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A Threshold Flux Phenomenon for Colloidal Fouling in Reverse Osmosis Characterized by Transmembrane Pressure and Electrical Impedance Spectroscopy

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ABSTRACT

The dependence of membrane fouling on flux has been investigated using silica as the model foulant in a crossflow membrane module operated at constant flux. Electrical impedance spectroscopy (EIS) was used to monitor the electrical properties of the fouling process.

We show that the nature of a flowing colloidal suspension of silica on the membrane surface changes when a transition or threshold flux is reached. This transition was well-defined and was reflected in the changes of the slope of transmembrane pressure (TMP) with flux and the conductance of the diffusion polarization (DP) layer determined by EIS. The threshold flux increased with increasing crossflow velocity. The effect of a spacer in the feed channel was also investigated and the presence of spacer increased the threshold flux. The conductance of the diffusion polarization layer (G_{DP}) derived from the low frequency region in the EIS was identified as the most important EIS parameter for signaling the onset of cake formation and the cake enhanced concentration polarization (CECP) effect. TMP measurements on their own provided limited information on these phenomena. The threshold flux was affected strongly by the crossflow velocity and this was also illustrated in the change in the minimum of the G_{DP} with increasing flux. This study suggests that EIS could be applied “online” using a side-stream, ‘canary’ cell to continuously monitor a reverse osmosis system to ensure its operations remain below the threshold flux.

Keywords

Electrical impedance spectroscopy; Threshold flux; Diffusion polarization; Cake enhanced concentration polarization (CECP); Transmembrane pressure

1. Introduction

Reverse osmosis (RO) is widely employed in wastewater treatment and reclamation plants to produce high quality water. This is because of the numerous advantages it offers, such as small footprint with modular construction, process stability and its ability to produce permeate with excellent water quality [1-3]. Despite the widespread use of RO systems in water treatment, fouling remains a major obstacle that limits its applications. Membrane fouling refers to the

deposition of unwanted materials on the membrane surface which is likely to cause undesirable consequences, including permeate flux decline in constant pressure filtration or increase in transmembrane pressure (TMP) in constant flux filtration, an increase in energy and operational costs, reduced membrane lifetimes, down-time for chemical cleaning as well as costs associated with chemicals and their disposal. There may also be a loss in water quality [4]. There are several types of particulate fouling, including colloids, suspended solids and microbial cells. However, colloidal fouling remains a persistent problem in the applications of water treatment [5].

Fouling tends to be flux-driven and one of the measures to mitigate fouling and improve the filtration performance is to operate the system below a certain flux. For example, the concept of critical flux was first introduced in 1995 by Field et al. [6] for microfiltration (MF) which asserts that “on start-up there exists a flux below which a decline of flux with time does not occur whilst above this “critical flux”, fouling will occur. This critical flux level would depend on the hydrodynamics and probably other variables. Others discussed a ‘transition’ between concentration polarization and cake formation for colloids [7]. Howell [8] pointed out “a flux below which there is no fouling by colloidal particles” which then leads to the concept of “sub-critical flux operations of microfiltration” which provides a basis for sustainable flux [9].

Operation above the critical flux would result in the deposition of a colloidal layer on the membrane surface and lead to an additional resistance to the permeate flow, which is known as the cake resistance and this increases the overall hydraulic resistance [10]. For RO membranes, the deposited layer on the membrane surface could hinder back-diffusion of solutes, such as salt, leading to the cake-enhanced concentration polarization (CECP) phenomena as identified by Hoek et al. [11]. Further, the solutes in this ‘unstirred’ cake layer are not exposed to the shear

forces of the crossflow, causing the concentration and the osmotic pressure of solutes at the membrane surface to be enhanced further [10, 11]. Thus, the loss of overall RO performance results both from the increase in hydraulic resistance and the cake enhanced osmotic pressure (CEOP) effect.

The concept of critical flux is useful but alone does not give sufficient guidance for plant operators to optimize the performance in real situations [12]. A more practical concept is that of a ‘threshold flux’, introduced by Bacchin et al. [9, 12], and defined as the “flux at or below which a low and near constant rate of fouling occurs but above which the rate of fouling increases markedly.” Thus, threshold flux is a transition between low (negligible) fouling and significant fouling. Studies of transitional fluxes in RO have been relatively limited. However in previous work [10] using a similar model colloidal silica foulant, operated over a range of fixed fluxes, it was observed that the deposition rate ($d(\text{mass})/dt$), estimated from a tracer technique, was flux dependent. A flux for transition from negligible to detectable net deposition was identified and termed ‘critical flux’ although it more correctly satisfies the definition of threshold flux. In this paper we use the term threshold flux to identify the fouling transition.

