Research article

Recovery of sulfuric acid aqueous solution from copper-refining sulfuric acid wastewater using nanofiltration membrane process

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\textbf{ABSTRACT}

We used a nanofiltration (NF) membrane process to produce purified aqueous sulfuric acid from copper-refining sulfuric acid wastewater. Wastewater generated from a copper-refining process was used to explore the membrane performances and acid stabilities of six commercial NF membranes. A combination of permeate flux, sulfate permeation, and metal ion rejection clearly showed that two polyamide membranes and a polyacrylonitrile-based membrane achieved recovery of a purified sulfuric acid solution. Acid-stability and long-term performance tests showed that the polyamide membranes were unsuitable for copper-refining wastewater treatment because of their low acid stabilities. In contrast, the polyacrylonitrile-based composite membrane showed excellent acid stability, and gave greater than 90% metal ion rejection, with the exception of calcium ions, for 430 d. We also evaluated the recovery performance in 1 ton/d pilot-scale process using wastewater from copper-refining process; 90% metal ion rejection was achieved, with the exception of calcium ions, even at 95% recovery rate.

\section{1. Introduction}

Enormous amounts of highly concentrated acid wastewaters are discharged by various industries such as the metal, pulp/paper, and leather industries (Visser et al., 2001; Awadalla and Kumar, 1994; Andres et al., 1994; Wisniewski and Wisniewska, 1997; Jönsson, 1987; Galiana-Aleixandre et al., 2005). Among these industries, the copper industry emits SO$_2$ and SO$_3$-containing flue-gases that are generated by sulfur in the copper ore during the copper smelting process. During the process for the treatment of this flue-gas, SO$_3$ is dissolved in the washing water in the wet desulfurization process, and sulfuric acid wastewater having strong acidity is generated. The wastewaters from this process contain highly concentrated acids and various types of metal ions. The acids contained in the wastewater are corrosive to body tissues and cause skin irritation when contacted, and heavy metals can cause vomiting, jaundice, and may damage the liver and kidneys (Chuttani et al., 1965). Therefore, the removal of harmful acids and heavy-metal ions from industrial wastewaters is an important environmental issue.

The acidic substances and metal ions in industrial wastewaters from copper refining are currently eliminated by neutralization and flocculation/precipitation. However, these processes use large amounts of chemical neutralizing agents and flocculants. In economic terms, the use of such large amounts of chemicals is undesirable. Furthermore, because secondary pollutants are generated during these processes, an additional process for disposing the neutralized precipitate is required.

Recently, membrane processes have become widely used for water treatment in various fields because of their advantages such as low energy consumption, time efficiency, and a small footprint compared with other water treatment technologies such as distillation, chemical treatment, adsorption (Li et al., 2011). Among various membrane types, nanofiltration (NF) membranes are considered to be the best for purifying acid wastewaters because they give high selectivity and permeate fluxes at relatively low pressures compared with those achieved using reverse osmosis (Rautenbach and Gröschl, 1990; Mohammad et al., 2015; Vergili, 2013; Chang et al., 2014; Homayoonfal et al., 2010; Bunani et al., 2013; Li et al., 2010; Ortega et al., 2005; Unlu et al., 2009; Jakobs and Baumgarten, 2002). Because of these advantages, NF membranes have been studied in various fields such as the reuse of organic solvents and reactants, metal ion recovery (Shang et al., 2014; Fodi et al., 2017; Didaskalou et al., 2017), and the application to acid wastewater treatment is also being studied (Galiana-Aleixandre et al., 2005).
Mendoza-Roca et al. purified the acid wastewaters from pickling and tanning processes using an NF membrane (Galiana-Aleixandre et al., 2005). They achieved high sulfate retention (> 90%) and obtained highly purified water. However, all the acidic substances and metal ions remained in the concentrate and had to be removed using conventional processes. Jakobs et al. also used an NF membrane for treatment of industrial nitric acid solutions (Jakobs and Baumgarten, 2002). The acid permeation and cation exclusion properties of the NF membrane enabled a purified nitric acid solution to be obtained from the nitric acid solution used in picture tube production. The recycling rate of the NF membrane process was 80–90%. This result clearly shows that NF membranes can be used to obtain purified acid solutions from acid wastewaters. The use of NF membrane systems to recover sulfuric acid aqueous solutions from sulfuric acid wastewater produced during copper smelting reduces the amount of discharged pollutants. However, to the best of our knowledge, no research has been performed to determine which type of membrane is most suitable for sulfuric acid solution recovery from copper-refining wastewater. Furthermore, membrane damage under strongly acidic conditions has not been sufficiently investigated. Further research is therefore needed on the selective ion rejection properties and durability under extremely acidic conditions of NF membranes for the treatment of sulfuric acid wastewater.

