

Recovery of Copper(II) and Nickel(II) from Plating Wastewater by Solvent Extraction^{*}

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Abstract The solvent extraction technology was applied to recover Cu^{2+} and Ni^{2+} from plating wastewater. Lix984N was chosen as the extractant due to its good extraction performance. The influence parameters were examined. The results show that the separation of Cu^{2+} and Ni^{2+} from sulphate medium can be realized by adjusting pH value with the help of Lix984N. For extracting Cu^{2+} and Ni^{2+} , the optimal pH values are 4 and 10.5, and the maximal extraction percentages are 92.9% and 93.0%, respectively. With recovered Cu^{2+} and Ni^{2+} stripped in 170 $\text{g}\cdot\text{L}^{-1}$ and 200 $\text{g}\cdot\text{L}^{-1}$ H_2SO_4 medium, the stripping percentages of Cu^{2+} and Ni^{2+} are 92.9% and 93.0%, respectively. This method is simple and can be used to recover Cu^{2+} and Ni^{2+} from plating wastewater. And a flow sheet for separation of Cu^{2+} and Ni^{2+} is presented.

Keywords recovery, copper, nickel, solvent extraction, plating wastewater

1 INTRODUCTION

Copper and nickel are important strategic resources [1, 2]. They are mainly produced from some raw materials, such as oxidic, silicate and sulphide ore [3]. On the other hand, the wastewater from the process of plating Cu and Ni alloy is a suitable resource because it contains abundant Cu^{2+} and Ni^{2+} . However, it is difficult to use the classical precipitation method to separate these metals effectively [4]. Solvent extraction is considered as a feasible method to recover and separate copper and nickel from plating wastewater [5–7].

Many commercial extractants [8–15] have been used for recovering copper by hydrometallurgy method, such as Lix622, Lix63, Lix84, Lix64, Lix860, Kelex100, Kelex120, and P5100 [16–20], which are vitriolic. However, the literature about using these extractants to extract nickel is rare.

Lix984 and Lix984N are good vitriolic extractants. The active components of Lix984 are 2-hydroxy-5-dodecylsalicylaldoxime and 2-hydroxy-5-nonylacetonphenoneoxime. Lix984N is a mixture of 2-hydroxy-5-nonylacetonphen oxime and 5-nonylsalicylaldoxime. Lix984 and Lix984N are both applied to extract copper successfully, and Lix984N is better for the high acidic solution. Thus Lix984N is chosen as the extractant for this experiment. The extractant has high viscosity, so kerosene solution is added to improve its fluidity [21].

In this study, Lix984N dissolved by kerosene is used to separate copper and nickel from a simulated solution. The major technological parameters are examined, such as initial pH of aqueous phase, extraction efficiency, extractant concentration, phase ratio

and extraction time. The experiments are carried out at room temperature (25–30 °C). Based on the investigation, a flow sheet is proposed.

2 EXPERIMENTAL

Lix984N was supplied by Henkel and used as extractant. Copper sulphate and nickel sulphate (analytical reagent grade) were used to prepare Ni^{2+} and Cu^{2+} solutions. The experimental procedure is as follows. Lix984N is diluted with 260[#] kerosene to desired concentration. The prepared Ni^{2+} and Cu^{2+} solutions are mixed with the diluted Lix984N-kerosene mixture, and the pH value of the mixed solution is adjusted with 20% (by volume) sulphuric acid solution or 50% (by volume) ammonia water. And the sample is taken under the experimental conditions.

The pH value of the mixed solution was measured by pH-meter. The concentration of metal ions in the aqueous phase before and after the extraction was measured by ICP, and the concentration of metal ions in the organic phase was obtained from the concentration difference of the aqueous phase before and after the extraction.

