Analyzing the spatial and temporal characteristics of membrane fouling
A. G. Agwu Nnanna, Jinsong Yu and Ishita Biswas

ABSTRACT

Fouling characteristics of crossflow flat-sheet membranes for two Nanofiltration (NF), one Ultrafiltration (UF), and one Microfiltration (MF) membranes were analyzed using 12.5 parts per million (mg/L) FeCl₃ solution and 350 mg/L copper nano fluid. FeCl₃ solution represents dissolved contaminant whereas copper nano fluid simulates particulate contaminant. The spatial and temporal fouling evolutions were captured using digital photography and analyzed using ImageJ software. FeCl₃ fouling studies for one NF membrane showed uniform fouling whereas for the other NF membrane, isolated fouling was apparent and the fouling initiated at the outlet then gradually extended towards the inlet. Copper nanoparticle fouling studies analyzed through gravimetric and image processing revealed spatial and temporal fouling developments. Both non-equilibrium and equilibrium fouling stages/regions were evaluated through fouling density analysis.

Key words | fouling density, membrane filtration, membrane fouling, nano fluid, visualization

INTRODUCTION

Membrane filtration processes have been widely applied to remove contaminants from water. One major drawback associated with various membrane filtration processes, however, is the tendency of the membranes to be fouled by the contaminants in the water.

Membrane fouling is often attributed to the chemical and physical interactions between particulate/dissolved species and the surface and pores of the membranes (Wakeman & Tarleton 1991; Davis 1992). The basic mechanisms of membrane fouling had been studied in the 1980s (Howell et al. 1980; Matthiasson 1985; Aimar et al. 1988) and more recently, studies on membrane fouling for particular membranes (Nanofiltration (NF) or Ultrafiltration (UF) or Microfiltration (MF)), in particular modules (hollow fiber or tubular), and by particular contaminants (organic species or nanoparticles) have been reported (Pradanos et al. 1996; Meng et al. 2006; Geng et al. 2007; Zhang et al. 2012; Qu et al. 2012). Nevertheless, the general consensus is that membrane fouling is a collective result of phenomena including pore blockage, cake layer formation, and concentration polarization. The rapid initial drop in permeate flux is largely attributed to the blockage of membrane pores. Further flux decline after pore blockage is attributed to the formation and growth of the cake layer on the membrane surface. Such cake layer creates an additional resistance to the permeate flow, and the resistance of the cake layer increases with the increase in its thickness.

Membrane fouling is often indirectly monitored through permeate flux reduction. A general practice is to regenerate the membrane once the permeate flux is below a preset critical value. The disadvantage of such practice is that it is determined by the collective permeate flux reduction. It should be noted that while the total fouling may still be tolerable, some local areas may have already been critically fouled and cannot be regenerated. The membranes therefore can gradually lose the functional areas and eventually may have to be replaced sooner than expected. Indeed our preliminary studies on membrane fouling have shown that membrane fouling depends on the location along the feed flow direction. In order to prolong the life-span of membranes, it is desirable to develop methodologies that can be used to determine the fouling progress along the feed flow direction (spatial distribution) and with respect to operation time (temporal distribution).

doi: 10.2166/wst.2013.504
Different technologies have been studied for the direct monitoring of membrane fouling phenomena, including photointerrupt sensor array (Tung et al. 2012), ultrasonic time domain reflectometry (UTDR) (Xu et al. 2009; Sim et al. 2012), electrical impedance spectroscopy (Sim et al. 2013), thermogravimetric (Tay et al. 2005), confocal scanning laser microscopy (Ferrando et al. 2005), and direct observation techniques (Mores & Davis 2001; Kang et al. 2004; Marselina et al. 2009; Yeo et al. 2013). Among these technologies, the direct observation techniques are particularly of interest, largely due to its simplicity and little reliance on sophisticated instruments. However, reports of direct observations on the effects of membrane materials on dissolved contaminant fouling behaviors are scarce. On the other hand, fouling density (FD) analysis on the pictogram of the spent membranes can be a simple but powerful tool. It can be used to understand how the fouling formation progresses and the obtained information can be very helpful to implement more efficient mitigation strategies. Such FD analyses, however, have been rarely reported. This study attempts to fill such knowledge gaps.

