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Fouling in reverse osmosis: Detection by non-invasive techniques

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Abstract

Two non-invasive techniques were demonstrated to detect silica fouling in reverse osmosis. The first technique, the sodium chloride tracer test, enabled the estimation of concentration polarisation (CP) level during the fouling process, where the polarisation was greatly enhanced by the formation of an unstirred layer. Using colloidal silica at a concentration of 200 ppm as model foulant and 2000 ppm NaCl as background ionic solution, and operation at a constant flux of 30 L/m²h, it was found that the CP level increased by 75% whereas only 22% increase in the fouling resistance (R_f) was observed. The second method, ultrasonic time domain reflectometry, was used to monitor the growth of the fouling layer. The change in amplitude of the reflected signal was correlated to the amount of silica deposited on the membrane layer. Both techniques are valuable in the study of fouling or can be applied as early warning systems to provide critical information such as the level of concentration polarisation and the extent of the fouling layer.

Keywords: Concentration polarisation; Fouling; Reverse osmosis; Tracer test; Ultrasonic time domain reflectometry

1. Introduction

Reverse osmosis (RO) is widely used in desalination and water reclamation to convert seawater

or wastewater to potable quality water. However membrane fouling is still a bottleneck in RO technology, which greatly reduces the filtration flux in constant pressure filtration or increases the trans-membrane pressure (TMP) in constant flux

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filtration. Many precautionary and preventative steps have been developed to combat fouling, however their success depends on how much we know about the fouling process. Current methods to monitor the fouling process are via flux decline or pressure rise data; while membrane autopsy is performed on a fouled membrane to gain details of the deposits present on the membrane. These methods have limitations as the measurement of TMP or flux is an average reading that reflects the overall changes in the membrane system; it does not recognise the actual location of the fouling deposits. Moreover, membrane autopsy is an undesirable method if the membrane has to be sacrificed. So, it is important to develop non-invasive, in-situ and real time tools to monitor fouling to enable an accurate determination of the fouling process. In this study, we show how two non-invasive techniques, namely the step tracer response test and the ultrasonic time domain reflectometry (UTDR), can be applied simultaneously to monitor the progress of fouling at constant flux operation. Colloidal silica was used as a model fouling species in the RO study.

2. Theory

Inevitably, fouling in RO is linked to concentration polarization (CP), a phenomena that arises when the rejected solutes accumulate at the surface of the membrane. Various attempts have been made to develop mathematical models for predicting the CP level in a clean membrane system. However, in the event of formation of a fouling layer, which can be considered as an unstirred layer, the back diffusion of salt ions from the membrane surface to the bulk solution is hindered. As a consequence, the concentration at the membrane surface is significantly increased and so is the osmotic pressure. The increase in osmotic pressure means a decrease in the effective trans-membrane pressure. This ‘cake enhanced osmotic pressure’ effect, defined by Hoek et al. [1] was often neglected, but instead the drop in performance was

attributed solely to the build up of a high resistance fouling layer of particles. This assumption leads to an over estimation of the actual amount of fouling layer. Conversely, it means that a relatively low load of particles on the membrane can produce a greater impact on performance than anticipated from ‘cake resistance’ considerations alone. In this study, a simple NaCl tracer response technique was used to study the ‘cake enhanced osmotic effect’ in an RO system under constant flux operation. This technique makes use of the unique property of an RO membrane to reject NaCl salts. Before the NaCl spike, flux can be expressed as

$$J_v = \frac{(\text{TMP} - \text{CP} \cdot \Delta\Pi_b)}{\eta(R_m + R_f)} \quad (1)$$

where CP is the concentration polarization modulus $(C_w - C_p)/(C_b - C_p)$. When a spike of NaCl is injected into the system, this causes an increase in the osmotic pressure. In order to maintain constant flux operation, the TMP of the system has to be raised. Therefore,

$$J_v = \frac{(\text{TMP}_s - \text{CP} \cdot \Delta\Pi_{bs})}{\eta(R_m + R_f)} \quad (2)$$

where $\Delta\Pi_{bs}$ is the osmotic pressure and TMP_s is the trans-membrane pressure of the system during the spike. Combining the above two equations, yields

$$\text{CP} = \frac{\text{TMP}_s - \text{TMP}}{\Delta\Pi_{bs} - \Delta\Pi_b} \quad (3)$$

Therefore, by knowing the trans-membrane pressure of the system as well as the conductivity of feed and permeate (conductivity can be easily converted to osmotic pressure) before and during the NaCl spike, CP can be determined.