In this study, we used an NF membrane process to produce sulfuric acid aqueous solutions from industrial wastewaters containing sulfuric acid. We explored the selective ion rejection properties and acid stabilities of various NF membranes, i.e., polyamide, polyacrylonitrile-based, and polyethersulfone (PES) membranes, with different molecular-weight cutoffs, using actual sulfuric acid wastewater from a copper-refining plant. Based on the results of the selective separation and acid resistance evaluation, a membrane suitable for acid recovery was selected. Pilot-scale tests using the membrane were conducted to confirm that this method could be used for actual sulfuric acid treatment.

2. Materials and methods

2.1. Materials

Sulfuric acid wastewater was obtained from a copper-refining plant. The sulfuric acid wastewater contained about 10 wt% sulfuric acid (pH 1–2) and more than 2000 mg/L of metal ions such as calcium, copper, iron, and magnesium. The original concentrations of ions in the wastewater are shown in Table S1. A polytetrafluoroethylene (PTFE) flat-sheet membrane with a pore size of 0.1 μm was purchased from Advantec-MFS, Inc. (USA). Two kinds of polyamide composite membranes (NE40, NE70) were supplied by Toray Chemical Korea Inc. The non-polyamide composite membranes (MPS-34, MPS-36) (Piedra et al., 2015) was purchased for Koch membrane system. Polyethersulfone (PES) based membrane (NP010, NP030) was purchased from Nadir.

The membrane specifications are summarized in Table 1.

2.2. Separation performance

The membrane performances were evaluated based on filtration of actual sulfuric acid wastewater. Prior to NF membrane filtration, the membranes were wetted by pressurization at 30 bar for 30 min. The membrane filtration tests were performed with applied pressures of 10, 20, and 30 bar under dead-end conditions, in which the feed solution was continuously concentrated in the cell without being discharged. The performance was evaluated based on the permeate flux, sulfate permeation, and metal ion rejection, which were calculated using the following equations:

\[ J_v = \frac{\text{permeate volume}}{\text{membrane area} \times \text{filtration time}} \]  

(1)

\[ P = \frac{C_{mp}}{C_{mf}} \times 100 \]  

(2)

\[ R = \frac{C_{mi} - C_{mp}}{C_{mi}} \times 100 \]  

(3)

where \( J_v \) is the permeate flux [L/(m² h), LMH], \( P \) is the sulfate permeation (%), \( C_{mf} \) is the sulfate in the permeate (ppm), \( C_m \) is the initial sulfate concentration (ppm), \( R \) is the metal ion rejection (%), \( C_{mi} \) is the initial metal ion concentration (ppm), and \( C_{mp} \) is the metal ion concentration in the permeate (ppm). The concentrations of sulfate ions in the feed and permeate were determined using ion chromatography ( Dionex, ICS-3000). The concentrations of metal ions in the feed and permeate were determined using inductively coupled plasma atomic emission spectroscopy ( Shimadzu, ICP-7510) with errors within 2%. The metal ions investigated were calcium, copper, iron, and magnesium.

2.3. Stability under sulfuric acid wastewater conditions

The three membranes selected through sulfuric acid separation performance evaluation (NE40, NE70, and MPS-34) were immersed in sulfuric acid wastewater for 430 d. Membrane degradation was confirmed by examination of the chemical structure and surface morphology. The membrane chemical structure was determined using attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). ATR-FTIR spectra were recorded in the range 2000–750 cm\(^{-1}\) (Thermo Scientific Nicolet 6700 IR spectrometer). XPS was performed using a Thermo VG Sigma Probe spectrometer with a monochromatic Al Kα (1486.6 eV) X-ray source. The membrane surfaces were examined using field-emission scanning electron microscopy (FE-SEM; JEOL JSM 7600F). Prior to the FE-SEM observations, all samples were coated under vacuum with platinum. Long-term performance of the membranes was confirmed by periodic measurements of performance changes.

