, as this quality of water contains too much particulate matter for the non-porous, semi-permeable membranes, which would foul at an unacceptably high rate. RO membrane manufacturers can usually provide a rough estimate of the range of anticipated operating fluxes based on the type of source water, which is roughly associated with a corresponding range of SDI values. A summary of these estimates is the following: for surface water with SDI in the range 2–4%/min, the estimated RO flux is in the range 13.6–23.8 $L/m^2/h$; and for groundwater with SDI < 2%/min, the estimated RO flux is in the range 23.8–30.6 $L/m^2/h$ [5]. The recommended maximum SDI value for acceptable RO feed water has been reported as 3 s/L^2 [6].

Many studies have reported that the main difficulty with these fouling indices, SDI in particular, is the lack of reproducibility when

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performing the tests with various membrane materials and even within the same batch of manufactured filters. Many studies have reported that SDI measurements can vary from test to test, with the operator, and that water temperature and the specific type of membrane used will affect the results. Consequently, it is important that the results are given for comparable conditions when evaluating SDI data [5,7]. Alhadidi et al. [7] studied membrane properties (pore size, membrane thickness, contact angle, bulk porosity, zeta potential and roughness) that affect the SDI method by testing eight different 0.45 µm membranes. It was reported that there is significant variation in the SDI results obtained using membranes within the same batch. Similar findings established that SDI values will vary with the filter material and type of filter used [8]. This is further corroborated by another researcher who studied the effect of three different filter holders on SDI/MFI values and reported > 100% difference in the SDI values and only 20% in the measured $MFI_{0.45}$ values for the same feed water [9]. The SDI method gives recommendations, however, does not specify the exact type of filter holder to be used in measurements. Several factors like the filter holder and the filter material need to be studied so as to give recommendations because it is not clearly specified in the standard.

Furthermore, as reported in the literature [5,7–12], the SDI shows several deficiencies, e.g., no linear relation with concentration of suspended and colloidal matter; no correction for temperature; and is not based on any filtration mechanism. The $MFI_{0.45}$ (based on 0.45 µm filtration) is a superior alternative since it: shows a linear relation with particle concentration; is corrected for temperature; and is based on the cake filtration mechanism. However, there is a need to perform reproducibility tests to validate the effect of testing factors like the filter holder, the filter support plate, and the filter material on the $MFI_{0.45}$. The ASTM $MFI_{0.45}$ method recommends the use of a replaceable highly porous foam support pad to be placed on the bottom of the filter holder while for the SDI test such a recommendation is not prescribed.

An additional interest from practice is to link water quality parameters with fouling potential, and at the moment there is no reported comprehensive dataset of monitoring of these parameters over long periods. There is, therefore, a need to study and to assess the fouling potential of seawater, especially particulate fouling, to establish the correlation between seawater characteristics and fouling indices. Such a correlation would be particularly useful to be able to predict or determine the fouling potential of seawater during algal blooms.

Summarizing, the specific objectives of this study were: *i*) to study the effect of filter holder and filter material in SDI and $MFI_{0.45}$ tests, and *ii*) to apply the SDI and $MFI_{0.45}$ in the monitoring of NSW. The research questions were: *i*) what is the effect of the filter material on the SDI/$MFI_{0.45}$ measurement?, *ii*) what is the effect of the support plate in the filter holder on the SDI/$MFI_{0.45}$ measurements?, *iii*) can algal bloom events and their fouling potential be monitored by measuring the SDI and $MFI_{0.45}$ values?

1.1. Theoretical background of the SDI and $MFI_{0.45}$

The SDI method relies on filtration through a 0.45 µm membrane, with a constant pressure of 207 kPa (or 210 kPa) and in dead-end mode. This index corresponds to the measurement of the flux decline over time (or "the percentage decrease in the filtration rate per minute"), which depends on the rate of plugging of the filtering media. The SDI index can be calculated using Eq. (1).

$$SDI = \frac{100\%}{t_f} \times \left(1 - \frac{t_1}{t_2}\right) = \frac{\%P}{t_f} \qquad (1)$$

where: t_1 = the time elapsed after 500 mL filtration, t_2 = the time elapsed after 500 mL filtration started 15 min (t_f) after the start of the first measurement, $\%P$ = plugging ratio (%). SDI is expressed in %/min. Maximum values to be reported are limited by the 75% plugging ratio as follows: SDI_{15} = 5 (max 6.7), SDI_{10} = 7.5 (max 10) SDI_5 = 15 (max 20), and for SDI_3 = 25 (max 33). The ASTM protocol recommends that if SDI_5 is not applicable, then another test methods should be used to analyze particulate matter [2]; nevertheless SDI_1 values can be found in literature for waters with high clogging/fouling potential.

The $MFI_{0.45}$ test consists of feed water filtration through a 0.45 µm filter, with a constant applied pressure and is operated in dead-end mode. This method considers that cake filtration is the dominant mechanism and contrary to SDI it allows to estimate the fouling potential of a given feed water during RO. The derivation of the formula has been presented in detail in previous studies [4,13] and considers the resistance of an incompressible cake during constant pressure filtration provided the retention of particles is constant. In the MFI, the fouling index I is defined as the product of the specific cake resistance per unit weight (α) multiplied by the concentration of particles per unit volume of filtrate (C_b). The specific cake resistance can be calculated according to the Carman-Kozeny [14] equation (Eq. (2)) for spherical particles where α increases with a reduction in the porosity of the cake (ε) or a decrease in particle diameter (d_p). Where ρ_p is the density of the particles forming the cake.

$$\alpha = \frac{180\cdot(1-\varepsilon)}{\rho_p\cdot d_p^2\cdot\varepsilon^3} \qquad (2)$$

The $MFI_{0.45}$ can be calculated from the slope of the linear region found in the plot t/V vs. V as illustrated in Fig. 1 of the equation derived for constant pressure filtration and cake filtration mechanism (Eq. (3)) as follows:

$$\frac{t}{V} = \frac{\eta\cdot R_m}{\Delta P\cdot A} + \frac{\eta\cdot I}{2\cdot\Delta P\cdot A_m^2}\cdot V \qquad (3)$$

where: t = the time (s); V = the filtrate volume (m^3); η = the water dynamic viscosity (Ns/m^2); R_m = the membrane resistance (m^{-1}); ΔP = the pressure gradient across the membrane (kPa); A_m = the membrane area (m^2); I = the fouling index (m^{-2}).

Substituting the Carman-Kozeny in Eq. (3) gives Eq. (4). This equation shows that MFI is a function of the dimension and nature of the particles forming a cake on the membrane, and directly dependent on particle concentration in water.

$$MFI = \frac{\eta\cdot 90\cdot(1-\varepsilon)\cdot C_b}{\rho_p\cdot d_p^2\cdot\varepsilon^3\cdot\Delta P\cdot A_m^2} \qquad (4)$$

In the reference conditions (that is T = 20 °C, $\Delta P = \Delta P_O$ = 207 kPa, and $A_m = A_O = 13.8 \times 10^{-4}\, m^2$), the index value I is obtained by taking the minimum of the slope of the curve t/V versus V which equals to tan α. This value can be used to determine the MFI values according to Eq. (5):

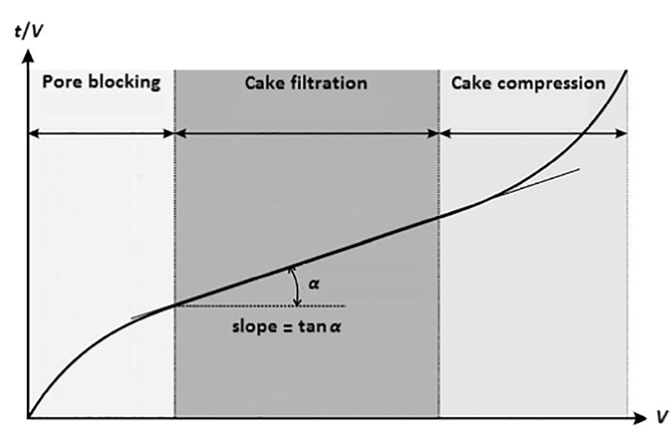

Fig. 1. Particulate fouling mechanisms including calculation of MFI.

$$MFI = \tan\alpha \times \frac{\eta_{20}}{\eta} \times \frac{\Delta P}{\Delta P_0} \times \left(\frac{A_m}{A_0}\right)^2 \quad (5)$$

Eq. (4) has been plotted in Fig. 14 (Supplementary information S1) to illustrate the influence of particle size and cake porosity in the MFI value.

