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Published in:
Separation and Purification Technology

Link to article, DOI:
10.1016/j.seppur.2012.06.009

Publication date:
2012

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):

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Treatment of dairy effluent by shear-enhanced membrane filtration: The role of foulants

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A B S T R A C T

Treatment of dairy effluent by membrane filtration permits to recover both reusable water and nutrients, but its advantages are weakened by concentration polarization and subsequent membrane fouling as they cause flux decline and permeate quality deterioration. In order to control flux decline, model dairy effluent was treated by shear-enhanced membrane filtration in this study, and the role of foulants was analyzed. For ultrafiltration (UF) of dairy effluent, protein adsorption and deposition caused flux decline and hydrophobic modification of membranes can reduced this fouling. While for nanofiltration (NF), flux decline was mitigated by the presence of casein micelles, and when the caseins were removed by UF pretreatment, free calcium ions increased due to the absence of casein micelles, also inducing flux decline at high concentration factor. Thus, the two-step UF/NF process was not found advantageous as it did not improve the average permeate flux nor permeate quality, while increasing significantly the process energy consumption. This conclusion was valid not only for rotating disk module (RDM) but also for vibratory shear-enhanced process (VSEP), which is available in large membrane area with a low energy consumption.

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1. Introduction

Wastewaters from agro-industries are characterized by high levels of chemical oxygen demand (COD), together with the presence of nitrogen and phosphorus. The dairy industry is particularly concerned as its effluents are responsible for a 1–3% loss in milk components, mainly carbohydrates, proteins and fats. These effluents result in both water eutrophication and nutrients loss when they are discarded without purification. Thus, treating dairy effluent is of crucial importance, not only for the environment, but also for recycling water and organic matters. Among available technologies for wastewater treatment, coagulation and constructed wetlands are the most frequent methods used to recycle organics [1,2], where the sludge generated by the coagulation can be used as animal food [3] or fuel substrate [1]. Coagulation is a simple and rapid method to reduce organic content, but it can only be used as pretreatment because generally its effluent quality cannot satisfy the emission standards [1]. Constructed wetlands method benefits from their relatively low capital costs and maintenance requirements, but it is not generally applicable for all the cases and appears to be limited by the organic loading rate [2]. Furthermore, the water treated by both methods cannot satisfy the standards for domestic or industrial reuses and needs a secondary treatment. Nanofiltration (NF) and reverse osmosis (RO) membrane technologies have been considered as promising approaches to convert wastewater into reusable water, making wastewater treatment more sustainable [4,5]. Through sieving effect and electrostatic repulsion, almost all of nutrients are retained by NF/RO membranes, and the concentrate can be reused as substrates for productions of bioenergy [6]. Moreover, the wastewater recycling by membrane is not only cost and energy efficient, but also easy to combine with other technologies, such as coagulation, bioreactor and fermentation, to improve its permeate quality and organic utilization [7,8].

However, a major limitation in applying membrane process for wastewater treatment is the permeate flux decline due to concentration polarization and fouling [9,10], especially for concentrated mixtures. In order to control the flux decline during the concentration of dairy effluent by NF, Luo et al. [6] proposed a two-stage ultrafiltration (UF) and NF process to reutilize wastewater combined with algae cultivation and anaerobic digestion, and through UF pretreatment, the irreversible fouling of NF membranes was greatly reduced when compared with single NF treatment. Moreover, the fractionation of nutrients by a two-stage UF/NF could improve its utilization efficiency in subsequent biohydrogen production [7,8].
and when shear rate was more than 2 rapidly at the initial stage for concentrating brackish water by RO, flux. Shi and Benjamin[15] indicated that flux declined much more decreased with rotation rate and increased with initial permeate tatively insensitive to particle concentration in the feed, and fouling high rotational speed, permeate flux of microfiltration was rela-

