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Colloidal fouling of RO membranes: an overview of key issues and efforts to develop improved prediction techniques

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Abstract

One of the most important considerations in applying membrane technology is the inevitable fouling of membranes which has very serious operational, economic and environmental implications. To select an appropriate pretreatment scheme and to optimize the design of membrane desalination plants, one needs reliable estimates of feed water fouling propensity. The currently employed tools for such predictions (e.g. SDI—Silt Density Index) are widely considered inadequate. An account is presented of the complex problem of colloidal fouling of desalination membranes and filtration membranes in general. The multitude of colloidal species, factors and synergisms that may be potentially harmful to membrane operation are discussed and the complicated subject of understanding and modeling colloidal fouling is touched upon with the aim of highlighting key issues and current trends. Reports from the scientific literature on operational experience of membrane processes are also reviewed. On the basis of this discussion, the problems associated with current practices for colloidal fouling assessment are highlighted and an approach for developing improved prediction techniques is outlined. Additionally, experiments carried out in this Laboratory are presented on RO membrane colloidal fouling. Two kinds of reference fouling species are tested, i.e. humic acids and iron oxide as typical organic and inorganic foulants, respectively. In parallel, SDI measurements are performed with feed waters similar to those in the fouling tests. A range of fouling species concentrations is observed, over which a linear relationship prevails between concentration and fouling rate. On the basis of such a relationship, projections of membrane performance for fouling species concentrations encountered in practice and an assessment of SDI predictions may be made. It is observed that the SDI exhibits a significant sensitivity with particles for which retention in the test microfilter is negligible. However, the new RO fouling data obtained suggest that the SDI may not be conservative enough.

Keywords: RO membranes; Colloidal fouling; Organic fouling; Iron oxide colloidal particles; Humic acids; Silt density index

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1. Introduction

1.1. Colloidal species and membrane fouling

According to Potts et al. [1] and references cited therein, particulate matter in natural waters and waste waters can be classified as settleable solids (>100 μm), supra-colloidal solids (1 μm to 100 μm), colloidal solids (.001 μm to 1 μm) and dissolved solids (<.001 μm). The above cut-offs are more or less arbitrary and different values are set by different authors. The chemical composition of particulate solids is of a wide variety and a major distinction is between inorganic and organic matter. The most common inorganic particles are aluminum silicate clays, ranging in size between 0.3 and 1 μm, and colloids of iron, aluminum and silica. Organic particles include proteins, carbohydrates, fats, oils and greases, and various surfactants. Polyphenolic aromatic complexes such as humic acids, lignin and tannin are decay products of woody tissues of plants and often occur as very small colloids. Polysaccharides that constitute cell walls of microorganisms and plants are also prominent. Some of the types of colloids that exist in natural waters, especially in the sea, are listed in Table 1 [2].

Dissolved or dispersed materials can potentially deposit on membranes and brine flow channels and interfere with membrane operation. Solubility limits of dissolved salts may be exceeded in the brine (which is typically concentrated 2–5 times) and precipitation on the membranes or in the bulk may occur. Calcium carbonate, sulfates of calcium, barium and strontium, and calcium fluoride are the most common examples. Particulate matter, preexisting or not, can agglomerate and adhere to the membranes due to increased concentration, salinity, compaction, flocculation, surface interactions and other physical and chemical factors. Ferric, aluminum and manganese hydroxides and silica grow through polymerization and bridging with organic and inorganic matter and form gels on membranes. Aromatic acids, such as humic acids, often present as very small colloids, become unstable and are more likely to foul as the pH of the feed waters is lowered and brine salinity increases. Biotic debris such as polysaccharides and dead cellular matter contribute greatly to membrane fouling. Synthetic polymers used in water pretreatment such as antiscalants and dispersants can also deposit on membranes. It is clear therefore that the distinction between *colloidal*, *organic*, *biological* and *precipitation fouling* of membranes is not sharp but there exists a certain degree of overlap. However, this distinction is a useful one since methods of fouling prediction, prevention through pretreatment and operating measures, as well as fouling deposit removal through cleaning, are categorized in the same manner.

Table 1
Colloidal matter in natural waters

Microorganisms
Biological debris (plant and animal)
Polysaccharides (gums, slime, plankton, fibrils)
Lipoproteins (secretions)
Clay (hydrous aluminum and iron silicates)
Silt
Oils
Kerogen (aged polysaccharides, marine snow)
Humic acids, lignins, tannins
Iron and manganese oxides
Calcium carbonate
Sulfur and sulfides

1.2. Key issues and parameters in colloidal fouling

Despite a significant amount of research efforts and numerous papers published on colloidal fouling of membranes (mainly MF and UF) a comprehensive theory to quantitatively predict the fouling effects is not available. However, significant progress has been made over the years to identify the important parameters determining the fouling behavior of colloidal particles. An assessment of modelling of colloidal fouling is made elsewhere [3]. Two such important operational parameters are the *fluid shear* at the membrane surface and the *permeation flux*. These parameters control the length of membrane required for concentration polarization effects to become important, which is roughly proportional to shear rate but inversely proportional to permeation flux cubed. Hence, it is important to recognize that increasing the shear rate and permeation flux by proportional amounts would not cancel out their effects on fouling. The significant effect of permeation flux is consistent with membrane manufacturer recommendations to maintain lower membrane specific flux at higher SDI (Silt Density Index) values. It also has led to the concept of "critical flux", associated with a sharp increase of concentration polarization and fouling. Turbulence promoted by the membrane spacers in spirally wound elements generally assists in reducing concentration polarization. Yet, it must be kept in mind that the shear field is inhomogeneous and deposition may be more severe near the points where the spacer contacts the membrane, yielding a deposit distribution pattern similar to the spacer geometric pattern.

