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Fouling behavior of dairy wastewater treatment by nanofiltration under shear-enhanced extreme hydraulic conditions

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1. Introduction

Membrane technologies have been considered as a promising method to treat wastewater because they can produce reusable water, especially with nanofiltration (NF) [1] and reverse osmosis (RO) [2]. But the advantages of membrane filtration in wastewater treatment are weakened by concentration polarization and subsequent membrane fouling as they cause flux decline and permeate quality deterioration [3]. Increasing fluid velocity can reduce solutes accumulation at membrane surface for crossflow modules, but also results in a large pressure drop between inlet and outlet of membrane module, which leads to a significant increase of local nonuniform transmembrane pressure (TMP). By using a rotating disk or by rotating or vibrating the membranes, a high shear rate can be generated at membrane without creating large pressure drops [4]. This shear rate effectively decreases concentration polarization, thus improving both solutes rejection and permeate flux, so that a NF membrane in shear-enhanced module may produce the same permeate quality as a RO membrane in crossflow filtration [4]. However, even a high shear rate cannot wipe off all the membrane fouling, such as foulants adsorbed on pore wall. There are few reports about fouling behavior in shear-enhanced membrane process. Frappart et al. [2] found that, at a shear rate of about \(1 \times 10^2 \text{ s}^{-1}\) and TMP of 40 bar, RO of diluted skim milk could be operated at a quasi stable flux of more than 100 Lm \(^{-2}\) h \(^{-1}\) for 6 h. Shi and Benjamin [5] reported that inorganic scale occurred in desalination of brackish water by a vibratory shear enhanced RO process (shear rate = \(1-5 \times 10^4 \text{ s}^{-1}\)) but with negligible organic fouling. Therefore, under a high shear rate, the fouling evolution of NF/RO membranes is quite slow but still exists, and needs to be further investigated.

In membrane mediated wastewater reclamation, fouling is typically caused by inorganic and organic materials present in water that adhere to the surface and pores of the membrane. First, inorganic scale, induced by minerals supersaturation, has two possible growth tracks, surface crystallization, and crystal deposition [6]. The former is scale formation on the membrane surface through lateral growth of crystals, while, in the latter, crystal particles shaped in concentration polarization layer and deposit on membrane surface [7]. Secondly, organic fouling, first derived from adsorption of foulants and particles deposition, is due to two mechanisms, pore blocking and cake layer formation [8–10]. Furthermore, the combined fouling resulting from calcium–organic complexation was found in many cases [9,11]. All typical fouling is more or less affected by solute concentration near the membrane...
surface, and that is the reason why decreasing concentration polarization can reduce membrane fouling. Concentration polarization is effectively controlled when operating at a high shear rate, and the particles may not deposit and form a cake layer on the membrane, and the high lateral shear force sweeps the membrane surface, preventing crystal or cake growth. Usually the permeate flux in shear-enhanced membrane process is quite high and also has a cleaning effect on foulant adsorption at pore wall. However, adsorption fouling cannot be avoided because it is mainly gov-

erned by the affinity between solutes and membrane materials [12], and even with a highly hydrophilic NF270 membrane at high shear rate, membrane fouling still occurred and was possibly caused by inorganic–organic complex adsorption [13].

Milk proteins, lactose and mineral salts present in dairy wastewater are the possible ingredients of fouling layer on/in NF membranes. By comparing the infrared absorbance between new fouled membranes, Rice et al. [14] found that protein and calcium phosphates were the main foulants during NF of dairy ultrafiltration (UF) permeate, and calcium-related fouling mechanism, whether cake layer or scaling, was completely dependent on the origin of crystallization, either in the bulk flow or at the membrane surface. While treating skim milk by NF membrane, Rabiller-Baudry et al. [15] concluded that for neutral to alkaline pH, inorganic fouling mechanism could retard fouling formation.

The main compositions and characteristics of model dairy wastewaters are given in Table 2 [17].