3 RESULTS AND DISCUSSION

3.1 Extraction performance of Lix984N for Cu^{2+} and Ni^{2+}

3.1.1 Influence of initial pH of aqueous phase on extraction efficiency

Figures 1 and 2 show the experimental results for concentration of Lix984N 15% (by volume), diluted

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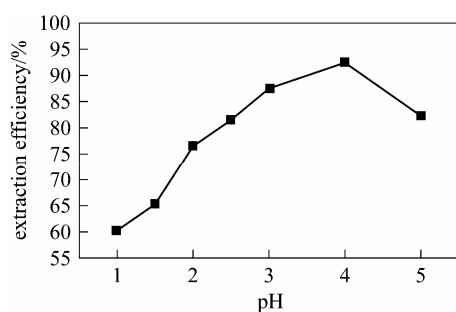


Figure 1 Effect of initial pH of aqueous phase on Cu^{2+} extraction efficiency

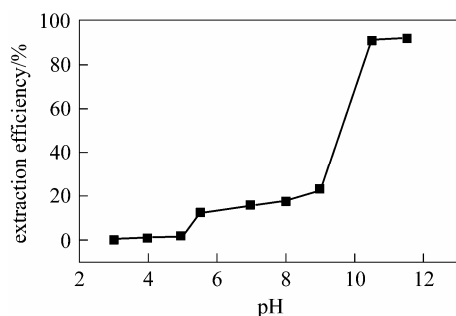
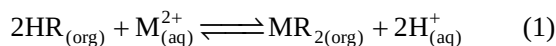


Figure 2 Effect of initial pH of aqueous phase on Ni^{2+} extraction efficiency

Lix984N mixed with a solution containing $0.02 \text{ mol} \cdot \text{L}^{-1}$ CuSO_4 or NiSO_4 , phase ratio (A/O) of 1, and extraction time of 5 min. The initial pH value of the solution greatly affects the extraction efficiency. The extraction efficiency of Cu^{2+} is considerable in the pH range of 1–5 and the maximum efficiency is obtained at pH of 4. The extraction efficiency for Ni^{2+} is at very low level for pH of 1–5.5, but it is greatly increased in the pH range of 9–11.

The most possible reason for above results is that Lix984N is an acidic extractant. The extraction principle is



where HR denotes extractant and M denotes metal. Eq. (1) indicates that 1 mol extractant releases 1 mol H^{+} , so the pH value affects the equilibrium of Eq. (1). If the pH value is low, the equilibrium of Eq. (1) moves to the left, so that the extraction efficiency will be gradually reduced, while at higher pH value, the extraction efficiency will increase to a high level. However, for pH value >5 , the precipitation of Cu^{2+} occurs. Moreover, Ni^{2+} is hardly co-extracted in the pH range of 1–5, so that the selectivity of Lix984 for Cu^{2+} is better than that for Ni^{2+} at pH of 1–5. The result indicates that Cu^{2+} and Ni^{2+} can be recovered separately by adjusting solution pH value in the solvent extraction. Some other common metal ions, such as Co^{2+} and Fe^{3+} , are hardly extracted in the pH range of 1–5 and 9–11 by Lix984N.

3.1.2 Influence of extractant concentration on extraction efficiency

For phase ratio (A/O) of 1 and extraction time of 5 min, the influence of extractant concentration on extraction efficiency was studied. Fig. 3 shows the experimental results for the aqueous solution containing $0.02 \text{ mol} \cdot \text{L}^{-1}$ CuSO_4 and NiSO_4 and Fig. 4 shows those for the aqueous solution containing $0.02 \text{ mol} \cdot \text{L}^{-1}$ NiSO_4 . At pH of 4, the extraction efficiency increases with extractant concentration. When the extractant concentration is higher than 15% (by volume), the extraction efficiency of Cu^{2+} is $>90\%$ and changes less, while that of Ni^{2+} is very low. Fig. 4 shows that Lix984N is suitable to extract Ni^{2+} at pH of 10.5, and the curve is similar to that of Cu^{2+} . Since high concentration of extractant is not favorable to phase splitting, the concentration of extractant is 15% (by volume) for the following experiments.