Another crucial issue in colloidal fouling is the *physicochemical interactions* between the suspended colloids as well as between colloids and membrane. Provided that concentration polarization effects are minimized (which is likely with RO membranes having fluxes usually much smaller than UF or MF membranes) these interactions determine the efficiency of attachment of particles on the membranes, and may be controlled to advantage. Indeed, many examples exist of better performance of charged membranes with charged particles or hydrophilic UF membranes with organic foulants. But even if concentration polarization effects exist, still the colloidal interactions are important in determining the back-transport properties of the concentrated colloidal layers near the membrane surface. It is usually demonstrated in colloidal fouling experiments, and also theoretically predicted, that during the initial stages flux decline follows standard cake filtration behavior. With highly stable colloids a steady state is fairly rapidly approached, whereas when stability is reduced more deposition and continuing gradual flux decline occur. Colloidal stability is usually promoted by significant particle charge (absolute value of ζ-potential >30 mV [4]) and it is recognized in manufacturers recommendations by setting less strict SDI limits. However, it must be pointed out that the ionic environment (which determines or influences particle charge and stability) is not uniform in an RO array, since salt concentration in the brine increases along the membrane. It increases even more near the membrane surface due to rejected salt concentration polarization. Particle charge may also change in concentrated dispersions, such as the concentration polarized particle layers. It is finally noted that the charge of naturally occurring colloids and organic molecules, which is usually negative, decreases as the pH is lowered. Thus, the usual practice of lowering pH to reduce the scaling potential due to calcium salts may reduce stability and promote colloidal fouling.

1.3. Critique of the SDI and related indices

The most common and widely accepted tool for prediction of colloidal fouling is the SDI. Other indices are the MFI (Modified Fouling Index), which was developed in the Netherlands [5] and gained acceptance mainly there, and the MPFI (Mini Plugging Factor Index). All three are based on batch filtration of feed waters through a 0.45 μm Millipore microfilter. Recently, the MFI-UF has been introduced which employs ultrafiltration membranes instead of the Millipore microfilter. Other measurements, such as turbidity, particle counts, and particle electrophoretic mobility are also employed, but are not accepted as reliable tools for fouling prediction.

Membrane manufacturers recommend that SDI should not exceed 4 or 5 and set limits of membrane productivity depending on the SDI (i.e. 8–14 gfd for SDI 2–4, 14–18 gfd for SDI <2 and 20–30 gfd for SDI <1). However, despite the wide acceptance of the SDI in the RO industry, cases of poor correlation with fouling propensity are not rare. Moody et al. [6] and Kaakinen and Moody [7] reported severe colloidal fouling problems in RO membranes treating feed waters with SDI less than 1. A meticulous foulant component study with two different RO membranes revealed that colloidal fouling (due mainly to clay sized particles) accounted for 20–80% of flux decline, organic fouling for 20–40% and membrane compaction for 0–20% [7]. Colloidal fouling was more severe with the higher flux membranes although the ratio between cross-flow and permeation flux was kept constant in the two different membranes. On the other extreme, cases of economic viability of RO desalination with feed waters having SDI greater than 5 have been also reported [1]. Lipp et al. [8] compared SDI and membrane performance in a test rig by artificially increasing the concentration of inorganic and organic foulants. No clear correlation of SDI and fouling behavior was found. Furthermore, increasing the concentration of inorganic foulants beyond a limit resulted in smaller fouling indices, a trend which was not reflected in the fouling behavior. Paasen et al. [9] reported severe colloidal fouling problems in a NF pilot plant due to iron oxides although standards were met (Fe <0.3 mg/L and MFI <3 s/L^2). Similarly, Butt et al. [10] reported severe colloidal fouling mainly due to iron and silica, which limited useful membrane life to 2 years in a commercial RO desalination plant. A synergistic effect in the presence of iron and aluminum oxides is known to exist which promotes silica precipitation at concentrations below the solubility limit [11]. Sung et al. [12] measured quality parameters (color, turbidity and TOC), as well as fouling indices (SDI, MFI and MPFI) for nine Florida groundwaters. The MFI correlated better with the quality parameters but the correlations were not strong. Furthermore, predictions of the decay rates in the membrane mass transfer coefficient (MTC) were close to actual decay rates in only two cases, whereas for surface waters the predictions were off by several thousand percent.

It should be emphasized that the SDI test is, strictly speaking, an empirical one and a very poor simulation of actual RO conditions. The absence of actual membrane–foulant interactions, the absence of shear (as opposed to the operation of cross-flow membrane modules), the significantly higher permeation rate (>1 cm/s in the filter vs. <.001 cm/s in RO membranes), and the doubtful rejection of particles smaller than 0.45 μm (nominal pore size of the filter) are the most important concerns. These poorly rejected particles are more likely to foul a membrane, since the resistance of a cake layer is inversely proportional to the square of particle size. Schippers et al. [13] state that particles smaller than 0.05 μm are responsible for flux decline in reverse osmosis membranes. Another criticism is that the index is not linearly related to colloid particle concentration, and does not distinguish between fouling mechanisms during the test (pore blocking, cake filtration, cake consolidation).