A new membrane was used for each series of experiments to ensure the same initial membrane conditions for the entire study. The membranes were soaked in deionized water for at least 48 h prior to use, and pre-pressured with deionized water for 30 min under a pressure of 40 bar. After stabilization, the pure water flux of membranes was measured at five pressures of 20, 16, 12, 8, 4 bar to calculate water permeability ($L_p$). Before the experiments started, the feed was heated to 35 °C, and was fully recycled in the system at zero TMP, and this process lasted about 20 min for each test. Then experiments were performed at a constant TMP of 40 bar and a feed flow rate of 180 L/h with permeate and retentate recycling. After each series of tests, the filtration system was flushed with deionized water until the rinsing water came out clear, and $L_p$ was measured again to determine the degree of permeability loss.

2.2. Test fluid

Model dairy wastewater was prepared from commercial UHT skim, semi-fat, and whole milks, respectively (Lait de Montagne, Carrefour, France), diluted 1:2 to one-third of normal concentra-

tion with deionized water (Aquadem E300, Veolia Water, France). The main compositions and characteristics of model effluents are described in Table 2.

2.3. Experimental procedure

A new membrane was used for each series of experiments to ensure the same initial membrane conditions for the entire study. The membranes were soaked in deionized water for at least 48 h prior to use, and pre-pressured with deionized water for 30 min under a pressure of 40 bar. After stabilization, the pure water flux of membranes was measured at five pressures of 20, 16, 12, 8, 4 bar to calculate water permeability ($L_p$). Before the experiments started, the feed was heated to 35 °C, and was fully recycled in the system at zero TMP, and this process lasted about 20 min for each test. Then experiments were performed at a constant TMP of 40 bar and a feed flow rate of 180 L/h with permeate and retentate recycling. After each series of tests, the filtration system was flushed with deionized water until the rinsing water came out clear, and $L_p$ was measured again to determine the degree of permeability loss.

2.3.1. Long-term batch tests

Two long-term batch tests were carried out at a rotating speed of 2000 rpm, for a total operating time of more than 17 h per test, spread over 7 days. New effluents were used for each batch filtration. For the first batch test, mild chemical cleaning with pH ~ 10 was carried out after each batch in first 3 days, and from the 5th day, the cleaning pH was increased to 11. For the second batch test, only water rinse was carried out after each batch in first 5 days. On the 6th day, chemical cleaning was done after each 2 h of filtration. The membrane compartment was not disassembled during each test lasting 1 week and after every operation, membrane $L_p$ was measured.

The rotating disk module (RDM) equipped with NF270 membranes (DOW-Filmtec) with a high pressure of 40 bar and membrane shear rates of up to $2.05 \times 10^5 \text{s}^{-1}$ to carry out full recycle experiments in order to study the effect of lipid and shear rate on flux decline and membrane permeability loss. Then, two long-term batch filtrations with and without chemical cleaning were compared and fouling mech-

anisms were discussed. The focus of this study is to analyze fouling phenomena at very high shear rate as well as high permeate flux and to find a way to avoid severe flux decline and permeate quality deterioration during NF regeneration of dairy wastewater by shear-enhanced membrane modules.

### Table 1

Properties of NF270 membrane [17].

<table>
<thead>
<tr>
<th>Index</th>
<th>NF270</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane material</td>
<td>Polyamide</td>
</tr>
<tr>
<td>Molecular weight cutoff (Da)</td>
<td>~270</td>
</tr>
<tr>
<td>$L_p^*$ ($\text{Lm}^{-2} \text{h}^{-1} \text{bar}^{-1}$)</td>
<td>11.3 ± 0.3</td>
</tr>
<tr>
<td>Max. temperature (°C)</td>
<td>45</td>
</tr>
<tr>
<td>Max. pressure (bar)</td>
<td>41</td>
</tr>
<tr>
<td>Contact angle (sessile drop) (°)</td>
<td>30</td>
</tr>
<tr>
<td>Zeta potential (mV)</td>
<td>~66.5 (pH 6.7)</td>
</tr>
<tr>
<td>Isoelectric point (pH)</td>
<td>~3.2</td>
</tr>
</tbody>
</table>

*a* Pure water permeability, own measurement.

