Treatment of dairy wastewater by two-stage membrane operation with ultrafiltration and nanofiltration

Yan-Wen Gong, Hong-Xun Zhang and Xue-Ni Cheng

ABSTRACT

Treatment of dairy wastewater by a two-stage membrane process with ultrafiltration (UF) and nanofiltration (NF) was investigated. The results showed that the flux of UF was higher at pH = 4.6 than that at pH = 8 because the resistance of the fouling membrane was lower at the isoelectric point of protein (pH = 4.6) in UF operation. Protein rejection exceeded 99% by UF + NF operation. Lactose rejections were 98.5 and 54% for UF + NF90 and UF + NF270 respectively. Experiments on membrane cleaning showed that the fouling layer of UF and NF was mainly protein and casein which could be removed by aqueous NaOH with pH = 10. The result of long-term experiments showed that the chemical oxygen demand (COD) of NF90 permeates was below 70 mg/L consistently and the wastewater could be concentrated to 24% by a two-stage membrane process.

Key words | dairy wastewater, lactose, nanofiltration, protein, ultrafiltration

INTRODUCTION

Dairy industry generates a large amount of wastewater, which contains high levels of suspended solids, ammonia, protein and other nutrients (Sirianuntapiboon & Tondee 2000; Vourch et al. 2008). Both aerobic and anaerobic technologies have been used for dairy wastewater treatment (Demirel et al. 2005; Wichern et al. 2008). An immersed membrane bioreactor (IMBR) was also setup to improve the quality of treatment effluent (Kaewsuk et al. 2010). However, the bio-treatment process has a number of difficulties such as large plant area, sludge settlement, removal of nitrogen and phosphorus, etc.

Several membrane processes have been proposed for dairy wastewater treatment to produce purified water for water reuse or recover nutrients (Ivnitsky et al. 2005; Boussu et al. 2007). Unlike conventional methods, membrane technology is tolerant to variable levels of pollutants in the upstream and is four times smaller than conventional wastewater treatment plant (Bae et al. 2003). One-stage experiments such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) used in dairy wastewater treatment were investigated (Sarkar et al. 2006; Frappart et al. 2008). It has been shown that one-stage of UF only rejected proteins and UF permeates contained lactose and other small molecules which related to high chemical oxygen demand (COD). NF operation could reject lactose, and the NF permeate has lower COD. However, the membrane flux is lower because of the large amount of protein adsorbed on the NF membrane. The RO process could produce reusable water while it needs high transmembrane pressure (TMP) (about 4 MPa) and has lower membrane flux in operation. Two-stage operations such as UF + RO, NF + RO or RO + RO were also studied (Turan 2004; Balannec et al. 2005). NF + RO or UF + RO are an effective way to produce reusable water in dairy plants (Bae et al. 2003; Vourch et al. 2008). However, higher TMP and membrane fouling in RO operation weaken its application. The main fouling cake was protein, calcium phosphate which adsorbed on the membrane porous or surface and increased the membrane resistance (Rosmaninho & Melo 2006). To decrease the fouling effects, new membrane processes were proposed to be used in operation. Experiments have shown that vibratory or rotating disk modules could decrease the membrane fouling (Jaffrin 2008). Unfortunately, these new technologies are seldom used in scale up because of its complexity.

In this study, we investigated the treatment of dairy wastewater by a two-stage membrane process with UF + NF under lower TMP. UF operation could remove the protein in raw wastewater and decrease the membrane fouling in the NF process. Compared with RO operation, the TMP was lower (at 1 MPa) and the membrane flux was higher in NF
operation. The aim of this work was not to produce reusable water in dairy plants, only to produce water for discharge and recover the nutrient in wastewater by two-stage membrane with UF + NF operation. The recovered nutrient could also be used for feed production.

**METHODS**

Henna Huahuaniu dairy plant (China) discharges wastewater at 200 m$^3$/day. Data collected from dairy plant showed that dairy wastewater contains proteins, lactose and other nutrients. The properties of the raw wastewater are shown in Table 1.

The spiral wound UF membrane used in this study was polysulfone with a molecular weight cut-off (MWCO) of 10,000 g/mol which was manufactured by Tianjin Motian Membrane Eng. & Tech. Co. Ltd. (China) while NF270 and NF90 were made by Dow-Filmtec. All other chemicals used were reagent grade or better.

The scheme of the experimental setup is shown in Figure 1. Raw wastewater collected from the dairy plant was initially filtered by a ceramic microfiltration membrane (MF) with 0.2 μm pore size. The MF permeate was filtered by UF and then the UF permeates were filtered by the NF membrane module. The pH of the wastewater was adjusted with the addition of 1 mol/L HCl or 1 mol/L NaOH. The TMP was maintained by adjustment of the control valves. The UF or NF membrane was cleaned by aqueous NaOH with pH = 10 for 20 min and rinsed with permeates for 5 min after the process was operated for 120 min. Protein concentration was analyzed by the coomassie brilliant blue method and lactose was analyzed by the 3,5-dinitrosalicylic acid method. The COD of the sample was determined with rapid test tubes (oxidation with potassium dichromate/sulfuric acid/silver sulfate at 148°C).

The rejection of protein or lactose was calculated using the following equation:

$$R(\%) = \left(1 - \frac{C_P}{C_O}\right) \times 100$$

where $C_P$ and $C_O$ are permeate and retentate feed concentration, respectively.