With regard to other indices, considerable attention has been given to the MFI. This index is measured with the same equipment under the same conditions and is based on filtered volume measurements every 30 s. The part of the filtration curve which corresponds to cake filtration is used for the determination of the MFI. Some recommendations on MFI and MPFI are shown in Table 2.

It is commonly believed that the newer RO membranes, operating at lower pressures and having higher specific fluxes, as well as NF membranes are more sensitive to fouling compared to the conventional cellulose acetate based membranes. Since the relative resistance of deposited material to that of the clean membrane may determine the degree of fouling, part of this sensitivity must be attributed to the lower resistance of the above membranes. Thus, it is rather surprising that the recommendations are less strict for NF membranes. Linearity of the MFI with colloid concentration has been demonstrated in several test cases. However, the problems of inadequately coping with the effect of shear, membrane interactions, fluxes and particles smaller than 0.45 μm still remain. Boerlage et al. [15] state that there exists a poor correlation of the SDI and MFI with colloidal fouling observed at RO and NF installations, and attributed this problem to colloidal particles smaller than 0.45 mm.

Over the past few years a great deal of work has been performed and significant progress made in Delft [16–19], which have led to the development of the MFI-UF. As in the case of MFI, the approach is to establish conditions of cake filtration during the test and obtain representative values of the fouling resistance of the cake formed on the membrane. Then, the target is to deduce the rate of fouling in actual NF or RO installations. Various UF membranes, with regard to material and MWCO have been screened. In this way the disadvantage of previous indices of inadequately coping with particles smaller than 0.45 μm has been addressed. The predicted fouling indices are dramatically higher due to retention of such particles in the new tests. Several important issues have been also taken into consideration in the experimental and theoretical developments. These include cake compressibility and the difference in operating pressures between the test and actual installations, incomplete particle deposition due to the presence of cross flow in RO/NF membrane modules, and the effects of changing conditions inside a membrane train (i.e. ionic strength and fouling species concentration). Additional work and validation are still required for this new fouling index to become established. For example, significant times are required for cake filtration conditions to be established in the tests. Also, the UF membrane modules need to be chemically cleaned and re-used. Thus, the MFI-UF test is more time consuming and costly. Concrete recommendations on MFI-UF limits or criteria have not been established yet. Moreover, the problems of membrane–foulant interactions, absence of shear and high permeation rates still need careful consideration.

Table 2
Fouling index recommendations for acceptable RO/NF operation [14]

Fouling index	Range(s/L^2)	Application
Modified fouling	0–2	RO
index	0–10	NF
Mini plugging	0–3 × 10^{-5}	RO
factor index	0–15 × 10^{-5}	NF

In fouling index modifications, such as the MFI-UF, the target is to obtain the resistance of the deposits formed under cake filtration conditions. However, comparing UF and RO membranes, even if all colloidal and hydrodynamic parameters were the same (i.e. flux, cross flow, membrane material), the fouling behavior would not necessarily be the same. This is not only due to the different pressures (and associated stresses within the fouling deposits) in the two processes, but also due to effects related to salt rejection by the RO membranes. The mechanism of rejected salt back-transport within the deposit of an RO membrane is different from that over a clean membrane (i.e. pure diffusion through a porous medium vs. convective diffusion). Thus, on a fouled RO membrane, additional concentration polarization builds up, and flux is affected by the associated osmotic pressure [20]. Such an effect cannot be captured by UF membranes. On the other hand, pore restriction and blockage are absent in RO membranes. However, such differences do not necessarily imply that a correlation of the fouling behavior of different membranes should not exist.

Similar views regarding the criticism on SDI and other fouling indices, including the MFI-UF, are shared by Rabie et al. [21]. As a more reliable alternative, these authors propose a procedure for extracting information from pilot plant data in order to predict the performance of real plants. Whereas, such an alternative is as close as possible to realistic conditions, it has a clear disadvantage in terms of time and cost. Thus, the development of reliable, rapid, and low-cost predictive tools still remains of great significance.

1.4. Research approach towards development of improved techniques

In this paper progress is reported on a research approach towards the improvement of fouling prediction techniques and practices, which consists of three steps:

a) To generate reliable RO fouling data in the laboratory under realistic, yet well controlled conditions.
b) To assess the performance of existing indices on the basis of the RO fouling data.
c) In parallel, to investigate variations or modifications of existing fouling indices towards the development of improved ones, by performing filtration experiments with a variety of membranes and conditions.

Fouling species representative of organic and inorganic RO membrane fouling were selected for testing in the first step above. As discussed before, organic fouling is a major category not only in membrane desalination, but also in numerous wastewater treatment applications involving membrane pre-treatment (MF, UF), which have emerged in recent years. Since such membranes do not adequately reject organic macromolecules, the issue of organic fouling is crucial. It should be mentioned that little information is given in the recommended criteria for the fouling propensity of organic foulant groups. The only quantitative information available for the assessment of organic fouling propensity is by measurement of the concentration of TOC in water, which can only provide a rough guidance for problems to be encountered. Natural organic matter (NOM) compounds are divided into the more hydrophobic humic substances or polyhydroxyaromatics, and non-humic such as proteins, polysaccharides and aminosugars [22–24]. Humic substances were selected for testing in this study since they constitute a significant fraction of NOM. Several fundamental studies of NF membrane fouling by humic acids exist, highlighting the effects of physicochemical parameters, such as pH, ionic strength and hydrophilicity of compounds and membranes, as well as operating conditions such as cross flow and permeation flux [25–27]. Many more studies of UF and MF membrane fouling exist, where effects of adsorption, pore constriction and blockage play a dominant role [28–32]. However, similar studies with RO membranes have not been performed.

