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Highly efficient and selective membrane separation of copper from nickel in ammoniacal solution using mixtures of M5640 and BESO as membrane carriers

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Separation of copper from nickel in ammoniacal/ammonium chloride solution using a flat-sheet supported liquid membrane impregnated with mixtures of Acorga **M5640** and bis(2-ethylhexyl)sulfoxide (**BESO**) was investigated. The crucial parameters influencing copper transport and separation abilities of copper and nickel, such as carrier concentration of **M5640** and **BESO** in the membrane phase, initial concentration of ions in the feed phase, H_2SO_4 concentration in the strip phase and membrane stability, were discussed. The results show that the mixtures of carriers (20 vol% **M5640** + 20 vol% **BESO**) in the membrane have a considerable antagonistic effect on membrane transport of nickel, but favor copper transport. Nearly all of the copper was transferred from the feed phase to the strip phase after 12 hours with a flux of 2.05×10^{-5} mol m^{-2} s^{-1} under the following conditions: 100 mg L^{-1} each of the copper and nickel dissolved in 1.0 mol L^{-1} each of ammonia and ammonium chloride solution as the feed phase, 60 g L^{-1} H_2SO_4 as the strip phase, and stirring speed of 800 rpm in two aqueous phases. Meanwhile less than 3.8% of the nickel was transported into the strip phase over the same time. Copper and nickel were efficiently separated with a calculated factor of 26.3. Furthermore, satisfactory membrane stability was obtained with at least ten cycle runs in this separation system.

1. Introduction

The ammonia leaching process has been considered as a promising approach for the recovery of copper and nickel from associated minerals and various secondary materials.[1] It supports selective extraction of copper and nickel into solutions as their ammine complexes, and simultaneously separates them from the majority of insoluble impurities in ammoniacal solutions, such as calcite and magnesia.[2] This developed scheme could enhance the leaching medium utilization and reduce the cost in the later purification process, especially suitable for processing low-grade resources. As a result, the obtained pregnant solutions require an efficient separation of copper and nickel, which remains as a challenging task due to the similar chemical properties of these two metals.[3] Many strategies-based solvent extraction containing varieties of commercial extractants have been reported for recovery and separation of copper and nickel from different acid leaching solutions, in hydrometallurgical process. The general conclusion acquired from these researches reveal that copper could be exclusively extracted and then separated with nickel in acid media by using the conventional hydroxyoximes extractants (such as Lix84,[4] Lix984,[5] Lix84i,[6] LK-C2).[7] However, almost all of this desired extractants exhibit poor selectivity of extraction in ammoniacal media due to that copper and nickel always were co-extracted into organic phase. In view of this, the procedure of selective stripping with different acid solutions from co-extraction phase was established as a feasible way for the separation of copper and nickel.[8] For instance, Sridhar *et al.*[9] investigated that copper and nickel were both extracted by LIX984N form ammoniacal/ammonium carbonate medium, after that nickel and copper in organic phase were severally stripped by 10 g L^{-1} and 180 g L^{-1} H_2SO_4 aqueous solutions in sequence. Unfortunately, this method is also limited by the case if only one of the metals was desired, and it will increase additional stripping stages to remove another metal.[10] Therefore, considerable efforts have been devoting to develop more efficient routes for the selectively recovery and separation of copper and nickel from ammoniacal solutions.

Currently, a strategy suggested that mixtures of two different extractants can evidently enhance the separation efficiency of copper and nickel based on the antagonistic effects of extraction. Hu *et al.* modified the extraction ability of extractants LIX84I by Aliquat 336, the mixtures of them made separation efficiency of

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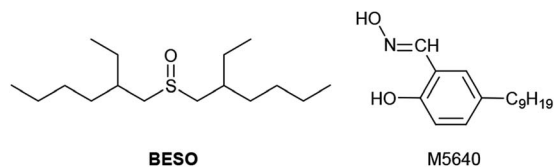
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Fig. 1   Representative structures of BESO and M5640.

copper and nickel improved obviously.[10] However, compared to the conventional solvent extraction method, the techniques of supported liquid membrane (SLM) also have been extensively studied for recovery and separation of low-concentration metals from aqueous solution because of its superiority combined solvent extraction with membrane separation.[11] It offers several advantages including less organic solvent and energy consumption, higher selective separation, and simultaneous extraction and stripping with one step procedure.[12] In view of this, Duan *et al.* studied transport and separation of copper from nickel in ammoniacal/ammonium chloride solution using supported liquid membrane containing antagonistic mixtures of **M5640** and TRPO as carrier.[13] The results indicated that the transport rate of nickel decreased from 51% to 6.1%, when the carrier concentration of TRPO rose from 0 vol% to 10 vol% at constant 20 vol% **M5640**, meanwhile copper transport rate only declined slowly during this process. This could lead to the increase of separation factors of copper and nickel. But the transport rate of copper also declined rapidly beyond 10 vol% concentration of TRPO which would result in the poor performance of membrane separation process. This may be owing to the excessive strength of hydrogen-bond interaction between **M5640** and TRPO also inhibited the extraction and transport of copper by **M5640** carrier.