**RESULTS AND DISCUSSION**

Prior to the long-term experiments, a number of short-term tests were carried out to optimize the operation conditions. Figure 2 shows the experimental data for filtrate flux as a function of filtration time under constant TMP ($\Delta P = 0.4$ MPa) at different pH and wastewater concentrations in UF operation. The flux declined quite rapidly at the start of the filtration and the rate of flux decline increased with increasing wastewater concentration because of the fouling cake formed on the membrane. The flux declined slightly

### Table 1 | Main characteristics of dairy wastewater samples from dairy plant

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.2–6.9</td>
</tr>
<tr>
<td>COD mg O$_2$/L</td>
<td>2,500–3,900</td>
</tr>
<tr>
<td>Protein g/L</td>
<td>1.01–1.31</td>
</tr>
<tr>
<td>Lactose g/L</td>
<td>0.47–0.59</td>
</tr>
<tr>
<td>TSS mg/L</td>
<td>500–750</td>
</tr>
</tbody>
</table>

![Figure 1](image1.png) **Figure 1** | Scheme of experimental set-up.

![Figure 2](image2.png) **Figure 2** | Effects of pH and wastewater concentration on UF flux at $\Delta P = 0.4$ MPa.
after 60 min for raw wastewater because the fouling layer resistance on the membrane became stable. At long operation times, the flux appeared to approach a nearly constant value for all conditions. Similar flux decline was observed under RO or UF wastewater treatment (Balannec et al. 2005; Ivnitsky et al. 2005).

The figure also showed that the membrane flux at pH = 4.6 was greater than that at pH = 8. It has been proved that the fouling cake is mainly proteins and the pH scope of the isoelectric point is 4.5–5.5 for proteins. The fouling cake was fluffy at the isoelectric point and thus decreased the membrane resistance. Rice et al. (2009) had also found that the flux at pH = 4.9 was higher than other pH values and fouling occurred most rapidly at high pH (8.9) due to the bulk precipitation of calcium phosphate and protein.

The effects of NF90 and NF270 on NF operation are shown in Figure 3 at $\Delta P = 1.0$ MPa. The feed of the NF was UF permeates in which the protein was removed by UF and mainly contained the lactose and other inorganic minerals. This flux decline behaviour is comparable to the commonly reported cake layer fouling mechanism of UF and MF membranes. The initial flux of NF270 was greater than that of NF90 because the diameter of the membrane pores was larger in NF270 than that in NF90. However, the membrane flux of NF270 was decreased to 60% after filtration time of 60 min, while the membrane flux of NF90 had decreased only by 20% for the same period. This might be because the protein adsorbed on the membrane pores in NF270 while it could not be adsorbed in NF90 because of the lower porous diameter. Kulozik & Kessler (1990) found that significant flux decline during RO operation was not found while the protein in dairy wastewater was removed by UF. Rice et al. (2009) researched the fouling of NF membranes by UF permeates of dairy and found that the fouling cake was mainly calcium phosphate and the small amount of protein played an important role in membrane fouling.

Table 2 presents the quality of UF permeates and NF permeates. The protein rejection exceeded 98% in the UF process. Thus, almost all protein was rejected by UF membrane. The effects of the TMP on protein rejection were small. The flux increased as the TMP increased, while the fouling resistance also increased at the same time. Thus the TMP was not higher in UF operation. Chollangi & Hosain (2007) studied the separation of protein and lactose from dairy wastewater by UF and found the MWCO of membrane significantly affected the recovery of lactose and protein, and the TMP was little affected in operation. The UF membrane could not reject lactose and other small molecules. The lactose rejections were 98.5 and 54% for the NF90 and NF270, respectively. Consequently, NF90 was suitable for lactose removal in the membrane process.

The effects of membrane cleaning are shown in Figure 4. The flux decreased 65% after 120 min filtration time for the new UF membrane. A soft white gel deposit, mainly caseins and whey proteins, was observed on the membrane surface after the experiments. However, the flux recovered 86% after cleaning with aqueous NaOH (pH = 10). This indicated that the gel deposit could be cleaned by aqueous NaOH.
The effects of NF membrane cleaning are also shown in Figure 4. The flux of NF decreased by 23% after 80 min filtration. It has been proved that casein sequestered calcium phosphate affected the calcium equilibrium and the fouling behaviour in the fouling process (Rosmaninho & Melo 2006). SDS-PAGE study also revealed the presence of casein macropeptides in the fouling layer under NF operation. The membrane flux recovered 95% after membrane cleaning with aqueous NaOH at pH = 10. This indicated that the UF and NF membrane could be cleaned at the same time in operation.

Finally, evolution of COD in NF permeates during the long-term experiment was performed to check the stability of the process. As shown in Figure 5, the CODs of NF90 permeates were below 70 mg/L. It has been proved that the COD of NF permeates was related to its concentration of lactose, protein and fat (Balannec et al. 2005). It has been verified in Table 2 that the protein and lactose removal exceeded 98% in the NF90 permeates. This accorded with the lower COD in NF permeates. The raw wastewater could be concentrated to 24% at the end and the nutrient in wastewater was recovered. The final quality of treatment wastewater by the UF + NF90 process consistently exceeded the quality required for discharge.

**CONCLUSION**

Treatment of dairy wastewater by the UF + NF90 process was studied under the TMP with 0.2 and 1 MPa for UF and NF respectively. The results showed that the flux of UF was higher at the pH = 4.6 than that at pH = 8 due to the fouling cake being fluffy at the isoelectric point of protein (pH = 4–5). Compared with NF90, the rate of flux decline in NF270 was rapid due to the small amounts of protein tending to be adsorbed on to NF270 membrane pores. Protein was almost rejected by UF operation and the lactose rejections were 98.5% and 54% for NF90 and NF270 respectively. The fouling layer could be removed by aqueous NaOH at pH = 10 in UF and NF operation. The result of long-term experiment showed that the COD was below 70 mg/L in NF90 permeates. Raw wastewater could be concentrated to 24% at the end and the nutrient in wastewater was recovered.

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