In this paper, FeCl₃ solution was used for dissolved contaminant fouling on two NF membranes and copper nanofluid was used for particulate contaminant fouling on one NF, one UF, and one MF membranes. The usages of FeCl₃ solution and copper nanofluid to study the fouling phenomena were based on the consideration that for membranes with relatively large pores (such as MF and UF) particulate contaminants (copper nanofluid) are mostly responsible for fouling; for membranes with very small pores (such as NF) dissolved contaminants (FeCl₃ solution) can induce additional fouling. Nanofluid fouling was investigated because nanoparticles are increasingly used and the filtration of nanofluids (either to remove or to recover) has become a more and more attractive application for membrane processes.

### METHODS

#### Membranes

Flat-sheet DK NF (molecular weight cut-off (MWCO) of 150–300 daltons), TFC-SR3 NF (MWCO of 200 daltons), HFK-328 UF (MWCO of 5000 daltons), and HFK-618 MF (0.1 μm mean pore size) were used in this study (Table 1).

#### Foultants

Ferric chloride (FeCl₃) (Mallinckrodt Co.) at 12.5 mg/L and copper nanofluid at 350 mg/L are representatives for dissolved and particulate foulants, respectively. Copper nanoparticles (≤70 nm) were purchased from Sigma Aldrich. Prior to the filtration experiments, the copper nanofluid was agitated using an ultrasonic transducer (UP 200 s Ultraschallprozessor, dr. hielscher, GmbH) for half an hour to minimize agglomeration and to promote homogeneity of the suspended solution.

#### Membrane system and filtration process

A crossflow flat-sheet membrane testing cell (Model CF042, Sterlitech Corporation) was used, as depicted in Figure 1(a) and the experimental setup is illustrated in Figure 1(b), including a 3-phase 230 V Hydracell diaphragm pump (Model M-03 s, Wanner Engineering), a variable speed drive (VS1MX, Baldor Electric), two pressure gauges (Sterlitech Corporation and Blach Corporation), a pulsation dampener (Wanner Engineering), and a needle valve (Sterlitech Corporation). Temperature was measured by A k type (Omega Co.) thermocouple. The volume of permeate was measured with A&D GX 800 digital balance. DI water filtration for 24 h to establish a stable filtration condition was carried out before switching to feed solution. Various feed flow rates have been applied, ranging from 0.025, 0.044, 0.063 and 0.088 L/s corresponding to

### Table 1 | Membrane characteristics and test conditions

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Membrane name</th>
<th>Membrane manufacturer</th>
<th>Pore size</th>
<th>Membrane material</th>
<th>Foultant</th>
<th>Concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF</td>
<td>TFC-SR3</td>
<td>Koch</td>
<td>0.2K-MWCO</td>
<td>PA</td>
<td>Cu-Nf</td>
<td>350</td>
</tr>
<tr>
<td></td>
<td>DK</td>
<td>GE</td>
<td>0.15–0.3K-MWCO</td>
<td>Hydrophilic thin-film</td>
<td>FeCl₃</td>
<td>12.5</td>
</tr>
<tr>
<td>UF</td>
<td>HFK-328</td>
<td>Koch</td>
<td>5K-MWCO</td>
<td>PA</td>
<td>Cu-Nf</td>
<td>350</td>
</tr>
<tr>
<td>MF</td>
<td>HFK-618</td>
<td>KMS</td>
<td>0.1 μm</td>
<td>PES</td>
<td>Cu-Nf</td>
<td>350</td>
</tr>
</tbody>
</table>

PES – polyethersulfone.
PA – thin film composite polyamide; NF – nanofluid.
crossflow velocities of 0.26, 0.46, 0.66 and 0.93 m/s. The flow channel has an effective height of 24 mm, width of 46 mm, and length of 92 mm. For feed flow rates below 0.044 L/s, laminar flow conditions are present throughout the channel; for feed flow 0.088 L/s, fully developed turbulent flow is established before the retentate exit. Turbulent flow generally results in an entrance length, associated with minimal foulant deposition.