1.2. Theoretical calculation of fouling potential of algal suspension

The fouling potential of algal suspension (without presence of algal organic matter) was calculated using the model Eq. (6) as described by [15].

$$MFI = \frac{15{\cdot}\pi{\cdot}d_p{\cdot}C_p}{\varphi^2}{\cdot}\frac{(1-\varepsilon)}{\varepsilon^3}{\cdot}\frac{\eta_{20}}{\Delta P_0{\cdot}A_0^2} \quad (6)$$

where: ε = cake porosity, φ = sphericity of the particles, C_p = particle concentration (count/mL), d_p = diameter of particles in the cake, η_{20} = water viscosity at 20 °C (Pa·s), ΔP_0 = reference feed pressure (2.07 kPa), A_0 = reference membrane area (13.8×10^{-4} m^2). Note: C_p is the particle concentration in terms of particle count per mL while C_b is in terms of mg/L.

1.3. MFI prediction model

Prediction of the fouling rate in RO systems, considering cake filtration as fouling mechanism is based upon Eq. (7) (see [16–18] for its derivation).

$$\Delta P = \eta{\cdot}R_m{\cdot}J + \eta{\cdot}I{\cdot}\Omega{\cdot}J^2{\cdot}t \quad (7)$$

where: ΔP = net driving pressure (N/m^2), η = viscosity (N·s/m^2), R_m = membrane resistance (m^{-1}), I = fouling potential derived from MFI (m^{-2}), Ω = deposition factor (−), J = flux (m^3/m^2·s), t = time (s). Eq. (7) has been plotted in Fig. 2.

We note that the presented model does not consider a more recent prediction model including the effect of the cake-enhanced osmotic pressure effect as proposed by previous works [19,20]. This model might be more appropriate when using other fouling indices such as the MFI-UF [21,22].

2. Materials and methods

2.1. Experimental setup for SDI and $MFI_{0.45}$ measurements

The set-up for constant pressure filtration and dead-end filtration mode is illustrated in Fig. 3. The feed water was transferred to the

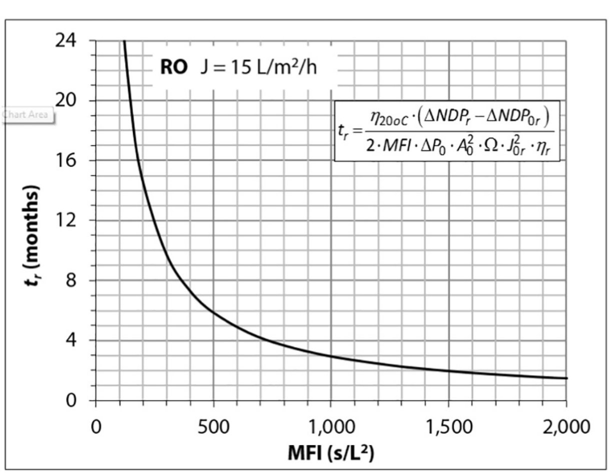

Fig. 2. Projections based on MFI values. Time (in months) for an increase in Net Driving Pressure (ΔNDP_r - ΔNDP_{0r}) = 1 bar in a RO system operating at flux = 15 L/m^2/h, Ω = 1 (worst case), T = 20 °C.

pressure vessel (max volume 4 L). The required pressure was achieved by applying pressurized nitrogen gas adjusted by a pressure sustaining valve (FESTO, model LRP: ¼–4) with a maximum operating pressure of 4 bar. Then, feed water was passed through a membrane filter where permeate was collected in a beaker set on an electronic balance (Mettler Toledo, Model PB 602-S). The scale has an RS-232 interface connected to a computer to acquire permeate weight from the balance.

Data sets of collected filtrate weight and filtration time are recorded and imported into a MS Excel spreadsheet using data acquisition software (WinWedge, USA). The recording interval was fixed at 10 s prior to the filtration run. The spreadsheet was adapted to include a graph of the calculated value of $MFI_{0.45}$ versus time and the minimum $MFI_{0.45}$ value was reported.

2.2. Filters

Three hydrophilic membrane materials of 0.45 μm nominal pore size and 25 mm external diameter were used during this study for measuring SDI and $MFI_{0.45}$ values. The studied materials were cellulose acetate (CA, Carl Roth), nylon 6.6 (NN, Pall), and mixed cellulose nitrate (NC, Millipore). The filters were flushed with demineralized water before testing with the real sample.

2.3. Filter holders

Seven different commercially available filter holders with various types of filter support plates were tested. Fig. 4 presents the photos of the filter holders and Table 3 presents the properties of the filter holders. Before testing, the analyst verified that air was not trapped inside the filter holder.

2.4. Clean water membrane resistance

Clean water flux experiments (CWF) were performed for all the filters tested in this work. The CWF measurements were performed with ultra-pure water under constant pressure. The clean water resistances of the membranes (R_m) were calculated using Darcy's law. The membrane resistance can be used as an overall indicator for the membrane properties, including, e.g. membrane porosity, pore size and thickness. The membrane resistance was used to study its relationship with SDI and $MFI_{0.45}$ values.

Based on the Hagen-Poiseuille equation and Darcy's equation for flow, the membrane resistance can be calculated from Eq. (8).

$$R_m = \frac{8{\cdot}\tau{\cdot}\Delta x}{\varepsilon{\cdot}r^2} \quad (8)$$

where: τ = membrane tortuosity (−), ε = membrane porosity (−), Δx = membrane thickness (m), r = radius of the pore size (m). In Eq. (8) the membrane resistance R_m increases proportionally with increasing membrane thickness, and is inversely proportional to the membrane surface porosity and to the square of the pore radius.

2.5. Water samples

Two water sources were used in this study. Delft canal water (DCW) was 10× diluted with Delft tap water (DTW) and used for studying the effects of filter material and filter holder in both SDI and $MFI_{0.45}$ tests. Some of the properties of DCW are presented in Table 1.

Raw North Sea water (NSW) was monitored in the period November 2016 to July 2017. Filtered NSW is the raw NSW after 2 μm glass media filtration pumped at a pressure of 0.8 bar. The NSW was sampled in Kamperland (province of Zeeland), the Netherlands.