In a previous publication using EIS, we showed that there is a threshold phenomena during RO crossflow filtration when the nature of the foulant layer undergoes a transition that was reflected in changes in the electrical conductance of the concentration polarization layer [13]. In this current work, we have investigated the dependence of the nature of the polarized or deposited foulant layer on flux. This was done by measuring the TMP as a function of flux and crossflow velocity using the flux-step method. EIS was simultaneously used to characterize the electrical properties of the diffusion polarization (DP) layer as a function of the flux. The effect

of crossflow velocity and the presence of a spacer on the feed side were also investigated to compare TMP data and EIS measurements around the transition.

2. Overview of EIS

This section provides a brief overview of EIS and the rationale for choosing EIS for the detection of the threshold flux measured by the TMP method.

2.1. Theoretical background and equivalent circuit model

Impedance measurements are conducted by the injection of small sinusoidal alternating currents, $i = i_o \sin(\omega t)$ at a series of known frequencies ω and amplitude i_o into the system and measuring the voltage $v = v_o \sin(\omega t - \theta)$ across the sample. The voltage amplitude v_o and phase difference θ between the voltage and current are measured. The magnitude of the impedance is given by,

$$|Z| = \frac{v_o}{i_o} \quad (1)$$

Impedance is a complex quantity, with real and imaginary components. The impedance can be decomposed into these components using the following expression:

$$Z = |Z| e^{j\angle Z} = \frac{v_o}{i_o} e^{-j\theta} = \frac{v_o}{i_o} (\cos \theta - j \sin \theta) \quad (2)$$

where $|Z| (= \frac{v_o}{i_o})$ and $\angle Z (= -\theta)$ define the impedance magnitude and phase respectively. This

gives the impedance in terms of the measureable parameters, such as i_o , v_o , θ and the imaginary unit vector, j where $j^2 = -1$.

The admittance is derived from the reciprocal of impedance and is represented by

$$Y = \frac{1}{Z} = \frac{i_o}{v_o} e^{j\theta} = \frac{i_o}{v_o} (\cos \theta + j \sin \theta) \equiv G + j\omega C \quad (3)$$

Here, the admittance is expressed in terms of a conductance element, G in parallel with a capacitance element, C describing its ability to conduct and store charge respectively. This single conductance in parallel with a capacitance is known as a Maxwell-Wagner element, where the impedance measurement provides a measure of,

$$G = \frac{1}{|Z|} \cos \theta \text{ and } C = \frac{1}{\omega |Z|} \sin \theta \quad (4)$$

where $\omega = (2\pi f)$ is the angular frequency. The variation or dispersion of G and C with frequency can be used to determine the number of circuit elements with different time constants present in the system. In the context of membranes, such elements arise from layers within the system and diffusion polarization layers or processes. This provides a means of real time and in-situ monitoring of the accumulation of particulates that could potentially foul the membrane [14].

Rearrangement of Eq. (3), leads to

$$Z(\omega) = \frac{1}{G + j\omega C} \quad (5)$$

Eq. (5) can also be expressed as

$$Z(\omega) = \frac{G}{G^2 + C^2\omega^2} - j \frac{C\omega}{G^2 + C^2\omega^2} \quad (6)$$

Since Z is a complex variable, $Z = Z_{\text{Re}} - jZ_{\text{Im}}$ where Z_{Re} represents the real part of Z and Z_{Im} refers to the imaginary component of Z . Therefore,

$$Z_{\text{Re}} = \frac{G}{G^2 + C^2\omega^2} \text{ and } Z_{\text{Im}} = \frac{C\omega}{G^2 + C^2\omega^2} \quad (7)$$

The impedance data can be presented graphically on Cartesian coordinates as a Nyquist plot in which $-Z_{\text{Im}}$ is plotted against Z_{Re} . The Nyquist plots consist of a number of overlapping semicircles where a single Maxwell-Wagner element produces a semicircular plot. The number of semicircles and the degree of overlapping are determined by the number of elements with different time constants and how close those time constants are to each other. In most cases, the Nyquist plot provides direct insights into the layers as well as the electrochemical transport processes occurring.

The frequency dependent complex impedance of the membrane can be modeled using a number of circuit elements in series representing internal and external layers in the membrane. This is the so-called Maxwell-Wagner model. Detailed explanations of the equivalent Maxwell-Wagner circuit model have been described in the literature [15, 16]. Briefly, at low frequencies (<10 kHz), there exists an element representing the diffusion polarization of ions at the membrane-solution interface. At mid frequencies, the dispersion in capacitance can be ascribed to elements representing membrane substrate, membrane skin layer and partial diffusion polarization effect. At higher frequencies (>10 kHz), there is an element representing the electrolyte connected in series with membrane [15-17].