Therefore, in order to obtain the higher separation efficiency of copper and nickel as well as transport rate of copper, bis(2-ethylhexyl)sulfoxide (**BESO**, Fig. 1) was selected for new modifier of **M5640** (Fig. 1) in present work.[14] Compared with the P=O group of TRPO, the oxygen atom in the S=O group of **BESO** has a lower electronic density due to the fact that the sulfur electronegativity (2.58) is higher than phosphorus (2.19), resulting in a weaker strength of hydrogen bond between O of S=O group and H of hydroxyl group that belong to **M5640**.[15] The weaker hydrogen-bond interaction between **M5640** and **BESO** could make it easier for **M5640** carrier to extract and transport copper, because the hydrogen bond need to be broken before extraction reaction. Thus, selective membrane separation of copper from nickel in ammoniacal solution using mixtures of **M5640** and **BESO** as membrane carrier were studied. The fundamental parameters influencing copper transport and separation abilities of copper and nickel were discussed, including carrier concentration of **M5640** and **BESO** in the membrane phase, initial concentration of ions in the feed phase, H_2SO_4 concentration in the strip phase and the membrane stability.

2. Experimental

2.1. Chemicals and materials

The commercial extractant **M5640** was supplied by Cognis Co., Ltd. **BESO** was prepared in our laboratory according to the

procedure described earlier.[15] Kerosene was used as diluent and all other reagents ($CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, $NH_3 \cdot H_2O$ and NH_4Cl) were of analytical grade. The hydrophobic polyvinylidene fluoride[13] (PVDF, Millipore Durapore GVHP 4700) was employed as the solid support for a flat-sheet liquid membrane. The initial aqueous solution was composed of 100 mg L^{-1} each of copper and nickel, and 1.0 mol L^{-1} each of $NH_3 \cdot H_2O$ and NH_4Cl.

2.2. Solvent extraction

Solvent extraction was conducted by shaking separating funnel that with equal volumes (10.0 mL) of organic and aqueous phases at the vapor-bathing constant temperature vibrator (25 ± 1 °C, 200 rpm). A total shaking time of 10 minutes was performed to reach the extraction equilibrium. After that, the raffinate phase was analyzed by atomic absorption spectroscopy (AAS, Hitachi Z2000 spectrophotometer).

The extraction rate (% E) was estimated as the percentage of metal concentration in the organic phase to its initial concentration in the aqueous phase. The distribution ratios (D) were calculated using the ratio of metal concentration in the organic phase to aqueous phase. The separation factor of copper and nickel ($\beta_{Cu/Ni}$) was determined according to eqn (1):

$$\beta_{Cu/Ni} = \frac{D_{Cu}}{D_{Ni}} \tag{1}$$

2.3. Transport and separation

A separation device consisted of two acrylic compartments contacted with the flat-sheet supported liquid membrane (FSSLM, effective membrane area: 11.34 cm^2), was shown in Fig. 2.

The FSSLM was prepared by impregnating PVDF film with the mixtures of **M5640** and **BESO** in kerosene solution for 24 hours, before being placed in the membrane cell. The feed cell and strip cell were poured into equal volumes (150 mL) of initial metals solution and H_2SO_4 aqueous solution respectively. Two aqueous phases were stirred at 800 rpm by using the mechanical agitators in order to avoid the ionic concentration polarization of membrane interfaces, and transport experiments were operated in a thermostatic water bath at 25 °C. The concentration of metals in feed phase and strip phase were determined periodically by AAS.

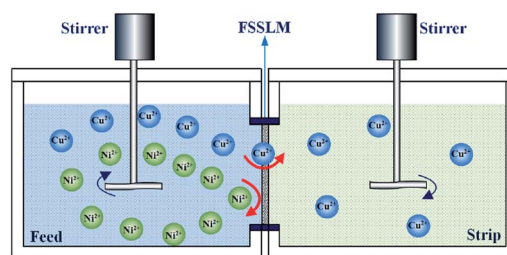The transport rate of copper (% T) was calculated according to eqn (2).

Fig. 2   Schematic illustration of FSSLM cell.

$$T(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \qquad (2)$$

The kinetic model of copper transport through membrane was given by eqn (3):[16]

$$\ln \frac{C_t}{C_0} = -\frac{A}{V}Pt \qquad (3)$$

The permeation flux (J, mol m^{-2} s^{-1}) was used for evaluating copper transport efficiency, which could be calculated by eqn (4):

$$J = P \times C_0 \qquad (4)$$

where P is permeation coefficient (P, m s^{-1}), A and V are the membrane effective area (m^2) and the volume of the feed phase (m^3) respectively. C_t and C_0 (mol L^{-1}) represent the respective concentrations of metals in the feed phase at a given time and the beginning time, and t is transport time (h).