Commercial formazin stock suspension of 4000 NTU, 100 mL (Hach, USA) was used in our work. The Formazin solution is produced and certified in accordance with ISO Guide 34:2009 and ISO/IEC 17025:2005. The reported median particle size of formazin is 1.5 μm

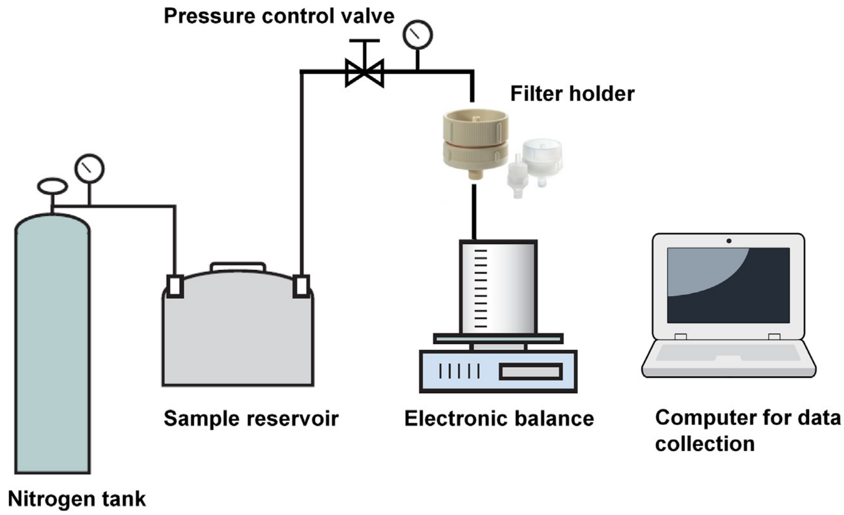

Fig. 3. Constant pressure, dead-end, filtration setup.

and the standard deviation of size is 0.6 μm [23]. Formazin standard solution was stored in the fridge when not in use. To minimize the effect of temperature, storage time, and concentration on size, shape, and aggregation, fresh solutions were prepared just before its use. Any formazin solution was discarded after 12 h. Formazin particles have many different shapes.

All SDI and $MFI_{0.45}$ measurements were performed in the laboratory facilities of IHE, 90 km from the sampling point in Kamperland, within 24 h after sampling. Amber glass bottles were used for sampling and they were transported and stored at cold temperature around 4 °C.

The counting of algal-cell density in water samples was performed using Haemacytometer (Burker-Turk counting chamber) slides and a light Nikon microscope (Olympus BX51). Flagellate-type of algal species were immobilized with Lugol's iodine solution before counting. Samples were also collected to measure chlorophyll-a according to the Dutch standard NEN 6520 protocol [24].

Table 1
Summary of Delft canal water properties.

Parameter	DCW	DCW1
Date	4 Jan 2017	4 July 2017
pH	7.3 ± 0.1	7.6
Turbidity, NTU	2.9 ± 0.1	3.6
Elec. conductivity, mS/cm	1.07 ± 0.06	1.1
DOC, mg/L	15.9 ± 1.8	17.5
SUVA, L/mg/m	3 ± 0.2	3.2

3. Results and discussion

3.1. Filter properties

The ASTM standard provides some indications on the recommended filters for the SDI test. The method describes that, for a range of pressures (91.4–94.7 kPa), the water flow should be around 25–50 s per 500 mL. Based on this information, the recommended permeability of the filters at 20 °C was calculated to be 21,911 L/m^2/h/bar to 45,405 L/

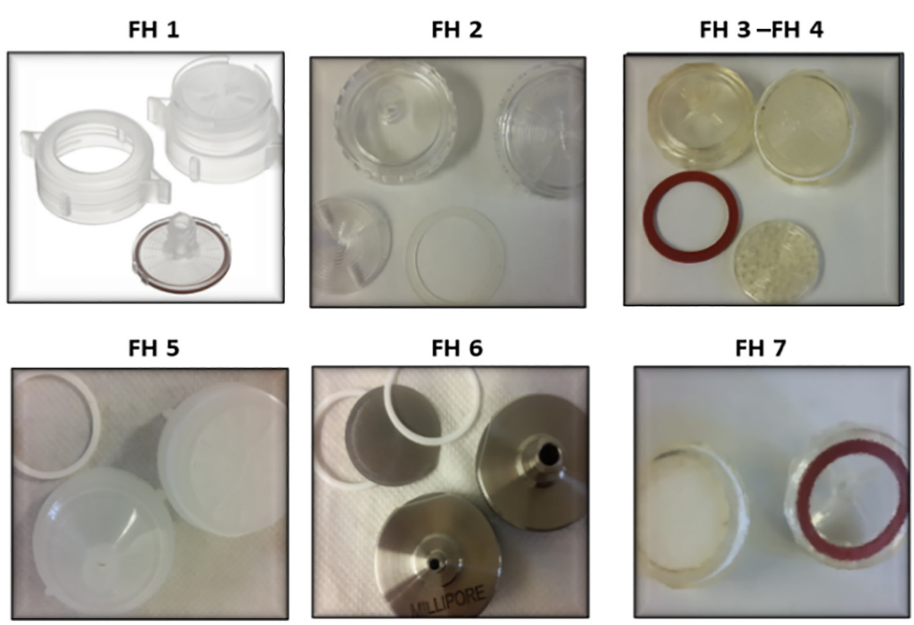

Fig. 4. Images of the filter holders.

Table 2
Filter properties.

Code	Filter material	Thickness[a], μm	Bubble point[a], bar	Permeability[b], $L/m^2/h/bar$
CA	Cellulose acetate[c]	106	> 2.4	B1: 31,020 ± 926 (3%) B2: 28,072 ± 2443(9%)
NN	Nylon 6.6	144–170	2.2–2.5	22,764 ± 579 (3%)
NC	Mixed cellulose nitrate[c]	150	> 2.1	44,438 ± 1259 (3%)

[a] Information from manufacturer.
[b] Measured using filter holder FH4 (Table 3) n = 10.
[c] ASTM recommended material.

$m^2/h/bar$. Comparing the results obtained from the three filters, the NC filter has the highest permeability in comparison to CA and NN. The measured permeabilities as shown in Table 2, suggest that all the tested filters are appropriate according to the recommendations of the ASTM.

Before SEM imaging, the samples were dried overnight in a 30 °C oven under vacuum. After drying the samples were sputtered with a gold layer. Top view SEM images were taken using a scanning electron microscope (Jeol, JSM-6010 LA).

Fig. 5 shows similarities in the pore morphology among the three filter materials. NN shows a smoother surface than the other NC and CA. The shape of the pores is not well defined and they are not homogenously distributed over the surface. In general, we can conclude that the membranes used in this work all have different pore shapes at the surface. Also from SEM images we can qualitatively observe the surface porosity for each type of membrane used. The NC filter shows higher surface porosity than the CA and NN. Back sides of the filters were not studied.

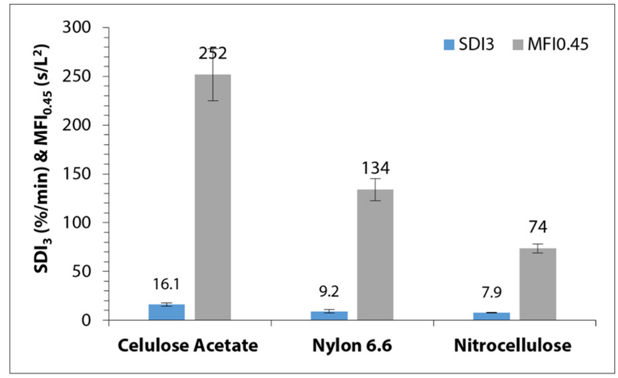

Fig. 6. SDI_3 and $MFI_{0.45}$ values measured with various filter materials (n = 10). DCW, FH4.

