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Dielectric measurements of fouling of nanofiltration membranes by sparingly soluble salts

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ABSTRACT

The dielectric spectroscopy of three industrial nanofiltration (NF) membranes NF90, NF270 and NF-, before and after fouled by $CaCO_3$, $CaSO_4$, $BaSO_4$, $SrSO_4$, were measured. The fouling process and different fouling mode caused by the different membrane pore radius were monitored by dielectric spectroscopy. The NF270 and NF- were mainly fouled in the inner of the membrane pore and NF90 was fouled both in the inner of the membrane pore and on the membrane surface where a scaling layer formed. By analyzing the dependence of dielectric parameters on the fouling time, the relaxation mechanisms of different membrane systems were explained: for the membrane NF270 and NF-, the relaxation observed at the initial stage of fouling process was the result of cooperation of interfacial polarization (between the fouled membrane and deionized water) and the concentration polarization (near the membrane surface) which is from the dissociation of the scale formed by insoluble salts (denoted as CP hereafter), and for that of membrane NF90, in addition to the above two mechanisms, the interfacial polarization between fouling layer and deionized water also contributes. The relaxation after 4 h was mainly controlled by the interfacial polarization between the fouled membrane and solution interface. Further, taking the membrane fouled by $CaSO_4$ as an example, the dielectric analysis was carried out by introducing a constant-phase-element (CPE) to circuit to describe the fouled membrane and the scaling layer. Our finding indicates that the size of membrane pore would influence the fouling process. The feasibility of dielectric spectroscopy as a noninvasive method to monitor the fouling process of internal and surface of membrane was also discussed.

1. Introduction

Nanofiltration (NF) membrane is widely used in drinking water production, water treatment and so on [1]. However, membrane fouling caused by sparingly soluble salt that adhere to pores and the surface of the membrane reduces the membrane separation efficiency, increases costs and shortens membrane life [2]. Therefore, the research on membrane fouling has attracted extensive attention.

Understanding of the micromechanism of membrane fouling is of vital importance to membrane fouling control and cleaning. Although there is no generally accepted theory to explain the complex question, traditionally, the initial decline of membrane flux is attributed to concentration polarization [3], while the long-term decline is attributed to membrane fouling [4]. Despite the mechanisms of concentration polarization and membrane fouling are totally different from each other, the presence of CP phenomenon leads to elevated concentration of solutes and/or particles at the membrane surface and the concentration of these solutes can reach oversaturated easier, which increases the risk of membrane fouling. Hence, it is necessary to take the CP phenomenon into consideration when studying the membrane fouling process.

Up to now, several methods could be used for membrane fouling study, which includes identification of pollutant component and morphology and monitoring the formation process of pollutant. In addition to chemical analytic methods, some characterization techniques, such as scanning electron microscope (SEM) [5], atomic force microscope (AFM) [6], X-ray fluorescence spectrometry (XRF) [7] and so on, could also provide information about pollutant's morphology, structure and elements, etc. However, these off-line techniques could not track the formation process of the pollutant on membrane surface.

Methods for in situ detection of membrane fouling mainly consists of direct observation of particle deposition on membrane

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surfaces by a microscope [8,9]; in situ observation of the change of particle cake layer using laser technique [10,11]; the processes study of scaling layer formation and particle deposition on membrane surface with ultrasonic time-domain reflectometry (UTDR) [12,13]. However, relatively expensive equipment and complicated operation make these methods above hard to popularize in practice. Meanwhile, some methods for concentration polarization study have also been developed, which mainly consists of shadowgraph [14], Magnetic resonance imaging (MRI) [15], Electron diode array microscope (EDAM) [16], etc. These methods could provide information on solution concentration within the concentration polarization layer and the thickness of concentration polarization layer and so on, however, complicated operation limit their application area.

