Desalination and Water Treatment
www.deswater.com

18 (2010) 187–191
June

doi: 10.5004/dwt.2010.1769

Comparison of fouling indices in assessing pre-treatment for seawater reverse osmosis

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Received 1 June 2009; Accepted 21 December 2009

ABSTRACT

In this study, different processes such as flocculation with ferric chloride ($FeCl_3$) and deep bed filtration (sand filtration and dual media filtration) as a pre-treatment were used for seawater desalination. The performance of these pre-treatments was determined in terms of silt density index (SDI) and modified fouling index by using microfilter (MF-MFI), ultrafilter (UF-MFI), and nanofilter (NF-MFI) membrane. MFI and SDI indicated that deep bed filtration with in-line flocculation was better pre-treatment than flocculation alone as colloidal particles are removed after this pretreatment. UF-MFI and NF-MFI indicated that these pretreatment cannot remove dissolved organic matter as the fouling reduction was smaller. Detailed molecular weight distribution (MWD) of seawater organic matter was examined after different pretreatments. MWD of the initial seawater mainly ranged from 1510 Da to 130 Da. Deep bed filtration with in-line flocculation removed relatively large molecular weight of organic matter (1510–1180 Da), while the small molecular weights (less than 530 Da) were not removed.

Keywords: Fouling index; Pre-treatment; Seawater desalination; Reverse osmosis

1. Introduction

Recent advances in membrane technology have led to broad application, and reverse osmosis (RO) systems now represent the fastest growing segment of the desalination market. Nevertheless the operation of membrane-based desalination plants still remains complex mainly due to membrane fouling. Membrane fouling can be classified as particulate/colloidal or organic fouling. Both particulate/colloidal and organic fouling can be controlled by pre-treatment. As a result, good pre-treatment of seawater can provide good quality of feed water for the RO desalination plant. A relative and a simple method to evaluate the pre-treatment is essential. Fouling indices can be a good indicator to compare different pretreatments.

There is a sustained interest in suitable bench-scale methods that are able to characterise feed water properties, predict membrane performances, and allow condition monitoring in plants. Among these, the Silt Density Index (SDI) is a standardised tool for the indication of the particulate content of feeds [1]. SDI determination involves filtering relatively low turbidity (<1 NTU) water through a 0.45 µm membrane at constant 30 psi (207 kPa) pressure, and measuring the rate of plugging by collecting a certain permeate volume (100–500 mL) and recording time intervals. The Silt Density can be determined relatively quickly with simple equipment but this method has many shortcomings. It requires large sample volumes, and the reported indices substantially

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vary with equipment and the skills of operators [2]. Various studies [3–5] emphasised that SDI tests do not correlate well with RO membrane fouling. The index values show an exponential relationship with the mass of captured particles [6], thus measurement errors tend to increase with SDI values. A recent improvement to the SDI method [7] allows data normalisation and establishes meaningful comparisons. Instead of using an exact reference time as set in the standard, the improved SDI is determined from a number of discrete SDI values at exactly 75% plugging.

The Modified Fouling Index (MFI) was introduced by Ref. [8] to address shortcomings of SDI. This index is based on cake filtration for constant pressure where the increase of total resistance is attributed to cake formation on the membrane (Equation 1).

$$\frac{t}{V} = \frac{h \cdot R_m}{\Delta P \cdot A} + \frac{h \cdot a \cdot c_v}{2 \cdot \Delta P \cdot A^2} \cdot V \tag{1}$$

With

$$a = \frac{h \cdot R_m}{\Delta P \cdot A}, \quad MFI = \frac{h \cdot a \cdot c_v}{2 \cdot \Delta P \cdot A^2},$$

Equation 1 can be simplified to

$$\frac{t}{V} = a + MFI \cdot V \tag{2}$$

with membrane surface area, A, particle concentration, c_v, in feed water, particle diameter, dp, applied trans-membrane pressure, ΔP, flow rate, Q, membrane resistance, R_m, filtration time, t, filtrate volume, V, average specific cake resistance, a, and water viscosity, h.

The MFI is the value of the gradient of the linear section of the plot of t/V versus V, and reported after corrections to reference conditions.

