Reducing industrial wastewater and recovery of gold by direct contact membrane distillation with electrolytic system

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ABSTRACT

To recover gold, this work used a novel direct contact membrane distillation (DCMD) reactor with a hybrid electrolytic process. Analytical results demonstrate that permeate flux increased as feed temperature and feed flow rate increased. Permeate flux increased from 2.8 to 17.6 kg m⁻² h⁻¹ when temperature increased from 30 to 70 °C, and increased from 9.2 to 19.9 kg m⁻² h⁻¹ when the feed flow rate increased from 10 to 50 L h⁻¹. A strong negative correlation between feed conductivity and permeate flux existed. Flux decreased about 21% following an increase in Au wastewater concentration in the feed from 5,600 to 55,000 μS cm⁻¹. The gold and total organic carbon concentrations increased as the concentration ratio increased. The Au concentration reached around 165 mg L⁻¹ with a concentrating efficiency exceeding 17-fold. After the DCMD process, 90% of the concentrated gold solution was recovered by electrolysis. Performance recovery rate increased about 20 times from 10.6 to 252 mg A⁻¹ h⁻¹. These positive results show that the new hybrid process integrating a DCMD reactor with electrolysis methods can be applied effectively to treat low concentrations of gold in wastewater.

INTRODUCTION

Heavy metals have atomic weights of 63.5-200.6, and a specific gravity exceeding 5.0 [1]. Such industries as metal plating, mining, fertilizer production, leather tanning, battery production, and paper and pesticide production discharge wastewater with heavy metals directly or indirectly into the environment, especially in developing countries. Unlike organic contaminants, heavy metals cannot be biodegraded and typically accumulate in living organisms. Many heavy metal ions are toxic or carcinogenic. Toxic heavy metals, including zinc, copper, nickel, mercury, cadmium, lead, and chromium, are of particular concern when treating industrial wastewaters. Chen et al. developed new technology for treating lead frame nickel-plating wastewater [2].

Electroplating discharges huge amounts of wastewater to wastewater treatment plants with large amounts of different valuable metals in the wastewater, such as gold, silver, copper, and nickel. In recent years, interest has increased in developing effective electrochemical methods to remove metal ions from wastewaters [2-4]. Metal ions were effectively recovered from a dilute solution using the ion exchange technique, but the high cost of resin limits its application [5,6]. The electrolytic process has advantages for metal recovery without further sequential treatment.

Recovering gold using electrolysis directly is difficult because of the low gold concentration in electroplating wastewater; however, membrane distillation (MD) can be used to treat gold-containing wastewater to obtain pure water and gold concentrate.

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Over the past years, membrane processes, such as reverse osmosis (RO), ultrafiltration (UF) and nanofiltration (NF), have wide applications in wastewater treatment [7]. According to Ng et al., combining NF and UF with an RO membrane achieved excellent removal efficiency (90-99%) for all target compounds [8]; however, its high operation cost is a major obstacle. In recent years, membrane processes, such as MD, have been developed [6-9]. MD is a process for volatile compounds evaporating through a non-wetted porous membrane [9,11,12]. The MD process has been studied since the 1960s [13,14]. Membrane manufacturers in the 1980s developed commercial membranes with desired properties. Improvements in module design and a better understanding of phenomena occurring in a layer adjacent to a membrane contributed to renewed interest in MD [15-18].

The MD processes have many important advantages, including complete rejection of dissolved, non-volatile species, processes with low operating pressure, reduced vapor space, and low operating temperature [19]. Utilizing alternative energy sources, such as solar, wave, or geothermal energy, is particularly attractive [20,21].

Among the different MD processes, the direct contact MD (DCMD) process is frequently used to prepare salt-concentrated solutions [22-30]. This is a thermally driven membrane separation process, in which two solutions at different temperatures are separated by a microporous hydrophobic membrane. The driving force of DCMD is the different vapor pressures on either side of the membrane, resulting from the temperature gradient in the boundary layers which are adjacent to the membrane surface. Thus the solution can be further concentrated even over the saturation concentration. The DCMD process has been applied for water desalination [9,31-33], wastewater reuse [25,34,35], and other concentration processes [36,37].

