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Research article

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

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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.

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.,

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2005; Jakobs and Baumgarten, 2002). 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 from 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:

$$Jv = \frac{permeate\ \ volume}{membranearea \times filtrationtime} \tag{1}$$

$$P = \left(\frac{C_{sp}}{C_{si}}\right) \times 100 \tag{2}$$

$$R = \left(\frac{C_{mi} - C_{mp}}{C_{mi}}\right) \times 100 \tag{3}$$

where J_v is the permeate flux [L/(m^2 h), LMH], P is the sulfate permeation (%), C_{sp} is the sulfate in the permeate (ppm), C_{si} 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, ICPS-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
Specifications of candidate membranes.

Designation	NE40	NE70	MPS-34	MPS-36	NP010	NP030
manufacturer	Toray chemical		Koch membrane systems		Nadir	
Materials	piperazine based polyamide		proprietary (cross-linked modified polyacrylonitrile)		polyethersulfone	
Structure	Composite membrane		Composite membrane		Asymmetric membrane	
Molecular weight cut off (MWCO)	1000 Da	350 Da	200 Da	1000 Da	1000 Da	400 Da
Water flux (LMH)	55–59[a]	31.8[a]	59–63[b]	250–263[b]	> 200[c]	> 40[c]
Rejection (%)	20-60[a](0.2% NaCl)	40-70[a](0.2% NaCl)	35[b](5% NaCl)	10[b](5% NaCl)	10[c](NaCl)	30[c](NaCl)
	97[a](0.2% $MgSO_4$)	97[a](0.2% $MgSO_4$)			35-75[c] (Na_2SO_4)	80-95[c](Na_2SO_4)
pH resistance	2–11	2–11	0–14	0–14	0–14	0–14

[a] Measured at 5.2 bar.
[b] Measured at 30 bar.
[c] Measured at 40 bar.