### Table 1

<table>
<thead>
<tr>
<th>Designation</th>
<th>NE40</th>
<th>NE70</th>
<th>MPS-34</th>
<th>MPS-36</th>
<th>NP010</th>
<th>NP030</th>
</tr>
</thead>
<tbody>
<tr>
<td>manufacturer</td>
<td>Toray chemical</td>
<td>Koch membrane systems</td>
<td>proprietary (cross-linked modified polyacrylonitrile)</td>
<td>polyethersulfone</td>
<td>Nadir</td>
<td>polyethersulfone</td>
</tr>
<tr>
<td>Structure</td>
<td>Composite membrane</td>
<td>Composite membrane</td>
<td>Asymmetric membrane</td>
<td>Asymmetric membrane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular weight cut off (MWCO)</td>
<td>1000 Da</td>
<td>350 Da</td>
<td>200 Da</td>
<td>1000 Da</td>
<td>1000 Da</td>
<td>400 Da</td>
</tr>
<tr>
<td>Water flux (LMH)</td>
<td>55–59(^{a})</td>
<td>31.8(^{\circ})</td>
<td>59–63(^{\circ})</td>
<td>250–263(^{\circ})</td>
<td>&gt; 200(^{\circ})</td>
<td>&gt; 40(^{\circ})</td>
</tr>
<tr>
<td>Rejection (%)</td>
<td>20–60(0.2% NaCl)</td>
<td>40–70(0.2% NaCl)</td>
<td>35(5% NaCl)</td>
<td>10(5% NaCl)</td>
<td>10(0.1% Na2SO4)</td>
<td>30(0.1% Na2SO4)</td>
</tr>
<tr>
<td>pH resistance</td>
<td>2–11</td>
<td>2–11</td>
<td>0–14</td>
<td>0–14</td>
<td>0–14</td>
<td>0–14</td>
</tr>
</tbody>
</table>

\(^{a}\) Measured at 5.2 bar.  
\(^{\circ}\) Measured at 30 bar.  
\(^{\circ}\) Measured at 40 bar.
Performance of candidate membranes at 30 bar.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>NE40</th>
<th>NE70</th>
<th>MPS-34</th>
<th>MPS-36</th>
<th>NP010</th>
<th>NP030</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeate flux (LMH)</td>
<td>8.2</td>
<td>8.4</td>
<td>6.25</td>
<td>82.5</td>
<td>97.9</td>
<td>17.8</td>
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<tr>
<td>Sulfate permeation (%)</td>
<td>80.0</td>
<td>76.3</td>
<td>78.0</td>
<td>101.5</td>
<td>102.3</td>
<td>97.8</td>
</tr>
<tr>
<td>Metal ion rejection (%)</td>
<td>99.3</td>
<td>98.6</td>
<td>96.4</td>
<td>43.9</td>
<td>28.5</td>
<td>53.7</td>
</tr>
<tr>
<td>Ca</td>
<td>96.1</td>
<td>98.5</td>
<td>92.2</td>
<td>37.3</td>
<td>25.6</td>
<td>49.8</td>
</tr>
<tr>
<td>Mg</td>
<td>98.1</td>
<td>99.2</td>
<td>95.5</td>
<td>55.6</td>
<td>27.9</td>
<td>54.6</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Separation performances of candidate membranes