### Table 2

Main characteristics of model dairy wastewater.

<table>
<thead>
<tr>
<th>Index</th>
<th>Model dairy wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Casein ($\text{gl}^{-1}$)</td>
<td>8.5</td>
</tr>
<tr>
<td>Whey protein ($\text{gl}^{-1}$)</td>
<td>2.1</td>
</tr>
<tr>
<td>Lactose ($\text{gl}^{-1}$)</td>
<td>15.3</td>
</tr>
<tr>
<td>Calcium ($\text{gl}^{-1}$)</td>
<td>0.40</td>
</tr>
<tr>
<td>Sodium ($\text{gl}^{-1}$)</td>
<td>0.17</td>
</tr>
<tr>
<td>Lipid ($\text{gl}^{-1}$)</td>
<td>Skim &lt;0.33 semi-fat 5.2 whole 12</td>
</tr>
<tr>
<td>COD (g O$_2$ L$^{-1}$)</td>
<td>36</td>
</tr>
<tr>
<td>Conductivity ($\mu$Scm$^{-1}$)</td>
<td>1500–1600</td>
</tr>
<tr>
<td>pH</td>
<td>~6.7</td>
</tr>
<tr>
<td>Dry mass ($\text{gl}^{-1}$)</td>
<td>32</td>
</tr>
</tbody>
</table>
2.3.2. Cleaning procedure

Alkaline cleaning was carried out by using a P3-ultrasil 10 (Ecolab, USA) detergent to remove protein residues, at 0.05% concentration, and a pH of 10 which was raised to 11 after the 4th day. In addition, acid cleaning (HCl, pH ~ 2) was carried out before alkaline cleaning on the 7th day of first test and on the 6th day of second test. Moreover, a detergent wastewater (pH ~ 7.5) collected from a detergent factory was used as cleaning solution on the 4th day of the first test, without adjusting pH and on 7th day with adjusting pH to 11 by NaOH. The chemical cleaning lasted 30 min at a temperature of about 25 °C. When operated without chemical cleaning, the system was first washed with pure water for 4 h test using NF270 membrane, indicating that lipids below 0.89 for this RDM system), and lipids do not deposit on the membrane. However, as seen in Fig. 2, flux decline was a little larger at higher lipid concentration, and permeate flux decreased by 3.1% without lipid against 7.6% at 12 gL⁻¹ lipid. After 4 h of filtration, membrane permeability loss was almost the same at lipid concentration from 0.3 to 5.2 gL⁻¹, but became

This is mainly due to the high shear rate and the perfect hydrophilicity of NF270 with a low contact angle (see Table 1), and lipids do not deposit on the membrane. However, as seen in Fig. 2, flux decline was a little larger at higher lipid concentration, and permeate flux decreased by 3.1% without lipid against 7.6% at 12 gL⁻¹ lipid. After 4 h of filtration, membrane permeability loss was almost the same at lipid concentration from 0.3 to 5.2 gL⁻¹, but became

2.4. Calculated parameters

The permeate flux (J) was calculated by:

\[ J = \frac{1}{A} \frac{dV_p}{dt} \]  

(1)

where A is the effective membrane area, \( V_p \) is the total volume of permeate, and t is the filtration time.

The pure water permeability \( (L_p) \) was calculated from the water flux as follows:

\[ L_p = \frac{J}{\text{TMP}} \]  

(2)

The permeability loss index \( (PL) \) is given by:

\[ PL(\%) = \frac{L_{pi} - L_{pf}}{L_{pi}} \times 100 \]  

(3)

where \( L_{pi} \) and \( L_{pf} \) are the initial and final hydraulic permeabilities.

The mean membrane shear rate on membrane \( (\gamma_m) \) can be calculated by the following equations [4].

\[ \gamma_m = 0.0164R^{8/5}(ko)^{9/5} \frac{R}{\pi^{3/5}} \]  

(4)

where \( R \) is the outer membrane radius and \( k \) is the velocity factor (0.89 for this RDM system), \( \omega \) the disk angular velocity, \( v \) the fluid kinematic viscosity.

