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In-situ monitoring of inorganic and microbial synergistic fouling during nanofiltration by UTDR

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ABSTRACT

This study describes an ultrasonic time-domain reflectometry (UTDR) as an non-invasive real-time technique for in-situ monitoring of the early-stage $CaSO_4$ and microbial synergistic fouling on nanofiltration (NF) membranes. The fouling experiments were carried out with 1.0 g/L and 1.5 g/L calcium sulfate solution at the operating pressure of 0.7 MPa, the temperature of 25±0.5°C and the flow rate of 0.13 cm/s. The number of bacteria incubated from lake was 5×10^6 cell/ml. A commercial nanofiltration membrane was utilized in this study. The permeate flux, rejection and ultrasonic measurements were made at regular intervals during cross-flow NF. Results show that the flux obtained in the experiment with bacteria declined subtly slower than that without bacteria in the early phase, and then declined to the same level in the later phase of the fouling process. The rejection obtained in the experiment with bacteria was higher than that without. Furthermore, the acoustic measurements indicate that the fouling layer obtained with bacteria was thicker and looser than that without bacteria under the condition of low concentration solution. However, the layer becomes thicker and denser under the condition of high concentration solution. It implies that bacteria could accelerate deposition of inorganic scaling on NF membrane. Independent measurement such as flux-decline date, SEM analysis and weight measurement corroborate the ultrasonic measurement. Overall, this study suggests that the ultrasonic technique, due to its powerful capabilities and its use in monitoring devices, can be of great significance in the membrane industry.

Keywords: Nanofiltration; Membrane fouling; $CaSO_4$ and microbial synergistic fouling; Ultrasonic time-domain reflectometry

1. Introduction

Nanofiltration (NF) has been paid more attention as the optimized step in water treatment technology. Having characteristics half-way between ultrafiltration (UF) and reverse osmosis (RO), NF requires a much lower operating pressure than RO, offers higher permeate flux compared to that of RO, and allows rejection of multivalent ions and dissolved organic compounds [1–3]. These advantages have popularized the application of NF technologies in drinking water treatment and wastewater effluents reclamation as an alternative for RO. However, like other membrane processes, fouling is always a big challenge to the membrane operation.

Numerous investigations were performed to study the membrane fouling mechanism in order to support much more important theoretic date for the optimization of membrane operation. Foulants can be categorized into several groups such as sparingly soluble (inorganic) salts, organic substances, colloidal and particulate matter and biological growth [4]. In drinking water treatment, colloidal and organic substances are the main foulants of all. Hence, many researchers have studied the membrane fouling of organic substances and colloidal [1–5]. The fouling

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mechanisms were (a) "cake-enhanced osmotic pressure" (CEOP) for individual colloidal fouling, (b) NOM-calcium complexation for individual NOM fouling and (c) CEOP and NOM-calcium complexation for the combined fouling [1]. The $CaSO_4$ fouling layer during NF process was analyzed by Lee et al. [6]. The inorganic fouling of calcium carbonate on RO membranes were also monitored by ultrasonic time-domain reflectometry (UTDR) by Mairal et al. [12] and Sanderson et al. [13].

The fouling caused by inorganic salts, organic substances, colloidal and particulate matter can generally be controlled by reduction of foulant concentration in the water phase, but biofouling is much more complex and inevitable attributed to the reproduction of microorganisms depending on the consumption of the nutrient in water. Many studies about biofilm have been done from the structure, density, thickness and the factors that affect the growth of biofilm [7–11]. Microorganisms can multiply even if their number is strongly diminished, and they will do so if nutrients are available. The adhesion of microorganisms on the solid surface seems to be the strategy of bacteria to survive, forming biofilms capable of scavenging nutrients in very low concentration in the feed water. The three general phases of biofilm development may be described as follows [7]: (1) the induction phase, with primary colonization (Attachment); (2) the logarithmical growth phase (Growth) and (3) the plateau phase (Stability even detachment). The first phase is most important for the prevention of biofilm developments. To prevent the adhesion of microorganisms is the most effective method to control membrane biofouling. However, many studies focused on the already-formed biofilm or the whole growth process. Studies about the early-stage of biofilm (the microorganism cells alone, no growth) are not very usual.

The focus of this study was to understand the combined fouling of microorganism cells and $CaSO_4$ on NF membrane. Especially, in recent years, the ultrasonic time-domain reflectometry (UTDR) as an in-situ, non-invasive technology has been used in detection of membrane fouling and cleaning as well as early-stage biofilm growth on polymeric surfaces [12–21]. However, it was seldom used to monitor the combined fouling of membrane. The objective of this study was to monitor the combined fouling of microorganism cells and $CaSO_4$ by UTDR in order to get a further understanding of fouling mechanism.