Another solution for flux decline is to enhance the shear rate on the membrane surface. Higher shear-induced back diffusion can decrease the solutes concentration and particles precipitation on/ in the membrane, thus reducing concentration polarization and membrane fouling. Shear-enhanced membrane modules, for example, rotating disk module and vibratory membrane module, can produce high shear rate without pressure drop, and independent of fluid velocity[11]. This technology allows very high concentration factors and high water recovery during wastewater treatment, which makes it more economical and applicable. For example, in the case of a disk with vanes rotating at 2000 rpm, the dry matter reached 32% (w/v) in UF of undiluted skim milk[12] and reached 26% (w/v) in NF of diluted skim milk still having a flux of 145 Lm$^{-2}$h$^{-1}$. Although fouling is mild for shear-enhanced membrane filtration, the fouling evolution still exists and causes flux decline in long-term operation. There are few reports about fouling behavior and mechanism in shear-enhanced membrane filtration. Engler and Wiesner[14] found that using a rotating membrane disk with high rotational speed, permeate flux of microfiltration was relatively insensitive to particle concentration in the feed, and fouling decreased with rotation rate and increased with initial permeate flux. Shi and Benjamin [15] indicated that flux declined much more rapidly at the initial stage for concentrating brackish water by RO, and when shear rate was more than 2 × 10$^4$ s$^{-1}$, the fouling rate at the initial stage did not decrease with increase of shear rate any more, while the fouling rate later in the runs was approximately linearly related to the shear rate. It was speculated that high shear rate reduced fouling by controlling the deposit morphology when the deposit was first laid down [15]. However, Luo et al. [16] found that, with permeate and retentate recycling, permeate flux was relatively stable at the initial stage when treating dairy effluent by NF at high shear rate (>10$^4$ s$^{-1}$), and afterward flux decline occurred in two steps: first adsorption fouling stage (low fouling rate) and then cake fouling stage (high fouling rate). These results implies that the fouling behavior and mechanism are greatly affected by shear rate, and the previous investigations only focus on the fouling rate at different shear rates and filtration stages. Some work about fouling mechanism at high shear rate needs to be further developed.

Although UF and NF of dairy effluent by using shear-enhanced filtration systems have been already investigated separately [12,13], the comparison between two-stage UF/NF and single NF has not yet been carried out, and the separation and fouling mechanisms under high shear rate also needs to be clarified during concentration of dairy effluent by UF and NF. In this work, several UF membranes with different molecular weight cut-off (MWCO) and materials were used to treat dairy effluents, and different UF permeates, along with the original effluent were concentrated by NF270 in order to compare fouling mechanisms. Most experiments were conducted by using a rotating disk module (RDM), but these results were also compared with those using a vibratory shear-enhanced process (VSEP), which has more industrial references.

2. Materials and methods

The RDM, described in detail elsewhere [13], has been designed and built in our laboratory (Fig. 1a). A flat membrane, with an effective area of 176 cm$^2$ (outer radius $R$ = 7.72 cm, inner radius $r$ = 1.88 cm), was fixed on the cover of the cylindrical housing in front of the disk. The disk equipped with 6 mm-high vanes can rotate at up to 2500 rpm, inducing high shear rates on the membrane (5 × 10$^4$–3 × 10$^5$ s$^{-1}$). The VSEP vibrating filtration system Series L (New Logic Research Inc., Emeryville, CA), shown in Fig. 1b, was equipped with a single annular membrane of 503 cm$^2$ area (outer radius $R$ = 13.5 cm, inner radius $r$ = 4.7 cm), supported by a central shaft. Vibrations are produced by an eccentric drive motor at the bottom plate, and this torsion spring amplifies and transmits them to the membrane located at its top. Because of vibrations, the membrane oscillates azimuthally with a displacement amplitude of 30.2 mm at the membrane periphery at the resonant frequency of 60.75 Hz, inducing a high shear rate on the membrane (~4 × 10$^4$ s$^{-1}$).

Seven commercial UF membranes fabricated by MICRODYN-NADIR GmbH were tested in the present study and their properties are summarized in Table 1, according to the manufacturer’s information. NF270 (DOW-Filmtec), a thin-film polyamide NF membrane with polysulphone support, was chosen in this study due to its high retention–permeability properties and strong antifouling performance, as described in [13]. Its molecular weight cut-off (MWCO) is about 270 Da. The membrane permeability could be recovered at 90% by P3-ultrasil 10 cleaning solution [16], but we found that it was not good at pore cleaning and the search for a better chemical cleaning agent is in progress.

2.2. Test fluid

A model dairy effluent was prepared from commercial UHT skim (Lait de Montagne, Carrefour, France), diluted 1:2 to one-third
of normal concentration with deionized water (Aquadem E300, Veolia Water, France). The composition and main characteristics of this diluted dairy effluent are described in Table 2. According to the previous reports [4,13], the effluent compositions and filtration behaviors for this model dairy effluent and the real dairy wastewater are very similar.