Another approach that can be applied to monitor the formation of a colloidal silica layer is the

ultrasonic time domain reflectometry (UTDR) technique [2]. This technique was pioneered by Greenberg and Krantz [2] for application to membrane systems. UTDR is a direct measurement method which is based on (i) the change in amplitude of the reflected ultrasonic signal from the fouling layer-membrane interface, and (ii) the time of flight or the amount of time for the sound to travel through the fouling layer. The principle of UTDR measurement is illustrated in Fig. 1.

A high frequency transducer (5 MHz) is fixed on the external wall of a flat sheet membrane module. A pulsar/receiver is used to send/receive the ultrasonic signal and the signals are recorded with an oscilloscope. When incident waves hit surfaces A and B, reflected echoes are generated from these surfaces. Other surfaces such as the bottom plate are not detected due to the limited penetration depth of the transducer. The signals, A and B, will remain unchanged as long as no fouling occurs. Once fouling is initiated on the membrane surface, the acoustic impedance difference of the membrane changes, resulting in a change in the amplitude of B, and this is labelled as echo B'. Furthermore, if the fouling layer has reached the detectable limit of the UTDR, a new echo C will appear as there is formation of a new interface. The thickness of the fouling layer can be calculated from the difference between the arrival time of echo B and C, provided the sound velocity of the fouling layer is known.

3. Materials and methods

A commercial RO membrane (FilmTec, model BW30) was used in all the tests. The membrane

came in 1×1 m size and was cut to fit the RO cell. Membranes were stored dried in a refrigerator at 4°C and soaked in Milli-Q water (Millipore) for 24 h before use. Colloidal silica (Sigma Aldrich, Ludox) was used as fouling agent. The silica was supplied in the form of 34 wt% in deionised water at pH 7.0 and has a mean particle diameter of 20 nm. Sodium chloride (Sigma Aldrich) was used as background ionic solution and for the tracer test. Milli-Q water was used to prepare the concentrated NaCl solutions and was filtered with a $0.45 \mu\text{m}$ filter (Millipore, model HAWP04700) before use.

The set up of the reverse osmosis system is shown in Fig. 2. The RO cell has parallel plate geometry and a flow channel of $310 \times 60 \times 0.8$ mm. The effective membrane area is 0.0186 m^2 . Test solution was delivered from the 10 L feed tank using a high pressure pump (Cats Pump, model 277) to the RO cell. The temperature of the feed water was kept constant at $25 \pm 1^\circ\text{C}$ with cooling water from a chiller (AR Engineering, custom made). An overhead stirrer (IKA, model Eurostar) was installed at the feed tank to ensure the solution was well mixed. System pressure and crossflow rate were controlled by a back pressure regulator (Veriflo Corporation, model ABP 1ST52BP4) and a flow control valve (Cole Parmer, model CP-32505-40) respectively. Pressures of the feed and permeate stream were monitored with pressure transducers (Bourdon Haenni, model E913); meanwhile flow rate of the stream was monitored with a turbine flow meter (McMillan, model 114). The amount of permeate withdrawn, which fixes the flux, was controlled with a mass flow controller (Brooks Instrument, model 5882), which

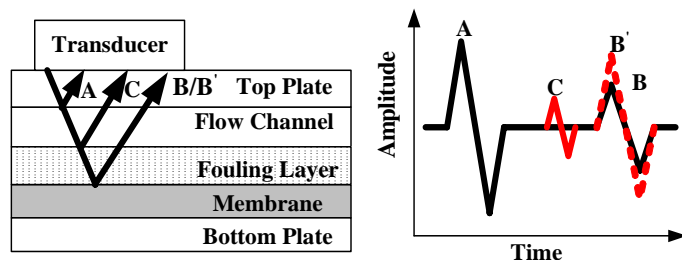


Fig. 1. Principle of ultrasonic detection of fouling layer.