As the element at low frequencies represents the phenomena occurring at the membrane-solution interface, the electrical properties of this element are of special interest. This diffusion polarization (DP) layer originates from a phenomenological event caused by the alternative accumulation and depletion of ions at the membrane-solution interface during the measurement of impedance using AC currents. During one half cycle (Fig. 1a), when the injected AC current is towards the feed side of the membrane, there is a transport of Na^+ towards membrane at the feed side and Cl^- away from membrane. In the membrane the electric current carried by the

cations and anions may not be equal; that is, they have different transport numbers. This can arise, for instance if the membrane has a net residual charge as is the case of the RO membranes used which are slightly negatively charged. Thus the fraction of the electric current in the membrane carried by Na^+ is larger than that carried by Cl^- , whilst in the feed solution these fractions are more equal. As a result, there will be a depletion of Na^+ ions at the surface. Similarly, fewer Cl^- ions arrive through the membrane at the membrane surface than are transported away in the feed solution, thus also lowering the Cl^- ion concentration at the membrane surface. The opposite effect occurs at the permeate side. Further, the entire profiles reverse during the next half cycle of the AC current when the electric current is reversed, as illustrated in Fig. 1b. The occurrence of electrical diffusion polarization only occurs for low frequencies of the AC current injected when the half cycle is long enough for substantial changes in the ion concentrations to build up near the surface of the membrane. At high frequencies there is insufficient time in each half cycle for concentration profiles to build up. Thus, the AC ion concentration perturbations are frequency dependent. If the conductance G has a real (G_R) and an imaginary component (jG'), that is, if

$$G = G_R + jG'(\omega) \quad (8)$$

This imaginary component appears as a frequency dependent capacitance. The capacitance can be written in terms of the imaginary part of the admittance in Eq. (3) as:

$$C = \frac{I_m\{Y(\omega)\}}{j\omega} \quad (9)$$

Substitution of Eq. (8) into Eq. (3) with Eq. (7) gives the total capacitance:

$$C^*(\omega) = C + \frac{G'(\omega)}{\omega} \quad (10)$$

This can be written as:

$$C^*(\omega) = C + C'(\omega)$$

$$\text{where } C'(\omega) = \frac{G'}{\omega} = \frac{\beta}{\omega} \quad (11)$$

where β is a constant describing the magnitude of this frequency dependent capacitance arising from diffusion polarization.

For a salt rejecting membrane, like RO, ions such as Na^+ and Cl^- also tend to accumulate on the RO membrane surface during filtration as a result of the pressure driven flux as illustrated in Fig. 1. This is the so called concentration polarization effect. It should be noted that the DP layer defined here is not identical with the pressure driven concentration polarization layer but is very sensitive to the concentration profile of the Na^+ and Cl^- near the membrane surface, both at the feed side as well as at the permeate side (Fig. 1). The DP profile will be asymmetry due to the differences in NaCl concentration on both sides of the membrane.

Modeling using a series combination of Maxwell-Wagner elements allows the determination of the conductance of the AC DP layer, designated here as G_{DP} . This parameter allows one to probe the changes at the membrane-solution interface in order to provide clearer understanding of the events occurring below, around and above threshold flux.

Figure 1.

2.2. Rationale for choosing EIS

EIS has been successfully employed to characterize various types of membranes, including synthetic [14-21] and biological membranes [22-24]. The porosity of the membrane can be estimated from the capacitance determined from EIS when the dielectric constant and the

thickness of the membrane polymer are known [16, 25]. This technique is also capable of detecting fouling or scaling in membrane processes in a real time and in a non-invasive manner [13, 26-29]. EIS has also been proven to be applicable beyond laboratory scale studies such as to detect real foulants on the membrane surface in the treatment of wastewater from a fermentation process [30]. To the best of our knowledge, most studies of threshold flux have focused on examining the relationship between parameters such as TMP and flux. Apart from studies using a direct observation through the membrane (DOTM) in MF [31], there are few studies, which focus on understanding the phenomena occurring in-situ at the membrane surface around the critical or threshold flux conditions. In-situ monitoring techniques for membrane filtration processes are of paramount importance for facilitating our understanding in the fundamental processes governing membrane fouling [32]. To date, EIS has not been correlated directly with flux nor used to detect changes at the membrane surface below, at and above the threshold flux. This study demonstrates the ability of EIS to characterize the threshold flux phenomena during the reverse osmosis processing of a colloidal silica suspension.