The permeability recovery after chemical cleaning is calculated by:

\[ \text{Recovery}(\%) = \frac{L_{pc}}{L_{pi}} \times 100\% \]  

(5)

where \( L_{pc} \) is the membrane water permeability after cleaning.

The flux decline index \( (FD) \) is expressed as a percentage of feed flux decrease after a continuous operation:

\[ FD(\%) = \frac{J_{fa} - J_{fd}}{J_{fa}} \times 100 \]  

(6)

where \( J_{fa} \) and \( J_{fd} \) are initial and final feed fluxes, respectively.

3. Results and discussion

3.1. Effect of lipid on fouling and filtration behaviors

Lipids inevitably exist in dairy wastewater but, to our knowledge, there has been no report yet regarding the effect of lipid on NF membrane filtration. Fig. 1 shows the flux profiles and permeate conductivity using diluted UHT skim, semi-fat and whole milk for 4 h test using NF270 membrane, indicating that lipids below 12 gL⁻¹ have negligible effect on filtration behaviors in short term.
higher at 12 gL⁻¹. This implies that, even at low concentration, some lipid molecules still adsorb to membrane surface by their hydrophobic parts, reducing the hydrophilicity of membranes. This effect may be amplified in long-term runs without chemical cleaning. To make the fouling behavior clearer, diluted skim milk was employed as model wastewater in following studies.

3.2. Effect of shear rate on fouling and filtration behaviors

Fig. 3 compares the permeate flux and conductivity variations with time at rotating speeds of 1000, 1500, and 2000 rpm, corresponding, respectively, mean shear rates of 0.59 × 10⁵, 1.22 × 10⁵, and 2.05 × 10⁵ s⁻¹. Flux decline and permeate quality deterioration are not obvious in these cases because all shear rates are above 10⁴ s⁻¹, much higher than that in crossflow modules. As shown in Fig. 4, flux decline and permeability loss decrease above 1000 rpm because the reduction in solute concentration at membrane increased the membrane hydrophilicity and reduced permeability loss. However, little improvement was seen above 1500 rpm (γₘ > 10⁴ s⁻¹). The mechanism of concentration polarization reduction by high shear rate can be explained as follows: at constant driving pressure, solute accumulation at membrane surface is governed by solute back diffusion coefficient, and with increase of shear rate, shear-enhanced back diffusion strengthens, and thus more solutes go back to the bulk solution. Here, in this study, a mean shear rate above 10⁴ s⁻¹ can be classified as high shear and a shear rate in the range of 10³–10⁴ s⁻¹, corresponds to medium shear.

3.3. Effect of chemical cleaning on fouling and filtration performance in long-term batch filtrations

Fig. 5a shows the permeate flux and conductivity variations during the first long term test with chemical cleaning after every batch. For each batch, a high and stable flux near 400 Lm⁻² h⁻¹ was obtained, which decayed slightly after each cleaning. At the beginning of the 4th day, the flux fell to 350 Lm⁻² h⁻¹, but still remained stable, implying that a cleaning solution at pH ~ 10 could not remove all the fouling. At the end of the 4th day, a detergent wastewater replaced the alkaline cleaning solution, but the cleaning efficiency was not good. So on the 5th day, an alkaline cleaning at pH ~ 11 was carried out before filtration and the flux increased a little as compared to 4th day. This was due, according to Dalwani et al. [17], to increase in membrane pores size after alkaline cleaning. Unexpectedly, on the 6th day, flux decreased by 27%. This was probably due to a higher pore fouling on 5th
day because they were enlarged and to a pore shrinking during the night. On the 7th day, flux increased after acid and alkaline cleanings, and increased again by 27% after another alkaline cleaning after 4 h, before declining slowly, confirming that the membrane became looser after alkaline cleaning. In Fig. 5a, it is also seen that, when cleaning at pH 10, permeate conductivity was almost constant during the filtrations, while with cleaning at pH 11, the permeate conductivity rose before decreasing with time.