The separation factor ($\alpha_{Cu/Ni}$) of copper and nickel was expressed as eqn (5).[17]

$$\alpha_{Cu/Ni} = \frac{(C_{Cu}/C_{Ni})_{strip,t}}{(C_{Cu}/C_{Ni})_{feed,0}} \qquad (5)$$

where $(C_{Cu}/C_{Ni})_{feed,0}$ is the ratio of the initial concentration of copper to nickel in the feed phase, and $(C_{Cu}/C_{Ni})_{strip,t}$ is the ratio of the concentration of copper to nickel in the strip phase at a given time.

3. Results and discussion

3.1. Solvent extraction studies

The extraction of copper and nickel from ammoniacal solution was investigated by varying concentrations of **M5640** ranging from 0.1 vol% to 1.0 vol%. As shown in Fig. 3(a), copper and nickel were both extracted by sole extractant **M5640**, nearly all of copper and 91.3% of nickel in initial aqueous phase were transferred to the organic phase as the **M5640** concentration increased to 1.0 vol%. The results show that it is difficult to achieve selective extraction and separation of two metals from ammoniacal solution only by using extractant **M5640**. In view of this, **BESO** as the desired modifier was used for adjusting the extraction abilities of **M5640**. Before that, the extraction behavior of sole **BESO** also was examined. As can be seen from Fig. 3(a), sole **BESO** as extractant exerted a poor extraction performance compared with **M5640**.

Then, the extraction experiments were performed by varying the **BESO** concentrations from 0 to 1.0 vol% mixed with a fixed concentration of 1.0 vol% **M5640**. It can be seen from Fig. 3(b), the nickel extraction rate decreased sharply from 91.3% to 4.3% as the **BESO** concentration increased from 0 to 1.0 vol%. Meanwhile the extraction efficiency of copper received the neglectable impact, and its extraction rate was consistently over 99.4% with the change of **BESO** concentrations. A maximum of separation factor of copper and nickel was obtained at a mixed concentration of 0.6 vol% of **BESO** with 1.0 vol% of **M5640**.
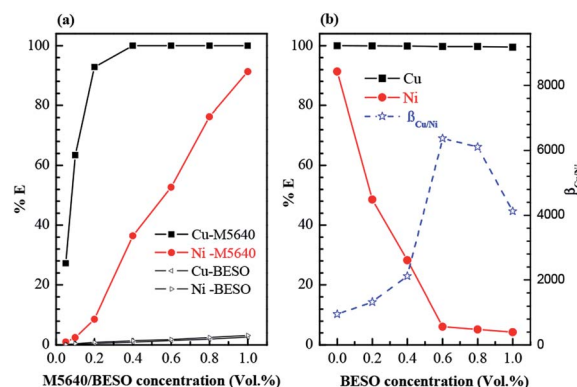

Fig. 3 Extraction of copper and nickel using **M5640** and **BESO**, (a) the sole **M5640** or **BESO** as extractant, (b) the mixtures of **BESO** and 1.0 vol% **M5640** as extractant. Conditions: aqueous phase = 100 mg L^{-1} each of Cu^{2+} and Ni^{2+}, 1.0 mol L^{-1} each of NH$_3$ and NH$_4^+$.

These results suggest that the strategy developed with the mixtures of extractant **M5640** and modifier **BESO** dissolved by kerosene as organic phase could be used for selective extraction of copper and separation with nickel from ammoniacal solution.

The chelate complex of **M5640** and metals (Cu, Ni) is represented on Fig. 4. Before chelation reaction happen, **M5640** and **BESO** tend to co-associate through hydrogen bonding involving the –OH and S=O groups when they were mixed together. Generally, the mixtures of **M5640** and **BESO** may hinder the formation of chelate metal complexes, and reduce kinetics of the metal chelate reaction. That is, this would result in antagonistic effects on extraction of both copper and nickel. However in fact, the antagonistic effect had a negligible impact on copper extraction compared with nickel according to the above experimental result. The distinction of antagonistic effect on two metals provided the theoretical support for efficient separation of copper and nickel from ammoniacal solution.