3. Materials and methods

3.1. Design considerations

3.1.1 EIS equipment

The main components of the EIS equipment are a crossflow impedance cell fitted with a pair of current injecting electrodes, a pair of electrodes for measuring the voltage across the membrane, the EIS spectrometer and an amplifier unit. The current injecting plates (plates 3 and 6 in Fig. 2) serve as the current electrodes and the RO membrane was placed between these two plates, insulated by a plastic gasket. The voltage electrodes are mounted in the top and bottom of

these two plates (but insulated from them) to measure the voltage developed across the membrane. Plates 1 and 8 are present to allow operations at high pressures. All of the stainless steel plates are insulated by the plastic gaskets (plate 2, 4 and 7) and cylindrical insulating tubes around clamping bolts to prevent the filtration cell from being electrically short circuited. Both the current and voltage electrodes are made of stainless steel. The phase difference between the current and voltage was measured by the spectrometer in the specified range of frequencies and recorded through dedicated software. The measured parameters then yield the capacitance and conductance (as detailed in Section 2.1) of the sample at each frequency. The amplifier unit contains a reference circuit (Randall circuit) so that the accuracy for the measurements over a wide range of frequencies can be optimized. This system employs the four-terminal method† where four electrodes are used for the measurement of impedance to eliminate the complicating effects of the frequency dependent impedance at the voltage electrode-solution interface [26].

The dimension of the cell is 302 mm x 60 mm x 0.95 mm with an effective membrane area of 0.01812 m². The cell was connected to an INPHAZE™ Electrical Impedance Spectrometer (Sydney, Australia) and the electrical properties of the membrane were measured at frequencies ranges from 10⁻¹ to 10⁵ Hz. This spectrometer has a phase resolution of 0.001° and is therefore capable of measuring the capacitance even at low frequencies where the admittance is dominated by the (high) conductance. Three replicates of impedance spectra were obtained per scan and the time required per scan over the frequency range (10⁻¹ to 10⁵ Hz) was approximately 30 minutes.

†Problems associated with the impedance of the interface between the electrode and the solution and changes in this interfacial impedance can be eliminated by using the four-terminal technique for impedance measurement. In this technique, the current is injected via one set of electrodes whilst the potential developed across the membrane is measured by the second set of electrodes. The latter is accomplished using a buffer amplifier which has very high input impedance, much higher than the impedance of the electrodes-solution interface. The voltage measurements therefore are not affected by that impedance.

Figure 2.

3.2. Model foulant, background electrolyte and membrane

Colloidal silica (Sigma-Aldrich, Ludox TMA) was used as the model foulant in this study as well as in our previous studies [13]. It was supplied in the form of a 34 wt% suspension in deionized water at pH 7.0. The nominal size of the silica particles was 20 nm based on the datasheet provided by the manufacturer. Sodium chloride (Merck) was used as the background electrolyte. Milli-Q water was used to prepare the silica and sodium chloride solution. A 0.45 μm filter (Millipore, model HAWP04700) was used to filter the sodium chloride solution to remove unwanted particulate impurities before use.

Commercial RO membranes (DOW FilmTec, TW30) with a membrane hydraulic resistance of $1.06 \times 10^{14} \text{ m}^{-1}$ were used. The observed salt rejection of the membranes was about 97%, measured at a constant flux of $25 \text{ l/m}^2 \text{ h}$ with 2000 ppm NaCl aqueous solution. RO membranes were wetted in ethanol for 2 hours and rinsed thoroughly before storing them in Milli-Q water for at least 24 hours before use. Most of the studies used a spacer-free feed channel but one set of experiments used a conventional diamond-shaped spacer.

3.3. RO setup

A schematic diagram of the RO setup is shown in Fig. 3. A high pressure pump (Hydra-Cell Pump, model D03) was used to deliver the solution from a 10 L feed tank to the RO-EIS crossflow cell. An overhead stirrer (Panasonics, model MX8G5B) was installed in the feed tank to ensure that the solution was mixed thoroughly throughout the experiment. The temperature in

the feed tank was maintained with cooling water from a chiller (PolyScience, model 9106) at 23 ± 1 °C. The reject and permeate were recycled back to the feed tank in the course of filtration where the permeate flux was controlled by a mass flow controller (Brooks Instrument, model 5882). The system pressure was controlled by a backpressure regulator (Swagelok, model KBP series) while the pressures of the feed and permeate were monitored using pressure transducers (Ashcroft, model 302174). The flow of the feed stream was measured with two flow meters (Cole-Palmer, model PMR1-010640 and model PMR1-010-210) while conductivity meters (Eutech Instruments, model Alpha COND 500) were installed to measure the conductivity of the feed and permeate. Pressure, flux and conductivity readings were recorded with a data acquisition system (National Instrument, model PCI-6014 and LabView 10).

Figure 3.

4. Experimental procedure

4.1. Membrane compaction

The membrane was compacted at a flux of $40 \text{ l/m}^2 \text{ h}$ for at least 48 hours prior to the fouling experiments. This was to ensure that there were no significant changes in the membrane properties as these changes are detectable by EIS. The final concentration of NaCl solution in the feed tank was adjusted to 2000 ppm to simulate brackish water conditions.