Fig. 5b describes the second long term test with longer filtration periods, but less chemical cleaning. On the 1st day, a flux higher than 410 Lm$^{-2}$ h$^{-1}$ was maintained for 4 h, then it decayed slowly. After 6 h of filtration, the membrane was rinsed several times. On the 2nd day, the flux kept stable only for 1.5 h, and declined very rapidly, before being restored by water rinses. Similar flux declines occurred in next 4 days, while at the same time, permeate conductivity increased rapidly with time. On the 6th day, an alkaline cleaning was carried out after 2 h and another batch filtration was filtrated. The flux increased to the same level as in the 4th day and declined slowly in 2 h. On the 7th day, due to a chemical cleaning at the end of 6th day, flux remained nearly stable for 2 h and declined rapidly afterwards. This suggests that membrane fouling and chemical cleaning may permanently reduce the hydrophilicity of the membrane surface [18]. By comparing these two long term tests, it is concluded that, water rinse, even with warm liquid, cannot remove foulants adsorbed at membrane surface which can induce subsequent severe fouling layer formation. While, with frequent chemical cleaning, a high and stable flux can be obtained for a long-term under extreme hydraulic conditions.

In order to quantify the effect of chemical cleaning on membrane permeability, the $L_p$ values after cleaning, filtration, and water soaking in two tests are shown in Fig. 6a and b. Fig 6a shows that, as expected $L_p$, drops after filtration and was restored by chemical cleaning. But surprisingly $L_p$ decreased significantly after the membrane was soaked in water during the night in all cases to the same level as after filtration for 2nd, 3rd, and 4th days. This difference confirms pore swelling by alkaline cleaning and a subsequent slow pore shrinking for the NF270 membrane. In Fig. 6a, on the 4th day, the $L_p$ after chemical cleaning was much lower than others when detergent wastewater was used as cleaning solution. On the 6th day, the permeability decay after a night was greater than after other nights and $L_p$ after filtration was lowest. Both effects were probably caused by starting filtration immediately after alkaline cleaning. Fig 6b shows this permeability decay overnight did not occur in the absence of chemical cleaning on 2nd and 3rd days. Water rinsing restored the permeability completely on 3rd day and partially on 4th and 5th days and there was no permeability decay overnight. When comparing Figs. 6 and 5, it is found that permeate fluxes seems to be correlated with $L_p$ values before filtration. However even if fluxes remained very stable in first test (Fig. 5a), $L_p$ values after filtrations were still much lower than before filtration (Fig. 6a). This finding means that during the filtration, the decrease of $L_p$ does not reduce the flux, but it is the $L_p$ decay during overnight soaking which produces a negative effect on the flux for the next batch.

3.4. Effect of cleaning mode on membrane permeability recovery
The membrane permeability recovery for the test of Fig. 6a, defined by Eq. (5) and shown at top of Fig. 7, decreased with time because our cleaning modes could not remove all the fouling and membrane hydrophilicity may have decreased. But it remained above 85%, while acid cleaning gave a recovery of only 65%. The
combination of acid and alkaline cleanings had the same efficiency as a single alkaline cleaning, indicating that inorganic fouling was negligible in this process. Detergent wastewater was first time used to clean fouled membrane but only newborn fouling could be removed. This detergent solution had low surface tension\[19\] and could not penetrate the deep fouling layer.

However, Fig. 6a showed that permeability recovery by chemical cleaning was cancelled after one night of membrane soaking. After a water rinse at room temperature (as seen in Fig. 6b), \( L_p \) did not change, and actually increased a little after warm water cleaning. This difference indicates that alkaline cleaning did not really remove all the fouling but caused membrane swelling, and warm water cleaning only removed some loose fouling but did not affect membrane properties.