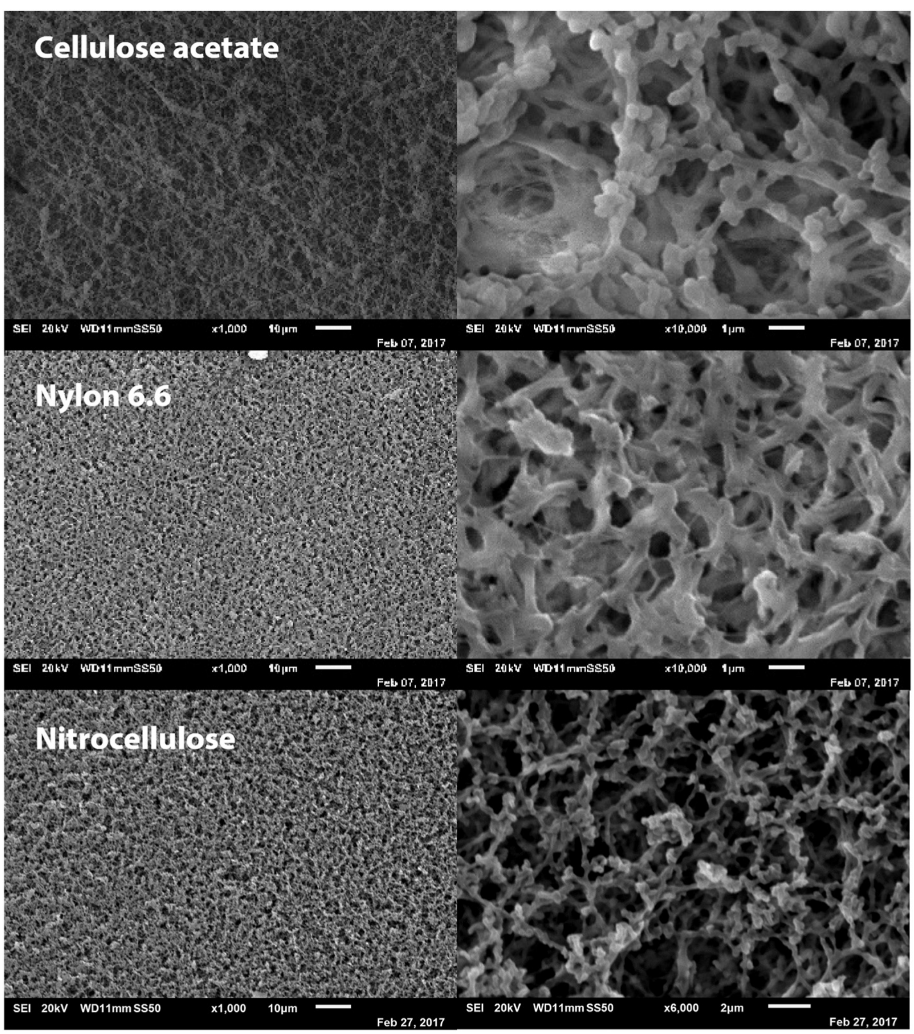

Fig. 5. SEM top view images of the three tested filters at different magnifications (1000× for left images, 10,000× for top right images, and 6000× for bottom right image).

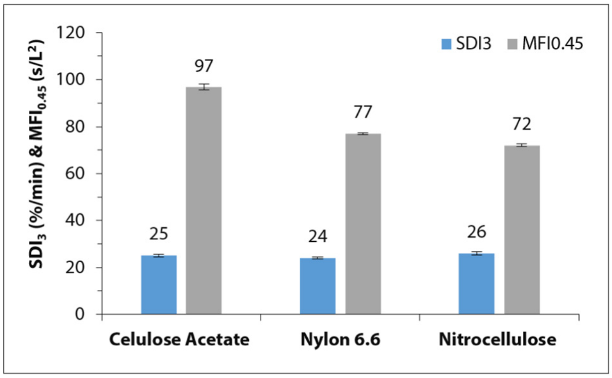

Fig. 7. SDI_3 and $MFI_{0.45}$ values measured with various filter materials (n = 10). Formazin (NTU = 15), FH4.

3.2. Effect of filter material on SDI and $MFI_{0.45}$ values

Fig. 6 (for Delft canal water) and Fig. 7 (for Formazin solution) present the SDI and $MFI_{0.45}$ values obtained for the three filter materials using the same filter holder. For DCW from Fig. 6, both SDI_3 and $MFI_{0.45}$ show that the material of the filter influences the results. When we refer to the material of the filter we refer to the filter properties (pore size, pore size distribution, surface porosity, thickness, tortuosity, surface charge) as influenced by the material during the manufacturing process and presented in Eq. (6). The NC filter gave the lowest SDI_3 value of 7.9%/min, followed by NN with an increased value of 9.2%/min, and CA 16.1% min. However, the relative error for the NN filter is 20%, for the CA is 10%, and for the NC 6%. Hence, the NC filter is more uniform than the CA in the obtained results. Furthermore, for all three filters the SDI_{15}, SDI_{10}, and SDI_5 could not be experimentally measured due to exceeding the 75% plugging ratio value recommended by the method.

Additionally, from the Fig. 6, it can be observed that the $MFI_{0.45}$ is more dependent on the material used and this can be attributed to the morphology of the membrane (pore size distribution, surface porosity, tortuosity of the pores) and to the fact that $MFI_{0.45}$ considers a filtration mechanism (i.e., cake filtration) in the calculation. $MFI_{0.45}$ value is 252 s/L^2 for the CA, 134 s/L^2 for NN, and 74 s/L^2 for NC. The relative error for CA, NN, and NC is 11%, 8%, and 6%, respectively. NC filters show the lowest variation for both SDI and $MFI_{0.45}$. In the supplementary information section S2, we present the t/V versus V figures for a representative test for the three filter materials. From these figures can be seen that cake filtration is the dominant fouling mechanism in the CA and NC filters, and pore blocking followed by cake filtration was observed for the NN filter.

In Fig. 7 it can be observed that using a solution of Formazin, the measured SDI_3 remains stable, regardless of the filter material. The SDI_3 value is 25%/min for the CA, 24%/min for the NN and 26%/min for the NC. Unlike for Delft canal water, with Formazin solution, the measured $MFI_{0.45}$ values are similar for NN and NC (77 s/L^2 for NN and 72 s/L^2 for NC, with low relative errors 0.7% and 0.8%, respectively). However, a larger $MFI_{0.45}$ value is obtained with the CA filter (97 s/L^2 and 1.3% relative error). The thinner thickness and clean water permeability of the CA cannot directly explain the higher $MFI_{0.45}$ value compared to the NC and NN filters when testing Delft canal water. It is possible that the surface charge of the filter and the interaction with the particulates and organic matter present in DCW influence the measured fouling potential.

In Fig. 6 we use DCW with a mix composition of particulates (organic matter, bacteria, inorganic particles and colloids) while in Fig. 7 we use Formazin solution with particles of uniform size that are not compressible. In Fig. 7 we observed that SDI shows uniform results for a solution of Formazin while large variations (in Fig. 6) with DCW. In the case of the $MFI_{0.45}$ we observed that the variations are not so significant due to the filter material when testing the Formazin solution. This suggests that besides the filter material, the nature of the particles present in the water will also influence the results in SDI and $MFI_{0.45}$.

R_m can be used as a general indicator of the membrane properties (e.g. membrane porosity, pore size, and thickness). In our study, the NC membranes have the lowest R_m values ($9.35 \times 10^9\,m^{-1} \pm 5.4\%$) followed by CA membranes ($1.39 \times 10^{10}\,m^{-1} \pm 6.6\%$) and NN membranes ($1.86 \times 10^{10}\,m^{-1} \pm 4.5\%$) with the highest R_m values. The ASTM (D4189-14) requirement of the pure water flow can be converted into clean water membrane resistance limits at 20 °C, as follows: $0.86 \times 10^{10}\,m^{-1} < R_m < 1.72 \times 10^{10}\,m^{-1}$.