4.2. Silica fouling

4.2.1 Flux step method

The system was adjusted to the desired (lowest) flux and crossflow velocity before silica was added into the feed tank. After the system was stabilized, concentrated silica was added to the feed tank to achieve the desired silica concentration of 200 ppm. The fouling stage at a particular flux was maintained for 2 hours and EIS measurements were taken at 1 and 2 hours intervals. The flux was then increased incrementally after a fixed duration and the sequence continued until the highest desired flux was reached.

Some prolonged fouling experiments were conducted and lasted for about 24 hours and EIS measurements were recorded regularly to monitor the membrane responses throughout the experiment.

5. Results and discussion

5.1. Rationale for results presentation

Nyquist plots (Fig. 4) are one of the most useful ways to represent EIS data, where each data point is obtained from a particular frequency as detailed in Section 2.1. This uses Eq. (7) and is a plot of $-Z_{\text{Im}}$ with respect to Z_{Re} whereby the shape of the plots and shift in the plots provide real time information of the onset of fouling processes as well as the type of foulant [13]. When the experimental data were fitted to the Maxwell-Wagner model, it reveals the presence of various elements and processes occurring in the system. The fitting is done using the INPHAZETM Structure Refinement Software (Sydney, Australia). As explained in section 2.1, elements at low frequencies ($\sim 1\text{-}10$ Hz) correspond to the DP layer and its conductance. G_{DP} values were derived from the fitted values as explained in Section 2.1. The detailed procedure for fitting has been described elsewhere [15, 26]. Fig 4 shows a typical Nyquist plot for a RO system, where the low frequency element corresponds to the DP layer, mid frequencies correspond to the

membrane layers and solution is the dominant feature in high frequencies range. The remaining discussions in this paper are in terms of the Nyquist plot and the parameter, G_{DP} which provides insights into the interfacial layer at the membrane surface when the operating conditions approach the threshold flux and the onset of the CECF effect.

Figure 4.

5.2. Threshold flux determined by the flux step method

The critical flux as originally defined [6] is usually determined by the flux step method. This is preferred over the pressure step due to the more manageable control of flux and a constant flow of foulants towards the membrane can be established more easily [33, 34]. Therefore, we adopted a similar flux step procedure, coupled with EIS measurements to investigate the effect of flux on the nature of the concentration polarization layer.

5.2.1 TMP and EIS measurement using the flux step method

The TMP with foulant as well as the salt rejection profiles for the flux step method are presented in Fig. 5a. The TMP values remained almost constant from 15 to 25 $\text{l/m}^2 \text{ h}$ throughout the course of filtration. A slope change occurred at about 30 $\text{l/m}^2 \text{ h}$, suggesting the onset of detectable foulant deposition and membrane fouling. As shown in Fig. 5b, the threshold flux (J_{th}) was found to be $\sim 28 \text{ l/m}^2 \text{ h}$ from the intersection of the $d\text{TMP}/dt$ slopes.

Figure 5

Fig. 6 presents the Nyquist plots of the flux step method for silica fouling. The Nyquist plot shifted to the right as the flux increased from 15 to 30 $\text{l/m}^2 \text{ h}$. When the system was operated

beyond J_{th} , the movement of the Nyquist plot changed direction and shifted to the left. The shift to the left of the Nyquist plot was due to a decrease in the overall Z (hence increase in G). The trend was similar to observations in a previous study by our group [13].

Figure 6

The G_{DP} values derived from the theoretical fitting result as detailed in Section 2.1 are shown in Fig. 7a. The G_{DP} decreased as flux increased from 15 to 30 $l/m^2 h$ and this is likely due to the presence of the flowing colloidal suspension of non-conducting particles near the membrane surface which would reduce the overall conductance (per unit volume) of that layer. The nature of this flowing colloidal suspension in the boundary layer might be such that the mass transfer coefficient for the salt that controls the concentration polarization at the surface is not affected substantially as the layer remains hydrodynamically active. When the flux exceeded the threshold level of 30 $l/m^2 h$, G_{DP} started to rise. It is proposed that this was because the concentration of salt in the DP layer increased as a result of cake enhanced concentration polarization (CECP). This would be expected if the salt mass transfer coefficient was decreasing due to hindered diffusion. That would imply that the nature of the foulant layer has undergone a transition from a flowing colloidal suspension or loose cake structure to a stagnant cake [7].

Figure 7

It decided to investigate if there was silica deposition on the membrane surface below the measured threshold flux in our study. For this, SEM images were taken for the membrane removed after 2 hours of filtration at an imposed flux of 25 $l/m^2 h$. Interestingly, a modest amount of silica particles was observed on the membrane surface even below the threshold flux as depicted in Fig. 8a. This confirmed that the decrease of G_{DP} prior to threshold flux is most

likely due to the accumulation of silica particles close to and on the membrane surface. Above the threshold flux ($35 \text{ l/m}^2 \text{ h}$), there was a greater accumulation of silica on the surface as shown in Fig. 8b where there were fewer voids and patches as compared to that at $25 \text{ l/m}^2 \text{ h}$ (Fig. 8a). However, denser silica layers did not result in lower G_{DP} values which is consistent with the notion that the dense cake structure resulted in a significantly hindered back transport of NaCl, which produces the CECF effect.