We explored the permeate fluxes, sulfate permeations, and metal ion rejections of the NF membranes to determine whether these membranes were suitable for producing purified sulfuric acid aqueous solution from sulfuric acid wastewater. We used real sulfuric acid wastewater discharged from a copper-refining plant to investigate the membrane performances. Figs. S1 and S2 show the changes in the performances of the candidate NF membranes with applied pressure. The permeate fluxes and metal ion rejections increased with increasing applied pressure (Figs. S1a and S2). The sulfate permeation decreased with increasing applied pressure (Fig. S1b). Similar trends have been observed in previous studies, and they are attributed to different permeability increases of the dissolved substances with increasing pressure (Pulido and Fèrez, 2015; Ortega et al., 2008). Table 2 shows the performance of the candidate membranes at 30 bar. The sulfate permeations of all the candidate membranes were above 75%, even at 30 bar. The sulfate permeation of the neat polyamide membranes was above 75%, even at 30 bar. Therefore, the sulfate permeation results of the membranes indicate that sulfuric acid could be recovered by the NF membranes. The permeate fluxes of the membranes were lower than those stated in the membrane specifications because of the high ion concentration in the wastewater from the copper-smelting process. Among the membranes, those with high permeate fluxes (MPS-36, NP010, and NP030) gave poor metal ion rejections, below 60%, for all metal ions at all pressures. In contrast, the other membranes (NE40, NE70, and MPS-34) gave excellent metal ion rejections, above 90% at 30 bar, although they had low permeate fluxes, below 10 L/m²h (LMH). These results suggest that NE40, NE70, and MPS-34 could recover purified aqueous sulfuric acid at 30 bar from which metal ions had been removed by selective permeation. The long-term stabilities of NE40, NE70, and MPS-34 were therefore evaluated.

3.2. Long-term stability of candidate membranes in sulfuric acid wastewater

NF membranes for treating copper-refining sulfuric acid wastewater must be stable under strongly acidic conditions. The acid stabilities of the polyamide membranes (NE40 and NE70) and a polyacrylonitrile membrane (MPS-34) were evaluated based on destruction of the chemical structures of the membranes during immersion in actual sulfuric acid wastewater. The ATR-FTIR spectra of NE40, NE70, and MPS-34 before and after exposure to sulfuric acid wastewater are shown in Fig. S3(a). The spectra of NE40 and NE70 after exposure to sulfuric acid wastewater for 30 d had clear IR bands at 1670 cm⁻¹, corresponding to carboxylic acid C=O stretching, and the spectra of the original piperazine-based polyamide membranes, i.e., before exposure to sulfuric acid wastewater, had IR bands at 1628 cm⁻¹, corresponding to amide C=O stretching. This change is attributed to polyamide degradation through acid-catalyzed hydrolysis. In addition, XP spectra of the polyamide membranes (Fig. S4) after exposure to sulfuric acid wastewater showed a peak at 533 eV, corresponding to the O 1s binding energy of carbonyl groups, indicating polyamide degradation through acid-catalyzed hydrolysis. These results show that the polyamide membranes were chemically unstable under strongly acidic conditions. In contrast, the ATR-FTIR spectra of MPS-34 before and after exposure to acid wastewater for 30 d were almost the same. These results show that only MPS-34 was chemically stable under sulfuric acid wastewater conditions.

FE-SEM was used to investigate the morphological changes in the membrane surfaces after exposure to acid wastewater for 30 d. Fig. 2 shows FE-SEM images of the surfaces of NE40, NE70, and MPS-34. The neat piperazine-based polyamide membranes had a uniform surface morphology. However, many pinholes caused by severe degradation of the active layer were observed on the surfaces of these piperazine-based polyamide membranes after immersion in sulfuric acid wastewater for 30 d. The pinhole density for NE40 was higher than that for NE70. This indicates fast degradation of NE40 because of its loose active layer structure. In contrast, the surface structure of MPS-34 was preserved after exposure to acid wastewater. These results indicate that MPS-34 did not decompose under acidic conditions, i.e., only MPS-34 had good stability in sulfuric acid wastewater.