3.5. Discussion of fouling mechanisms

By monitoring pH and conductivity of retentate during each batch filtration, it was found in Fig. 8 that, for both new and cleaned membranes with a stable flux, retentate properties did not change. While for a fouled membrane used again and again without chemical cleaning, the permeate flux declined with time, and pH in retentate decayed and conductivity increased \[13\]. When the flux did not decline during filtration with chemical cleaning as in test of Fig. 5a, the tank remained very clean after a single water rinse, as seen in Fig. 9a, when the flux decreased from the 2nd to the 6th day for the test of Fig. 5b, fouling fractions flaked away from membrane due to the very high shear rate, and were retained by the mesh at the bottom of feed tank, as seen in Fig. 9b, implying that a cake fouling layer has formed. This cake layer must contain some weak acid radicals in addition to protein and calcium ions since retentate pH decreased.

According to our data and previous works \[20–22\], the fouling in dairy wastewater treatment by NF under extreme hydraulic conditions can be divided into two stages following the steady flux one, fouling by adsorption and formation of a cake layer, as described in Fig. 10. During the stable flux stage, due to the high shear rate, concentration polarization forms quickly, and solute molecules do not deposit on the membrane (Fig. 10a). Then, adsorption fouling by small solutes such as lactose and calcium ions or their aggregates occurs, possibly causing pore narrowing and charge screening, decreasing membrane hydrophilicity and causing a slow flux decline (See Fig. 10b). In the first two stages, the foulant-membrane interaction is the main fouling mechanism. In the third stage, protein molecules bridging by acid radicals and calcium ions deposit on the adsorption layer and aggregate, forming rapidly a cake fouling layer, resulting a severe flux decline (Fig. 10c). In this stage, the cake formation is mainly controlled by foulant-foulant interaction. Because acid radicals precipitate from feed solution in this

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**Fig. 7.** Membrane recovery tendency and effect of cleaning mode on membrane permeability recovery. (a) Alkaline cleaning; (b) acid cleaning; (c) acid + alkaline cleaning; (d) detergent wastewater cleaning (pH 11).

**Fig. 8.** Variation profiles of flux, pH and conductivity in retentate with time for different membrane conditions.

**Fig. 9.** Membrane recovery tendency and effect of cleaning mode on membrane permeability recovery. (a) Alkaline cleaning; (b) acid cleaning; (c) acid + alkaline cleaning; (d) detergent wastewater cleaning (pH 11).
stage, more hydrogen ions are generated by electrolysis and pH in retentate decreases when flux decline. If chemical cleaning is carried out before the third stage, adsorbed solutes can be removed and cake formation can be avoided, so that a high stable flux can be maintained for a long time under extreme hydraulic conditions. However, the P3-ultrasil 10 is not good at pore cleaning as it is not intended for NF membranes. That is the reason why the permeate flux could not be fully restored after chemical cleaning (See Figs. 5a and 6a). The next goal is to find a suitable cleaning agent for NF270 membrane with strong pore cleaning ability and causing no membrane swelling.

4. Conclusion

The first part of this work demonstrated that lipids present in dairy wastewater could accelerate adsorption fouling during NF treatment, but, under extreme hydraulic conditions of highest TMP with high shear rate (>10⁵ s⁻¹), a high and stable flux up to 420 Lm⁻¹ h⁻¹ could be obtained for at least 4 h. For skim milk, after the stable flux period, a slow flux decline caused by surface adsorption of foulants (lactose, multivalent salt ions and their aggregates) occurred. In this adsorption fouling stage, pore narrowing and blocking governed by foulant–membrane interaction was the main fouling mechanism. In absence of chemical cleaning, this adsorption fouling could induce cake fouling formation by inorganic–organic aggregates, resulting in severe flux decline. P3-ultrasil 10 cleaning solution could remove organic fouling at membrane surface but not in the membrane pores, and it caused membrane swelling. If feed filtration was started immediately after this alkaline cleaning, membrane pore fouling was aggravated in next filtrations. These findings not only clarify the fouling behaviors in high shear rate NF process, but also provide valuable advice for membrane cleaning in NF operations under extreme hydraulic conditions.

Acknowledgments

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References