Figure 8

Whilst the properties of these layers cannot be determined from the SEM images, their impact on TMP and the G_{DP} would indicate substantial differences. As observed in Fig 7a, there was a distinct minima around J_{th} where G_{DP} increased sharply with increasing flux and this is interpreted to coincide with the formation of a more structured cake layer from the incipient silica fouling layer on the membrane surface. It is assumed that above J_{th} , as the cake layer grew thicker and denser it enhanced the CECF resulting in a higher salt concentration at the membrane surface which gave rise to the higher G_{DP} as the fouling proceeded further (compare 1 and 2 hr data after flux adjusted in Fig 7a). The higher G_{DP} values at fluxes beyond J_{th} for fluxes maintained for 1 and 2 hours lead to slightly different estimates of J_{th} from ~ 31 to $29 \text{ l/m}^2 \text{ h}$. The latter is closer to the value of J_{th} of $\sim 28 \text{ l/m}^2 \text{ h}$ derived from the TMP data. It is evident that the threshold flux defined here is somewhat dependent on the time scale and in this case the threshold flux from the G_{DP} plot was $\sim 29 \text{ l/m}^2 \text{ h}$ for a flux step of 2 hours each.

In order to study the fouling behavior of colloidal silica below and above the threshold flux, prolonged silica fouling experiments were conducted below and above the threshold flux (imposed flux of $25 \text{ l/m}^2 \text{ h}$ and $35 \text{ l/m}^2 \text{ h}$) to investigate the change of G_{DP} as opposed to TMP

with time. Below the threshold flux, the G_{DP} decreased for the first 3.5 hours of filtration and then increased as shown in Fig. 9a. This phenomenon was previously observed by Sim et al. where the Nyquist plot was originally shifted to the right direction and then to the left [13]. This further confirms that there is a transition for the foulant layer from loose cake to stagnant cake where CECF becomes dominant. However, the nature of this layer above the threshold appears to be different as discussed above. Above J_{th} , the cake formed more rapidly (note different time scales in Figs 9a and 9b) which reduced the mass transfer coefficient of NaCl, leading to a significant CECF effect at the initial stage of the fouling. This can also be observed from Fig. 9b where the G_{DP} increased immediately as fouling proceeded.

The TMP profile (Fig. 9c) shows insignificant changes throughout the course of filtration of 20 hours below the threshold flux. It would appear that the in-situ EIS method is more sensitive than the TMP method in determining the incipient silica fouling event.

Figure 9

It is also worth noting that changes of ion concentration in the DP layer on the permeate side caused by flux adjustment could also impact the G_{DP} value. When the flux was increased in the sub-threshold flux region, the concentration of salt on the permeate side decreased due to the increased salt rejection as shown in Fig. 5a, therefore, resulting in decreased G_{DP} . When the J_{th} is exceeded, the cake forms and the salt concentration rises on the feed side with increasing flux. The increased salt concentration leads to a decrease in salt rejection in the permeate which would lead to an increase in the G_{DP} on the permeate side.

The conductance of the skin layer (G_{skin}) and base layer (G_{base}) of the membrane were also deduced using the INPHAZETM Structure Refinement Software. Fig. 7b shows the changes

in G_{skin} as the flux was increased. The change in G_{skin} was not as distinct as G_{DP} around the J_{th} although it does show a minor minima around $30 \text{ l/m}^2 \text{ h}$. G_{base} , as shown in Fig. 7c does not differ much before and around the J_{th} . These results confirm that the diffusion polarization layer was the dominant layer where fouling behavior can be observed.

5.2.2 Effect of crossflow velocity

The critical flux is known to be dependent on the crossflow velocity [6, 10, 31, 35]. Likewise, we would expect the threshold flux to increase with crossflow velocity. This was examined in a separate series of experiments. The dTMP/dt data versus flux in Fig 10 shows J_{th} at two crossflow velocities (0.15 and 0.30 m/s). The trend of J_{th} with crossflow velocity is similar to that observed in the case of critical fluxes [10, 31, 35]. In the present study, the J_{th} with the increased crossflow velocity (from 0.15 to 0.30 m/s) resulted in a higher J_{th} of $\sim 37 \text{ l/m}^2 \text{ h}$ (up from $30 \text{ l/m}^2 \text{ h}$). The turning point for G_{DP} also shifted to a higher flux of around $40 \text{ l/m}^2 \text{ h}$ that is relatively close to the TMP-derived J_{th} (Fig. 11). It is suggested that the increase crossflow provides a greater shear rate, causing increased back transport of particles from the membrane-solution interface and a thinner layer of silica below the J_{th} . Beyond the threshold flux of about $40 \text{ l/m}^2 \text{ h}$, however, the cake would start to form at the surface leading to CECP and a rise in the G_{DP} as before.

