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Published in:
Bioresource Technology

Link to article, DOI:
10.1016/j.biortech.2011.05.012

Publication date:
2011

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

Link back to DTU Orbit

Citation (APA):
A two-stage ultrafiltration and nanofiltration process for recycling dairy wastewater

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\textbf{Article info}

Article history:
Received 21 February 2011
Received in revised form 5 May 2011
Accepted 7 May 2011
Available online 13 May 2011

Keywords:
Ultrafiltration
Nanofiltration
Dairy wastewater
Water regeneration
Waste recycle

\textbf{Abstract}

A two-stage ultrafiltration and nanofiltration (UF/NF) process for the treatment of model dairy wastewater was investigated to recycle nutrients and water from the wastewater. Ultrafiltration (UF) membranes were found to be the most suitable for this purpose. In the first stage, protein and lipid were concentrated by the Ultracl PLGC UF membrane and could be used for algae cultivation to produce biodiesel and biofuel, and the permeate from UF was concentrated by the NF270 membrane in the second stage to obtain lactose in retentate and reusable water in permeate, while the NF retentate could be recycled for anaerobic digestion to produce biogas. With this approach, most of dairy wastewater could be recycled to produce reusable water and substrates for bioenergy production. Compared with the single UF process, this two-stage UF/NF process had a higher efficiency and less membrane fouling.

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1. Introduction

Large amounts of wastewater, composed of dilute milk (lipid, protein and lactose) and cleaning chemicals (acids, alkalis and detergents), are generated in dairy processing plants and represent a waste of water and nutrients as well as pollution. Among available technologies for wastewater treatment, membrane technology, especially nanofiltration (NF) and reverse osmosis (RO), has been often considered as a promising method because it can permit both water reuse and protein and lactose recovery in the same operations (Sarkar et al., 2006; Luo et al., 2010a). RO permeate water can be recycled in the plant, and the concentrated retentate can be used as feed supplement for animals (Selmer-Olsen et al., 1996), as substrates for biosynthesis of biodegradable plastics (Bosco and Chiampo, 2010) or for anaerobic digestion to produce hydrogen (Mohan et al., 2008; Guo et al., 2010).

Ultrafiltration (UF) of dairy wastewater yields a high permeate flux at low transmembrane pressure, but its permeate water is not reusable as it contains too much lactose (Chollangi and Hossain, 2007). Permeate water obtained from NF/RO treatment of dairy wastewater can be discharged in river or reused, but with the increase of organic solutes and inorganic salts in retentate during a concentration process, concentration polarization and osmotic pressure increase rapidly, leading to a large flux decline (Balannec et al., 2005). Even using a rotating disk membrane (RDM) module with a high shear rate at membrane surface (2–3 \texttimes 10^5 s\textsuperscript{-1}), NF permeate flux decreased from 500 to 120 L m\textsuperscript{-2} h\textsuperscript{-1} when 12 L real dairy wastewater was concentrated to 1.5 L (Luo et al., 2010a). Another problem for NF/RO treatment of dairy wastewater is the difficulty of nutrients recovery. That is, because cleaning chemicals contained in dairy wastewater, which are all retained by NF/RO membranes, contaminates the nutrients (lipsks, proteins and lactose), and lipids have a negative impact on anaerobic digestion because they are difficult to degrade and thus plug the sludge bed (Demirel et al., 2005; Passeggi et al., 2009). Also proteins in substrates decrease the hydrogen production rate because hydrogen consumption occurs in the fermentation of protein (Sreethawong et al., 2010; Xiao et al., 2010).

A two-stage UF/NF process was proposed for utilization of whey protein and lactose, as proteins were retained by UF membrane and lactose in UF permeate was concentrated by NF (Atra et al., 2005; Yorgun et al., 2008). For dairy wastewater treatment, similar approach can also be applied. Fig. 1 shows the flowsheet diagram of the two-stage UF/NF process. In this process, with a suitable UF membrane, lipids and proteins can be concentrated and collected by UF in the first stage, while small solutes (lactose, chemicals and salts) can easily pass through the UF membrane, the osmotic pressure in UF retentate will not increase significantly and consequently flux decline can be small when shear rate at membrane surface is high. The UF retentate could be used for algae cultivation to produce biodiesel and biofuel (John et al., 2011; Pittman et al., 2011). Considering the high absorption and utilization of nitrogen (N) and phosphorus (P) by algae, the problem of N and P removal from dairy wastewater could be solved (Demirel et al., 2005). While in NF stage, lactose and chemicals in UF permeate can be concentrated and

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recycled as substrates for anaerobic digestion to produce biogas (Ganzle et al., 2008), avoiding the negative effect of lipids and proteins on hydrogen production. This approach could simultaneously eliminate pollution, produce reusable water, and recycle waste.