3.2. Membrane separation studies

The transport of copper and nickel through FSSLM using **M5640**, **BESO** and their mixtures as membrane carriers respectively were studied. Fig. 5(a) shows the concentration of copper and nickel in the feed phase gradually decreased with transport time. Nearly all of copper and 49.4% of nickel were transported from the feed phase to the strip phase after 12 hours by using 20 vol% **M5640** as membrane carrier. Besides, the slight decline of metals concentration in feed phase indicated that **BESO** (20 vol%) could be regarded as the noneffective carrier using for the transport of copper and nickel compared with **M5640**. However, as can be seen Fig. 5(b), the nickel
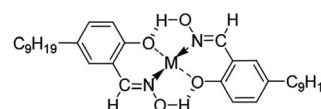

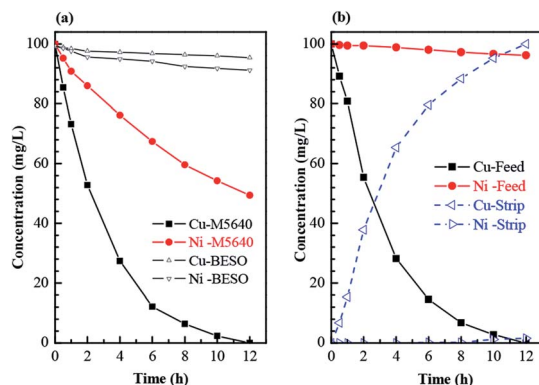**Fig. 4** The chelate complex of **M5640** and M^{2+} (M = Cu, Ni).

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Fig. 5 Concentration profiles of copper and nickel in feed/strip phase. (a) The sole M5640 or BESO as membrane carrier, (b) the mixtures of M5640 and BESO as membrane carrier. Conditions: feed phase = 100 mg L^{-1} each of Cu^{2+} and Ni^{2+}, 1.0 mol L^{-1} each of NH$_3$ and NH$_4^+$; strip phase = 60 g L^{-1} H$_2$SO$_4$; stirring speed = 800 rpm.
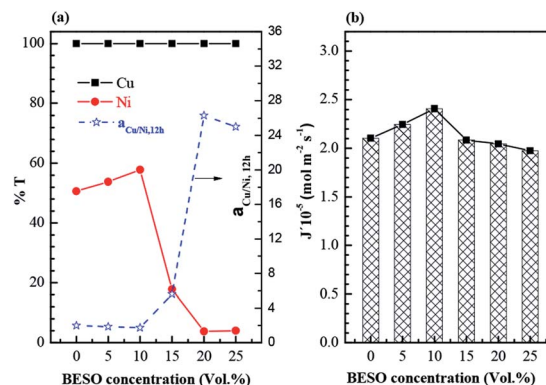

Fig. 6 Effect of the BESO content in the membrane phase on the separation of copper and nickel (a), as well as the transport of copper (b). Conditions: feed phase = 100 mg L^{-1} each of Cu^{2+} and Ni^{2+}, 1.0 mol L^{-1} each of NH$_3$ and NH$_4^+$; strip phase = 60 g L^{-1} H$_2$SO$_4$; stirring speed = 800 rpm.

transport rate decreased significantly from 49.4% to 3.8% over a period of 12 hours, after employing the mixtures of 20 vol% M5640 and 20 vol% BESO as membrane carrier.

Meanwhile, high-efficiency transport of copper had hardly changed in this system. The results of membrane separation of copper and nickel agree well with that obtained by above solvent extraction. Subsequently, the specific studies were conducted to evaluate the separation abilities of copper and nickel by using the flat-sheet supported liquid membrane containing the mixtures of M5640 and BESO as carrier.

3.2.1. Effect of the concentration ratio of M5640 and BESO in membrane phase.
Too high concentration of carrier in membrane could be result in the slow transport efficiency as the higher viscosity of liquid membrane.[18] Some studies suggested that the 20–30 vol% concentration of membrane carrier is generally an ideal control condition.[19] In this case, the concentration of M5640 was firstly determined as typical 20 vol%. The effects of modifier BESO concentration varying from 0 to 25 vol% mixed with a fixed 20 vol% M5640 as membrane carrier on metals transport were investigated. The results were illustrated in Fig. 6. The nickel transport rate slightly increased as the BESO concentration was increased from 0 to 10 vol%. This could be due to the weak chelating character of M5640 modified with BESO against nickel, resulting in the easier nickel stripping ability in the strip/membrane phase interface.[19] Then the transport rate of nickel was followed by a sharp decrease when the BESO concentration more than 10 vol%. Coupled with negligible influence on copper transport rate regardless of the absence/presence of BESO, it is clear that the separation factors of copper and nickel for a period of 12 hours ($\alpha_{Cu/Ni,12\ h}$) increased significantly from 1.73 to 26.3 as the BESO concentration increases from 10 to 20 vol%. This behavior should be explained by the fact that the weaker chelating character of M5640 modified with more BESO against nickel, leading to the more difficult nickel extracting ability in the feed/membrane phase interface. Furthermore, as can be seen from Fig. 6(b), these two effects caused by different concentrations of

BESO also had led to slight increase, and then decrease in the copper permeation flux. As a result, an excellent separation factor (26.3) of copper and nickel was obtained with a carrier of (20 vol% BESO + 20 vol% M5640) in the membrane phase, where the transport rates of copper and nickel respectively were 99.99% and 3.8%. To evaluate the influencing parameters on the membrane transport of copper and separation efficiency of copper over nickel, further studies were conducted by using the mixtures of 20 vol% and 20 vol% BESO as membrane carrier.