Electrochemical impedance spectroscopy (EIS) method has also been widely used to study membrane fouling due to its relatively simple experiment equipment. Chilcott et al. [17] and Gaedt et al. [18] proposed its feasibility for investigating membrane fouling, the results indicate that the method has potential for monitoring the deposition of particulate that can lead to fouling. Park et al. [19] investigated bovine serum albumin (BSA) fouling of the cation-exchange membrane and anion-exchange membrane using impedance spectroscopy. Differences in the dispersions arising from fouling were identified by subtracting the impedance of the solution from those of unfouled and fouled IEMs in solution. They also [20] studied the fouling phenomena of an anion-exchange membrane by BSA using the current–voltage (*I*–*V*) relation and electrical impedance spectroscopy. Two distinguishable slopes were observed in the over-limiting current density(LCD) region of *I*–*V* curve, indicating the change of resistance was caused by the structure changes of the BSA fouling layer formed on membrane surface. Lee et al. [21] investigated ion exchange membrane fouling by sodium dodecylbenzenesulfonate (SDBS). The equivalent circuits show that an additional layer formed on the membrane surface, increasing the electrical resistance to permeation of ions through the membrane. Kavanagh [22] analyzed the electrical property change of reverse osmosis membrane before and after fouled by $CaCO_3$ using the equivalent circuit and found that fouling could potentially be measured by the increased impedance at frequencies below 100 Hz. Moreover, electrochemical impedance spectroscopy could also be used to study concentration polarization. Zhao et al. [23,24] investigated the concentration polarization phenomena in ion-exchange membrane/solution system under application of d.c. bias voltage, the conductivity of the reduced ion concentration and the thickness of the concentration polarization layer were obtained by modeling analysis. Sang et al. [25] discussed the formation and structure of concentration polarization layer (CPL) on ion-exchange membrane-solution interface under high frequency AC electrical field, and investigated the relations of CPL thickness with the electrolyte concentration and ion-exchange membrane property. In recent years, Antony et al. [26] studied the fouling of reverse osmosis membrane during the filtration of water containing $CaCO_3$. They found that dielectric structural modeling was able to detect and characterize five electrically distinct layers and a concentration/diffusion polarization. Sim et al. [27] used Silica and BSA as model foulants, and studied the fouling process of single and binary foulants on the reverse osmosis (RO) membrane by EIS. Hu et al. [28] used EIS to measure the electrical properties changes during calcium sulfate scaling in a reverse osmosis system. They found that the conductance signal of 10–100 Hz can signal the nascent stages of scale formation. Cen et al. [29] detect the fouling of reverse osmosis membranes, during filtration of industrial (molasses) waste water and model feeds containing silica and BSA foulants. They found that the low frequency (1 Hz) capacitance was the most sensitive measurement and was more sensitive than either conductance or fluxdecline.

From the reviews above, we can see that the studies about membrane fouling and concentration polarization using electrochemical impedance spectroscopy were mainly focused on the systems of ion-exchange membrane/solution and reverse osmosis membrane, and few researches on the nanofiltration membrane fouling and the accompanying concentration polarization phenomenon.

In the present work, the fouling process of three types of nanofiltration membrane (NF90, NF-, NF270) fouled by $CaCO_3$, $CaSO_4$, $BaSO_4$, $SrSO_4$ solutions was simulated in the laboratory. Dielectric measurements for the three nanofiltration membranes fouled at different time were carried out over a frequency range from 40 Hz to 11 MHz. The dielectric parameters and phase parameters of membranes were obtained by dielectric analysis. By analyzing the dependence of these parameters on the fouling time, the feasibility of dielectric spectra for monitoring NF fouling and concentration polarization caused by sparingly soluble salt was assessed.

2. Experiment and materials

2.1. Chemicals and membranes

Na_2CO_3, $CaCl_2$, $BaSO_4$ and $SrSO_4$ were analytical grade and $CaSO_4 \cdot 2H_2O$ was chemical grade. Deionized water (D.W.) was used in the experiment. Three commercial NF membranes (Dow, USA), NF90, NF270 and NF-, were used. Some parameters of the membranes are shown in Table 1.

2.2. Preparation of scaling solution

2.2.1. Preparation of saturated $CaCO_3$ solution

Solutions of Na_2CO_3 and $CaCl_2$ having the same concentration (6 mM) were mixed fully with a volume ratio of 1:1. After standing for some time, the supernatant fluid was used as the scaling solution.

2.2.2. Preparation of saturated $CaSO_4$ solution

The $CaSO_4$ powder was dissolved directly in deionized water and the supernatant fluid was used as scaling solution. The preparation methods of $BaSO_4$ and $SrSO_4$ solution are the same as $CaSO_4$ solution.

2.3. Simulation of membrane fouling and dielectric measurements

The experiment is divided into two stages. The first stage is to simulate the fouling process of nanofiltration membrane and the second stage is to carry out dielectric measurements for the fouled membrane.

2.3.1. Experiment of membrane fouling

The experimental set-up for membrane fouling is shown in Fig. 1. The membrane fouling experiment is a single channel cross-flow filtration process. The NF membrane is fixed in the middle of a rectangular cell with a cylinder chamber, separating the cylinder chamber into two chambers. The effective surface area of the membrane is actually the bottom area of the cylinder. The scaling solution was pumped from a stirred tank using peristaltic pump to the rectangular cell, flowing along the active layer of NF membrane, and then recycled back to the stirred tank. During filtration, as crystals would deposit at the membrane surface, saturated feed solution was added into stirred tank to ensure the feed concentration was constant. Flow pressure and temperature were kept at 0.055–0.075 MPa and 20 ± 1 °C, respectively.