We explored the permeate fluxes, sulfate permeations, and metal ion rejections of the NF membranes as a function of immersion time in sulfuric acid wastewater to determine the durability of the NF membranes for long-term operation. The membrane performances of the polyamide membranes were recorded for 30 d because membrane decomposition occurred within 30 d at pH 1–2. The initial permeate fluxes of NE40 and NE70 were about 8 LMH; their permeate fluxes increased to above 1000 LMH with increasing immersion time because of degradation of the polyamide active layers, as expected from the ATR-FTIR spectra and FE-SEM images (Fig. 3a). Fig. 3(b and c) shows that the sulfate permeation rates of all the polyamide NF membranes increased steadily during exposure to sulfuric acid wastewater for 30 d. The rejections of calcium, copper, iron, and magnesium ions by NE40 decreased significantly after immersion for 7 d in the copper-refining sulfuric acid wastewater (Fig. 4b). The rejection performance of NE70 declined considerably after immersion for 15 d in sulfuric acid wastewater. The rejection performances eventually reached almost 0%, with
the exception of magnesium ion rejection (ca. 30%). These changes in the permeate flux, sulfate permeation, and metal ion rejections are ascribed to decomposition of the polyamide active layer and generation of pinholes by the copper-refining sulfuric acid wastewater. All the polyamide NF membranes tested are therefore unsuitable for sulfuric acid wastewater treatment because of acid-induced decomposition of the active layer.

The membrane performance of MPS-34 was monitored for 430 d because it had high acid stability, unlike the polyamide membranes. The water permeability of MPS-34 was well maintained for 430 d with immersion time. The sulfate permeation of MPS-34 did not change significantly for 200 d, but increased after 200 d and was then maintained again. This change in the sulfate permeation is thought to be caused by changes in the wastewater composition during long-term evaluation, i.e., for more than one year, because the membrane was intact. Membrane MPS-34 gave an excellent rejection performance, i.e., above 90%, except in the case of calcium ion rejection (about 80%); this was well maintained for 430 d. Its selective ion rejection properties and durability under extremely acidic conditions indicate that MPS-34 is the most suitable NF membrane for recovering aqueous sulfuric acid from sulfuric acid wastewater.

3.3. Pilot-scale (1 ton/d) tests using MPS-34 spiral wound module

The suitability of MPS-34 for use in wastewater treatment was evaluated in pilot-scale tests, with a 1 ton/d treatment capacity, using an MPS-34 spiral-wound module. Fig. 5 shows the changes in the membrane performance of MPS-34 with applied pressure. The permeate flux and metal ion rejections increased with increasing applied pressure, and the sulfate permeation decreased with increasing applied pressure (Fig. 5). These trends are the same as those observed in flat-sheet membrane experiments. The permeate flux was increased by the cross-flow effect, and this effect did not change significantly in the range 2–6 L/min because agitation was sufficiently large compared to the feed enrichment speed (Fig. S5).

Fig. S6 shows the changes in the MPS-34 membrane performance with recovery rate in the pilot-scale experiments. The permeate flux decreased with increasing recovery rate (Fig. S6a). This is attributed to the increase in osmotic pressure caused by concentration of the feed solution. The sulfate permeation decreased with increasing recovery rate for the same reason (Fig. S6b). Metal ion rejection was not significantly affected up to 95% recovery rate, despite ion enrichment. The membrane process could therefore be used to concentrate wastewater up to a high recovery rate, indicating that a large amount of sulfuric acid solution can be recovered. These results suggest that the NF membrane process is suitable for the recovery of highly purified sulfuric acid aqueous solution from copper-refining sulfuric acid wastewater.

4. Conclusion

In this study, we developed an NF membrane process for the recovery of aqueous sulfuric acid from copper-refining industrial wastewater. We examined the permeate fluxes, sulfate permeations, metal ion rejections, and acid stabilities of six commercial NF membranes, using actual copper-refining sulfuric acid wastewater, to determine
whether NF membranes are suitable for producing purified sulfuric acid aqueous solution from sulfuric acid wastewater. A combination of the permeate flux, sulfate permeation, and metal ion rejection results showed that NE40, NE70, and MPS-34 could separate purified sulfuric acid solution from sulfuric acid wastewater. However, the polyamide membranes were unsuitable for copper-releasing wastewater treatment because of their low acid stabilities. ATR-FTIR spectroscopy and FE-SEM showed that MPS-34 was acid resistant; it gave above 75% sulfate permeation and greater than 90% metal ion rejection, with the exception of calcium ions, for 430 d. In addition, pilot-scale (1 ton/d) tests showed that the separation performance was maintained even at a high recovery rate of 95%. NF processes using membranes with good selective acid permeations and excellent acid stabilities provide attractive and eco-friendly methods for the recovery of various acid solutions from industrial acid wastewaters. Currently, studies are under way to improve the recovery efficiencies of NF membranes.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.

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