This work is to apply the DCMD process to concentrate gold in wastewater. Effects of feed temperature, permeate flux, feed flow rate, and conductivity on process performance are discussed. Additionally, the electrical recovery rate for gold recovery is determined.

**MATERIALS AND METHODS**

1. Materials

Raw industrial wastewater was obtained from Taiwan Electroplate Company. This company collects wastewater with a low gold concentration. Table 1 shows wastewater quality.

2. DCMD Process

Figure 1 is a schematic of the DCMD apparatus, which consists of two thermostatic cycles, with a feed cycle and permeate one. The membrane module is equipped with a flat-sheet membrane with an effective area of 70 cm². The membrane, hydrophobic polytetrafluoroethylene (PTFE) with 0.5 μm pore size, is placed between the two identical chambers.

<table>
<thead>
<tr>
<th>Table 1. The quality of wastewater</th>
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<tbody>
<tr>
<td><strong>Unit</strong></td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Au mg L⁻¹</td>
</tr>
<tr>
<td>TOC mg L⁻¹</td>
</tr>
<tr>
<td>COD mg L⁻¹</td>
</tr>
<tr>
<td>Conductivity μS cm⁻¹</td>
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Fig. 1. The DCMD process (1) Membrane Cell (2) Feed Reservoir (3) Pump (4) Heating System (5) Permeate Reservoir (6) Pump (7) Cooling System (8) Condenser (9) Distillation (10) Thermometer (11) Conductivity Monitor.
3. Electrolysis for Gold Recovery

After the DCMD process was complete, the electrolytic system (OMIT recovery system) was used for gold recovery. Figure 2 shows the experimental setup of the electrolytic reactor. The double electrode cell has an inside diameter of 4.3 cm, and height of 23 cm for the dimensionally stable anode (DSA) net as the anode, and diameter of 7.3 cm and height of 24 cm for the stainless steel cylinder as cathode. The DSA is titanium net coated with a thin layer of RuO/IrO₂. Experiments were performed with 1.4 L solution in a 2-L acrylic electrolytic reactor with a 527 cm² effective cathode surface area. The cylindrical reactor was operated at a constant current mode. The recycling pump was used to mix the solution. Recovery rate is evaluated.

RESULTS AND DISCUSSION

1. Effect of Feed Temperature

To investigate the water vapor permeability of the membrane, a set of experiments was carried out using pure water as feed. Feed temperature varied at 30-70 °C, while permeate temperature was maintained at 25 °C. Figure 3a shows the effect of feed temperature on permeate flux. Permeate flux increased significantly from 2.0 to 17.9 kg m⁻² h⁻¹ as temperature increased. This exponential rise in flux as feed temperature increased has been previously reported [38-40]. According to the Antoine equation, this flux enhancement following the rise in feed temperature was attributed to vapor pressure rise:

\[ P^0 = \exp \left( \frac{23,238 - 384}{T - 45} \right) \]  (1)

where, \( P^0 \) is water vapor pressure, and \( T \) is feed temperature. Additionally, the water vapor pressure is correlated with flux, as in Eq. 2:

\[ \text{Flux} = K \Delta P \]  (2)

where the \( K \) is a constant value, and \( \Delta P \) is the difference in water vapor pressure between the feed and permeate.

Indeed, flux increases significantly with feed temperature (Fig. 3a). This can be attributed to the fact that water vapor pressure, being the driving force for water flux, increases exponentially with temperature.

2. Effect of Feed Flow Rate

The effect of feed flow rate is assessed under feed temperature of the hot solution of 70 °C, and coolant temperature of 25 °C. Figure 3b shows changes in permeate flux for various feed flow rates. Permeate flux increased from 9.2 to 19.9 kg m⁻² h⁻¹ as feed flow rate increased from 8.5 to 48.8 L h⁻¹.

Increasing the feed flow rate through the flow channel increases velocity, which leads to an increase in the Reynolds number (Re):

\[ \text{Re} = \frac{\rho u L}{\mu} \]  (3)

where, \( \rho \) is density, \( u \) is velocity.
cross-sectional area of the duct or pipe, \( L \) is characteristic length, and \( \mu \) is dynamic viscosity.