Iron oxide was also selected in this study as a typical inorganic colloidal foulant, due to its importance as evidenced by the frequent appearance in membrane autopsies [2], and the specific reference in manufacturer recommendations [33–36]. Iron is encountered in two major forms. The water-soluble form is known as the ferrous state and has a +2 valence state. The solubility is limited by its carbonate [37,38]. Iron in the soluble Fe^{2+} form is rejected by RO membranes as effectively as any divalent ion. Fouling can occur, however, when hydrogen sulfide reacts with Fe^{2+} forming an insoluble black precipitate, ferrous sulphide. Soluble iron can be also oxidized into the more troublesome insoluble compounds, such as $Fe(OH)_3$, FeOOH and Fe_3O_4, by the introduction of air, e.g. after storage in tanks or through leaky pump seals. In the presence of strong oxidizing agents, such as chlorine, potassium permanganate and ozone, iron will oxidize readily even under acidic conditions. The solubility of Fe^{3+} is governed by the solubility of $Fe(OH)_3$, which is less than 1 ppb over a pH range of approx. 5–9. Typically, RO manufacturers recommend that combined iron levels should be less than 0.05 ppm in the RO feed. In the present experiments Fe^{3+} is introduced in the feed water and precipitates to form colloidal particles. Thus, the procedure followed simulates phenomena taking place in actual membrane installations and only skips the oxidation step of dissolved ferrous ions [38].

In the following section a laboratory scale experimental set-up is described, where filtration experiments are performed. Then, experimental results are presented of RO membrane fouling by species representative of organic and inorganic fouling, namely humic acids and iron oxide colloidal particles. Finally, an assessment of the performance of the SDI is performed on the basis of the RO fouling data obtained.

2. Experimental materials and methods

RO fouling experiments were performed in a laboratory unit with a narrow-gap channel-type of test section which employs flat sheet membrane pieces of active filtration area of 130 cm^2. A schematic diagram of the experimental set-up is shown in Fig. 1. A 30 L vessel contains the feed solution which is pressurized via a Grundfos CRNE 2 pump. Pressure and cross-flow rate are monitored through digital sensors and controlled through two needle valves at the

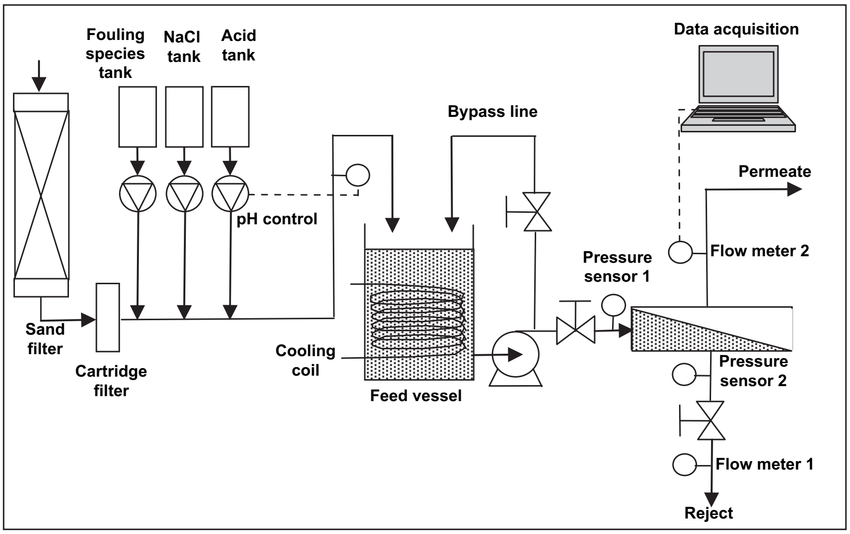

Fig. 1. Schematic diagram of the experimental set-up employed in the RO fouling experiments.

entrance and exit of the test section. Permeate flow is monitored through a Humonics 1000 digital flowmeter connected to a PC for automatic data acquisition. Temperature is controlled in the system through a cooling coil connected to a water cooler at 25 ± 0.1°C.

The type of membrane employed was a brackish-water RO membrane (Osmonics AG) in flat sheet form. In all the experimental runs a constant cross-flow rate of 0.5 L/min was maintained in the channel, which corresponds to an average velocity of 17 cm/s. This is in the same range of typical cross-flow velocities encountered in spirally wound RO membrane elements. The feed water flow rate in the feed vessel was 1.8 L/min, and thus the mean residence time of water and fouling species in the system was approx. 15 min. Feed water passed through a sand filter and a cartridge filter to reach an SDI close to 2 and a turbidity typically less than 0.1 NTU, whereas raw water has an SDI close to 4 and a turbidity close to 1 NTU.

It is frequently mentioned in the literature that a certain period of time is required for *membrane setting*, which refers to membrane adjustment to the pressure applied and to the ionic environment of the feed water. During this period, flux drops and rejection increases. This behavior was found to be largely independent of the type of feed water used (tap water, sand filtered tap water, deionized water, Nanopure water, RO water). In all the experimental runs 48 h or more were dedicated to membrane setting with clean feed water. Although flux drop was not completely eliminated it was reduced to about 0.2% per hour or less. A typical experimental run including membrane setting and fouling measurements lasted approximately one week. In the present experiments, open loop operation was established by continuous introduction and withdrawal of water and foulant in the system.