2. Experimental

2.1. Cross-flow nanofiltration and UTDR measurement systems

Figure 1 shows a schematic of the NF experimental setup and UTDR measurement system. The apparatus

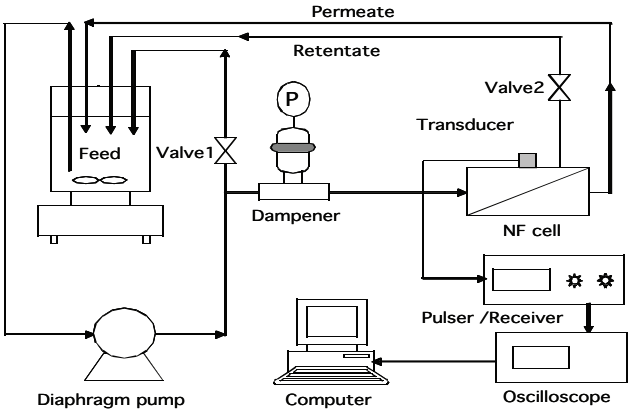

Fig. 1. Schematic NF experimental setup and UTDR measurement system.

consisted of a 5 L feed tank for storage and supply of the feed solution, a diaphragm pump for pressurization of the feed solution, a rectangular test module (200 mm length and 110 mm width), a stirring system, analog pressure gauge and valves. The cross-flow membrane system had one feed stream entering the system, one rejection stream (brine) and one permeate stream (purified water) leaving the system. These three streams were circulated back to the feed tank in the experimental setup.

The ultrasonic measurement system consisted of a 10 MPa ultrasonic transducer (Panametrics V111), a pulser-receiver (Panametrics 5058PR) and a 350 MHz digital oscilloscope (Agilent 54641A) with sweep speeds from 50 s per division to 1 ns per division and 2 mV per division sensitivity. The transducer was externally mounted in contact with the top plate of the separation module. The incident wave from the transducer was perpendicular to the membrane surface. The oscilloscope connected to the pulsar-receiver captured and displayed the data signal as amplitude changes on its front panel. Each set of ultrasonic data generated consisted of 5000 data points. These data can be stored on a computer's hard drive for the further analysis. The principle and application of ultrasonic measurement on the membrane fouling monitoring can be found elsewhere [13–17].

2.2. Experimental procedure

A thin-film composite nanofiltration (NF) membrane (XLE-DOW/Filmtech) was used in all the experiments. The membrane samples were cut into the pieces with a size of 16 × 7.5 cm and stored in deoinized water at 4°C. The deoinized water was regularly replaced. All membrane samples were rinsed thoroughly with deoinized water prior to use. The surface morphology of the fouled membrane samples were analyzed using a scanning electric microscope (SEM QUANTA200, FEI).

This investigation was performed in two parts—to culture the microorganism and to foul the membrane by $CaSO_4$ solution alone or combined $CaSO_4$-microorganism solution. The first part was to obtain the microorganism cells at a high concentration. The microorganism population was extracted from a lake, and then incubated in the culture medium of sterile peptone, beef extract and sodium chloride stored in swaying bed at 37°C. The microorganisms multiplied rapidly in 24 hours. The extraction of cells was obtained by centrifugation in physiological saline at 4000 r/min. The number of cells could be calculated according to the adsorption of visible light. The centrifuged microorganism cells were used as a kind of foulant for the following fouling processes. The second part was to foul the NF membrane by $CaSO_4$ solution combined with microorganism. The fouling processes were monitored by the ultrasonic measurement. In order to compare the synergistic fouling mechanism of $CaSO_4$ and microorganism on the membrane, NF fouling experiment carried out with $CaSO_4$ alone was conducted under the same conditions. The ultrasonic signals were captured synchronously during $CaSO_4$ deposition processes.

The scaling experiments were performed with 1.0 and 1.5 g/L $CaSO_4$ solution with and without microorganisms (5×10^6 cell/ml). Before the fouling, each experiment commenced with pure water being circulated through the system at the desired flow rate, applied pressure and temperature (0.13 cm/s, 0.7±0.01 MPa and 25°C) for 2 h in order to attain a steady state. Once a steady state with respect to the permeate flux and the ultrasonic signal was attained, the feed was displaced by the $CaSO_4$ solution or $CaSO_4$-microorganisms solution. The experiments continued until the flux and ultrasonic response had stabilized (360 min). During the experiments, the flux, ultrasonic signal and the concentration of Ca^{2+} in the permeate solution were measured at a regular time. The reproducibility of experimental results was also investigated.

