Recovery of copper and nickel from ammoniacal medium through double supported liquid membranes containing N902 as carrier

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Abstract. In this paper, simultaneous recovery and separation of copper and nickel from ammoniacal medium through double supported liquid membranes containing N902 as carrier were investigated. The results show that copper was continuously transported across double membranes, but nickel only was transported through one of them. Therefore, more than 92.4% of nickel and 94.0% of copper in the mixed feed phase were separated into the two different strip phases within a transport time of 30 hours under the conditions: 6 g/L and 180 g/L H₂SO₄ solutions as two different strip phases, 100 mg/L each of two metals dissolved in 2.0 mol/L total ammoniacal solution as the feed phase, and 25 vol.%N902 as the carrier in two membranes.

1. Introduction
The scarcity of natural resources and environmental destruction are becoming main factors of restricting the social sustainable development. Copper and nickel as the momentous nonferrous metals, their high-grade sulphide ores have been consumed in the recent several decades. Meanwhile, large amounts of waste generated in the production and consumption of copper and nickel metal is destroying the ecological environment, such as solid waste pollution of electronic products and heavy metal pollution in the water. Therefore, it is very significant to develop the efficient approach for utilization of copper and nickel from the secondary resources (e.g. low grade ore, electronic waste, and electroplated sludge/wastewater). Currently, the operational procedure of ammonia leaching-extraction-separation is regarded as one of the most promising routes for recovery of the valuable metals containing copper and nickel. Ammonia leaching provides the characteristic advantage for selective dissolution copper and nickel due to the formation of metal ammine complexes [1, 2]. This method facilitates the initial purification between the valuable metals and undesired impurities (e.g. calcite and magnesia). However, there is still a challenge for high-efficiency separation of copper and nickel in ammoniacal medium due to their similar physico-chemical properties [3].

Almost all of commercial extractants (e.g. M5650, Lix984 and N902) have been used for solvent extraction of copper and nickel from ammoniacal solutions. It was found that two metal ions both easily transfer into organic phase from aqueous solution [4, 5]. Although two metal ions could be separated with different acid solutions in the stripping stage, it needs torun a number of stripping steps and result in the poor separation efficiency of copper and nickel [6]. Therefore, many researchers have been working on the preferable method for separation of copper and nickel. It is well known that...
the technique of supported liquid membrane (SLM) combines the functions of both solvent extraction and membrane separation, and it supports simultaneous extraction and stripping in a single step [7]. In present work, the separation strategy of double supported liquid membranes was established for the simultaneous recovery and separation of copper and nickel from ammoniacal solution.

2. Experimental

2.1 Chemicals and materials

The N902 extractant was purchased from Shanghai Laiyashi Co., Ltd., which was utilized as a membrane carrier. Kerosene was used as diluent of the extractant and all other chemicals (CuSO\(_4\)·5H\(_2\)O, NiSO\(_4\)·6H\(_2\)O, NH\(_3\)·H\(_2\)O, (NH\(_4\))\(_2\)SO\(_4\)) were analytical reagent grade. The initial aqueous solution included 100 mg/L each of Cu\(^{2+}\) and Ni\(^{2+}\), 1.0 mol/L each of NH\(_3\)·H\(_2\)O and (NH\(_4\))\(_2\)SO\(_4\). The polyvinylidene fluoride (PVDF) membrane was employed as the solid support for the liquid membrane [8].

2.2 Solvent extraction

Equal volumes (10.0 mL) of organic and aqueous solution were poured into a separating funnel. Then solvent extraction was conducted in a gas bath thermostatic oscillator (25 ± 1 °C), with the mechanical shaking of 200 rpm for 5 min. The concentrations of metals in the raffinate were determined by atomic absorption spectroscopy (AAS, Hitachi Z5000) after two phase disengagement. The extraction rate (%E) of each metal was calculated using Eq. (1):

\[
\%E = \frac{C_0 - C_e}{C_0} \times 100\% (1)
\]

Where \(C_0\) is the concentration of each metal in initial aqueous solution, \(C_e\) is the corresponding metal concentration in the raffinate after extraction.

2.3 Transport experiments

Transport experiments were operated in a permeation device consisting of three acrylic compartments in contact with double supported liquid membranes, and two membranes area both are 11.34 cm\(^2\). The illustration of transport model was shown in figure 1. Two PVDF membranes were impregnated with 25 vol.% N902 solution for 12 hours before they were placed in permeation device. The feed phase (150 mL) was composed of 100 mg/L each of Cu\(^{2+}\) and Ni\(^{2+}\), 1.0 mol/L each of NH\(_3\)·H\(_2\)O and (NH\(_4\))\(_2\)SO\(_4\). The strip phase 1 and strip phase 2 were composed of 6 g/L and 180 g/L H\(_2\)SO\(_4\) aqueous solution respectively, and the volumes of two strip phases also both were 150 mL. Three aqueous phases both were mechanically stirred with 800 rpm to facilitate metal ion diffusion between the membrane interfaces and the bulk of the solutions. 0.5 mL of each aqueous phases was taken out periodically and analysed by AAS during the course of the transport experiment.