Fig. 8 shows the variation of the SDI_3 (a) and $MFI_{0.45}$ (b) as a function of normalized R_m. Contrary to what was reported in literature, the results do not show a clear correlation on high SDI values with low R_m. In addition, no correlation between $MFI_{0.45}$ and R_m was observed.

3.3. Can we normalize the results for material differences?

The hypothesis is that each filter material will produce a different slope when testing MFI vs. Formazin concentration. Each slope could be used for normalizing the results with various filter materials. Formazin solution has been used in the past as a model solution to demonstrate the proportionality of concentration with $MFI_{0.45}$ and SDI values [4]. In this study the $MFI_{0.45}$ and SDI values for various concentrations of Formazin (expressed as NTU) in the range 0–30 NTU were measured.

The results presented in Fig. 9 show that SDI values increase when the Formazin concentration goes from 0 to 10 NTU, but remain constant afterwards. $MFI_{0.45}$ linearly increases in value when the concentration of Formazin, and thus of particles, increases. The slopes of $MFI_{0.45}$ vs. Formazin concentration show that there is no significant difference among the three filter materials and thus we cannot use Formazin solution for normalizing the results.

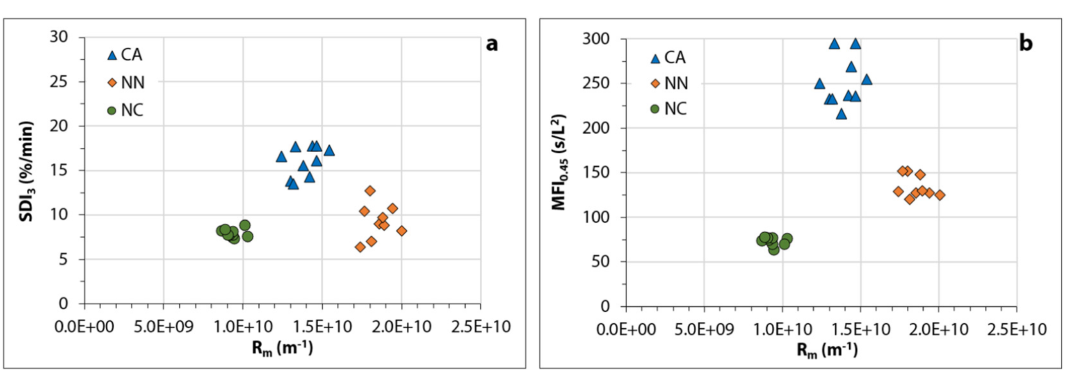

Fig. 8. SDI_3 (a) and $MFI_{0.45}$ (b) as a function on R_m (n = 10). DCW. FH4.

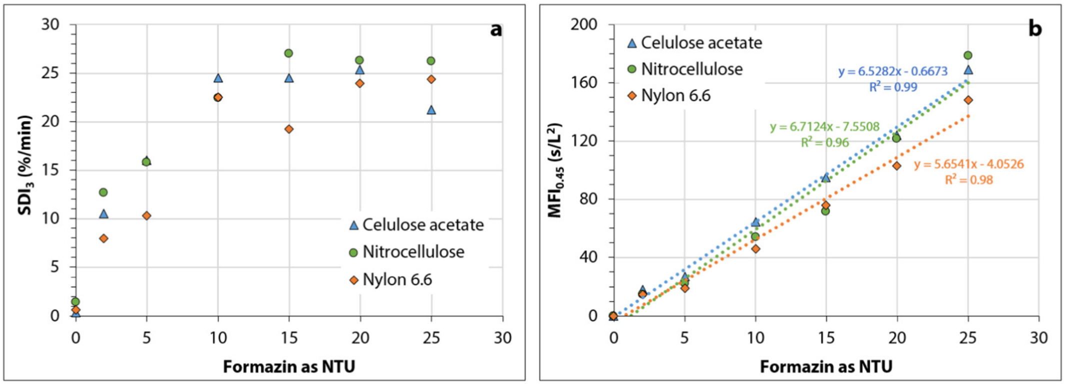

Fig. 9. SDI_3 (a) and $MFI_{0.45}$ (b) values measured for Formazin solution with three filter materials and FH4 support plate.

3.4. Effect of filter holder support plate on effective filtration membrane area

The CA filter was used for determining the effective (or real) filtration membrane area influenced by the support plate of each filter holder. A solution of powdered activated carbon was prepared and filtered through CA filters with the various filter holders to get the engraved design of each filter support as shown in the Fig. 10. From the engraving, the real effective filter area (EFA) was determined by measuring the permeable part of the filter which is covered in black. Table 3 shows the values of the real effective area for the different filter holders.

By comparing the values of the effective filter area in Table 3, it can be observed that the lowest value was obtained for the FH4 filter holder, with a channel support plate (EFA is about 56% of the FA) while the value was maximal for the FH7 (EFA is 100% of the FA). This might be explained by the fact that the FH7 support plate is porous, allowing to maximize the filtration area through the filter. In the case of the FH7, the support plate of the filter holder is thus not influencing the filtration membrane area.

When comparing the values of the EFA for FH3 and FH4, which come from the same manufacturer and are both made of polysulfone, it can be noticed that the perforated support plate influenced slightly less the filtration area (EFA is 63% of the FA) than the channel support plate (EFA is 56% of the FA), in those conditions. However, channel support plates could still lead to relatively high corrected effective filter areas.

When considering the filter holder having a channel support plate (FH1, FH2, FH4 and FH5), it can be seen that the support plate made of Makrolon was the one that influences the less the filtration membrane area (EFA is 77% of the FA). The support plate of the Millipore stainless steel filter holder (FH6) appears to be more uniformly porous and not that simple to determine. From the image, the effect of an air bubble can clearly be observed since the filter is not transparent and it is difficult to remove.

3.5. Effect of filter holder on SDI and $MFI_{0.45}$

The results for SDI_{15} and SDI_5 obtained for all filter holders exceeded the 75% plugging ratio and thus SDI_3 values are reported in Fig. 11.

The FH3, was the only filter holder producing results for SDI_5 of 10.8%/min ± 5%. This could be attributed to the filter support, which has perforations that appear to be equal in size. The perforations seem to be randomly distributed and more concentrated at the center. Thus, the flow appears to be trickling through the filter and takes more time to collect the same volume, hence the observed SDI_5. The perforations are likely to create more resistance to the flow.

Filter support structure has a significant impact on $MFI_{0.45}$ but not so much on SDI. The SDI values cannot be corrected for considering the effective membrane area due to the filter support plate, as the SDI formula only considers the time between two measurements and the total volume that is filtered in that time which is depending on the flow rate.