2.3. Experimental procedure

A new membrane was used for each experiment to ensure the same initial membrane conditions for the entire test. 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 0.6 MPa for UF and 4.0 MPa for NF. After stabilization, the pure water flux of membranes was measured. Before the experiments started, the feed was heated to 35 °C, during which the feed was fully recycled in the system at zero TMP, and this process lasted about 10 min for each test. Then experiments were performed at a feed flow rate of 120 Lh⁻¹ in two series: short-term full recycle tests, long-term concentration tests.

2.3.1. Series 1: short-term tests with full recycling

In order to rapidly evaluate the membrane performance in dairy effluent treatment, these tests were performed with permeate and retentate recycling on a 3 L volume. A pre-filtration was carried out for 10 min at lowest tested TMP and a rotating speed of 2000 rpm, to ensure membranes stabilization. Afterward, the TMP was increased in steps and then decreased gradually until the original starting pressure. Samples were collected in permeate 5–10 min after the beginning of each TMP increment in order to obtain stabilized flux and transmission data. The mean flux decline was calculated by comparing fluxes during stepwise TMP increase and decrease and taking their average.

2.3.2. Series 2: long-term concentration tests

In this series, the permeate was not returned to feed tank and 12 L of model dairy effluent were concentrated to 1 L by UF membranes, and then the 11 L of UF permeate was concentrated to 2 L by NF. For single NF treatment, 12 L of model dairy effluent were directly concentrated to 3 L by NF. Samples were taken from every 0.5 L (0.2–0.3 L when retentate less than 3 L) of collected permeate. After filtration, the membrane system was flushed with deionized water until the rinsing water came out clear, and water flux was measured again to evaluate the degree of irreversible fouling.

2.4. Analytical methods

Turbidities of permeate were measured with a Ratio Turbidimeter (Hach, USA). COD was measured using Nanocolor Kits (Machery-Nagel, Hoerdl, France) in order to quantify organic matter concentration, and the overall measurement accuracy was estimated to be 8% including experimental error. Conductivity was measured with a Multi-Range Conductivity Meter (HI 9033, Hanna, Italy) and pH was measured with pH Meter (MP 125, Mettler Toledo, Switzerland). Dry mass was determined by measuring the weight loss after drying samples at 105 ± 2 °C for 5 h in an oven. Powers of feed pump under different pressure were measured with Power & Energy Monitors (Metric MX240, Chauvin Arnoux, France).

### Table 1

Properties of MICRODYN-NADIR ultrafiltration membranes tested.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Surface material</th>
<th>Molecular weight cut-off (kD)</th>
<th>Water permeability (Lm⁻²h⁻¹bar⁻¹)ᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>UPO05P</td>
<td>PES</td>
<td>5</td>
<td>15–16</td>
</tr>
<tr>
<td>PO10F</td>
<td>PES</td>
<td>10</td>
<td>26–29</td>
</tr>
<tr>
<td>PO20F</td>
<td>PES</td>
<td>20</td>
<td>41–44</td>
</tr>
<tr>
<td>UH030F</td>
<td>PESH</td>
<td>30</td>
<td>40–50</td>
</tr>
<tr>
<td>UH050P</td>
<td>PESH</td>
<td>50</td>
<td>&gt;50</td>
</tr>
<tr>
<td>PES50</td>
<td>PES</td>
<td>50</td>
<td>&gt;70</td>
</tr>
<tr>
<td>US100P</td>
<td>PSH</td>
<td>100</td>
<td>&gt;80</td>
</tr>
</tbody>
</table>

PES, Polyethersulphone; PESH, Permanently hydrophilic polyethersulphone; PSH, Permanently hydrophilic polysulphone.

ᵃ Own measurement at 25 °C and 0.1–0.5 MPa.

### Table 2

Main characteristics of model dairy effluent.

<table>
<thead>
<tr>
<th>Index</th>
<th>Model dairy wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Casein (gL⁻¹)</td>
<td>8.5</td>
</tr>
<tr>
<td>Whey protein (gL⁻¹)</td>
<td>2.1</td>
</tr>
<tr>
<td>Lactose (gL⁻¹)</td>
<td>15.3</td>
</tr>
<tr>
<td>Calcium (gL⁻¹)</td>
<td>0.40</td>
</tr>
<tr>
<td>Sodium (gL⁻¹)</td>
<td>0.17</td>
</tr>
<tr>
<td>Lipid (gL⁻¹)</td>
<td>&lt;0.33</td>
</tr>
<tr>
<td>COD (gO₂L⁻¹)</td>
<td>36</td>
</tr>
<tr>
<td>Conductivity (μS cm⁻¹)</td>
<td>~1580</td>
</tr>
<tr>
<td>pH</td>
<td>~6.7</td>
</tr>
<tr>
<td>Dry mass (gL⁻¹)</td>
<td>32</td>
</tr>
</tbody>
</table>

Fig. 1. Schematics of (a) RDM module and (b) VSEP module.
2.5. Calculated parameters

Volume reduction ratio (VRR) is defined as:

\[
VRR = \frac{V_o}{V_R} \tag{1}
\]

where \(V_o\) is initial feed volume and \(V_R\) retentate volume.