For the organic fouling experiments a commercial humic acid (Aldrich) was used. A concentrated solution in distilled water was injected to the feed water line. No dialysis or other treatment was performed in order to maintain the small MW compounds. In the iron fouling experiments, a stock $FeCl_3$ solution of appropriate concentration was injected in the feed stream at a rate of 10 mL/min and pH was adjusted to 7.

3. Results and discussion

3.1. Organic fouling experiments

Several experiments have been performed in order to explore the influence of fouling species concentration, feed water salinity and initial membrane flux. For this purpose, in a first set of experiments tap water was employed as is, with a TDS of 500 ppm. The initial membrane flux prior to fouling species introduction was close to 30 LMH. In a second set of experiments, a concentrated solution of NaCl (18% w/w) was injected in the feed in order to bring salinity up to 2000 ppm in TDS, and the flux was kept close to 27 LMH. In a third set of experiments with the same salinity, pressure was increased so that initial membrane flux was kept close to 40 LMH.

In preliminary experimental runs with humic acids no detectable flux decline could be discerned. Thus, in order to increase the aggregation tendency of humic acids and the efficiency of attachment to the membrane, calcium concentration was increased to 2 mM/L by injecting a concentrated solution of $CaCl_2$ to the feed water line. It is well known that calcium promotes intra- and inter-molecular bridge formation and aggregation of humic acids [32]. Typical raw data on membrane flux variation, before and after the introduction of humic acid, are shown in Fig. 2.

As can be observed, a clearly detectable decline of permeation rate, linear in time is

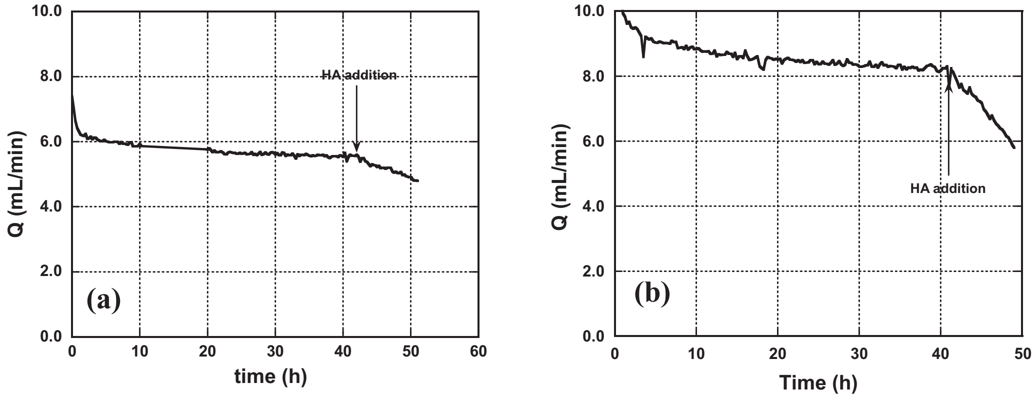

Fig. 2. Raw experimental data of permeate flow rate as a function of time before and after fouling species introduction. Feed water TDS: 2000 ppm; Humic acid concentration: 20 ppm; Pressure: (a) 116 psi, (b) 155 psi.

obtained. To extract fouling rates, the permeate flux rate is written as:

$$J = \frac{\Delta P}{R_m + R_f} \approx \frac{\Delta P}{R_m}\left(1 - \frac{R_f}{R_m}\right) \tag{1}$$

Here ΔP is the applied pressure, R_m the membrane resistance and R_f the fouling resistance. The fouling resistance is taken to be composed of two parts: one due to membrane setting effects (R_s), and another due to the deposition of the fouling species (R_d). Considering the short duration of the fouling tests and the small decline in flux prior to and after fouling species introduction, both terms can be assumed to be linear in time, i.e. $R_s = R_s{}'t$ and $R_d = R_d{}'t$. Then the above equation can be written

$$\begin{aligned} J &= \frac{\Delta P}{R_m}\left(1 - \frac{R_s' t}{R_m}\right), \text{ and} \\ J &= \frac{\Delta P}{R_m}\left[1 - \frac{R_s' t}{R_m} - \frac{R_d'(t - t_0)}{R_m}\right], \end{aligned} \tag{2}$$

for $t < t_0$, and $t > t_0$, respectively, where t_0 is the time when fouling species are introduced. From the raw data, the normalized flux decline variation can be obtained, as shown in Fig. 3.

The analysis of the three sets of experimental data is presented in Table 3.

Finally, the fouling resistance coefficient, $R_d{}'$, as a function of fouling species concentration is shown in Fig. 4. A clear effect of fouling species concentration on the fouling rate can be observed. The linear relationship obtained may be used to predict the fouling rate at lower concentrations with a satisfactory degree of confidence. It may be also observed that the initial membrane flux has a clear effect on the rate of fouling since it affects the rate at which fouling species are brought to the membrane surface.