By correcting for the effective filter area, the $MFI_{0.45}$ results obtained with the different filter holders (Fig. 11 b) are closer to each other (247 s/L^2 ± 10.8%) in comparison with the average without considering the area effect (400 s/L^2 ± 27.6%). In the MFI formula, the area plays a significant role; if the area is halved then the MFI will be quartered. Thus, the vast variation in the MFI values for filter holders

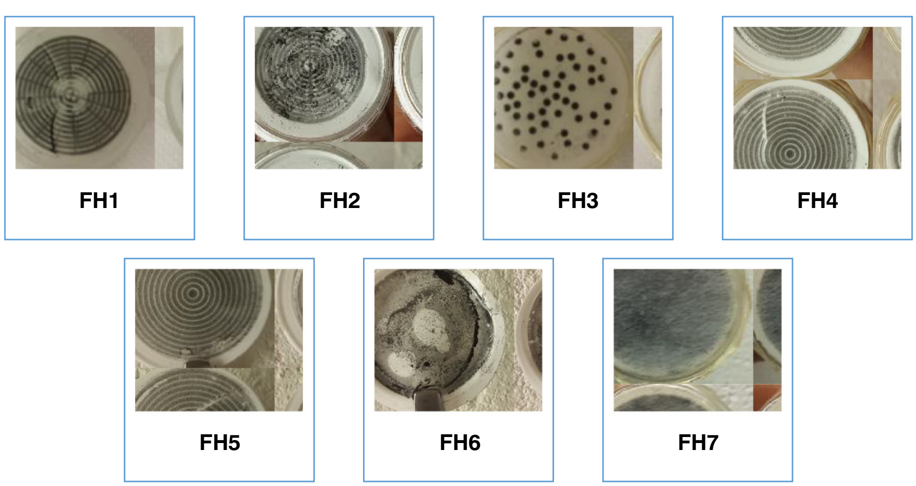

Fig. 10. View of the support of the filter holder after filtration with powder activated carbon.

Table 3
Filter holder properties.

Code	Filter holder	Support	Material	MOP[a] (bar)	FD[b] (mm)	FA[c] (mm^2)	EFA[d] (mm^2)
FH1	Whatman	Channel	Polypropylene	3.5	21	346	242 (70%)
FH2	Sartorius Stredim	Channel	Makrolon	7	21	346	269 (77%)
FH3	Schleicher & Schuell	Perforated	Polysulfone	7	21	346	218 (63%)
FH4	Schleicher & Schuell	Channel	Polysulfone	7	21	346	193 (56%)
FH5	Swintex Millipore	Channel	Polypropylene	3.5	21	346	232 (67%)
FH6	Millipore stainless steel	Grid	Stainless steel	6.9	21	346	–
FH7	Akvoregia (filter support) in FH3 holder	Porous	Polysulfone	7	21	346	346 (100%)

[a] MOP, maximum operating pressure.
[b] FD, filter diameter.
[c] FA, filter area.
[d] EFA, effective filter area.

without area correction. Additionally, in the MFI the flow rate influences greatly the fouling potential of a water sample, so any effect that increases the flow rate through the membrane (like the channels in the filter support plates that reduce the effective filter area) will increase the fouling load of the membrane and consequently the measured $MFI_{0.45}$ will be higher.

Nahrstedt and Camargo-Schmale [9], studied the effect of the filter holder on SDI and $MFI_{0.45}$ by testing three filter holders, namely: Millipore inline 47 mm, Sartorius SM 47 mm, and Sartorius 25 mm. The study concluded that for the same feed water SDI values varied up to 90% and $MFI_{0.45}$ values varied up to 20% for the three filter holders. These differences were attributed to the effect of the corrected effective area and of the flow distribution inside the filter due to the filter support.

3.6. Application of SDI and $MFI_{0.45}$: water quality monitoring

3.6.1. Properties of North Sea water

The summary of the properties of North Sea water during the monitoring campaign is presented in Table 4. The pH and electrical conductivity values remained fairly stable during this period, pH around 8 and EC values of 48–49 mS/cm for the samples. Turbidity measurements ranged between 0.1 and 1.0 NTU for filtered North Sea water and between 0.9 and 45 NTU for raw North Sea water. The elevated turbidity results shown in Fig. 12, indicated by the peaks, can be attributed to high ocean tides and storms in the area.

Algal cell counts and chlorophyll-a are primarily used to indicate algal bloom occurrence. The chlorophyll-a concentrations measured in the period were below the detection limit of the method (LOD < 5 μg/L). According to the results presented in the Fig. 12 (b), the minimum and maximum algal count concentrations measured for raw North Sea water are 11 cell/mL and 1039 cell/mL, respectively. These values are considered normal due to the low temperature during the period until the end of April when the values rapidly increased, most likely due to a mild algal bloom. An algal cell count lower than 1000 cell/mL indicates that there is no algal bloom. On the contrary, an algal cell count higher than 60,000 cell/mL is an indicator of an acute algal bloom [25]. Based on the high algal cell numbers at the end of April until mid-May, it can be concluded that a mild algal bloom event took place at the testing location.

Table 4
Summary of seawater quality properties in the study period.

Parameter	Raw North seawater	Filtered North seawater
pH	8.0 ± 0.3	
Turbidity, NTU	Min = 0.9; Max = 45 Avg = 10.5 ± 11.0	Min = 0.1; Max = 1.0 Avg = 0.4 ± 0.2
Elec. conductivity, mS/cm	48.1 ± 1.6	
DOC, mg/L	2.1 ± 0.5	
SUVA, L/mg/m	1.8 ± 0.6	
Total algal count, cell/mL	Min = 11, Max = 1039	–
Chlorophyll-a, μg/L	< 5 (bdl) till end of March. In May ~7.5 μg/L	

bdl = below detection limit.

3.6.2. Particulate fouling potential of North Sea water

From October 2016 to July 2017, the SDI and $MFI_{0.45}$ values were measured for both raw and filtered North Sea water (Fig. 13). SDI_{15}, SDI_{10}, and SDI_5 could not be measured due to clogging of the filter, but the SDI_3 values were reported ranging between 6 and 26%/min for filtered and 9–28%/min for raw North Sea water.

$MFI_{0.45}$ measured for filtered North Sea water is in the range of 12–170 s/L^2 and for the raw seawater sample between 20 and 310 s/L^2, Fig. 13. Consistently higher $MFI_{0.45}$ values were obtained for the raw NSW (up to 8× higher) that has a higher particles content as compared to the filtered NSW.

The $MFI_{0.45}$ is much more sensitive than the SDI as the range of values obtained is much wider and higher values could be reached Considering that MFI0.45 is proportional to the concentration of

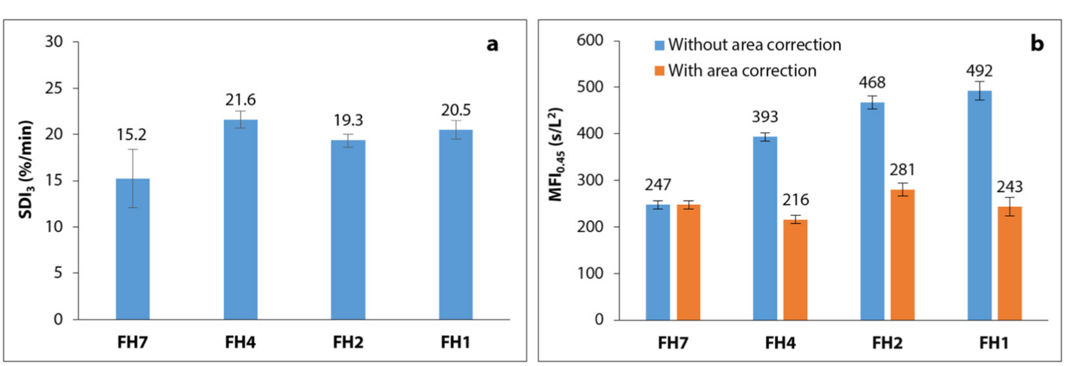

Fig. 11. SDI_3 (a) and $MFI_{0.45}$ (b) values measured with various filter holders (n = 10). DCW1. CA filter.