The mean membrane shear rate on membrane \(\gamma_m\) can be calculated by the following equations [11].

For RDM system:

\[
\gamma_m = \frac{0.0164 R^5 (k_0) 0.89}{v R^3} \tag{2}
\]

For VSEP system:

\[
\gamma_m = \frac{2d(R^2 - r^2)(\pi F)^{3/2}}{3R(R^2 - r^2)v^{1/2}} \tag{3}
\]

where \(R\) and \(r\) are the outer and inter membrane radius and \(k\) is the velocity factor (0.89 for this RDM system), \(\omega\) the disk angular velocity, \(v\) the fluid kinematic viscosity, \(d\) the membrane displacement at periphery and \(F\) is the oscillations frequency \((d = 30.2\ mm\ when\ F = 60.75\ Hz)\) [17].

The average flux decline (%) for each membrane is calculated by:

\[
\text{Flux decline} (\%) = \frac{\sum_{i=1}^{n} \frac{J_{ai} - J_{ai}}{J_{ai}} \times 100\%} \tag{4}
\]

where \(J_{ai}\) and \(J_{ai}\) are the permeate fluxes during stepwise TMP increase and decrease at each TMP, respectively and \(n\) is the number of TMP increases.

The permeability loss (PL) index, approximately representing the irreversible fouling, is given by:

\[
\text{PL} (\%) = \frac{L_{pi} - L_{pf}}{L_{pi}} \times 100\% \tag{5}
\]

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

The specific energy of the pump consumed per m³ of permeate \(E_c\) is represented as:

\[
E_c = \frac{P_p}{Q_f} \tag{6}
\]

where \(P_p\) is the pump power, and \(Q_f\) is the permeate flow for 176 cm² membrane area.

3. Results and discussion

3.1. UF membranes evaluation

The main task of UF process is to recover proteins from dairy effluent. Therefore, a UF membrane with high protein rejection and high flux, but low rejection of salt ions is preferable. As shown in Table 1 and Fig. 2, the UF permeate flux increases with membrane MWCO, except for P010F membrane, which has a higher flux than the P020F and it increased almost linearly with TMP from 0.1 to 0.6 MPa, indicating that a cake layer does not form at such high shear rate. As seen in Fig. 3a, the turbidity was less than 3 NTU for US100P, UH030P, P020F and UP005P membranes, but rose from 6 to 20 NTU for other membranes and was lower during the 2nd part of the test (decreasing TMP) due to increasing fouling with time. However, in Fig. 3b, it can be found that the permeate conductivity decreased with increasing TMP for all membranes, which was caused by a “dilution effect” due to higher flux. In fact, this change of conductivity mainly resulted from charged proteins and inorganic ions combined with proteins, since almost all free inorganic ions could pass through UF membranes. As described above, the caseins in dairy effluent were well retained by all tested UF membranes, and this also was confirmed by the direct observations, as all permeate samples looked very clear. It is worth mentioning that the average diameter of casein micelles is about 200 nm [18], while the average pore size is less than 20 nm [19] even for the US100P, and thus casein micelles cannot pass through these UF membranes. The higher turbidity data in Fig. 3a resulted possibly from a wide pore size distribution and adsorption in pores of casein monomer and whey protein. Furthermore, this pore adsorption could induce pore plugging and resulted in flux decline, as seen in Fig. 4 that the PES50 membrane with highest permeate turbidity had the largest flux decline. Except for UP005P membrane with smallest pore size, the fouling of all PES membranes was much higher than that of hydrophilic modified membranes (see Table 1 and Fig. 4). Therefore, US100P, UH050P and UH030P membranes, with high antifouling performance as well as high flux and low ions rejection, were chosen for subsequent concentration tests.