In the present work, a two-stage UF/NF process for the treatment of dairy wastewater was proposed and examined, aiming at realizing concentration of protein in the first stage of UF, and lactose concentration and reusable water production in the second stage of NF, with focus on the selection of UF and NF membranes in terms of solutes rejection, membrane permeability as well as antifouling performance. The performance of the two-stage UF/NF process was also compared with that of a single NF process. The outcome could be useful in membrane process development for utilization of dairy wastewater and bioenergy production from dairy wastewater by algae cultivation and biogas fermentation.

2. Methods

2.1. Feed solution and membranes

A model effluent was prepared from commercial whole milk (Sanyuan pure milk, Capital Agribusiness Group, China), skimmed by a refrigerated centrifuge (4k-15, Sigma, Germany) at 4 °C for 20 min (10,000 rpm, 10,733 g). Then the skim milk was diluted with deionized water (milk:water = 1:9) to one-tenth of normal concentration. The main characteristics of this model dairy wastewater are shown in Table 1. Three commercial UF membranes (UP005P, UH030P, Ultracel PLGC) and five NF membranes (NF270, NF90, Nanomax50, Desal-5 DL, Desal-5 DK) were tested in the present study. Properties of these UF and NF membranes, obtained from manufacturers’ data sheet and literatures (Morao et al., 2006; Zhu et al., 2007; Luo et al., 2010b), are summarized in Table 2.

2.2. Experimental set-up and procedure

The schematic diagram of the experimental set-up was the same as our previous work (Luo et al., 2010b). The dead-end filtration experiments were performed in a laboratory-constructed magnetically stirred cell in concentration mode. The suspended bar impeller (length: 20 mm, diameter: 6 mm) inside the cell was driven by a magnetic agitator (85-2, Shanghai Sile Instrument Plant, China). The stirring speed was monitored using a digital optical tachometer (RM-1000, Prova Instruments Inc., China). The gap between the impeller and the membrane was about 2.5 mm. The working volume of the cell was 12.0 mL. It could be fitted with a membrane disc having an effective diameter of 24 mm within the module, with an effective membrane surface area of $4.52 \times 10^{-4}$ m$^2$. The operating temperature was controlled by a water bath. Feed was first diverted into an injection column (Superloop 50 mL, Pharmacia, Sweden) through a by-pass of the switching valve (V-7, Pharmacia, Sweden) and then was pumped at constant flow rate into the filtration cell using a high performance HPLC pump (LC-20AT, Shimadzu Corp., Kyoto, Japan). By adjusting the switching valve, deionized water could be pumped into cell directly to measure the pure water permeability ($J_p$) of membranes. The transmembrane pressure (TMP) was continuously monitored by a pressure sensor (MLH040BSB09A, Honeywell, USA) and the data were collected automatically by a computer. All experiments were performed under constant permeate flux mode, at a temperature of 25 ± 0.5 °C and a stirring speed of 1200 ± 10 rpm.

![Fig. 1. Schematic diagram of a two-step UF/NF process for dairy wastewater treatment and utilization for bioenergy production.](image-url)
A new membrane was used for each experiment. New membranes were dipped in 50% ethanol solution for about 5 s to remove manufacturing residues from the membrane surface, then soaked in deionized water for at least 12 h prior to use. Once installed, each membrane was compacted at a high flux until its permeate conductivity remained constant (5 bar for UF, 30 bar for NF), and then soaked in deionized water for at least 12 h prior to use. Once removed manufacturing residues from the membrane surface, membranes were dipped in 50% ethanol solution for about 5 s to pass through the column temperature was 40 °C. The conductivity was measured by a conductivity meter (DDS-307A, Precision & Scientific Instrument, China) and pH was measured with a pH-meter (PHS-2F, Precision & Scientific Instrument, China).