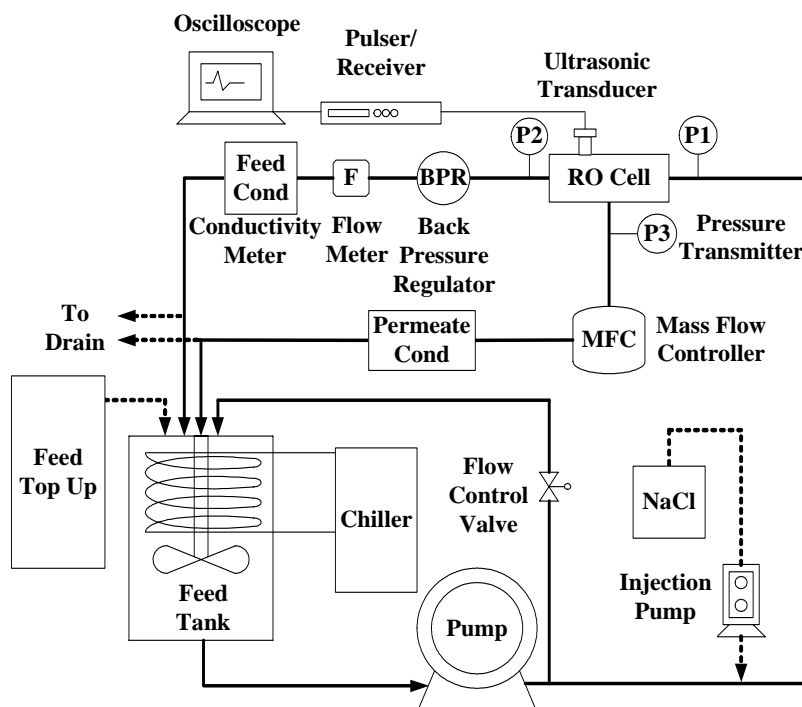


Fig. 2. Schematic diagram of reverse osmosis set up.

consists of a thermal mass flowmeter and a micro control valve, located on the permeate side of the RO cell. To achieve constant flux operation, the RO system was operated at excess feed pressure so that the mass flow controller self adjusted the permeate side pressure to meet the set permeate flow rate; i.e. only a transmembrane pressure of 3 bar was required to obtain a flux of 10 L/m²h, but instead the applied pressure was set to 20 bar, so the mass flow controller regulated the permeate side pressure to 17 bar. The quality of feed and permeate was monitored with conductivity meters (Mettler Toledo, model Seven Multi and Rosemount Analytical, model Solu Comp II, respectively). During tests, concentrate and permeate were recycled back to the feed tank. For the sodium chloride tracer test, sodium chloride solution was injected into the high pressure feed line to the RO cell via a metering pump (Pulsafeeder,

model Pulsatron). During the test, concentrate and permeate samples were removed and the feed solution was topped up in order to maintain a constant volume. Pressures, crossflow rate, flux, and conductivity readings were recorded with a data acquisition system (National Instrument, model PCI 6014 and LabView). The acoustic hardware included a pulsar-receiver (GE Panametrics, model 5800); a digital oscilloscope (Tektronix, model TDS5082) that enabled a 4 ns sampling rate; and a 5 MHz ultrasonic transducer (Shantou Ultrasonic Instrument Corporation, model 5P14) fitted on the top plate of the RO cell, near the exit region of the module.

The experiment was commenced with the compression of the membrane at 20 bar and a crossflow rate of 0.5 L/min for 2 h with Milli-Q water. Then, flux was set to the desired value, and the system was left to equilibrate for 12 h. For

test runs with NaCl in the background, this was followed by the addition of concentrated NaCl solution to achieve a final concentration of 2000 ppm NaCl and the system was left to equilibrate for another 2 h. Subsequently, the tracer test was carried out and this was used as reference point for the ‘clean’ membrane i.e. the CP value determined here was taken as the reading at $t = 0$ for the fouling test. In the tracer test, 200 g/L of NaCl was injected into the high pressure feed line via the metering pump, to give an additional of 500–1500 ppm NaCl to the feed solution entering the RO cell. The spike length lasted for 30 min. When the spiking was stopped, the system TMP and conductivity readings returned to the previous values and the system was left for equilibration for 1 h. Then the fouling test was initiated by adding colloidal silica suspension to the feed tank at a final concentration of 200 ppm silica. Several tracer tests were carried out during each fouling run. Samples were collected from the feed tank and the permeate line and analyzed for pH (Mettler Toledo, model SevenMulti), turbidity (Hach, model 2100AN) and total silica content with inductive couple plasma optical emission spectrometer (Perkin Elmer, model Optima 2000 DV).

4. Results and discussion

Silica fouling test was initially conducted without NaCl in the background. An example of TMP, feed and permeate conductivity profiles, as well

as the calculated CP values during one of the NaCl spikes is shown in Fig. 3a. As shown in the figure, even though the feed concentration was constant throughout the NaCl spike, instead of quickly reaching a steady value, the TMP values continued to increase during the spike. Similarly, the calculated CP values also increased with time and appeared to be very high. A possible reason was the interaction of NaCl with the silica forming aggregates; as such the silica stability was disturbed by the addition of NaCl and hence caused an exaggerated fouling. This was supported by the data from UTDR measurement, where the amplitude of the peak of fouling layer increased from 0.06 to 0.25 V, indicating there was significant cake fouling occurring during the spike. This would have made the assumption of negligible increase in the cake resistance during the NaCl spike to be invalid. After 30 min duration the spike was terminated and both TMP as well as the amplitude of the fouling layer’s peak returned to the original values. This suggests that the fouling process that had occurred was reversible.