3.2.2. Effect of the H$_2$SO$_4$ concentration in strip phase.
The original stability of copper complex with M5640 was destroyed by the additional modifier BESO. An appropriate concentration of H$_2$SO$_4$ in strip phase needs to be determined in order to attain optimal efficiency of copper decomplexation. Therefore, the effect of H$_2$SO$_4$ concentration in strip phase on copper transport was studied in the range of 20–100 g L^{-1}, and the results are presented in Fig. 7. As can be seen from Fig. 7(a), the permeation flux of copper increased from 1.71 × 10^{-5} mol m^{-2} s^{-1} to 2.05 × 10^{-5} mol m^{-2} s^{-1} as the H$_2$SO$_4$ concentration was increased from 20 g L^{-1} to 60 g L^{-1}, and then remains almost constant value beyond that. It is understandable that higher concentration of H$_2$SO$_4$ in strip phase could accelerate reaction of copper decomplexation at the membrane/strip phase interface, and promoting copper diffusion across the membrane. However, some studies[20] pointed out that the increase in H$_2$SO$_4$ concentration could reduce the interfacial tension between the membrane liquid phase and the strip phase, resulting in the faster loss of membrane carrier. Obviously, the H$_2$SO$_4$ concentration of 60 g L^{-1} was enough in this work.

Fig. 7(b) shows that the copper transport rate for a period of 12 hours is consistently high (>99.6%) with the increasing of H$_2$SO$_4$ concentration. Whereas the transport rate of nickel grows slightly, in despite of the fact that the majority of nickel in feed phase cannot be carried by membrane carrier. This also caused a decline of separation factor of copper and nickel. As a result, H$_2$SO$_4$ concentration in strip phase was finally
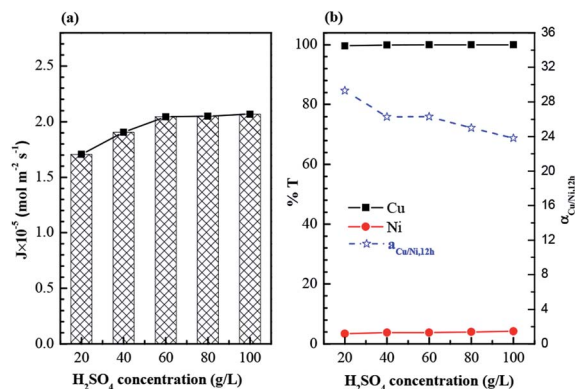
Fig. 7 Effect of the H_2SO_4 concentration on the transport of copper (a), and the separation of copper from nickel (b). Conditions: feed phase = 100 mg L^{-1} each of Cu^{2+} and Ni^{2+}, 1.0 mol L^{-1} each of NH_3 and NH_4^+; extractant carrier = 20 vol% **M5640** + 20 vol% **BESO** in kerosene; stirring speed = 800 rpm.
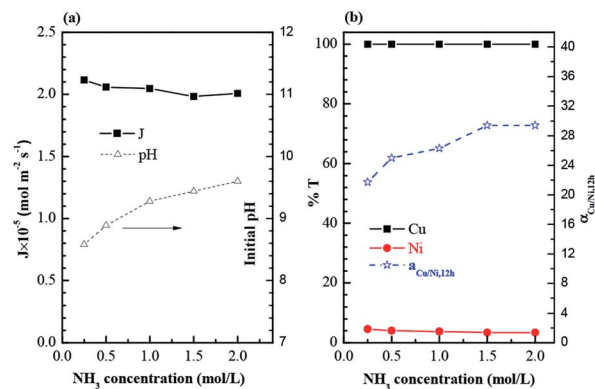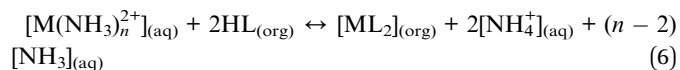

Fig. 8 Effect of the ammonia concentration on the transport of copper (a), and the separation of copper from nickel (b). Conditions: feed phase = 100 mg L^{-1} each of Cu^{2+} and Ni^{2+}, 1.0 mol L^{-1} of NH_4^+; extractant carrier = 20 vol% **M5640** + 20 vol% **BESO** in kerosene; strip phase = 60 g L^{-1} H_2SO_4; stirring speed = 800 rpm.

confirmed as 60 g L^{-1} by taking into consideration both the copper permeation flux and the separation efficiency of copper and nickel.

