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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.

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”

Abbreviations: RO, reverse osmosis; TMP, transmembrane pressure; CEOP, cake enhanced osmotic pressure; CECP, cake enhanced concentration polarization; EIS, electrical impedance spectroscopy; DP, diffusion polarization

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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(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, $i = i_0 \sin(\omega t)$ at a series of known frequencies ω and amplitude i_0 into the system and measuring the voltage $v = v_0 \sin(\omega t - \theta)$across the sample. The voltage amplitude v_0 and phase difference θ between the voltage and current are measured. The magnitude of the impedance is given by,

$$|Z| = \frac{v_0}{i_0} \tag{1}$$

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

$$Z = |Z|e^{j\angle Z} = \frac{v_0}{i_0}e^{-j\theta} = \frac{v_0}{i_0}(\cos\theta - j\sin\theta) \tag{2}$$

where $|Z|(=\frac{v_0}{i_0})$ and $\angle Z(=-\theta)$ define the impedance magnitude and phase respectively. This gives the impedance in terms of the measureable parameters, such as i_0, v_0, θ and the imaginary unit vector, j where $j^2 = -1$.

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

$$Y = \frac{1}{Z} = \frac{i_0}{v_0}e^{j\theta} = \frac{i_0}{v_0}(\cos\theta + j\sin\theta) \equiv G + j\omega C \tag{3}$$

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,

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

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

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

Eq. (5) can also be expressed as

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

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,

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

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