3. Results and discussion

3.1. Effect of microorganisms on membrane flux and Ca^{2+} rejection

As mentioned above, once steady state was attained after pure water (PW) filtration, the feed was switched to a scaling solution (1.0 g/L $CaSO_4$ solution alone or combined with microorganisms) to initiate the fouling experiments. The normalized flux and Ca^{2+} rejection under different operation conditions are summarized in Fig. 2a. It shows that the normalized fluxes drop to 33.9% and 23.2% of the initiate fluxes in the experiments with and without microorganisms after 45 min of fouling. The flux obtained with microorganisms kept 5–6% higher than that without microorganisms, and then declined nearly at the same level after 450 min fouling (7% of the initial flux). Meanwhile, the Ca^{2+} rejection in the experiment with microorganism is 2–7% higher than that without.

In order to consolidate the above observation, further experiments were carried out with 1.5 g/L $CaSO_4$ alone or combined with microorganisms. Similar results can be seen from Fig. 2b that the normalized fluxes are 17.9% and 12.5% of the initial fluxes in the experiments with and without microorganism after 45 min fouling. The tendency kept until the end of fouling experiment, and declined to 3% of the initial flux. The rejection obtained with microorganisms is 6–18% higher than that without.

Overall, these results suggest that the presence of the microorganisms can effectively slow down the permeate flux decline and increase the rejection of inorganic ions. Meanwhile, the higher concentration of scale solution can cause more serious membrane fouling.

3.2. UTDR measurements analysis

Ultrasonic measurements are based on the propagation of mechanical waves. A detailed description of the theory of ultrasonic measurements for membrane

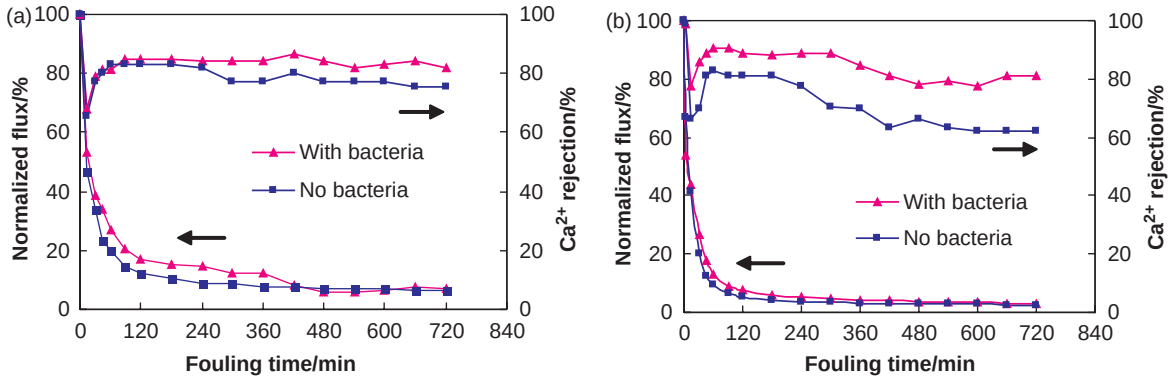

Fig. 2. Normalized flux and Ca^{2+} rejection vs. operation time: (a) 1.0 g/L$CaSO_4$; (b) 1.5 g/L$CaSO_4$.

applications has been presented previously [13–17]. The ultrasonic wave pulses are transmitted by the externally mounted transducer and propagate through the module. Briefly, a partial reflection of an acoustic wave can occur from any planar interface across which there is a difference in acoustic impedance. Since each of these waves will travel a different distance from and to the transducer, they can be distinguished on the basis of their different arrival times if sufficient signal resolution is available.

It is difficult quantitatively to interpret the signals received in ultrasonic testing and signal analysis processes when two or more signals are overlapping or a layer is much thinner than its support. A differential signal as one of the approaches for overlapping signal separation is defined as the difference between reference waveform and test waveform [17–18]. In this study, the waveforms obtained at the pure water state were considered as the references, and a fouled membrane waveform was used as the test waveform. The differential signal represents an echo signal of the scale layer on the membrane surface. In here, the differential signals obtained at 15, 60, 480, and 720 min of the fouling operation carried out with different solutions are illustrated in Figures 3–6.