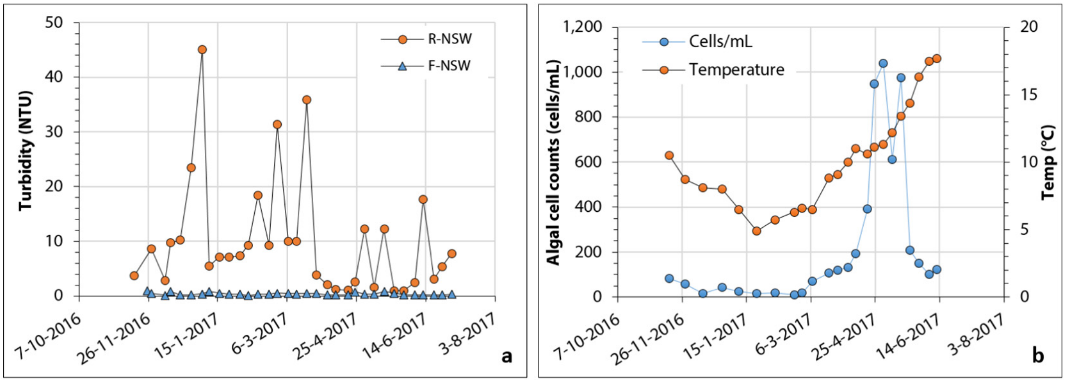

Fig. 12. Turbidity for raw NSW and filtered NSW (a) and algal cell counts and temperature of raw NSW (b) (n = 3 per sample).

particles (C_b) and also is influenced by the properties of the particles forming the cake layer expressed as specific cake resistance (α) (particle density, particle size, cake porosity) as illustrated by the Carman-Kozeny equation (Eq. (4)), the $MFI_{0.45}$ reflects more adequately than the SDI the variations of particulate fouling in North Sea water, whether or not the water has been filtered.

Considering an average size of algal cells of 10 µm, the maximum algal concentration measured in our work (1039 cell/mL), a porosity equal to 0.4 and sphericity value of 1 [15], the calculated MFI value using Eq. (6) (MFI for algal suspensions) is $< 0.1\ s/L^2$. This indicates that the contribution of algal cells to the fouling potential is very low. Our calculations confirm reported MFI values for pure algal suspensions with much higher concentrations where the MFI values are in the range 10–20 s/L^2 [15,26]. It is most likely that the fouling potential reported in our measurements originates from algal organic matter [15] and particulate material present in the water.

Based on the theoretical model for particulate fouling of RO systems presented in Section 1.3 we have predicted the fouling rate in RO systems based on the measured MFI values for filtered NSW. The period outside the algal bloom has an MFI value equal to $18\ s/L^2 \pm 7\ s/L^2$, while the maximum value during the algal bloom was about $170\ s/L^2$. The projected rate of fouling during the algal bloom period was about 0.06 bar/month increase in net driving pressure; or if we calculate the time for 1 bar pressure increase in NDP, the time would be about 17 months. As expected the $MFI_{0.45}$ values yield very low fouling rates in RO due to the large pore size of the filter.

The first part of the study has shown that the filter materials influence both SDI and $MFI_{0.45}$ measurements. The type of support plate of the filter holder is affecting $MFI_{0.45}$ but not SDI. As shown by the monitoring of North Sea water, the $MFI_{0.45}$ is more sensitive to monitor seawater quality variation. In order to limit the effect of the filter material on the $MFI_{0.45}$ measurement, we recommend to be consistent with using always the same filter material. To limit the effect of the support plate of the filter holder, a correction for the effective membrane area of the filter is necessary. We recommend the use of porous filter supports in the filter holder when performing an SDI and MFI test. The $MFI_{0.45}$ results of R-NSW and F-NSW have been used to predict the fouling rate of UF and RO systems. The predicted values are not sensitive enough as for matching real UF and real RO operation. For improving the predictive value of the MFI, it has been suggested by previous studies to use ultrafiltration membranes in the MFI test.

4. Conclusions and recommendations

The type of support plate of the filter holder influences the measurements of clean water flux, membrane resistance, and $MFI_{0.45}$. This effect can be controlled by correcting the effective membrane area of the filter. Porous support needs to be compared with the tested filter holders. SDI was not affected by the type of support of the filter holder. This is different from what was found by other researchers who obtained large differences in SDI values between filter holders but not an important influence in MFI values [9]. This could be explained by the

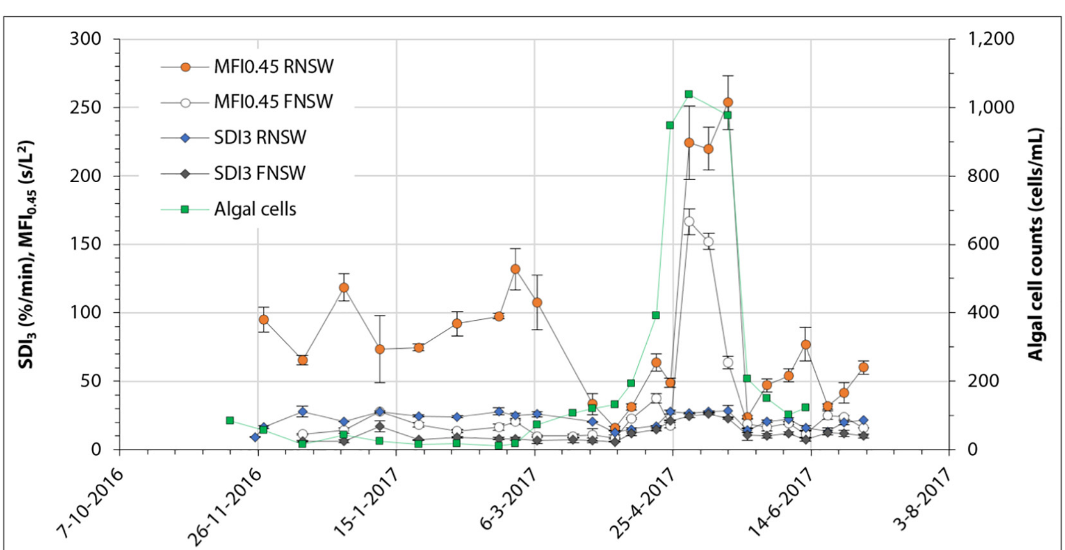

Fig. 13. SDI_3 and $MFI_{0.45}$ values of raw NSW and filtered NSW versus algal cell counts (n = 3). CA filter. FH4.

fact that the values measured in our study are in the range of 15.2–21.6%/min for SDI_3 and 247–492 s/L^2 for MFI, while in the study of Nahrstedt et al. [9] the range of values is 0.8–4.2%/min for SDI_{15} and 0.1–2.5 s/L^2 for MFI. The differences in sensitivity to the filter holder obtained between SDI and MFI could thus be dependent on the type of foulant.

The filter material influences the measurements of SDI and $MFI_{0.45}$. Different materials yielded different SDI and $MFI_{0.45}$ values. No correlation was found between the membrane resistance and the SDI and MFI values. This might be due to properties of the filters that we tested, with R_m values in the range recommended by ASTM and also with narrower R_m variation, in comparison with other studies [7] where the filters with high R_m influenced greatly the reported correlation.

North Sea water was monitored between November 2016 and July 2017. Raw NSW had 6–8 times higher $MFI_{0.45}$ values than the 2 μm filtered NSW. SDI values were reduced by a factor 3 only namely from around 25%/min to approximately 8%/min due to the 2 μm filtration.

The results of monitoring North Sea water indicate that $MFI_{0.45}$ is more sensitive parameter than SDI for assessing changes in particulate fouling potential in particular during algal growth.