The experiment was repeated with 2000 ppm of NaCl in the background. This would be a more typical condition for brackish RO. An example of TMP, feed and permeate conductivity profiles, as well as the calculated CP values during one of the NaCl spikes is shown in Fig. 3b. Unlike the previous test where the system experienced a continual increase in TMP, in this test the TMP rapidly increased from 12.3 to 15.8 bar and

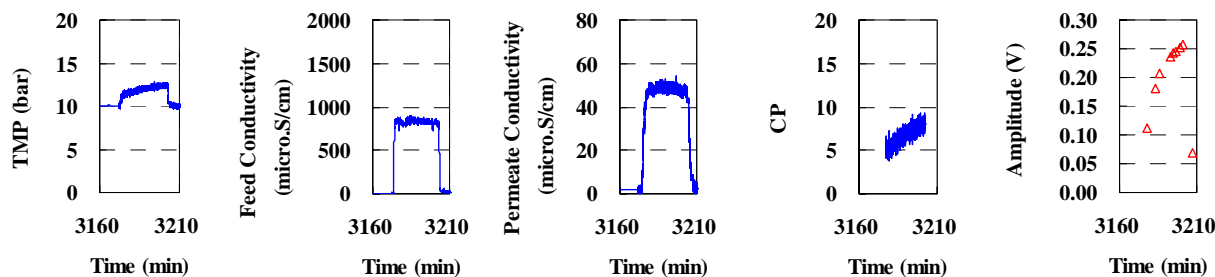


Fig. 3a. TMP, feed, permeate conductivity, calculated CP values and amplitude of UTDR signal of silica fouling without background NaCl solution during NaCl spike at time = 3172 min.

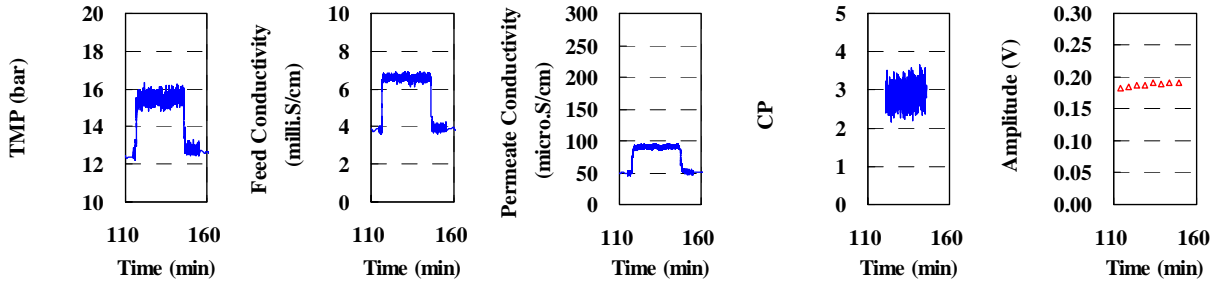


Fig. 3b. TMP, feed, permeate conductivity, calculated CP values and amplitude of UTDR signal of silica fouling with background 2000 ppm NaCl solution during NaCl spike at time = 116 min.

reached a steady value when NaCl was spiked into the system. There was only minor additional fouling during the spiking process as supported by the data from the UTDR measurement. The amplitude of the fouling layer peak remained constant at 0.19 V. Therefore the assumption of negligible fouling during the spike was valid. The average CP values and the ratio of the cake fouling resistance to the overall resistance, R_f/R_T , determined based on the TMP and conductivity profiles over a period of steady silica fouling are shown in Fig. 4. As shown, the CP values increased from an initial value of 2.0–3.5, showing an increase of 75%; whereas the fouling layer only contributed a maximum value of 22% to the total resistance. These results confirm that typical fouling layers in RO can significantly reduce apparent permeability, but that this is through a dramatic increase in CP and consequent loss in driving force rather than through an additional hydraulic resistance. It is also suggested that the ‘salt’ spiking response could be used as a diagnostic for fouling development.