3.2.3. Effect of ammonia concentration in feed phase. Ions of copper and nickel could form various metal ammine complexes ($Cu(NH_3)_n^{2+}$ and $Ni(NH_3)_n^{2+}$, $n = 1–6$) in ammoniacal solutions. The different complexes are relevant to pH of solution and ammonia concentration. In present ammonia system[21] (pH > 8.5), the predominant ammine species are $Cu(NH_3)_4^{2+}$, $Ni(NH_3)_4^{2+}$ and $Ni(NH_3)_6^{2+}$. In order to explore the effect of ammonia concentration on metals transport through membrane, ammonia concentrations variation studies in the range 0.25–2.0 mol L^{-1} were carried out at a fixed NH_4Cl concentration of 1.0 mol L^{-1}. It is observed from Fig. 8(a) that the initial pH of feed phase increased, and copper permeation flux rather slowly decreased with the increase of ammonia content. Kyuchoukov[22] et al. have explained that excess ammonia in the aqueous solution disfavor the extraction of copper and nickel owing to the fact that extraction reaction need to run through ion exchange and deamination process according to eqn (6) (where M represents Cu or Ni).

$$[M(NH_3)_n^{2+}]_{(aq)} + 2HL_{(org)} \leftrightarrow [ML_2]_{(org)} + 2[NH_4^+]_{(aq)} + (n-2)[NH_3]_{(aq)} \quad (6)$$

Besides, ammonia also could be co-extracted with copper and nickel by using hydroxyoxime extractants (including **M5640** used in this study) in the alkaline region,[23] and the higher ammonia concentration may result in the reduction of copper carrying capacity of membrane carrier in membrane phase. This is perhaps the reason of why the transport rate of nickel declined slightly as the increasing of ammonia concentration, then driving up the separation factor of copper and nickel (Fig. 8(b)). In fact, the ammonia content of actual solution derived from different industries is always inequable. In the present work, an ammonia concentration of 1.0 mol L^{-1} was maintained throughout the experimentation to keep the comparison ability of the results.

3.2.4. Effect of initial concentration of metal ions in the feed phase. There always encounter complicated solution containing metal ions of various concentrations in actual separation system. It is necessary to examine the effect of metals initial concentrations on their transport and separation in FSSLM model. Therefore, metal concentrations variation studies in the range 50–300 mg L^{-1} were performed, and Table 1 list the corresponding experiment results using different initial feed phases. It is obvious that copper permeation flux improved with the increase of the initial metal ions. In general, there existed the maximum of permeation flux that tend to be independent of initial metal concentration.[19] Obviously, the flux of 3.28 × 10^{-5} mol m^{-2} s^{-1} (initial metal concentration = 300 mg L^{-1}) may well have not touched this limitation. In this case, the initial copper concentrations (<300 mg L^{-1}) become rate determining of copper transport efficiency. In addition, it is observed that the copper permeation flux and transport rate had hardly changed since the initial concentration of Cu/Ni changed from 100/100 to 100/300 mg L^{-1}, but nickel transport rate increased as the nickel concentration was increased from 100 to 300 mg L^{-1}. In the meantime, separation factor of copper and nickel diminish slightly from 26.3 to 18.1. This means that elevated content of nickel in the feed phase has little influence on copper transport, in turn, favors the transport of nickel. Furthermore, it will be noted that there are both the superior separation factor of copper and nickel between the initial Cu/Ni concentration of 100/300 mg L^{-1} and 300/100 mg L^{-1} in the feed phase. The results indicate that the separation strategy developed in this work could accomplish the high-efficient separation of copper over nickel from various initial solutions composed of different mixture ratios of Cu/Ni. Of course, the preferable separation efficiency of copper and nickel could be obtained, if copper has a higher concentration than nickel in initial solution.

Table 1 Effect of the initial metal ions concentration on copper flux and separation factor of Cu(II)/Ni(II)[a]

$[Cu]_{feed}/[Ni]_{feed}$ (mg L^{-1})	Initial flux of copper J_{Cu} (mol m^{-2} s^{-1})	$T_{Cu,12\ h}\%$	$T_{Ni,12\ h}\%$	Separation factor, $\alpha_{Cu/Ni,12\ h}$
50/50	1.51×10^{-5}	99.99	7.6	13.2
100/100	2.05×10^{-5}	99.99	3.8	26.3
300/300	3.28×10^{-5}	93.4	4.3	21.9
100/300	2.02×10^{-5}	99.8	5.5	18.1
300/100	3.37×10^{-5}	93.8	3.4	27.6

[a] Conditions: feed phase = 1.0 mol L^{-1} each of NH$_3$ and NH$_4^+$; extractant carrier = 20 vol% **M5640** + 20 vol% **BESO** in kerosene; strip phase = 60 g L^{-1} H$_2$SO$_4$; stirring speed = 800 rpm.