2.3. Analytical methods

The protein concentration in solution was measured by the Bradford protein assay using BSA (bovine serum albumin) as a standard (Bradford, 1976). The amount of lactose was quantified by the Shimadzu UV-1601PC detector (RID-10A, Shimadzu Corp., Kyoto, Japan) and Shimadzu PHS-2F, Precision & Scientific Instrument, China). The volume reduction ratio (VRR) is defined as:

$$\text{VRR} = \frac{V_p}{V_R}$$

where $V_p$ is the retentate volume, 12.0 mL. The irreversible fouling index ($IF$) can be expressed as a percentage of pure water permeability decrease after the experiment.

$$IF \% = \left( \frac{L_p - L_{p, f}}{L_p} \right) \times 100$$

where $L_{p, f}$ and $L_p$ are the initial and final pure water permeability respectively.

3. Results and discussion

3.1. UF membrane selection for the first stage

A UF membrane with high rejection of protein and high flux but low rejection of lactose is desirable for the first stage treatment of dairy wastewater. Analysis of permeates obtained with three different membranes (see Table 1) shows that proteins could be completely retained by the UF005P and Ultracel PLGC membranes and largely retained by the UH030P membrane (the protein transmission with this membrane was only around 0.67%), while lactose could pass through the Ultracel PLGC and UH030P membranes, be slightly retained by the UP005P membrane. The measurement of conductivity in the permeate also shown in Table 1 indicated that the transmission of salts through the three membranes was in this order: Ultracel PLGC > UH030P > UP005P.

Fig. 2 shows the TMP variation with increase of VRR at a constant permeate flux of 26.6 L m⁻² h⁻¹ for the three UF membranes. For the UP005 membrane, the TMP increased distinctly with increasing VRR, because lactose could be partially retained and gradually accumulated in the retentate, as shown in Table 3, and salts could also be retained to some extents as shown in Table 1, and consequently leading to higher osmotic pressure in retentate. Moreover, the UP005 membrane had the smallest MWCO among...
the three membranes, thus the highest intrinsic membrane resistance would be expected. All these could be the reasons why the TMP with the UP005 membrane was the highest under the same operating conditions when different UF membranes were used (Fig. 2). When the Ultracel PLGC and UH030P membranes were used, lactose could pass through both membranes completely (see Tables 1 and 3) due to their much higher molecular weight (342.30 Da), reducing osmotic pressure. As a result, their TMP were about one-third of that of UP005. As can be seen in Table 3, proteins were almost completely rejected by these three UF membranes, and protein concentration in retentate increased during membrane filtration. With the Ultracel PLGC, TMP remained nearly constant with VRR because both lactose and salts was freely transmitted, and osmotic pressure did not rise. Since membrane fouling could be another important factor affecting TMP during membrane filtration, the TMP profile with the Ultracel PLGC implied that fouling with this membrane could also be very small. This is confirmed by the fouling index shown in Fig. 3, since the IF for the Ultracel PLGC was only 2.1%. As for the UP005P and UH030P membranes, their IF were 47.4% and 72.4%, respectively. The main reason was that the surface layer of Ultracel PLGC membrane was made from regenerated cellulose (RC) while the other two UF membranes were made from polyethersulphone (PES) (Table 2), and the anti-fouling performance of RC membrane was much better than that of PES membrane, as reported by Puro et al. (2010). Although the UH030P membrane had the highest MWCO and no retention of protein and salts, the TMP with this membrane increased from 0.76 to 1.62 bar, faster than that with the Ultracel PLGC membrane having lower MWCO. This could be attributed to serious membrane fouling with the membrane (IF = 72.4%), as can be seen in Fig. 3. Therefore, the Ultracel PLGC membrane was selected for the first stage as it showed excellent anti-fouling properties and the lowest TMP.