3.2. Comparison between two-stage UF/NF and single NF processes

3.2.1. Flux profile and permeate quality

The model dairy effluent was concentrated to VRR = 12 by three selected UF membranes, and results are shown in Fig. 5. With the US100P membrane, the permeate flux rose rapidly at first (Fig. 5a), at beginning of concentration, then decreased, first slowly, and fast at VRR > 5. Three tests were carried out with similar results. The initial flux increase may be related to the special property of surface material of US100P (hydrophilic polysulphone, see Table 1) but the real reason is unclear. With the UH050P membrane, the flux decreased fast initially, then varied similarly as for the US100P membrane when VRR > 1.25. The permeate flux of UH030P, first declined quickly, then remained almost constant until the final VRR. Unexpectedly, although these three flux profiles were different, their final fluxes at VRR = 12 were almost the same. This is because, in case of protein fouling, the initial flux behavior is highly dependent on membrane properties (foulant–clean-membrane interaction), while the long term flux behavior becomes independent of membrane properties (pore size, materials, etc.) and is largely controlled by foulant–deposited foulant interaction [20]. Table 3 shows that salt, ions and lactose passed easily through UF membranes, leading to high conductivity and COD in permeate, which was not reusable. Although the permeate COD for US100P membrane was slightly higher than for UH050P with a smaller cut-off, the turbidity of UH050P was much higher at 9.8 NTU than the US100P one, indicating a lower casein rejection for UH050P.

Subsequently, these three UF permeates were concentrated by a NF270 membrane to VRR = 5.5. As seen in Fig. 6a, NF permeate fluxes decreased linearly with VRR in semi-log coordinates when VRR was less than 3.4, which presumably corresponds to the mass transfer limited regime with negligible cake fouling. When VRR exceeded 3.4, NF permeate fluxes declined at a higher rate, especially for US100P permeate. This behavior is likely to be caused by membrane fouling and will be discussed in the next section. Table 3 and Fig. 6b shows that COD, conductivity and turbidity of NF permeates were fairly close and low, so that these permeates are potential to be reused for domestic or industrial purposes. According to the characteristics of reusable process water from several dairy factories in France [4], COD and conductivity in vapor condensate are lower than 40 mg L⁻¹ and 100 μS cm⁻¹, and here the conductivity of NF permeates (∼400 μS cm⁻¹) is much higher than this criteria. However, these NF permeate can be reused as cooling water in closed loop (conductivity < 1500 μS cm⁻¹) [4].

The variation of permeate flux without UF inNFRR is also plotted in Fig. 6a. It decayed linearly with increasing VRR at the same rate as NF permeate with UF pretreatment until VRR = 2.5 then it decreased a little faster as in the case with UF pretreatment.
to reach 150 Lm$^{-2}$ h$^{-1}$ at VRR = 6, Table 3 shows turbidity and conductivity in 9 L of collected NF permeate with and without UF. These values are very close, indicating that ion and lactose concentrations were similar in these permeates, although the VRR without UF was smaller at 4 than in NF permeates with UF (5.5).

By comparing the NF flux and permeate quality with and without UF treatment in Fig. 6 and Table 3, it is found that ultrafiltrations did not improve the efficiency of subsequent NF concentrations by the RDM system. As seen in Fig. 6a, since the NF permeate flux of original dairy effluent decreased regularly during the process, the final flux at VRR = 4 (permeate water was 9 L, the same as those with UF pretreatment), was much higher at 240 Lm$^{-2}$ h$^{-1}$ than with UF pretreatment at 40 Lm$^{-2}$ h$^{-1}$. Even if the single NF concentration operation went on, the permeate flux
still decreased linearly with VRR in semi-log coordinates, to be 127 Lm⁻² h⁻¹ when 12 L original dairy effluent was concentrated to 1.5 L [13]. The permeate quality for single NF treatment shown in Fig. 6b and Table 3 was very similar as with UF pretreatment, while retentate pH decayed slowly with increasing VRR for all tests. These results are different from previous data obtained from a dead-end filtration system with low shear rate [6], which can be attributed to different fouling behaviors at lower shear rates.

3.2.2. Fouling behavior
At low shear rate, due to their relatively low mobility, casein micelles and whey proteins rapidly form a concentration polariza-
tion layer, and when calcium phosphate is retained and accumu-
lates on the NF membrane, a complex organic–inorganic aggrega-
tion is formed through calcium phosphate bridges[21]. Thus, a
significant flux decline occurs during NF when both proteins and
multivalent salt ions are present in feed, causing increasing con-
centration polarization and fouling. While caseins and proteins
are removed by UF, this flux decline is greatly reduced during
the NF concentration step, as observed by Luo et al.[6]. However,
at high shear regime, the situation has changed, as seen in
Fig. 6a, that although fluxes with UF pretreatment were higher dur-
ing most of concentration process as their protein content were
lower, they declined rapidly at the end of concentrations, espe-
cially for US100P permeate, lowering it by 83% as compared to sin-
gle NF treatment, which indicates that, even if UF increases the
initial flux, it aggravates the fouling of NF process.