It should be noted that the salt spiking response could also be applied at constant TMP. In this case

the spike would also cause a rise in $\Delta\Pi_{bs}$, but this would result in a drop in flux from J_{V1} to J_{V2} . Assuming no significant change in cake resistance during the spike, and assuming CP remains unchanged (this is not strictly correct if flux changes), the CP equation based on Eqs. (1) and (2) for J_{V1} and J_{V2} respectively, becomes

$$CP = TMP \left(\frac{J_{V1} - J_{V2}}{J_{V1}\Delta\Pi_{bs} - J_{V2}\Delta\Pi_b} \right) \quad (4)$$

Comparisons of the constant flux and constant pressure CP determinations are planned.

Results from the UTDR measurements for the overall fouling process are presented Figs. 5a and 5b. As seen in Fig. 5b the change in the signal was correlated reasonably well with the amount of colloidal silica deposited on the membrane, which was estimated via the change in the concentration of feed solution. As the amount of silica deposited was increased, the amplitude of the reflected signal from the fouling layer also increased. This was due to the difference in the acoustic impedance of the fouled membrane

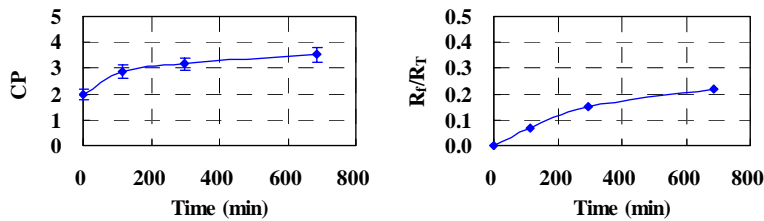


Fig. 4. CP levels and R_f/R_T vs. experimental run time.

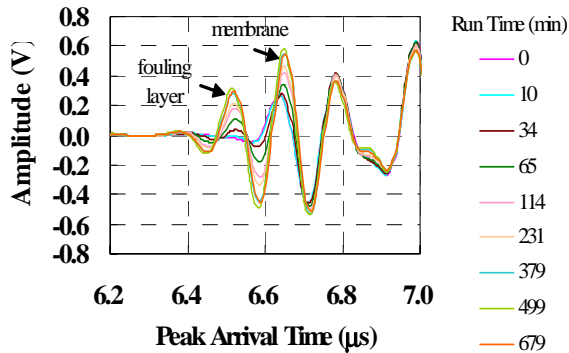


Fig. 5a. Ultrasonic response signals at different experimental run time.

compared to a clean membrane. However, the shift in the arrival time of the peak was not significant, which suggests that the silica deposit layer was not thick. This conclusion was in agreement with the thickness estimated from the amount of SiO_2 deposited. At a deposit load of $335 \text{ mg}/0.0186 \text{ m}^2$, a particle density of $2.31 \text{ g}/\text{cm}^3$ and an assumed porosity of 0.3–0.5, the calculated thickness was about 11–15 μm .

5. Conclusions

The results in this paper confirm earlier studies which showed that UTDR can indicate the development of incipient fouling layers [2], in our case particularly evident as a change in the amplitude of the reflected signal. Further evidence was obtained by the 'salt spike' response technique which allowed estimation of the 'cake enhanced osmotic effect' by monitoring TMP change at controlled flux (or flux change at controlled TMP). The techniques can be used individually or together, depending on the situation, for fouling evaluation or to obtain advanced warning of fouling events.

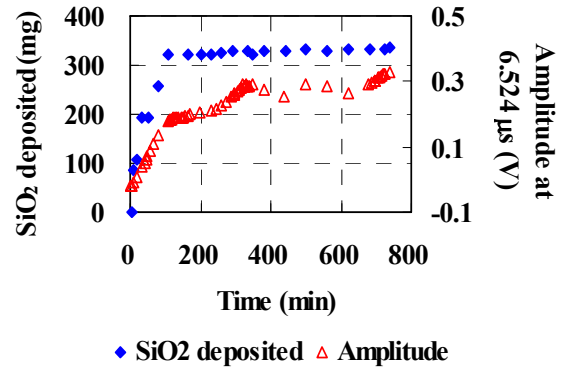


Fig. 5b. Amount of silica deposited and amplitude of UTDR signal vs. experimental run time.

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References

- [1] E.M.V. Hoek and M. Elimelech, M. Cake-enhanced concentration polarization: A new mechanism for salt-rejecting membrane. *Environ. Sci. Technol.*, 37 (2003) 5581–5588.
- [2] A.P. Mairal, A.R. Greenberg, W.B. Krantz and L.J. Bond, Real-time measurement of inorganic fouling of RO desalination membranes using ultrasonic time domain reflectometry. *J. Membr. Sci.*, 159 (1999) 185–196.