3.2. Inorganic fouling experiments

In a first set of experiments membrane flux prior to fouling species introduction was kept close to 8×10^{-4} cm/s (or 28 LMH or 17 gfd), which is representative of membrane fluxes typically encountered in RO applications. Tap water was employed as is, with a TDS of 500 ppm. In a second set of experiments, a concentrated solution of NaCl (18% w/w) was injected in the feed in order to bring salinity up to 2000 ppm in TDS. Finally, in a third set of experiments with the same salinity, pressure was increased so that

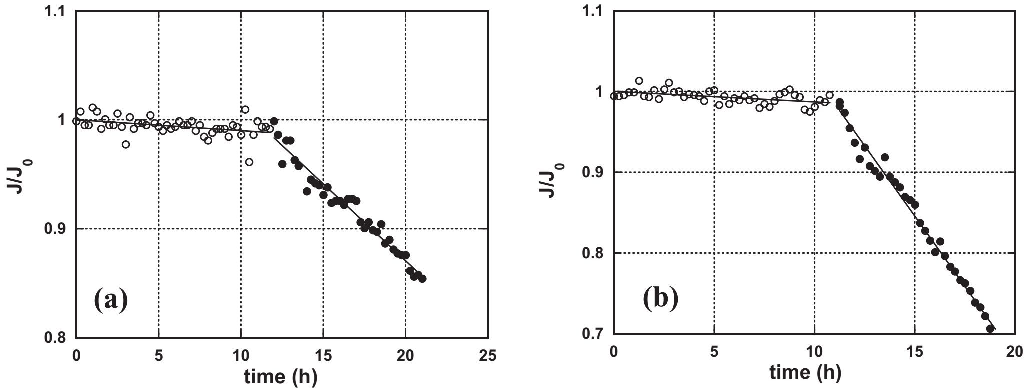

Fig. 3. Normalized membrane flux as a function of time before and after fouling species introduction. Feed water TDS: 2000 ppm; humic acid concentration: 20 ppm; pressure: (a) 116 psi, (b) 155 psi.

Table 3
Analysis of data from HA fouling experiments

c (mg/l)	J_0 (LMH)	ΔP (psi)	R_m (atm/LMH)	R_s' (atm/LMH/h)	R_d' (atm/LMH/h)
	Low flux experiments. TDS = 500 ppm				
5	29.5	181	0.42	5.5×10^{-4}	0.4×10^{-3}
5	31.5	162	0.35	5.9×10^{-4}	1.5×10^{-3}
10	29.9	181	0.41	5.8×10^{-4}	1.6×10^{-3}
15	29.3	181	0.42	7.8×10^{-4}	3.9×10^{-3}
20	29.9	162	0.37	7.2×10^{-4}	5.3×10^{-3}
	Low flux experiments. TDS = 2000 ppm				
5	24.9	132	0.36	2.6×10^{-4}	0.7×10^{-3}
7.5	27.4	116	0.29	3.2×10^{-4}	1.7×10^{-3}
10	26.9	118	0.30	9.8×10^{-4}	1.9×10^{-3}
15	27.2	116	0.29	1.4×10^{-4}	3.1×10^{-3}
20	25.9	116	0.30	3.1×10^{-4}	4.0×10^{-3}
	High flux experiments. TDS = 2000 ppm				
5	40.3	155	0.26	5.0×10^{-4}	1.7×10^{-3}
7.5	38.8	165	0.29	5.7×10^{-4}	2.6×10^{-3}
10	41.0	155	0.26	1.7×10^{-4}	4.6×10^{-3}
15	39.7	155	0.27	6.5×10^{-4}	6.5×10^{-3}
20	38.5	155	0.27	3.5×10^{-4}	9.2×10^{-3}

initial membrane flux was kept close to 40 LMH. Typical raw and normalized data obtained in an experimental sequence, which included pH adjustment, membrane setting and fouling species introduction are shown in Fig. 5.

A similar procedure, as described before for the humic acid deposits, was applied to extract the fouling resistance coefficient of the iron oxide particles. The results obtained are summarized in Table 4.

The fouling resistance coefficient R_d' as a function of iron concentration in the feed water is shown in Fig. 6 for the three sets of experiments. A clear effect of fouling species

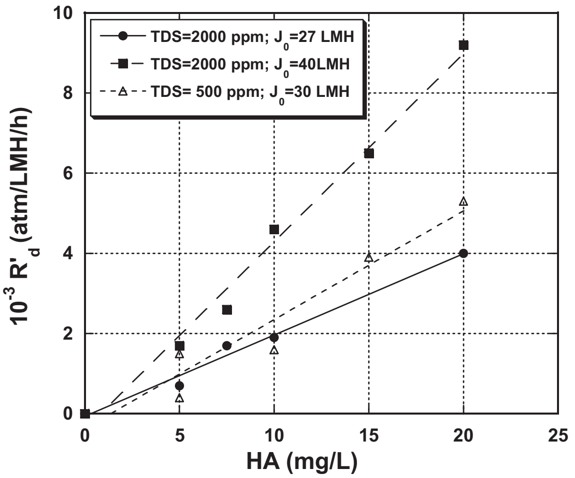

Fig. 4. Fouling resistance coefficient, R'_d defined in Eq. (2), as a function of humic acid concentration in the feed water.

concentration is observed, and a linear relationship between iron concentration and fouling resistance is obtained with a satisfactory degree of confidence. However, any effects of flux and feed water salinity are not evident or are small compared to the scatter in the data. This is a subject currently under investigation. It is clear that the present experimental results represent accelerated fouling conditions, since iron concentrations are far above the recommended values for membrane feed waters. However, on the basis of a discussion on precipitation kinetics and the effects of aggregation phenomena, it is proposed that the linear relationship found between fouling rate and iron concentration can be extrapolated to lower and more realistic concentrations [38].