Figures 3 and 4 show the differential signal (broken line) growth at 1.0 g/L $CaSO_4$ solution fouling alone and it combined with microorganisms. It can be seen from Fig. 3 that a differential peak appeared after 60 min of fouling and grew with 156 mV after 720 min of fouling. Similar phenomena can also be observed in Fig. 4. However, the peak obtained by 1.0 g/L $CaSO_4$ solution fouling alone is larger than that obtained by the combined fouling (94 mV). In order to confirm the above observation, further experiments were carried out with 1.5 g/L $CaSO_4$ solution. The growth of differential signal is present in Figures 5 and 6. It reveals that the amplitude obtained in the experiment of $CaSO_4$ and microorganisms combined fouling (281 mV) is larger than that obtained by $CaSO_4$ fouling alone (156 mV). The growth of amplitude is attributed to the increase in the density of the fouling layer [16]. In general, as the fouling processed, the amplitude of differential signal increased which implied that the density of fouling layer was increasing with the fouling time.

To get the overall growth and development of the fouling layer on the membrane surface, Fig. 7 plots the amplitudes of the differential signals as a function of operation time during the fouling experiments carried out with 1.0 and 1.5 g/L $CaSO_4$ solution with and

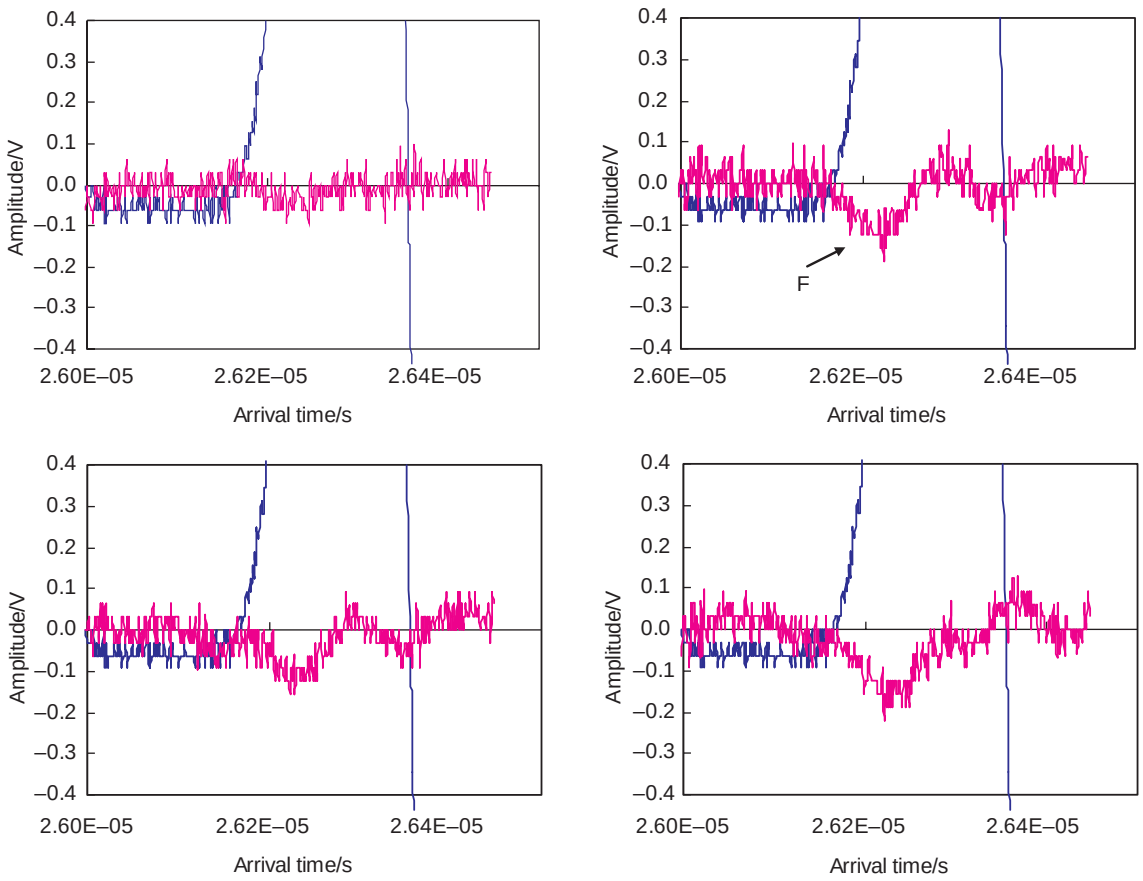

Fig. 3. Amplitudes of differential signals vs. operation time obtained at (a) 15 min, (b) 60 min, (c) 480 min and (d) 720 min in the experiments carried out with 1.0 g/L $CaSO_4$ solution alone.