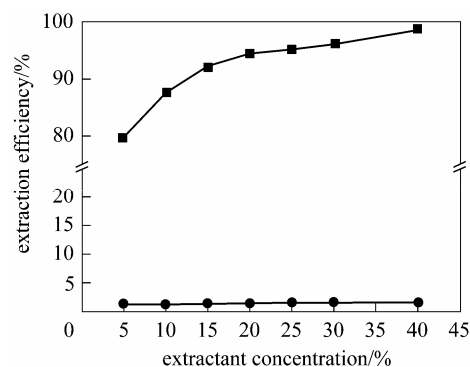


Figure 3 Effect of extractant concentration on extraction efficiency for Cu^{2+} and Ni^{2+} at pH of 4
■ Cu^{2+} ; ● Ni^{2+}

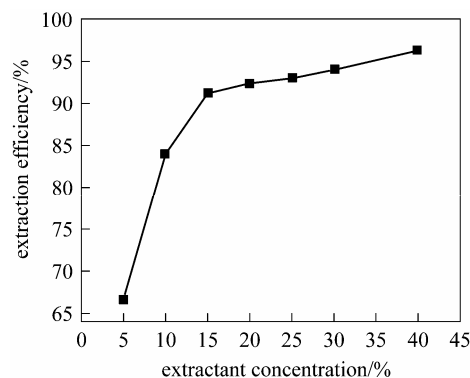


Figure 4 Effect of extractant concentration on extraction efficiency for Ni^{2+} at pH of 10.5

3.1.3 Influence of phase ratio (A/O) on extraction efficiency

For concentration of Lix984N 15% (by volume) and extraction time of 5 min, Fig. 5 shows the experimental results for the aqueous solutions containing $0.02 \text{ mol} \cdot \text{L}^{-1}$ CuSO_4 and NiSO_4 and Fig. 6 shows those for the aqueous solution containing $0.02 \text{ mol} \cdot \text{L}^{-1}$ NiSO_4 . Phase ratio (A/O) is an important factor for the

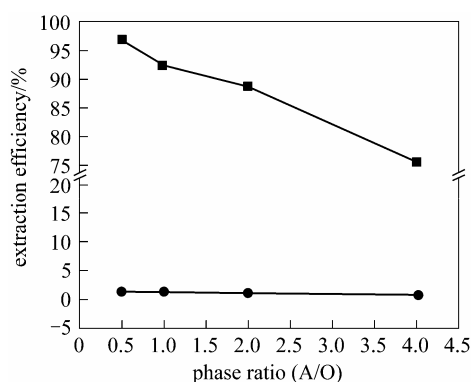


Figure 5 Effect of phase ratio on extraction efficiency for Cu^{2+} and Ni^{2+} at pH of 4

■ Cu^{2+} ; ● Ni^{2+}

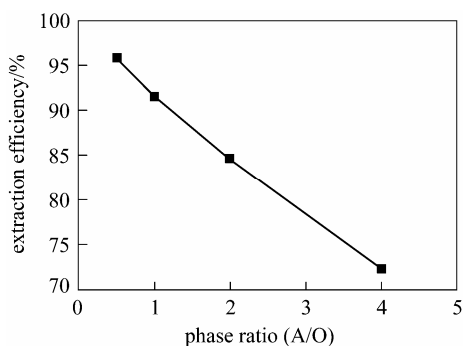


Figure 6 Effect of phase ratio on extraction efficiency for Ni^{2+} at pH of 10.5

extraction efficiency. The extraction efficiency decreases as phase ratio increases, but lower phase ratio results in more organic phase, which is unfavorable for stripping. Taking extraction efficiency and stripping into account, the phase ratio (A/O) chosen is 1.