3.3. SDI measurements

It is interesting to examine the predictions that would be obtained by SDI measurements if the same water were to be used as RO feed water. Feed water was prepared in the same way as for the fouling experiments and ferric ions or humic acid were added at various concentrations. With humic acids, measurable SDI values were obtained at concentrations up to approximately 200 ppb. If an extrapolation is made on the basis of Fig. 4 down to lower concentrations, a membrane operating under the same conditions with a feed water of SDI 3 or 4 would exhibit a 10% decline in flux to within less than 40 or 30

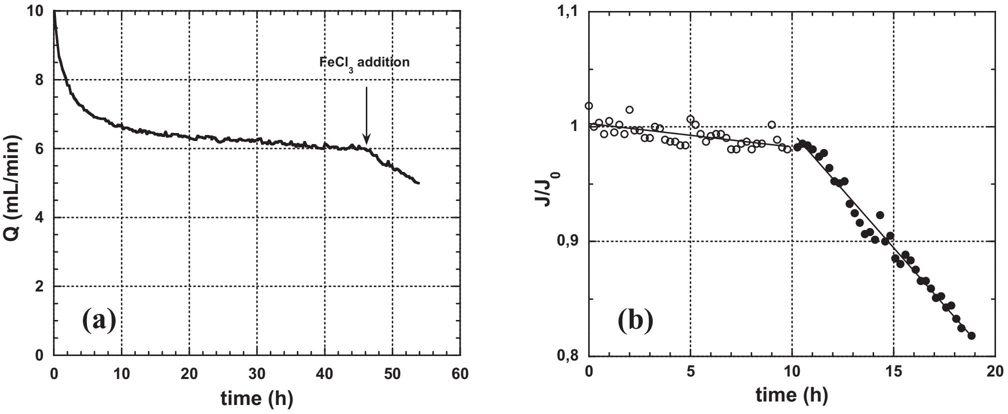

Fig. 5. Raw experimental data of permeate flow rate (a) and normalized membrane flux (b), as a function of time before and after fouling species introduction. Pressure: 147 psi; iron concentration: 3.5 ppm; feed water TDS: 500 ppm.

Table 4
Analysis of data from iron fouling experiments

c (ppm)	J_0 (LMH)	ΔP (psi)	R_m (atm/LMH)	R_s' (atm/LMH/h)	R_d' (atm/LMH/h)
	Low flux experiments. TDS = 500 ppm				
1	28.6	160	0.38	5.8×10^{-4}	3.3×10^{-3}
2	30	147	0.33	9.4×10^{-4}	4.8×10^{-3}
3.5	28.1	147	0.35	6.5×10^{-4}	6.5×10^{-3}
5	30.4	147	0.33	1.5×10^{-3}	1.03×10^{-2}
	Low flux experiments. TDS = 2000 ppm				
0.75	26.5	185	0.47	9.4×10^{-4}	1.82×10^{-3}
1.5	22.4	150	0.46	2.2×10^{-3}	4.7×10^{-3}
3.0	20.2	184	0.62	4.8×10^{-4}	7.7×10^{-3}
7.5	25.1	185	0.50	2.1×10^{-3}	1.48×10^{-2}
0.75	26.9	132	0.33	9.9×10^{-4}	1.84×10^{-3}
3	26.1	134	0.35	6.0×10^{-4}	5.18×10^{-3}
4	26.7	140	0.36	5.7×10^{-4}	6.58×10^{-3}
	High flux experiments. TDS = 2000 ppm				
0.5	39.7	165	0.28	3.1×10^{-4}	1.97×10^{-3}
1	37.7	170	0.31	7.8×10^{-4}	4.18×10^{-3}
2	39.0	180	0.31	2.8×10^{-4}	3.88×10^{-4}
4	39.3	175	0.30	5.1×10^{-4}	5.14×10^{-3}

days, respectively. Such a decline is considered severe; therefore, SDI appears to significantly underestimate the feed-water fouling propensity.

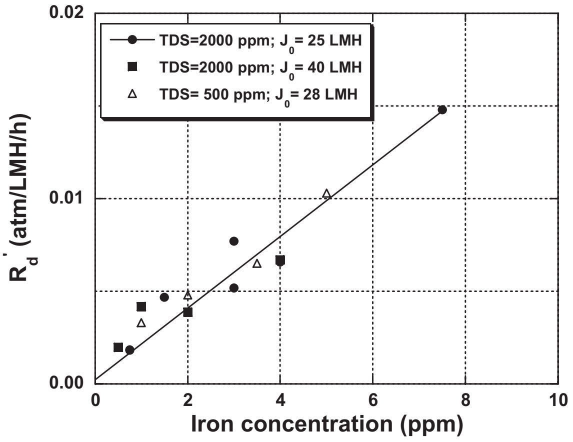

Fig. 6. Fouling resistance coefficient as a function of iron concentration in the feed water for the three sets of experiments.