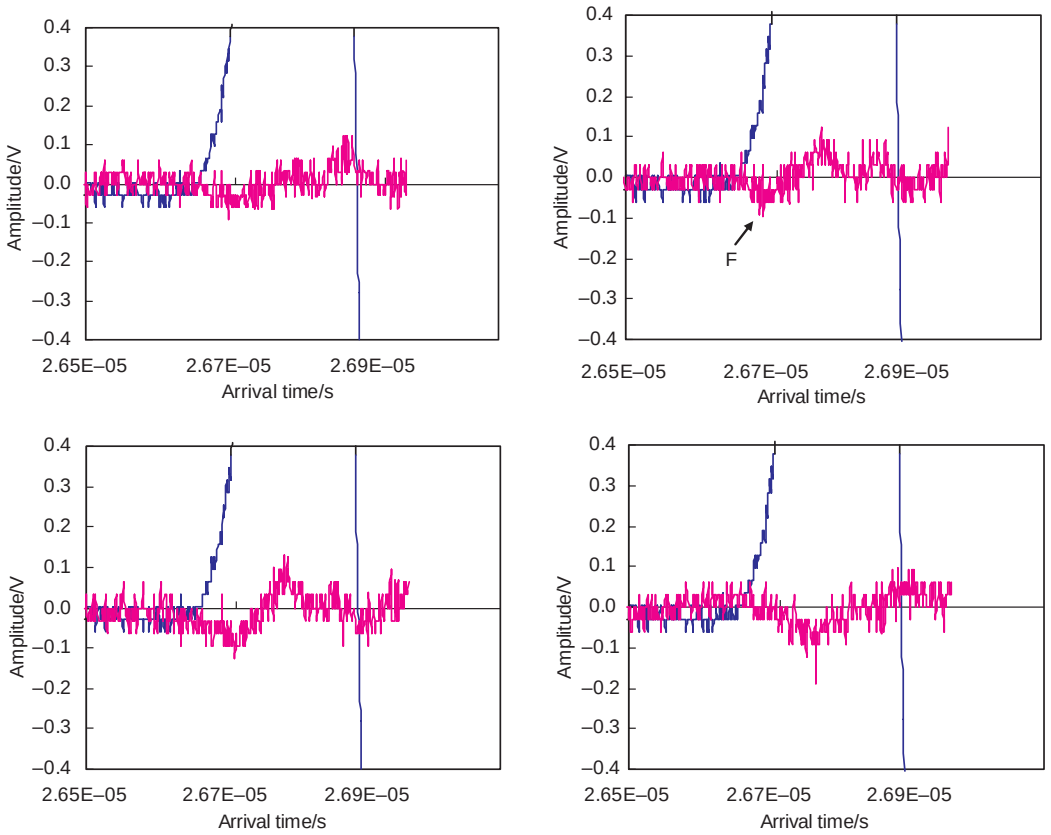

Fig. 4. Amplitudes of differential signals vs. operation time obtained at (a) 15 min, (b) 60 min, (c) 480 min and (d) 720 min in the experiments carried out with 1.0 g/L $CaSO_4$ solution combined with bacteria.