In this UF stage, lipids and proteins could be fully recovered in retentate and the pH of the concentrated solution could also be adjusted by diafiltration operation. After rinsing, the lipid/protein rich stream generated by UF could be used for animal feed, or utilized for algae culture to produce bioenergy (see Fig. 1). It was reported that with 25% dilution of dairy wastewater and mix algae of Chlorella sp., Microactinium sp., Actinodium sp., the biomass productivity was 59 mg L⁻¹ day⁻¹ and lipid content was 29% cell dry weight (Woertz et al., 2009). Moreover, the benthic freshwater algae could be preferred for treatment of this wastewater due to their higher nutrient uptake rate (Pittman et al., 2011).

### 3.2. NF membrane selection for the second stage

As UF permeate of dairy wastewater with the Ultracel PLGC membrane contains lactose and cleaning chemicals at low concentration, nanofiltration could be applied to obtain dischargeable or reusable water. Usually, the NF permeate can be reused as cleaning water, expected to contain acid or alkali. Therefore, a NF membrane with high rejection of lactose and high flux but low rejection of inorganic salts is desirable for this second stage. To evaluate solutes rejection and average TMP with different NF membranes, 12 mL of feed (UF permeate collected in the first stage) was first injected to the filtration cell, and then another 2 mL of feed was pumped into the cell. After releasing the first 1 mL of permeate for stabilizing the system, the subsequent 1 mL of filtration permeate and the corresponding retentate were collected for analysis.

Table 4 shows the solutes rejection and average TMP for different membranes. Because the MWCO of both Nanomax50 and Desal-5 DL were high, their lactose rejections were not high enough, and they were not suitable for concentration of UF permeate containing lactose. The Desal-5 DK membrane retained lactose well and partly transmitted inorganic salts, but its TMP was quite high, when compared with other membranes, leading to higher energy consumption. NF90 membrane had the highest lactose rejection due to its lowest MWCO, however, its conductivity rejection was too high and this made its TMP a bit higher. Moreover, with increase of VRR, inorganic salts would accumulate in retentate due to the high salts rejection of NF90 (94.7%), and thus leading to increasing TMP or declining flux. For the NF270, lactose rejection was 97.8% and salts rejection was only 62.3%, indicating that most lactose could be retained by the NF270, while salt could pass through easily.

Fig. 4 shows permeate flux variation with TMP for different NF membranes using deionized water. It can be seen that the f_p of NF270 was the highest (13.4 L m⁻² h⁻¹ bar⁻¹), followed by NF90.
Table 4
Solute rejection and average TMP for different NF membranes.

<table>
<thead>
<tr>
<th>Index</th>
<th>NF270</th>
<th>NF90</th>
<th>Nanomax50</th>
<th>Desal-5 DL</th>
<th>Desal-5 DK</th>
</tr>
</thead>
<tbody>
<tr>
<td>R&lt;sub&gt;app&lt;/sub&gt; of lactose (%)</td>
<td>97.8%</td>
<td>99.3%</td>
<td>67.6%</td>
<td>73.1%</td>
<td>96.0%</td>
</tr>
<tr>
<td>R&lt;sub&gt;app&lt;/sub&gt; of conductivity (%)</td>
<td>62.3%</td>
<td>94.7%</td>
<td>31.5%</td>
<td>53.4%</td>
<td>64.4%</td>
</tr>
<tr>
<td>TMP (bar)</td>
<td>4.56</td>
<td>5.97</td>
<td>9.51</td>
<td>12.45</td>
<td>14.40</td>
</tr>
</tbody>
</table>

Flux = 53.1 L m<sup>−2</sup> h<sup>−1</sup>, T = 25 °C, stirring speed = 1200 rpm.

(10.5 L m<sup>−2</sup> h<sup>−1</sup> bar<sup>−1</sup>), Nanomax50 (6.0 L m<sup>−2</sup> h<sup>−1</sup> bar<sup>−1</sup>), Desal-5 DL (4.0 L m<sup>−2</sup> h<sup>−1</sup> bar<sup>−1</sup>), and Desal-5 DK (3.9 L m<sup>−2</sup> h<sup>−1</sup> bar<sup>−1</sup>), which agreed well with the TMP values shown in Table 4. Comparison of L<sub>p</sub> for the five NF membranes also implied that the NF270 membrane would have higher productivity and lower operating cost in NF operation. Therefore, NF270 could be considered as the most suitable membrane for the NF step in terms of its solutes rejection and low TMP (i.e., high L<sub>p</sub>).