Digital photography and image analysis

The membrane surfaces were recorded using Canon Ultrasonic EDS 7D and then analyzed using ImageJ software (Ferreira & Rasband 2012). A filter system, ‘Gray values’, is applied to distinguish dark (fouled) from light (unfouled) regions. Gray values of 0 and 255 corresponded to dark and light, respectively with a reference gray value threshold of 135. Images are then converted into a binary format where gray values above 135 are considered background (unfouled). By summing the number of dark (fouled) pixels and dividing by the total pixels, the fouled percentage was calculated.

RESULTS AND DISCUSSION

Fouling by 12.5 mg/L FeCl₃ solution

Figures 2(a) and (b) show DK and TFC-SR3 NF membranes after filtering the FeCl₃ solution (laminar flow) at 2.76 MPa for different operation times, respectively. Figure 2(a) shows a rather uniform fouling formation on the DK NF, whereas
Figure 2(b) shows the fouling initiated at the outlet and gradually extends toward the inlet for the TFC-SR3 NF. Such drastic differences in fouling development shown in Figure 2 clearly suggest that the membrane’s properties may have profound impacts on the fouling development when dissolved foulants are concerned.

The phenomena depicted in Figure 2 indicated that strong interactions between membrane materials and the dissolved contaminants can occur and the fouling behaviors could be drastically different. However, very limited information in this regard was available in the open literature. A detailed chemistry analysis on the foulant and membrane material may be needed to further understand such observed phenomena. The exposed functional groups of the membrane materials may have played important roles.

**Gravimetric analysis of temporal and spatial variation in foulant accumulation**

The masses of fresh and air-dried spent membrane were measured with an analytical balance (Model M254AI, H&G Weighing Systems, precision of 0.1 mg) and the difference between fresh and spent membrane represents the solids deposited (including both that on the surface and that in the pores). Figures 3(a) and (b) show the temporal variation in foulant accumulation.

![Figure 3][1]

**Figure 3** | (a) Temporal and (b) spatial variations of nanoparticle deposition on membranes.

---

and spatial variations in the mass of the copper nanoparticles deposited on the membranes, respectively (insert in Figure 3(b) shows the dissection of the spent membrane into five pieces of equal width).

Data depicted in Figure 3(a) show that foulant accumulation behaviors for MF/UF/NF membranes tested in this study appeared to be similar (near linearly) with the calculated rates of deposition of 0.2, 0.28, and 0.22 mg/minute, respectively. It appears that MF membrane suffers from more severe fouling, which is understandable as pore blockage is generally more severe for MF than for UF and NF.

Figure 3(b) shows that the mass of the deposited foulants on five sections increases toward the outlet and more foulants are deposited on the middle sections. A total of five samples was used for the calculation for each section. The standard deviation for each part of the membrane is very similar and measured at about 0.1. This is different from the NF fouling depicted in Figures 2(a) and (b). The fouling by nano-sized particulate foulants appears to depend on the hydrodynamic conditions and to progress differently from dissolved foulants.

**FD analysis by ImageJ**

Images of spent TFC-SR3 NF membranes for three crossflow rates (0.044, 0.063, and 0.088 L/s) were captured and analyzed. The Reynolds numbers (Re) for the three crossflow rate tests were calculated to be 1826 (laminar), 2609, and 3652 (turbulent) for 0.044, 0.063, and 0.088 L/s and the corresponding fouled areas were 52, 57, and 87%, respectively. The increase in the fouled area with the increase in Re value could be understood by taking the turbulence effect into account, whereby acceleration and number of nanoparticles arriving at the membrane wall increased with the crossflow rate and turbulence.