The MFI 0.45 has been successfully used in the management of aquifer storage and recovery, using relatively turbid urban stormwater and organic reach feeds [9]. Since MF test membranes of 0.45 µm pore size do not take into account the fouling effect of colloids [10], the method was extended to use ultrafilter (UF) test membranes, named MFI-UF [11–12]. The MFI-UF with 13 kPa PAN test membranes was successfully used to characterise the fouling propensity of various feeds [13–14]. MFI-UF was evaluated to predict flux decline or pressure increase in RO systems [15–16], but the obtained results were not entirely satisfactory. It was suggested that MFI-UF determined at low constant fluxes would better simulate and predict RO membrane fouling [17]. The corresponding cake filtration index (constant flux MFI-UF) can be determined as the gradient of pressure increase with time. This index was measured within hours, substantially faster than the constant pressure MFI-UF, though there seem to be no reported uses. In discussing MFI, it was argued [18] that for the many feeds and cake filtration periods, a single number would not represent the evolution of fouling adequately.

All the above indices are measured in dead end filtration, whereas many plants use crossflow arrangement to reduce fouling and concentration polarization. Mosqueda-Jimenez et al., [19] evaluated various equipment used for UF and RO membrane tests, and concluded that dead-end cells gave significantly faster but different results than crossflow arrangement, thus their use was not recommended. Another approach proposed the selective removal of particles that are most likely to deposit and cause fouling in conditions that represent most RO processes [20]. This is accomplished by a cross flow sampler (CFS), in essence a membrane pre-filter employed upstream of a dead end MF fouling test cell. MFI values obtained after loose MF-CFS pre-filtration were significantly lower for standard dead-end MFI measurements but showed insignificant differences when tight MF/UF pre-filtration sampling membranes were used [21].

Khirani et al. [22] emphasized that many feeds have a significant fraction of small particles that pass through ultrafilters. Nanofiltration (NF) test membranes reject such small particles and also some solutes, and account for them in an MFI-NF index. It was proposed that a well-chosen loose NF membrane might provide effective foulant retention yet allow salt passage to avoid undesirable osmotic effects. Their method is practical, as it requires only about one hour to complete the measurement. However the choice of a standard NF membrane with high organic rejection and low salt rejection remains unresolved.

In this study the above mentioned fouling indices were applied to compare their effectiveness to assess pre-treatments. Different pre-treatments to seawater reverse osmosis (SWRO) were compared in terms of fouling potential. Fouling indices such as MF-MFI, UF-MFI, NF-MFI, pore blocking index (S_{pb}) and 15 minutes SDI (SDI_{15}) were measured and compared in order to study their suitability in comparing efficiency in terms of fouling reduction.

2. Materials and methods

2.1. Fouling indices measurement

The MFI of feed water was determined with a test membrane placed in a dead-end filter holder (membrane cell). The feed was conveyed from a 10 L Sartorius pressure vessel to the membrane at constant pressure provided from a nitrogen gas cylinder via a pressure regulator. All parts in contact with water are made of stainless steel and PTFE material. Permeate flow was measured with analytical balances (10 mg and 100 mg classes). Measured permeate mass, time, and temperature were

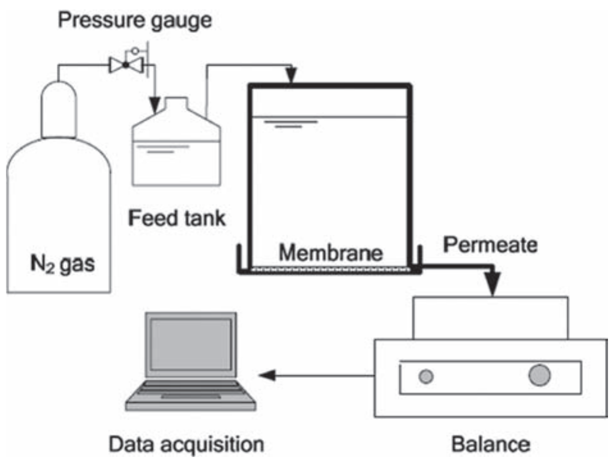

Fig. 1. MFI experimental setup.