For dealing with the measured differences in results obtained by different membrane (materials) manufacturers' and differences in filter holders, we recommend to following: *i*) using always the same filter material to avoiding inevitable differences and also for comparing data, *ii*) using always the recommended porous support prescribed by ASTM in the $MFI_{0.45}$ test. Additionally, as the SDI and $MFI_{0.45}$ can be measured with help of the same equipment, more alignment in the ASTM protocols for both methods is recommended. We recommend the desalination sector to measure the $MFI_{0.45}$ together with the SDI and eventually to abandon the SDI as the ultimate parameter for assessing RO feed water quality. Finally, due to the low sensitivity of the MFI measured with 0.45 μm filters, we recommend the implementation of other fouling indices such as the MFI-UF with membranes down to 10 kDa or less.

Nomenclature

A_m	membrane area [m^2]
R_m	membrane resistance [m^{-1}]
SDI	silt density index [%/min]
$MFI_{0.45}$	modified fouling index [s/L^2]
ΔP	applied pressure [Pa]
ΔP_0	applied pressure at 2 bar [207 kPa]
$t_{1,2}$	time to collect the first and second samples [s]
t_f	elapsed filtration time [15 min or 900 s]
V	filtered volume [m^3]
$V_{1,2}$	sample volume [m^3]
%P	plugging ratio [%]
NTU	nephelometric turbidity units [−]
J	flux [L/m^2/h]
DOC	dissolved organic carbon [mg/L]
SUVA	specific UV absorbance [L/mg/m]
EC	electrical conductivity [mS/cm]
LOD	limit of detection
I	fouling index [m^{-2}]
C_b	concentration of particles per unit volume of filtrate [kg/m^3]
d_p	particle diameter forming the cake [m]
Δx	membrane thickness [m]
r	radius of the pore size [m]

Greek letters

α	specific cake resistance per unit weight [m/kg]
η	water dynamic viscosity [Ns/m^2]
η_{20}	water dynamic viscosity at 20 °C [Ns/m^2]
ε	porosity of the cake [−]
τ	membrane tortuosity [−]
ρ_p	density of the particles forming the cake [kg/m^3]

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.desal.2018.12.006.

References

[1] DesalData, Global Water Intelligence (Ed.), IDA Desalination Plants Inventory, 2018.
[2] ASTM D4189 - 14, Standard Test Method for Silt Density Index (SDI) of Water, ASTM International, West Conshohocken, PA, 2014.
[3] ASTM D8002 - 15, Standard Test Method for Modified Fouling Index (MFI-0.45) of Water, ASTM International, West Conshohocken, PA, 2015.
[4] J.C. Schippers, J. Verdouw, The modified fouling index, a method of determining the fouling characteristics of water, Desalination 32 (1980) 137–148.
[5] S. Allgeier, B. Alspach, J. Vickers, USEPA (Ed.), Membrane Filtration Guidance Manual (EPA 815-R-06-009), USEPA, Cincinnati, 2005.
[6] M. Badruzzaman, N. Voutchkov, L. Weinrich, J.G. Jacangelo, Selection of pretreatment technologies for seawater reverse osmosis plants: a review, Desalination 449 (2019) 78–91.
[7] A. Alhadidi, A.J.B. Kemperman, J.C. Schippers, M. Wessling, W.G.J. van der Meer, The influence of membrane properties on the Silt Density Index, J. Membr. Sci. 384 (2011) 205–218.
[8] A. Mosset, V. Bonnelye, M. Petry, M.A. Sanz, The sensitivity of SDI analysis: from RO feed water to raw water, Desalination 222 (2008) 17–23.
[9] A. Nahrstedt, J. Camargo Schmale, New insights into SDI and MFI measurements, Water Sci. Technol. Water Supply 8 (2008) 401–412.
[10] A. Alhadidi, B. Blankert, A.J.B. Kemperman, J.C. Schippers, M. Wessling, W.G.J. van der Meer, Effect of testing conditions and filtration mechanisms on SDI, J. Membr. Sci. 381 (2011) 142–151.
[11] A. Alhadidi, A.J.B. Kemperman, B. Blankert, J.C. Schippers, M. Wessling, W.G.J. van der Meer, Silt Density Index and Modified Fouling Index relation, and effect of pressure, temperature and membrane resistance, Desalination 273 (2011) 48–56.
[12] J.C. Schippers, S.G. Salinas Rodriguez, S.F.E. Boerlage, M.D. Kennedy, Why MFI is edging SDI as a fouling index, Desalination & Water Reuse, Faversham House With the Cooperation of the International Desalination Association, UK, 2014, pp. 28–32.
[13] S.F.E. Boerlage, M.D. Kennedy, M.P. Aniye, E.M. Abogrean, D.E.Y. El-Hodali, Z.S. Tarawneh, J.C. Schippers, Modified Fouling Index ultrafiltration to compare pretreatment processes of reverse osmosis feedwater, Desalination 131 (2000) 201–214.
[14] P.C. Carman, Fundamental principles of industrial filtration (a critical review of present knowledge), Trans. Inst. Chem. Eng. 16 (1938) 168–188.
[15] L.O. Villacorte, Algal Blooms and Membrane Based Desalination Technology, CRC Press/Balkema, Leiden, 2014.
[16] S.F.E. Boerlage, M. Kennedy, Z. Tarawneh, R.D. Faber, J.C. Schippers, Development of the MFI-UF in constant flux filtration, Desalination 161 (2004) 103–113.
[17] S.G. Salinas Rodríguez, Particulate and Organic Matter Fouling of SWRO Systems: Characterization, Modelling and Applications, CRC Press, Balkema, Delft, 2011.
[18] S.G. Salinas Rodríguez, M.D. Kennedy, G.L. Amy, J.C. Schippers, Flux dependency of particulate/colloidal fouling in seawater reverse osmosis systems, Desalin. Water Treat. 42 (2012) 155–162.
[19] E.M.V. Hoek, M. Elimelech, Cake-enhanced concentration polarization: a new fouling mechanism for salt-rejecting membranes, Environ. Sci. Technol. 37 (2003) 5581–5588.
[20] A.H. Taheri, L.N. Sim, T.H. Chong, W.B. Krantz, A.G. Fane, Prediction of reverse osmosis fouling using the feed fouling monitor and salt tracer response technique, J. Membr. Sci. 475 (2015) 433–444.
[21] L.N. Sim, Y. Ye, V. Chen, A.G. Fane, Investigations of the coupled effect of cake-enhanced osmotic pressure and colloidal fouling in RO using crossflow sampler-modified fouling index ultrafiltration, Desalination 273 (2011) 184–196.
[22] S.G. Salinas Rodríguez, G.L. Amy, J.C. Schippers, M.D. Kennedy, The Modified Fouling Index Ultrafiltration Constant Flux for assessing particulate/colloidal fouling of RO systems, Desalination 365 (2015) 79–91.
[23] J. Downing, Turbidity Monitoring, Chapter 24, Environmental Instrumentation and Analysis Handbook, John Wiley & Sons, 2005, pp. 511–546.
[24] NEN, Water - Spectrophotometric Determination of Chlorophyll-A Content (NEN 6520:2006), NEN, Netherlands, 2006, p. 12.
[25] M.A. Darwish, H.K. Abdulrahim, A.S. Hassan, B. Shomar, Reverse osmosis desalination system and algal blooms part I: harmful algal blooms (HABs) species and toxicity, Desalin. Water Treat. 57 (2016) 25859–25880.
[26] N. Dhakal, S.G. Salinas-Rodriguez, A. Ouda, J.C. Schippers, M.D. Kennedy, Fouling of ultrafiltration membranes by organic matter generated by marine algal species, J. Membr. Sci. 555 (2018) 418–428.