3.3. Comparison between the two-stage UF/NF and a single NF processes

Based on the above experimental results, the Ultracel PLGC and NF270 membranes were selected for the two-stage UF/NF process to recycle dairy wastewater. Fig. 5 shows the TMP profiles of concentration process with the NF270 membrane in the two-stage UF/NF and a single NF processes. In the two-stage UF/NF process, UF permeate from the first stage was used as feed in the second stage of NF, the concentration by the NF270 was carried out at a constant flux of 53.1 L m<sup>−2</sup> h<sup>−1</sup>, and TMP remained less than 8.0 bar as VVR rose to five (Fig. 5a). However, in a single NF process without UF pretreatment, TMP in NF increased from 1.9 to 35.7 bar in 12 min at a constant flux of 53.1 L m<sup>−2</sup> h<sup>−1</sup>. In this case, permeate flux had to be lowered to ensure the TMP not exceeding the upper limit of the membrane during operation. When permeate flux was set to a lower value of 39.8 L m<sup>−2</sup> h<sup>−1</sup>, TMP dropped a little but rose quickly to 37.5 bar in 18 min. When the flux was further decreased to 26.6 L m<sup>−2</sup> h<sup>−1</sup>, TMP remained at 4.0–6.0 bar for about 100 min but rose again at VRR = 4. Finally, the flux had to be reduced to 13.3 L m<sup>−2</sup> h<sup>−1</sup> to stabilize TMP at about 5.0 bar (Fig. 5b). When VRR reached five, with UF pretreatment, the concentration time was 120 min with low and stable TMP, but without UF pretreatment, it took 248 min to concentrate the same volume of feed and TMP was high and unstable.

The higher TMP in single NF process was caused by the presence of proteins in feed. Because proteins have relatively low mobility, they form a concentration polarization layer, and when calcium phosphate is retained and accumulated on the NF membrane, a complex organic–inorganic aggregation is formed through calcium phosphate bridges (Bouzid et al., 2008). Thus, a “limiting flux” occurred in NF when both proteins and multivalent salt ions were present in feed, caused by increasing concentration polarization and fouling (Bouzid et al., 2008; Rabiller-Baudry et al., 2009). While proteins were removed by UF, concentration polarization and fouling were greatly reduced during NF concentration step. This was confirmed by the very low irreversible fouling of the NF270 membrane (IF = 2.64%) shown in Fig. 6 as compared with 59.1% for a single NF concentration process, after concentrating 60 mL of original feed to 12 mL. Due to the fouling layer, lactose rejection by NF270 improved, and the recovery of lactose for a single NF process was a bit higher than that for the two-stage UF/NF process, as can be seen in Table 5. However, this fouling
The NF270 membrane was suitable to treat the UF permeate in performance and high transmission of lactose and inorganic salt. The wastewater in the first stage because of its excellent antifouling performance and high transmission of lactose and inorganic salt. The NF270 membrane was suitable to treat the UF permeate in performance and high transmission of lactose and inorganic salt. The NF270 membrane was suitable to concentrate proteins and lipids in wastewater for bioenergy production (see Fig. 1), as discussed by John et al. (2011), Pittman et al. (2011) and Ganzle et al. (2008). Therefore, this two-stage UF/NF process seems more applicable for recycling dairy wastewater and more efficient in providing sub-

4. Conclusions

This work demonstrated that the two-stage UF/NF treatment of dairy wastewater was a viable and promising method to recycle water and nutrients for production of bioenergy. The Ultracel PLGC membrane was suitable to concentrate proteins and lipids in wastewater in the first stage because of its excellent antifouling performance and high transmission of lactose and inorganic salt. The NF270 membrane was suitable to treat the UF permeate in the second stage to obtain lactose in retentate and reusable water in permeate due to its high permeability and high lactose rejection as well as the low retention of salts.

Acknowledgements

We thank the International Cooperation Program, Ministry of Science and Technology of China (Grant No. S2011ZR0434) and the Program Cai Yuanpei 2010–2012, Egide of France (Grant No. 24039NA) for the financial support. The financial support of China Scholarship Council (CSC) for Jianquan Lou’s thesis fellowship is acknowledged. We thank FilmTec Corporation, USA for providing NF270, NF90 membranes.

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