3.2.5. Membrane stability. Membrane lifetime was evaluated by a series of continuous transport experiments associated with a fixed FSSLM, where the feed phase and strip phase were replaced with respective initial solutions after every 12 h. The transport results of 120 h (10 cycles) were displayed at Fig. 9. It is clear that copper transport rate appeared a slowly downward trend over 10 continuous cycles, but that still remain 97.6% on the tenth operation. Obviously, the decline of transport rate with recycle numbers could attribute to the gradual loss of effective carrier in membrane.[24]

However, it is unexpected that transport of nickel instead increased beyond the sixth transport, and then resulting in the decrease of separation factor of copper and nickel. The reason caused the abnormal phenomenon may be that the loss of **BESO** in membrane is more easy than **M5640**. Because it was observed that the visible viscosity of **BESO** is far below **M5640** during the experiment. In this case, it leads to the decline of the ratio of **BESO** to **M5640** in membrane, then result in the rise performance-based extraction nickel in feed/membrane phase interface. On the whole, the present FSSLM system nearly kept stable over six continuous cycles for high-efficiency separation of copper and nickel. Even at the tenth run, the transport rate of nickel was still lower than 8.6%, and together with a separation factor of 11.3. It's worth mentioning that the eighth separation efficiency of copper and nickel (separation factor = 16.4) in this work also exceeded the first operation (separation factor = 16.0)
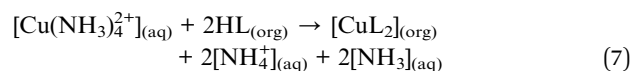

Fig. 9 Stability evaluation of the FSSLM system. Conditions: initial feed phase = 100 mg L^{-1} each of Cu^{2+} and Ni^{2+}, 1.0 mol L^{-1} each of NH$_3$ and NH$_4^+$; extractant carrier = 20 vol% **M5640** + 20 vol% **BESO** in kerosene; initial strip phase = 60 g L^{-1} H$_2$SO$_4$; stirring speed = 800 rpm.

employing **M5640**/TRPO as carrier.[13] These results indicate that the present FSSLM displayed a satisfactory successive performance of copper transport and separation with nickel.

3.2.6. Result comparison. Comparison of the results between this work and literature is presented in Table 2. As can be seen from the table, among these methods, the present work has the highest extraction of copper as well as separation efficiency of copper and nickel. In particular, the higher transport rate of copper and low transport rate of nickel was obtained with **BESO** than TRPO, and separation factor of copper and nickel has gone up by 64.0%. What is more, there is an essential difference between modifier of **BESO** and TRPO. TRPO can inhibit both the transport of copper and nickel, and this inhibition only has a lesser impact on copper transport compared with nickel. However **BESO** has almost no effect on high-efficient transport of copper, and it inhibits nickel transport with high selectivity. Therefore, the FSSLM system developed with **M5640**/**BESO** as the carrier could be a more useful tool for copper transport and separation with nickel.

3.2.7. Separation and transport kinetics. Fig. 10 illustrates the copper transport and separation with nickel from ammoniacal solution through the FSSLM. The reactivity of basic extractant **M5640** was adjusted by modifier **BESO**, and their mixture as membrane carrier become difficult to extraction and transport of nickel. Thus, the process of copper transport through FSSLM could be decomposed into following elementary steps.

(i) Copper and nickel ammine complexes in the feed phase diffused to the aqueous boundary layer (d_a) in the feed/membrane phase side.

(ii) A majority of copper were preferentially extracted by membrane carrier (**M5640**) in the feed/membrane phase interface, following the eqn (7).

$$[Cu(NH_3)_4^{2+}]_{(aq)} + 2HL_{(org)} \rightarrow [CuL_2]_{(org)} + 2[NH_4^+]_{(aq)} + 2[NH_3]_{(aq)} \tag{7}$$

(iii) The copper extracted complexes transfer through the membrane toward the membrane/strip phase interface.

(iv) In the membrane/strip phase interface, copper was stripped by H$_2$SO$_4$ solution, according to eqn (8).
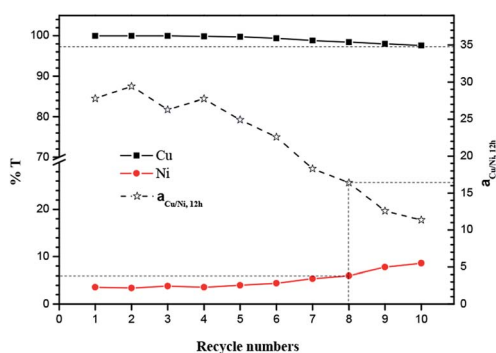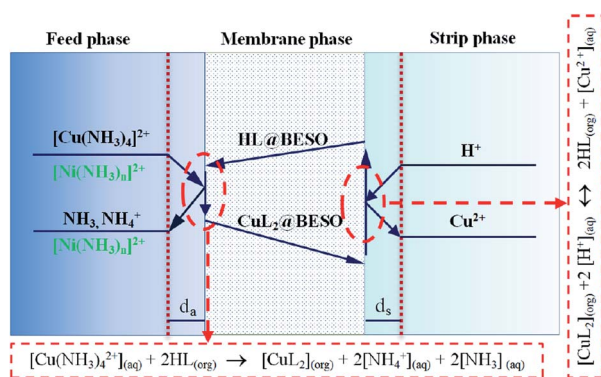
$$[CuL_2]_{(org)} + 2[H^+]_{(aq)} \leftrightarrow 2HL_{(org)} + [Cu^{2+}]_{(aq)} \tag{8}$$