Figure 10

Figure 11

5.3. Effect of spacer

Commercial RO systems and side-stream (canary) cells use spacer-filled channels. In the case of critical fluxes, several studies have shown that J_{crit} can be enhanced in spacer-filled channels [10, 36]. Consequently it was of interest to investigate the effect of a spacer on the threshold flux. This was done by the inclusion of a diamond shaped spacer in the feed channel. The $dTMP/dt$ in the spacer-filled channel is presented in Fig. 12 and the estimated threshold flux, J_{th} , was $\sim 33 \text{ l/m}^2 \text{ h}$ at the crossflow rate of 0.15 m/s . The spacer gave an enhancement of the J_{th} by $\sim 18\%$. The turning point of the G_{DP} plot also shifted to a higher flux as shown in Fig. 13 with a J_{th} as determined by EIS of $\sim 38 \text{ l/m}^2 \text{ h}$. This value is higher, but relatively close to the value obtained by $dTMP/dt$ analysis. A longer flux step period could bring the two methods closer, as suggested by Fig 7a. It has been suggested by Neal et al. [36] that the presence of the spacer introduces complex mixing behavior as the stream flows over and under the attached filaments, leading to a patchy and heterogeneous particle deposition and in the present study it led to a higher value of J_{th} . The fact that the EIS can determine J_{th} , which is dependent on the presence of spacers further supports the use of a side-stream ‘canary cell’ incorporating EIS to characterize plant performance [13, 37]. To simulate the plant, the canary cell requires spacers in the flow channel and the non-invasive detection method needs to provide a ‘membrane-averaged’ signal; EIS delivers this information.

Figure 12

Figure 13

6. Conclusions

EIS was employed to characterize the electrical properties associated with diffusion polarization as a function of the flux. The G_{DP} decreased with increasing flux due to presence of

a flowing colloidal suspension with enhanced concentrations of silica that result from the pressure driven flux. As the flux was increased beyond the threshold flux, the G_{DP} was found to increase, which is attributed to the formation of a stagnant/cake layer and the accumulation of salt in this layer, the so called cake enhanced concentration polarization (CECP) effect. This hypothesis was confirmed when a higher G_{DP} was obtained beyond J_{th} at longer filtration times when a thicker stagnant layer forms with a higher concentration of salt.

The threshold flux measured by $dTMP/dt$ increased with increasing crossflow velocity. The minima of G_{DP} also shifted to a higher flux, indicating the formation of a cake layer at a higher flux, which is attributed to the increased shear force at higher crossflow velocities that tends to drag and transport the particles along on the membrane surface. The efficacy of EIS in characterising the threshold flux was also confirmed in a spacer-filled channel. The enhanced J_{th} obtained by the $dTMP/dt$ measurement was also detected by EIS which revealed a shift of the turning point in the G_{DP} plots to higher flux values.

EIS is able to provide quantitative data for the onset of cake formation and the CECP effect while the TMP measurements on their own provide no direct information for these events. EIS is therefore a promising tool that could be incorporated into a side stream canary cell for fouling and cake formation monitoring in high pressure membrane systems to optimize plant performance. The flux that RO plants are operated at is often conservative and based on in-situ EIS measurements, the plant could be tuned to operate more efficiently at or just below the threshold flux.

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Nomenclature

i	alternating current
i_o	amplitude of current
v	voltage
v_o	amplitude of voltage
Z	impedance (ohms m ²)
j	imaginary constant
Y	admittance (ohms ⁻¹ m ⁻²)
G	conductance (S/m ²)
C	capacitance (F/m ²)
G_{DP}	conductance of diffusion polarization layer (S/m ²)
G_{skin}	conductance of membrane skin layer (S/m ²)
G_{base}	conductance of membrane support layer (S/m ²)

J_{th} threshold flux ($l/m^2 h$)

Abbreviation

RO Reverse osmosis

TMP Transmembrane pressure

CEOP Cake enhanced osmotic pressure

CECP Cake enhanced concentration polarization

EIS Electrical impedance spectroscopy

DP Diffusion polarization

Greek symbols

θ phase difference

ω angular frequency (rad/s)

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Fig. 1. Schematic illustration of electrical driven diffusion polarisation (DP) process at low frequencies. The profiles of concentration shown in (a) are for that part of the AC cycle when the electric current is towards the membrane from the feed side to the permeate side. It is assumed in this illustration that in the membrane the transport number (fraction of current carried) for Na^+ is greater than that for Cl^- . In the next half cycle of the AC current, the

concentration profiles are reversed as shown in (b). Note that a DP exists at both the feed and permeate sides of the membrane and the impedance elements associated with these are in series.