An increased \( Re \) enhances mixing in the flow channel and reduces thickness of the temperature boundary layer in the feed side. Mass and energy transport can be enhanced by increasing the feed flow rate.

Permeate flux increased rapidly as the feed flow rate increased. A similar asymptotic trend of increasing permeate flux as feed flow rates increased was also reported by Garcia-Payo et al. [41] for the separation of aqueous alcohol solutions. The selectivity of water decreased as feed flow rate of the solution increased. This behavior is due to membrane wetting at high flow rates.

3. Effect of Feed Concentration

In this work, gold-containing wastewater was concentrated by DCMD. The concentration ratio (CR) was calculated using the Eq. 4:

\[
CR = \frac{C_i - C_o}{C_o}
\]

where \( C_o \) is initial concentration, \( C_i \) is the concentrated concentration. Different CRs affected wastewater conductivity at a feed flow rate of 34 L h\(^{-1}\), hot side temperature of 70 \( \degree \)C, and cold side temperature of 25 \( \degree \)C (Fig. 4a).

When the wastewater CR was increased, wastewater conductivity increased dramatically and then reached a plateau (about 100,000 \( \mu S \) cm\(^{-1}\)) at CR about 12. When MCMD is used to desalt brackish waters, the desalting ratio can reach 99.5% for all CRs.

The gold concentration increased as wastewater concentration increased. When the CR was 17, the gold concentration and TOC were 165 and 111,000 mg L\(^{-1}\), respectively (Fig. 4b). Distillates produced from the permeate side of the membrane was generally gold-free.

Since the wastewater was concentrated, wastewater conductivity increased dramatically. The relationship between conductivity and flux is discussed. Figure 5 shows the effect of the concentration of gold wastewater under a hot side temperature of 70 \( \degree \)C and a cold side temperature of 25 \( \degree \)C. Permeation flux decreased approximately 21% from 16.7 to 12.9 kg m\(^{-2}\) h\(^{-1}\) following an increase in wastewater concentration from 5,600 to 55,000 \( \mu S \) cm\(^{-1}\) in the feed side.

The concentration of gold in wastewater strongly affected the flux. Polarization layers formed on either side of the PTFE membrane reduce water permeation in MD [42,43]. This reduction increases in intensity as the concentration increases.

4. Electrolysis Recovery Rate

After the DCMD process, 90% of the concentrated gold solution was recovered by electrolysis. A different weight of gold powder was obtained in each experiment; therefore, electrolysis recovery rate (RR) was calculated by Eqs. 5 and 6.

\[
m_i = \frac{A I t}{n F}
\]

\[
RR = \frac{m_c}{m_i}
\]
gold recovery efficiency in the electrolytic process.

Indeed, DCMD improves concentration, the RR for gold can reach 20 times than was 252 mg A h⁻¹. For the wastewater with a high gold conductivity reached 100,000 ìS cm⁻¹ when using DCMD and the RR for gold was 10.6 mg A h⁻¹. However, gold wastewater concentration was 187 and No. 101-EC-17-D-02-11-1200.

The conductivity of the initial gold concentrations. The conductivity of the initial Fig. 6 provides green product sources.

Finally, the DCMD reactor combined with the electrolytic system can be used in industrial applications to recover Au. At 70 °C and a 48.8 L h⁻¹ feed flow rate, the 17 times Au concentration can be enriched. After applying the DCMD process, 90% of concentrated gold in solution was recovered by electrolysis. RR for gold reached 252 mg A⁻¹ h⁻¹ when wastewater was concentrated at 100,000 ìS cm⁻². Finally, the DCMD reactor combined with the electrolytic system can be used in industrial applications to provide green product sources.

CONCLUSIONS

A DCMD combined with an electrolytic process was applied successfully to recover Au. At 70 °C and a 48.8 L h⁻¹ feed flow rate, the 17 times Au concentration can be enriched. After applying the DCMD process, 90% of concentrated gold in solution was recovered by electrolysis. RR for gold reached 252 mg A⁻¹ h⁻¹ when wastewater was concentrated at 100,000 ìS cm⁻². Finally, the DCMD reactor combined with the electrolytic system can be used in industrial applications to provide green product sources.

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