With the iron oxide particles, almost complete plugging of the filter occurred within the first two minutes of the test at a concentration of 1 ppm of iron. The range of concentrations, where measurable SDI values could be obtained, had an upper limit of approximately 20 ppb. Several interesting observations may be made by examination of the results in Fig. 7. First of all, it may be recalled that membrane manufacturer recommendations, for feed waters under conditions favoring oxidation, are that dissolved iron concentration should be less than 50 ppb. It may also be mentioned that fouling problems due to iron have been reported with NF membranes at even lower concentrations [10], and, therefore, this limit could be considered tentative. The upper limit of 20 ppb for precipitated iron obtained by the present SDI measurements is not only remarkably close to manufacturer recommendations, but also on the correct side. A second observation is that there is a notable sensitivity to particles much smaller than the

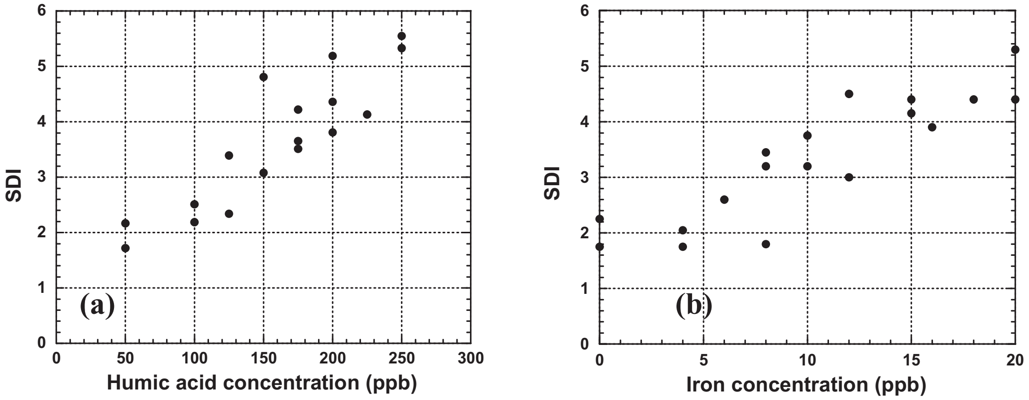

Fig. 7. SDI as a function of humic acid (a) and iron concentration (b) in the feed water.

pore size of the filter employed in the SDI test. In this case, the observed filter fouling is more likely due to pore restriction and plugging rather than cake formation. Thus, despite the negligible particle retention, significant effects are observed. It may be added here that in MFI measurements, where the index is based on the cake filtration regime, significant information from the initial stages of pore-blockage filtration regime may be lost. Finally, from the linear relationship obtained in Fig. 6 on the basis of the present RO fouling data, it may be projected that a similar membrane operating under similar conditions would exhibit a 10% drop in productivity within less than 75 or 50 days, if the feed water contained 10 ppb or 15 ppb of iron, respectively. These concentrations correspond to an SDI close to 3 or 5, respectively. Such rates of flux decline are rather severe, and suggest that, under the conditions of the present tests, the SDI is not conservative enough.

4. Conclusions

In view of the preceding discussion, it is suggested that there certainly exists the need for improved means of predicting the colloidal fouling propensity of feed waters, in the direction of determining actual flux decline and accounting for membrane type and operating conditions. The approach adopted in the present work, which includes obtaining basic RO fouling data and testing fouling index performance, is promising. Fouling index modifications can be tested by selecting membranes having greater resistance to water flow than the SDI filters. Important considerations in pursuing improvements in fouling indices is to simulate as closely as possible the conditions prevailing in actual RO membrane modules, namely flux, concentration polarization and membrane/foulant interactions, and to predict fouling rates.

In the present RO fouling study, humic acid was selected as a representative contaminant for organic fouling. Iron oxide was also selected as a typical inorganic colloidal foulant, due to its importance, as evidenced from the well-known manufacturer recommendations on iron concentrations in feed waters and from frequently encountered problems in membrane installations. The experimental procedure followed with the iron oxide particles simulates phenomena taking place in actual membrane installations and only skips the oxidation step of dissolved ferrous ions. A range of fouling species concentrations was identified where a linear relationship existed between flux reduction rate and concentration under the experimental conditions employed. Although the results obtained represent accelerated fouling conditions, it is proposed that the linear relationship can be extrapolated to lower and more realistic concentrations.

Despite the criticism that the filters employed in the SDI test have a pore size much larger than the size of potentially hazardous colloidal particles, a notable sensitivity of the SDI was also observed with particles and macromolecules for which retention is negligible in the test microfilter. Such sensitivity is mainly due to filter pore restriction and plugging. However, on the basis of the present RO fouling data, it may be projected that the SDI predictions may not be conservative enough. Furthermore, since the SDI cannot predict fouling rates it cannot discriminate between different types of membranes, nor can it predict the effect of operating conditions. For example, under the same conditions, an NF membrane would be expected to foul more rapidly and a seawater membrane to be less affected, since their resistances are different compared to that of the fouling cake.

Thus, until new more reliable indices are developed, the recommendations based on SDI should be respected but one should also be alert of possible fouling problems even when the SDI values are considered acceptable. In this respect, it must be stressed that care should be exercised during SDI measurements since, as reported by Walton [39], significant scatter in the results may exist due to materials employed (filter holders and filters), operator experience and strict adherence to the specifications of the testing conditions or lack thereof. Finally, a point on SDI variations or excursions must be highlighted; Kremen and Tanner [40] argue that unit increases in measured SDI correspond to geometric increases in the amount of foulant deposits and provide some supporting experimental evidence from SDI measurements at successive dilutions of a feed water. Consequently, their suggestion, that even infrequent excursions of the SDI above a recommended value may be quite harmful, appears very reasonable.

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