Fig. 2. Cross section (bottom) and explode view (top right) of the stainless steel RO-EIS crossflow cell for impedance measurement. (1 and 8 – metal plates, 2, 4 and 7 – insulating plastic gaskets, 3 and 6 – metal plates that form the chamber and also act as the current electrodes. The voltage electrodes protrude through the plates that act as the current injecting electrodes and are insulated from it. The tip of the voltage electrodes make contact direct with the solutions on either side of the membrane (feed or permeate). The bolts that clamp the components of the flow chamber together are insulated from the current injecting electrodes by plastic sleeves.

Fig. 3. Schematic diagram of the RO-EIS crossflow filtration system.

Fig. 4. Representative Nyquist plot of a silica-fouled RO system. Conditions: RO feed = 200 ppm silica with 2000 ppm NaCl; Flux = $30 \text{ l/m}^2 \text{ h}$; crossflow velocity = 0.15 m/s . The full line represents the fitted results obtained from the Maxwell Wagner model using the INPHAZETM Structure Refinement Software.

Fig. 5. (a) TMP, permeate flux and salt rejection versus time plot; (b) $d\text{TMP}/dt$ versus permeate flux for the flux step experiment. Conditions: RO feed = 200 ppm silica with 2000 ppm NaCl; crossflow velocity = 0.15 m/s.

Fig. 6. Nyquist plots obtained from EIS measurement with the flux step method. The points in the plot represent the measured data whereas the solid lines are obtained from the fitted data using the Maxwell-Wagner model. Error bars (generally smaller than the size of the symbols) were obtained from three scans for a particular imposed flux. Note that the x and y-axes of the plot are presented in different scale in order to better illustrate the shifts in the Nyquist plots. Conditions: RO feed = 200 ppm silica with 2000 ppm NaCl; crossflow velocity = 0.15 m/s.

Fig. 7. (a) G_{DP} (b) G_{skin} and (c) G_{base} of membrane obtained from the fitted model for silica fouling in the flux step method. The time in (a) indicates the duration after the flux has been adjusted to the desired one. Conditions: RO feed = 200 ppm silica with 2000 ppm NaCl; crossflow velocity = 0.15 m/s.

Fig. 8. SEM images of silica particles on membrane surface at x20,000 magnification after 2 hours of fouling at (a) 25 l/m² h; (b) 35 l/m² h and (c) clean membrane. Conditions: RO feed = 200 ppm silica with 2000 ppm NaCl; crossflow velocity = 0.15 m/s.

b

Fig. 9. (a) G_{DP} of membrane obtained from the fitted model for silica fouling as a function of time in a prolonged fouling experiment at a flux of 25 l/m² h. (b) G_{DP} of membrane obtained

from the fitted model for silica fouling as a function of time in a prolonged experiment at a flux of $35 \text{ l/m}^2 \text{ h}$ and (c) TMP at an imposed flux of 25 and $35 \text{ l/m}^2 \text{ h}$ in the prolonged fouling experiment. Conditions: RO feed = 200 ppm silica with 2000 ppm NaCl; crossflow velocity = 0.15 m/s .

Fig. 10. Comparison of $dTMP/dt$ versus flux plot for flux step experiments with different crossflow velocities. Conditions: RO feed = 200 ppm silica with 2000 ppm NaCl; crossflow velocity = 0.15 m/s and 0.30 m/s.

Fig. 11. Comparison of G_{DP} for flux step experiments with different crossflow velocities. Conditions: RO feed = 200 ppm silica with 2000 ppm NaCl; crossflow velocity = 0.15 and 0.30 m/s.

Fig. 12. $dTMP/dt$ versus permeate flux for flux step experiment with and without a spacer in the feed channel. Conditions: RO feed = 200 ppm silica with 2000 ppm NaCl; crossflow velocity = 0.15 m/s.

Fig. 13. G_{DP} of membrane obtained from the fitted model for silica fouling in the flux step experiments with no spacer in the feed channel and with a spacer in the channel. Conditions: RO feed = 200 ppm silica with 2000 ppm NaCl; crossflow velocity = 0.15 m/s.

Highlights

Electrical impedance spectroscopy (EIS) detects threshold flux (J_{th}) of colloids in RO

EIS detects phenomenological events at the membrane-solution interface

Conductance (G_{DP}) of the polarization layer has a minimum at J_{th}

G_{DP} rise after J_{th} due to cake-enhanced concentration polarization

EIS detects higher J_{th} at higher crossflow and for spacer-filled channel

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