![Figure 1. Separation model of double supported liquid membranes.](image)

The transport rate (%T) of each metal was determined according to Eq. (2):

\[
\%T = \frac{C_0 - C_t}{C_0} \times 100\% (2)
\]
Where \( C_0 \) is the concentration of each metal in initial feed phase, \( C_t \) is the corresponding metal concentration in the strip phase at a given time.

3. Results and discussion

3.1 Solvent extraction

The effect of N902 concentration varying from 0.2 to 1.0 vol.% on extraction of copper and nickel in different medium were illustrated in figure 2. It is clear from figure 2a that copper and nickel in ammoniacal medium both could be extracted by N902 extractant, nearly all of copper and 88.6% of nickel were transferred into organic phase when N902 concentration was increased to 1.0%. In addition, as can be seen from figure 2b, nickel in acid medium hardly was extracted by N902, but the extraction rate of copper increased evidently with the concentration of N902. The results indicate that extractant N902 supports selective extraction and separation of copper over nickel in acid medium.

![Figure 2](image-url)

**Figure 2.** Extraction of copper and nickel by N902, (a) Aqueous phase = 100 mg/L each of Cu\(^{2+}\) and Ni\(^{2+}\), 1.0 mol/L each of NH\(_3\) and NH\(_4^+\); (b) Aqueous phase = 100 mg/L each of Cu\(^{2+}\) and Ni\(^{2+}\), 6 g/L H\(_2\)SO\(_4\).

Thus, the new strategy of “extraction-stripping-extraction” could be established for recovery and separation of copper and nickel from ammoniacal solution. As expected, copper and nickel in ammoniacal medium firstly both are extracted into organic phase by N902, following the eqs. (3). Then two metals are returned back to aqueous phase with stripping extraction of H\(_2\)SO\(_4\) solution according to the eqs. (4). Finally, separation of copper and nickel would be accomplished using N902 once again in acid medium. Consequently, membrane transport and separation experiments would be performed in the sections below based on this strategy.

\[
[M(NH_3)_n]^{2+}_{(aq)} + 2[HL]_{(org)} \leftrightarrow [ML_2]_{(org)} + 2[NH_4^+]_{(aq)} + (n-2)[NH_3]_{(aq)} \quad (3)
\]

\[
[ML_2]_{(org)} + 2[H^+]_{(aq)} \leftrightarrow [M^{2+}]_{(aq)} + 2[HL]_{(org)} \quad (4)
\]

Where M denotes Cu and Ni, HL is extractant N902, and the subscripts \(aq\) and \(org\) represent the aqueous and organic phases.

3.2 Transport experiments

The concentration variation of copper and nickel in the three aqueous phases (Feed, Strip1 and Strip2) over transport time were illustrated in figure 3. Copper and nickel of feed phase firstly both were transported across SLM to strip phase 1, and their concentrations gradually decreased in feed phase. It is obvious from figure 3a that there is the higher transport efficiency of copper than nickel, nearly all of copper have left feed phase after transport of 12 hours. As can be seen from figure 3b, the copper...
concentration first increased and then decreased with the increasing transport time. This could be explained that copper in strip phase 1 could continue to be extracted and transported into strip phase 2 by membrane carrier of another SLM, due to $\text{H}_2\text{SO}_4$ concentration difference between two strip phases, following the Eqs. (5). Meanwhile it also results in the accumulation of copper in strip phase 2. Figure 3c show that few of nickel were transferred into strip phase 2, because nickel of acid solution could not be extracted and transported by N902 carrier. Thus, the concentration of nickel and copper gradually increased in the strip phase 1 and strip phase 2 respectively. Finally, More than 92.4% of nickel and 94.0% of copper from a mixed feed solution were separated into the two different compartments after 30 hours of transportation.

$$[\text{Cu}^{2+}]_{(\text{aq})} + 2[\text{HL}]_{(\text{me})} \leftrightarrow [\text{CuL}_2]_{(\text{me})} + 2[\text{H}^+]_{(\text{aq})} \quad (5)$$

Where the subscripts $\text{aq}$ and $\text{me}$ represent the aqueous and membrane phases. HL is extractant N902.

Figure 3. Concentration profiles of copper and nickel in feed/strip phase. (a) feed phase, (b) strip phase 1, (c) strip phase 2, (d) the transport rate.
### 3.3 Transport process
Transport process of metal ions through membrane was presented in figure 4. Firstly, copper and nickel were extracted by membrane carrier (HL) in the interface of feed phase and membrane, then carrier and its metal complexes (ML₂) diffused across the membrane by driving the concentration difference. Metal ions were stripped by H⁺ in the interface of membrane and strip phase basing on ionic-exchange. Finally, the metals were transported from feed phase to strip phase.

![Figure 4. Transport processes of ions through membrane, M represent Cu and Ni, HL is extractant N902.](image)

### 4. Conclusions
Simultaneous recovery and separation of copper and nickel from ammoniacal medium through double supported liquid membranes containing N902 as carrier was investigated. The results show more than 92.4% of nickel and 94.0% of copper from the mixed feed phase were separated into the two different strip phases with a transport time of 30 hours under the conditions: 6 g/L and 180 g/L H₂SO₄ solutions as two different strip phases, 100 mg/L each of two metal ions dissolved in 1.0 mol/L each of NH₃H₂O and (NH₄)₂SO₄ solution as the feed phase, and 25 vol.% N902 as the carrier in two membranes.

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