Table 1
Characteristics of MF, UF and NF membranes used.

Code	Material	MWCO* (daltons)
NTR 7410	Sulfonated polysulfones	17500
NTR 729 HF	Polyvinylalcohol/ polyamides	700
MF	Cellulose acetate	0.45 μm

*Molecular weight cutoff.

logged and displayed on a connected computer. Index values were determined from post-processed data, and corrected to reference conditions.

The characteristics of MF, UF and NF membranes used are given in Table 1.

2.2. Pore blocking index

Sometimes cake filtration does not give an exact prediction of fouling behaviour so, the pore blocking index was also measured and considered for prediction of the fouling behaviour of the feed water. This could be explained by the fact that the colloidal fraction plays an important role in pore blocking as in the resistance of the cake. Flocculation and adsorption were more efficient than MF for decreasing the MFI (cake filtration index) and S_{pb} (pore blocking index). Membranes with smaller molecular weight cutoffs are being tested and will allow a more precise comparison of the efficiency of the pretreatment related to pore blocking phenomena.

The pore blocking slope was determined from the gradient of the general filtration equation at constant pressure using a plot of t/V versus t.

$$\frac{t}{v} = S_{pb}t + b \tag{3}$$

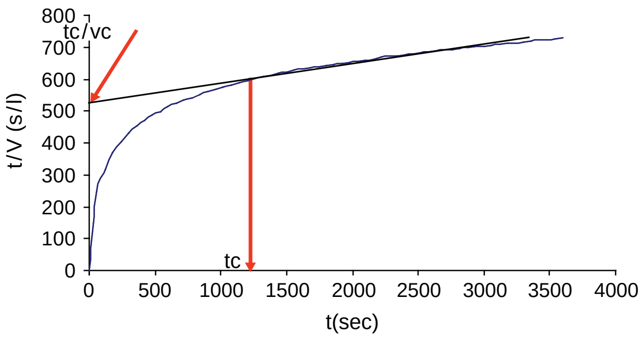

Fig. 2. t (time)/v (permeate volume) vs. t for feed water.

where,
v = total permeate volume (L)
t = filtration time (s)
S_{pb} = pore blocking slope by critical time – pore blocking index ($1/L$)
b = constant

Here, vc and tc are defined as the critical values above which we could obtain a linear relation between t/v and t.

S_{pb} was obtained from the slope of the straight line between t/v and t (from $t = 0$ to the critical point) (Fig. 2).

2.3. Molecular weight distribution (MWD) of organic matter

The seawater effluent after each pre-treatment was subjected to MWD measurement to investigate seawater organic matter (SWOM) removal. High pressure size exclusion chromatography (HPSEC, Shimadzu Corp., Japan) with a SEC column (Protein-pak 125, Waters Milford, USA) was used to determine the M_w distributions of SWOM (Fig. 3). Standards of M_w of various polystyrene sulfonates (PSS: 210, 1800, 4600, 8000, and 18000

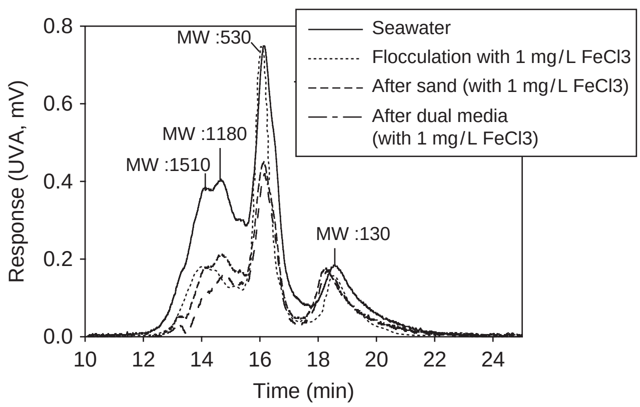

Fig. 3. MWD of SWOM (seawater organic matter) after different pretreatments.

Table 2
Comparison of different pre-treatment efficiency in terms of different fouling indices.