This unexpected phenomenon can be explained by the role of
foulants in dairy effluent during NF, as illustrated in Fig. 7. The
casein micelle is considered as a (homogeneous) matrix of caseins
in which the colloidal calcium phosphate nanoclusters are dis-
persed as very small “cherry stones”. Attached to the surface of
the nanoclusters are the centers of phosphorylation of the caseins.
The tails of the caseins, then associate to form a protein matrix,
which can be viewed as polymer mesh to avoid the further agglom-
erate [18]. Apparently, this formation of casein micelle can also
bind calcium ions, especially at high concentration and high pH
[22]. The possible interaction between calcium ions and whey pro-

table 3
Main characteristics of model dairy effluent and UF/NF permeates).

<table>
<thead>
<tr>
<th>Index (25 °C)</th>
<th>COD (mg O₂L⁻¹)</th>
<th>Conductivity (µS cm⁻¹)</th>
<th>Turbidity (NTU)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>36000</td>
<td>~1580</td>
<td>NA</td>
<td>-6.67</td>
</tr>
<tr>
<td>US100P permeate</td>
<td>23000</td>
<td>1542</td>
<td>1.33</td>
<td>6.55</td>
</tr>
<tr>
<td>UH050P permeate</td>
<td>22000</td>
<td>1527</td>
<td>9.80</td>
<td>6.41</td>
</tr>
<tr>
<td>UH030P Permeate</td>
<td>21500</td>
<td>1542</td>
<td>1.48</td>
<td>6.40</td>
</tr>
<tr>
<td>NF270 Permeate</td>
<td>38</td>
<td>409</td>
<td>0.68</td>
<td>6.20</td>
</tr>
<tr>
<td>US100P + NF270 permeate</td>
<td>50</td>
<td>430</td>
<td>0.64</td>
<td>6.20</td>
</tr>
<tr>
<td>UH050P + NF270 permeate</td>
<td>45</td>
<td>412</td>
<td>0.67</td>
<td>6.19</td>
</tr>
<tr>
<td>UH030P + NF270 permeate</td>
<td>33</td>
<td>430</td>
<td>0.65</td>
<td>6.19</td>
</tr>
</tbody>
</table>

NA, not available.

* 12 L feed; 11 L UF permeate; 9 L NF permeate.

Fig. 6. Variations of NF (a) permeate flux and (b) permeate conductivity and retentate pH with VRR during concentration of model dairy effluent or its UF permeate by NF membrane. TMP = 4.0 MPa; rotating speed = 2000 rpm.
tein is shown Fig. 7b. This phenomenon is largely attributed to the ability of calcium to combine with carboxyl groups in whey proteins and at the surface of NF membranes. When complexation happens near the surface of NF membranes, calcium ions serve as bridges, tightly linking whey proteins to a membrane surface. This promotes the deposition of foulants and makes the fouling layer more compact. Therefore, for NF of original dairy effluent, casein micelles with calcium phosphate are formed, and these colloids are so large (average diameter 200 nm [18]) that shear-induced diffusion is negligible [23], and thus it is difficult for these colloids to deposit and agglomerate into cake layer, which reduces fouling; secondly, free soluble calcium phosphate possibly decreases due to more casein micelles formation and thus osmotic pressure in feed can be reduced, but this effect is not visible until a high VRR. Thirdly, due to the lower mobility (diffusion coefficient) of casein micelles compared with whey proteins ($3.1 \times 10^{-12}$ vs. $6.2 \times 10^{-11}$ m$^2$ s$^{-1}$, $D_{c,\infty}$, 35 °C), their concentration polarization layer is thicker than that for UF permeate, leading to a lower permeate flux at first.

The US100P permeate contains few casein micelles (Turbidity = 1.33 NTU, Table 3) but whey proteins are abundant because molecular weights of α-Lactalbumin and β-Lactoglobulin, accounting for 63% of whey proteins, are 14 kDa and 18 kDa [24], respectively, so these proteins can easily pass through the 100 KDa US100P membrane. The size of whey protein is less than 10 nm so that shear-induced diffusion is negligible [23], and these proteins easily form a cake layer with bridging of calcium phosphate on NF membrane (see Fig. 7b) [25,26]. When the VRR is more than 3.4, at a high TMP of 4.0 MPa, solutes concentration at membrane surface becomes high enough to form agglomerates, causing a rapid flux decline (see Fig. 6a). Furthermore, as can be seen in Fig. 6b, the retenate pH for NF of US100P permeates drops a little during the flux decline period, which also confirms the formation of complex organic–inorganic aggregation [27]. However, since at a larger part of whey proteins are retained by UH050P and UH030P, as seen in Fig. 6a, their permeate fluxes do not decline as rapidly as that for US100P permeate, and a mild flux drop maybe caused by the increasing solute concentration [6,28,29].