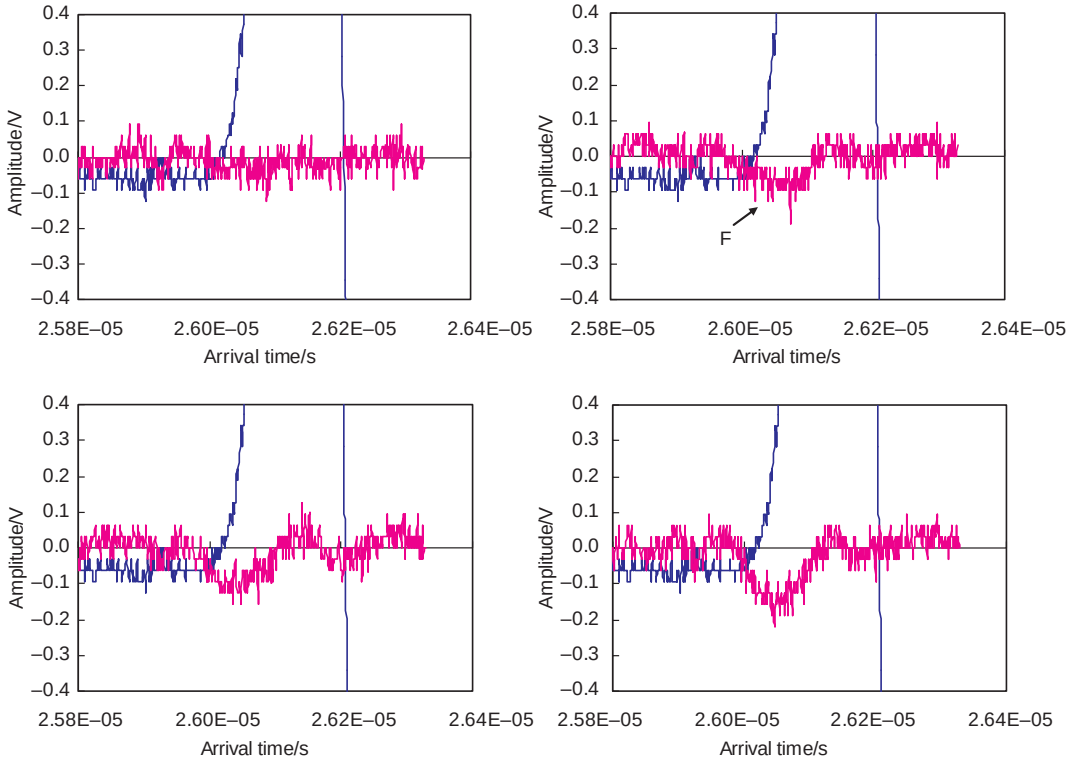

Fig. 5. Amplitudes of differential signals vs. operation time obtained at (a) 15 min, (b) 60 min, (c) 480 min and (d) 720 min in the experiments carried out with 1.5 g/L $CaSO_4$ solution alone.

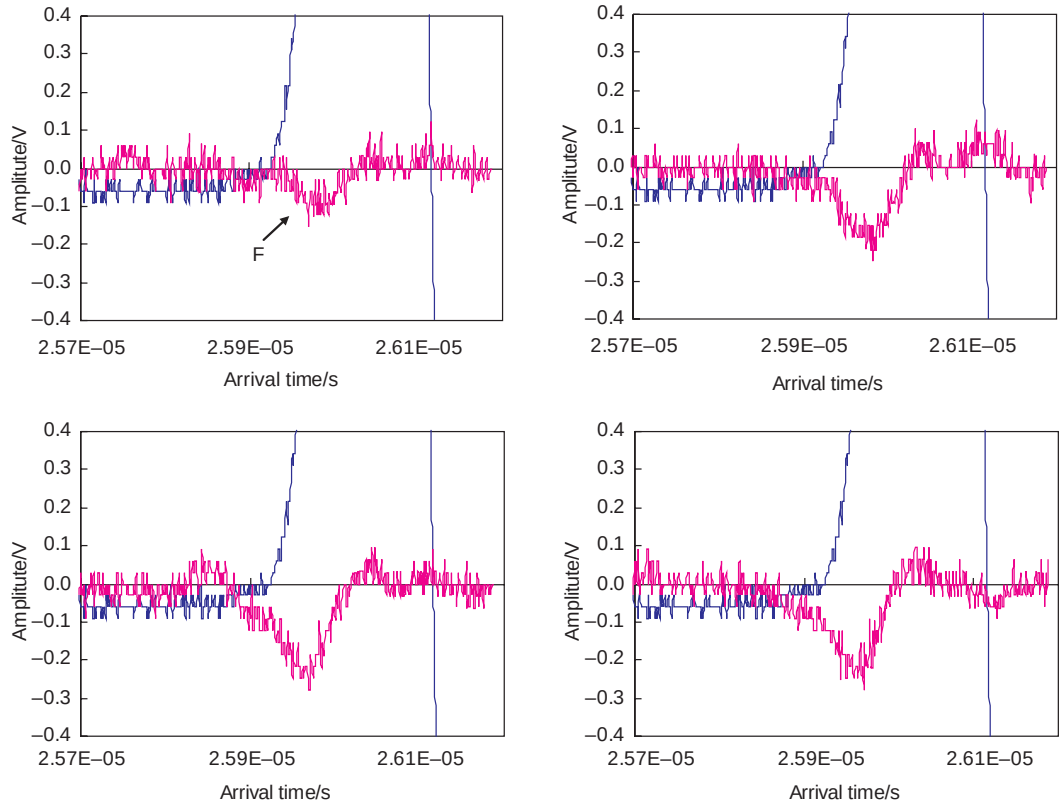

Fig. 6. Amplitudes of differential signals vs. operation time obtained at (a) 15 min, (b) 60 min, (c) 480 min and (d) 720 min in the experiments carried out with 1.5 g/L $CaSO_4$ solution combined with bacteria.