Types of feed water	SDI_{15}	S_{pb} (1/L)	MF-MFI (s/L2)	UF-MFI (s/L2)	NF-MFI (s/L2)
Seawater after MF alone	~5.8	0.22	214–256	22829	5E+08
Effluent from sand filter with 1 mg/L $FeCl_3$ flocculation	2	0.01	1.8	15228	1E+07
Effluent from dual media (sand+anthracite) with 1 mg/L $FeCl_3$ flocculation	1.9	0.01	<1	12949	4E+06

daltons) were used to calibrate the equipment. The weight-averaged molecular weight can be calculated from the following equation,

$$M_w = \sum_{i=1}^{n}\left(N_i M_i^2\right) \Big/ \sum_{i=1}^{n}\left(N_i M_i\right) \tag{4}$$

Where N_i is the number of molecules having a M_w of M_i and i is an incrementing index over all M_w present.

2.4. Pre-treatment

In this study, the following pre-treatment methods were used.

2.4.1. Deep bed filtration

Sand and dual media (sand and anthracite) filtrations were used as media for depth bed filters. The filter depth was kept at 80 cm for both the sand filter and the dual media filter. The velocity of the effluent was maintained at 10 m/h. Both media filters were operated for 6 hrs. The effluent was collected and different fouling indices were measured when turbidity removal became constant. Ferric chloride ($FeCl_3$) of 1 mg/L was used as inline flocculant.

3. Results and discussion

With the pre-treatment of contact flocculation-filtration of colloidal matter, it was possible to remove the colloidal particles; therefore the SDI_{15}, S_{pb} and MF-MFI values were lower after the pre-treatment. The SDI values decreased from 5.8 to 2 after flocculation followed by filter media pre-treatment. The same trend was observed in the values of S_{pb} and MF-MFI. The NF-MFI value decreased by 50–100 times when a pre-treatment of contact flocculation-filtration was provided. The higher decrease in NF-MFI was due to dissolved organic matter which was noted in the molecular weight distribution results.

3.2. Molecular weight distribution of seawater organic matter after different pretreatment

The MWD of SWOM in seawater was measured after each pre-treatment. The M_w of the untreated seawater ranged from about 1510 Da to 130 Da. Typical M_w peaks for the seawater was found at around 1510 Da, 1180, 530 and 130 (Fig. 3).

The M_w fraction of 1510 Da, 1180 Da, 530 and 130 Da found in this study represents fulvic acids I, fulvic acids II, low M_w acids (hydrolysates of humid substances), and amphiphilics, respectively (Source: http://www.doclabor.de/english_pages/Applications/Marine_Water/body_marine_water.html). Fig. 3 shows the MWD of SWOM with and without pre-treatment. All pre-treatments used in this study removed fulvic acids type organic compounds that are responsible for membrane fouling. In this study, flocculation with 1 mg/L $FeCl_3$ removed the majority of large M_w SWOM (1510–1180 Da) as observed in Ref. [23]. However, flocculation could not remove the small range of M_w (530–130 Da). Furthermore, deep bed filtration with inline coagulation removed both the large M_w (1510–1180 Da) and the majority of small M_w compounds (530 Da).

4. Conclusion

It is important to study the relationship between different fouling indices to identify the representative index for assessing the efficacy of the pre-treatment. The performance of these pre-treatments was determined in terms of silt density index (SDI) and modified fouling index by using microfilter (MF-MFI), ultrafilter (UF-MFI), and nanofilter (NF-MFI) membrane. MFI and SDI indicated that deep bed filtration with in-line flocculation was better pre-treatment than flocculation alone as colloidal particles are removed after this pretreatment. UF-MFI and NF-MFI indicated that these pretreatment cannot remove dissolved organic matter as the fouling reduction was smaller. In terms of detailed molecular weight distribution (MWD) of seawater organic matter, deep bed filtration with in-line flocculation removed relatively large molecular weight of organic matter (1510–1180 Da), while the small molecular weights (< 530 Da) were not removed. Correlating different fouling indices will give more complete information of the filtration phase with respect to fouling and provide extra information that are missed in a single MFI or SDI value.

Acknowledgement

This research is funded by Australian Research Council discovery grant (DP0772690).

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