Therefore, the differences between our previous work [6] and the present one can be explained as follows: at low shear rate ($<10^3$ s$^{-1}$) used in [6], concentration polarization layer of caseins and whey proteins are easy to form due to the low shear-induced back diffusion, and when these macromolecules are removed by UF pretreatment, polarized layer and fouling are largely reduced, thus sustaining the high permeate flux; while at high shear rate ($>10^5$ s$^{-1}$) of present work, caseins micelles are dispersed away from membrane surface by high shear-induced back diffusion, also taking away some calcium phosphate nanoclusters. Thus, in this case, UF pretreatment is almost useless, even deleterious at high concentration factor due to more free calcium ions in absence of casein micelles.

3.3. Comparison between RDM and VSEP filtrations

Since at high shear rate ($\gamma_{m,initial} = 2.15 \times 10^5$ s$^{-1}$ at 2000 rpm) and a high TMP (4.0 MPa), the two-stage UF/NF process gave little improvement in recycling dairy effluent, we have compared the RDM and VSEP systems at moderate shear rates and TMP using both single NF and UF + NF.

3.3.1. Flux profile and permeate quality

Fig. 8 shows the variation of permeate flux with TMP for RDM and VSEP systems. Corresponding shear rates, calculated by Eqs. (2) and (3), and listed in Table 4, were $0.59 \times 10^5$ s$^{-1}$ for the RDM at 1000 rpm and $0.40 \times 10^5$ s$^{-1}$ for the VSEP at 60.75 Hz frequency for diluted milk at 35 °C. In single NF, the RDM permeate flux was smaller than at 2000 rpm and reached a plateau of 195 L h$^{-1}$ m$^{-2}$ at 2.0 MPa, higher than with the VSEP. However the UF pretreatment increased their NF fluxes significantly above 2.0 MPa. Therefore, 2.0 MPa was chosen for the single NF concentration test and a higher TMP of 2.5 MPa was used for NF of US100P permeate.

In Fig. 9, it is found that the rapid flux decline during NF of US100P permeate present at VRR > 4 in the 2000 rpm, 4.0 MPa test does not appear in same test with single NF and in tests at moderate shear rate and TMP, but NF fluxes of UF permeate decay a little faster than those of original effluent, probably due to higher concentration of free calcium phosphate (higher osmotic pressure) in absence of casein micelles. Permeate fluxes at 1000 rpm for RDM were a little higher than those for VSEP due to the RDM greater shear rate. Table 4 shows that the VSEP has, in single NF, a higher permeate COD, but a slightly lower turbidity. It is worth mentioning that COD values in NF permeate are nearly related with the lactose concentration ($0.89$ g L$^{-1}$ lactose corresponding to $1$ g L$^{-1}$ COD) because proteins and other organic acids can be completely retained by NF270 [6]. Thus the lactose in NF permeate is less than 0.01 g L$^{-1}$ under different operating modes.

3.3.2. Membrane fouling

The permeability loss (PL) of NF membranes after concentration test under different conditions, with and without UF, is shown in Fig. 10. These losses with 100 kDa UF pretreatment are higher than
with 50 and 30 kDa due to the presence of whey protein in US100P permeate. Since whey proteins are removed by UH050P and UH030P membranes, membrane fouling of NF270 is greatly reduced, especially for UH030P pre-filtration which rejects most of proteins and reduced the PL to 0.5%. The PL for NF of US100P permeate is larger than that for single NF process, especially for RDM with 1000 rpm, which is caused by the increase of free calcium phosphate in the absence of casein micelles for US100P permeate. This indicates that whey proteins and calcium ions are the main foulants for NF membranes. Permeability losses were smallest for the VSEP and a little lower in single NF.