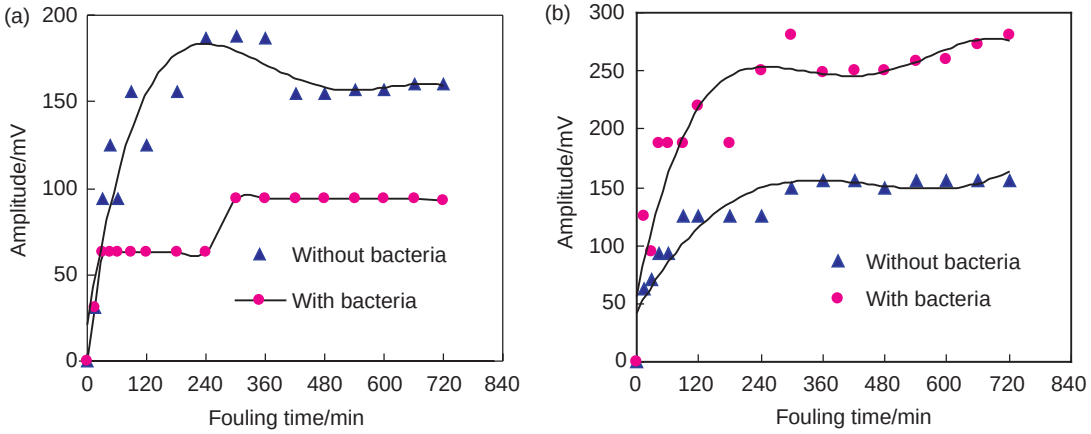

Fig. 7. Amplitudes of differential signals vs. operation time in the experiments carried out with (a) 1.0 and (b) 1.5 g/L $CaSO_4$ solution combined with and without bacteria.

without microorganisms. It can be seen in Fig. 7 that the amplitude of differential signals increased as the fouling progressed in the experiments [16]. An increase in the amplitude results from scaling deposition. The denser the fouling layer is, the better reflection and thus the larger the amplitude that is seen [15]. However, the amplitude of differential signal with microorganisms is lower than that in the scale fouling alone in the experiments performed with 1.0 g/L $CaSO_4$ solution, while it acts contrarily in the operation at 1.5 g/L scale solution. This is due to the different rate of $CaSO_4$ and microorganisms' content. In the low concentration (1.0 g/L) of inorganic ions experiments, the microorganisms can support a crystal nuclear during the deposition process which lead to a looser fouling layer than that in the scale fouling alone operation. When the concentration of inorganic ions is higher (1.5 g/L), the microorganisms content is relatively little for the foulant. Therefore the existence of microorganisms does less effect on the crystal formation and deposition.

According to the principle of UTDR, the thickness of fouling layer can be calculated from the differential signal curves. Figure 8 shows the thicknesses of the fouling layers as a function of operation time during the fouling experiments carried out with 1.0 and 1.5 g/L $CaSO_4$ solution with and without microorganisms. At two different concentrations of $CaSO_4$, the fouling layers in the experiments with microorganisms are thicker than that obtained by scale fouling alone. The foulant coverage on the membrane obtained by weight measurement can further confirm the above observations. The deposition coverage was 1.34 and 1.88 μg/cm^2 during the fouling experiments carried out with 1.0 and 1.5 g/L $CaSO_4$ solution alone, and 1.88 and 2.35 μg/cm^2 with microorganisms, respectively. It is obviously that the deposition coverage carried out with microorganisms is more than that obtained without microorganism.

3.3. Morphological characteristics of fouling layer

In order to get a further studies about the combined fouling behavior of inorganic ions and microorganisms, the fouled membrane samples were scanned by the scanning electronic microscope (SEM). The SEM micrographs

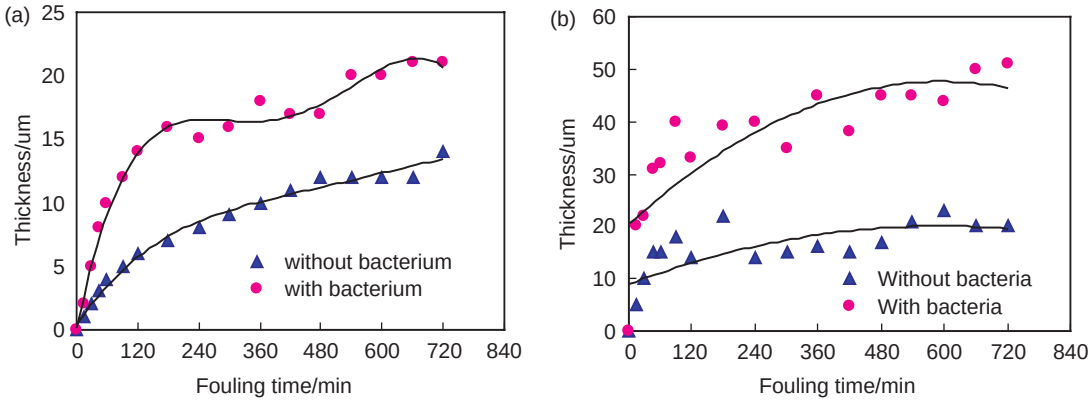

Fig. 8. Thickness vs. operation time in the experiments carried out with (a) 1.0 and (b) 1.5 g/L $CaSO_4$ solution combined with and without bacteria.