Table 2 Comparison of different methods for separation copper and nickel

Methods	Extractants	Cu extraction rate (% E_{Cu})	Ni extraction rate (% E_{Ni})	Separation ratio (E_{Cu}/E_{Ni})	References
Solvent extraction	LIX84I and A336	97.66	11.39	8.57	10
	M5640 and TRPO	99.96	6.6	15.15	15
FSSLM separation	Only **M5640**	99.99	51.0	1.96	13
	M5640 and TRPO	98.40	6.1	16.04	13
	M5640 and **BESO**	99.99	3.80	26.30	Present work

Fig. 10 Schematic of copper transport through FSSLM. (HL = **M5640**).

(v) Cu^{2+} diffused from the membrane/strip phase interface to the bulk of the strip phase.

(vi) Regenerated carrier HL transfer backed to the feed/membrane phase interface.

Among these steps, if the interfacial reactions of complexation extraction at the feed/membrane phase interface (ii) and the decomplexation at the membrane/strip phase interface (iv) occur instantaneously relative to other diffusion processes,[25] then copper transport efficiency is mainly controlled by the rate of diffusion of the extracted CuL_2 complexes through the membrane under the optimal conditions: mixtures of 20 vol% **M5640** and 20 vol% **BESO** in kerosene as carrier, 100 mg L^{-1} each of the copper and nickel dissolved in 1.0 mol L^{-1} each of ammonia and ammonium chloride solution as the feed phase, 60 g L^{-1} H$_2$SO$_4$ as the strip phase, and stirring speed of 800 rpm
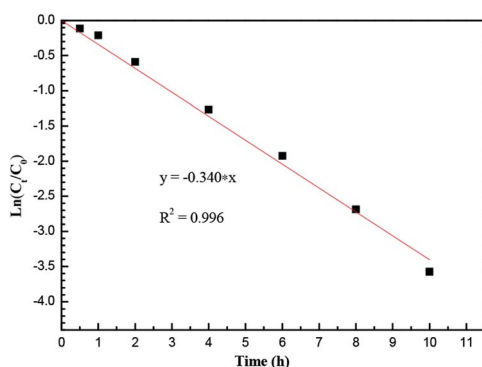

Fig. 11 The kinetic plot of copper transport through FSSLM.

in two aqueous phases. The transport of copper through the FSSLM follows first-order kinetics. The plot of $\ln(C_t/C_0)$ *versus* operation time for copper transport is presented in Fig. 11 and illustrates that $\ln(C_t/C_0)$ is a linear function of time with a slope of -0.340. Thus, the permeability coefficient (P) was calculated to be 1.26×10^{-5} m s^{-1}.

4. Conclusions

High-efficient and selective membrane separation of copper from nickel in ammoniacal solution using mixtures of Acorga **M5640** and bis(2-ethylhexyl)sulfoxide (**BESO**) as membrane carrier was studied. The preliminary solvent extraction studies illustrated that the mixtures of extractant **M5640** and modifier **BESO** in the organic phase exhibited an obvious inhibiting effect on the nickel extraction. In order to determine the optimum membrane separation conditions of copper and nickel, the crucial parameters influencing copper transport and separation abilities of copper and nickel, such as carrier concentration of **M5640** and **BESO** in the membrane phase, initial concentration of ions in the feed phase, H$_2$SO$_4$ concentration in the strip phase and the membrane stability were discussed. The results show that the mixtures of carrier (20 vol% **M5640** + 20 vol% **BESO**) in membrane favor copper transport, but exert considerable antagonistic effect on membrane transport of nickel. Nearly all of copper were transported from the feed phase to the strip phase after 12 hours with a flux of 2.05×10^{-5} mol m^{-2} s^{-1} under the following conditions: 100 mg L^{-1} each of the copper and nickel dissolved in 1.0 mol L^{-1} each of ammonia and ammonium chloride solution as the feed phase, 60 g L^{-1} H$_2$SO$_4$ as the strip phase, and stirring speed of 800 rpm in two aqueous phases. Whereas only less than 3.8% of nickel was transported into strip phase in the meantime. Copper and nickel were efficiently separated with a calculated factor of 26.3. Furthermore, satisfactory membrane stability was obtained with at least ten cycle runs in this separation system. The results achieved in this study indicate that the FSSLM system developed with **M5640**/**BESO** as the carrier could be a useful tool for facilitating transport and selective separation of copper from nickel in ammoniacal solutions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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