### 3.3.3. Energy consideration

It is interesting to see which process and operating conditions minimize the specific energy consumed per m³ of permeate. But energy measurements made on small pilots are generally not meaningful because the power consumed by internal friction of motors may be disproportionate. The upper line of Fig. 11a shows the power consumed by the feed pump measured at different TMP. This power is high as the feed flow used in the tests was 120 Lh⁻¹. So, we have deduced from these data the power corresponding to a feed flow of \( Q = 30 \) Lh⁻¹, which is more realistic considering the small membrane area of our pilots 176 and 503 cm². The first data on the left, 0.134 kW, represents the power consumed by the pump at zero TMP. Since the power consumed by fluid friction is proportional to \( Q^3 \), we can estimate the corresponding power at \( Q = 30 \) Lh⁻¹ to be 134/64 = 2.1 W at TMP = 0. Thus the line parallel to the upper one drawn through this point represents the power consumed by the pump at different TMP (Fig. 11a). This energy consumption for pump pressurizing is independent of mechanic and only relevant to the performance of membrane (flux behavior, concentration polarization and fouling, etc.).

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**Table 4**

Comparison of permeate quality under different operating modes for same NF permeate volume.

<table>
<thead>
<tr>
<th>Index</th>
<th>( \gamma_{mi} ) (s⁻¹) ( ^a )</th>
<th>Mode</th>
<th>COD (mg O₂ L⁻¹)</th>
<th>Conductivity (μS cm⁻¹)</th>
<th>Turbidity (NTU)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>RDM 2000 rpm</td>
<td>2.15 × 10⁵</td>
<td>Single NF</td>
<td>38</td>
<td>409</td>
<td>0.68</td>
<td>6.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>UF + NF</td>
<td>50</td>
<td>430</td>
<td>0.64</td>
<td>6.20</td>
</tr>
<tr>
<td>RDM 1000 rpm</td>
<td>0.59 × 10⁶</td>
<td>Single NF</td>
<td>83</td>
<td>726</td>
<td>0.79</td>
<td>6.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>UF + NF</td>
<td>60</td>
<td>630</td>
<td>0.73</td>
<td>6.27</td>
</tr>
<tr>
<td>VSEP 60.75 Hz</td>
<td>0.40 × 10⁷</td>
<td>Single NF</td>
<td>162</td>
<td>712</td>
<td>0.68</td>
<td>6.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>UF + NF</td>
<td>110</td>
<td>631</td>
<td>0.59</td>
<td>6.29</td>
</tr>
</tbody>
</table>

\( ^a \gamma_{mi} \) means the mean shear rate at the beginning of operations (for original model dairy effluent).

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The specific energies \( E_c \) of feed pump for the different processes (UF + NF) and NF were calculated using Eq. (6) and results are shown in Fig. 11b. For a RDM rotating at 2000 rpm or 1000 rpm, \( E_c \) is lowest for single NF operation and minimum at 2000 rpm. While for the VSEP, \( E_c \) is close for single NF and two-stage UF/NF processes and higher than for the RDM at 1000 rpm. One must keep in mind that we have omitted in the calculations the power consumed by the disk rotation or vibrations in the VSEP. This power would be twice larger in the UF/NF process than in the single NF one and will be less for a large VSEP unit than for a RDM of same membrane area.
The hydrophilic modified UF membranes are preferable for recovering proteins from dairy effluent because of their better anti-fouling performance, as compared with PES membranes. Although permeate fluxes are different for US100P, UH050P and UH030P membranes in short-term concentration of dairy effluent, their long-term fluxes are similar due to the dominant foulant–deposited foulant interaction. UF pre-filtrations did not improve permeate quality and flux decline control. At high or moderate shear rates (>4 × 10^4 s^-1), the presence of casein micelles in dairy effluent reduces UF membrane fouling possibly because these micelles can bind much calcium phosphate and are prone to be dispersed by shear forces, while caseins are removed by UF, a complex organic–inorganic aggregation is easier to be formed through calcium bridging whey proteins at high concentration factor. Thus, a single NF operation is preferable for recycling dairy effluent by shear-enhanced membrane filtration and can also lead to a lower specific energy consumption.

Compared with the RDM at similar shear rates, the permeability loss of NF membranes was a little lower for VSEP. Because their flux profile, permeate quality and energy consumption are quite similar, the results obtained from a laboratory RDM pilot can provide valuable information for industrial VSEP equipment.

Acknowledgments

We thank the Program Cai Yuanpei 2010–2012, embassy of France in China for the financial support (No. 24039NA). The financial support of China Scholarship Council (CSC) for Jianquan Luo's thesis fellowship is acknowledged. The authors thank FilmTec Corporation, USA for providing NF270 membranes.

References