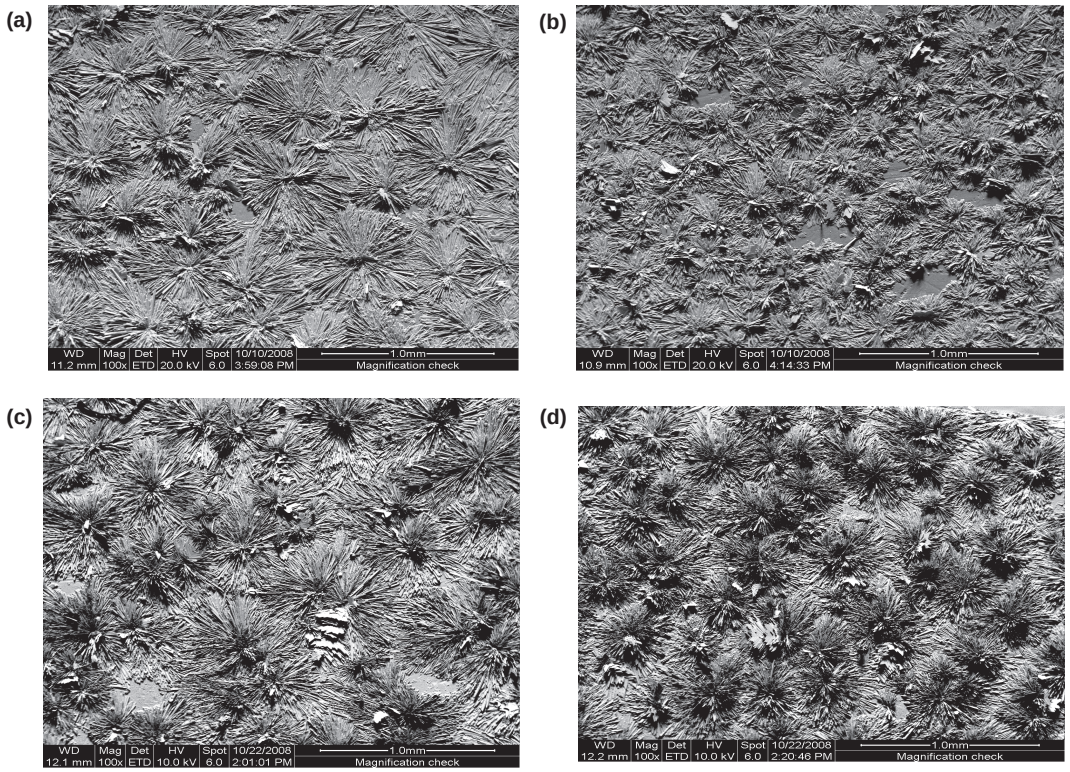

Fig. 9. SEM micrographs of membrane surface after 720 min of fouling operation in the experiments (a) 1.0 g/L $CaSO_4$ alone; (b) 1.0 g/L $CaSO_4$ and microorganisms; (c) 1.5 g/L $CaSO_4$ alone; (d) 1.5 g/L $CaSO_4$ and microorganisms.

of membrane surfaces are shown in Fig. 9. It obviously reveals that the crystal flowers rolled out around on the membranes when the membrane was fouled by $CaSO_4$ alone, while they grew upward when the membrane was fouled by the $CaSO_4$ and microorganisms. The presence of microorganisms affects the crystal formation and growth. That is the reason why the flux and rejection were improved in the combined fouling experiments of inorganic ions and microorganisms.

4. Conclusion

This study provides the evidence that ultrasonic measurements have successfully been employed to monitor the combined fouling processes of bacteria and $CaSO_4$ during NF separation. The results show that bacteria may be as crystallization nuclei favoring the deposition of inorganic salt ($CaSO_4$) on NF membrane. The UTDR can distinguish the fouling behaviors with the different fouling conditions. The flux decline is related not only to the thickness of scaling layer, but also to the scaling density. The ultrasonic results have a good agreement with the independent measurements including flux-decline date, SEM analysis and weight measurement.

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