Figure 4 shows the calculated FD (at 0.69 MPa), a measure of the degree of nanoparticle accumulation on the membrane surfaces. Figure 4 indicates that FD is small for the first 21 mm or so after the inlet for three flow rates and the change in FD with axial location was also small and negligible (compared with the drastic increase at distance ≥45 mm). This observation could be attributed to the effect of entrance length on the development of the concentration boundary layer. Such entrance length \(L_e\) was estimated to range from 19 to 23 mm (with \(L_e\) decreasing with the increase in Re) in this study. Similar dependence of \(L_e\) on the Re value was reported by Wu et al. (Wu & Howell 1992). Furthermore, calculation of the maximum FDs resulted in 0.016, 0.011, and 0.01 for Reynolds numbers of 3652, 2609, and 1826, respectively. Apparently, maximum FD is monotonically proportional to Re number. The FD peak locations were in the range of 45 to 55 mm, with the exact position pushed more towards the outlet as the flow rate (and correspondingly the Re number) increased.

The temporal and spatial evolutions of the FD profiles on TFC-SR3 NF membranes fouled by 350 mg/L copper nanofluid are presented in Figures 5(a) and (b). Data depicted in Figure 5(a) show the FD as a function of filtration time for two locations: \(x = 35\) mm and \(x = 65\) mm, with these two positions representing the onset position of non-equilibrium fouling and the location for maximum FD, respectively. Figure 5(a) shows that the FD at both locations generally increased with the increase in operational time. However, a transition stage (50 to 100 minutes) is apparent where negligible change in FD is observed. A possible explanation for this transition stage is that during this period, equilibrium fouling conditions may occur and the nanoparticles depositing onto and disassociating from the membrane surfaces cancel each other off, resulting in no appreciable change in FD. For the time before and after the transition stage, non-equilibrium fouling conditions occurred. While not shown in this paper, a similar transition stage was observed for MF membranes.

Figure 5(b) shows that the FD generally increases with the axial position. However, changes in FD are small for \(x \leq 35\) mm at a given time. Such a 35 mm can be viewed as a leading edge, over which the FD started to increase nearly linearly with the axial position. This observation is in good agreement with the result reported by Song (Song 1998), who reported that equilibrium fouling would be achieved first at the initial section of the filtration channel and that the cake layer thickness remains fairly constant in the equilibrium region, whereas the thickness in the non-equilibrium region grows with distance. The distance to reach the non-equilibrium region may depend on the...
properties of suspensions (such as the sizes and concentrations of the nanoparticles), operational parameters (such as TMP and crossflow rates), and membrane characteristics (such as surface morphology and pore sizes).

CONCLUSION

Understanding the spatial and temporal variations in membrane fouling is of practical interest to the development of more efficient membrane fouling mitigation protocols. In this study, digital photography and ImageJ analyses were employed to analyze the temporal and spatial variations in fouling for selected membranes. FeCl₃ solution and copper nanofluid were used as representatives for dissolved and particulate contaminants, respectively, as these contaminants are increasingly important to membrane filtration applications. Experimental results from digital photography, gravimetric, and software analyses show that membrane fouling induced by particulate and dissolved foulants can be drastically different: dissolved fouling may depend heavily on the membrane properties whereas nano-sized particulate fouling may be more influenced by the flow path and operating conditions. Such observation indicated that membrane materials need to be tailored towards specific dissolved contaminants. Moreover, both spatial and temporal variations in the fouling development have been observed and both equilibrium and non-equilibrium stages have been confirmed. An entrance length that has significant impacts on the fouling development has been confirmed through this study. In addition, it is determined that surface FD analysis for cake layer and gravimetric analysis for both cake layer and pore blockage should be combined to adequately describe the fouling situations.

REFERENCES


First received 7 December 2012; accepted in revised form 12 August 2013. Available online 25 October 2013