3.1.4 Influence of extraction time on extraction efficiency

For concentration of Lix984N 15% (by volume) and phase ratio (A/O) of 1, Fig. 7 shows the experi-

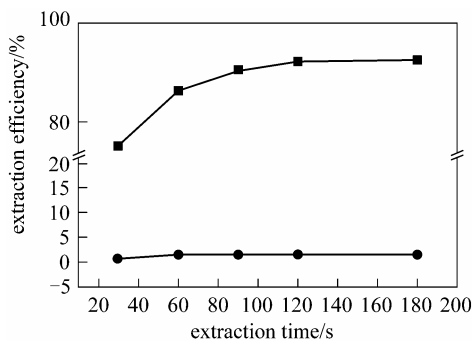


Figure 7 Effect of extraction time on extraction efficiency for Cu^{2+} and Ni^{2+} at pH of 4

■ Cu^{2+} ; ● Ni^{2+}

mental results for the aqueous solutions containing $0.02 \text{ mol}\cdot\text{L}^{-1}$ CuSO_4 and NiSO_4 and Fig. 8 shows those for the aqueous solution containing $0.02 \text{ mol}\cdot\text{L}^{-1}$ NiSO_4 . Extraction time is also an important factor for the extraction efficiency. The extraction efficiency increases with extraction time, and then approaches constant. In Fig. 7, the extraction efficiency of Cu^{2+} is 92.2% at 120 s but changes little later, while that of Ni^{2+} is very low. Thus the best extraction time is 120 s for the Cu^{2+} experiment. In Fig. 8, the extraction efficiency of Ni^{2+} is 92.7% at 240 s but increases little later, so the best extraction time is 240 s.

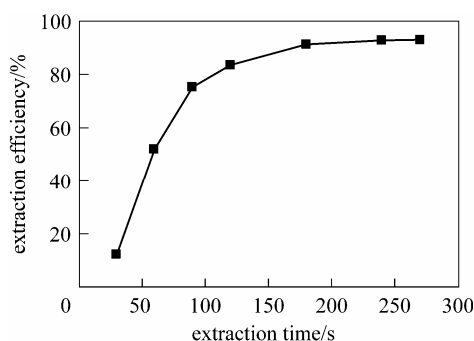


Figure 8 Effect of extraction time on extraction efficiency for Ni^{2+} at pH of 10.5

3.2 Recovery of Cu^{2+} and Ni^{2+}

The method to recover Cu^{2+} and Ni^{2+} [22] was used with stripping. Under the stripping conditions of phase ratio (O/A) of 1 and 8 min, a single-stage extraction was carried out. Fig. 9 shows that the stripping efficiency increases with H_2SO_4 concentration. When the H_2SO_4 concentration is $170 \text{ g}\cdot\text{L}^{-1}$ for Cu^{2+} stripping and $200 \text{ g}\cdot\text{L}^{-1}$ for Ni^{2+} stripping, the stripping efficiencies are higher than 90%, but the efficiency increases little as the concentration of H_2SO_4 increases further. Thus $170 \text{ g}\cdot\text{L}^{-1}$ and $200 \text{ g}\cdot\text{L}^{-1}$ H_2SO_4 are appropriate for stripping Cu^{2+} and Ni^{2+} , respectively.

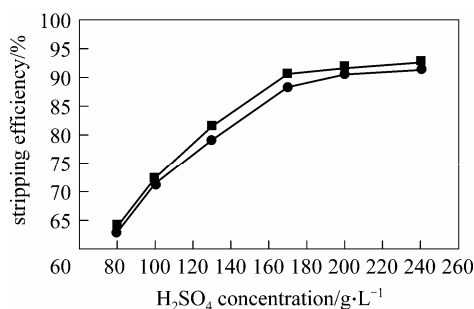


Figure 9 Effect of H_2SO_4 concentration on stripping efficiency of Cu^{2+} and Ni^{2+}

■ Cu^{2+} ; ● Ni^{2+}

In order to strip Cu^{2+} and Ni^{2+} effectively, a two-stage counter-current stripping was carried out.

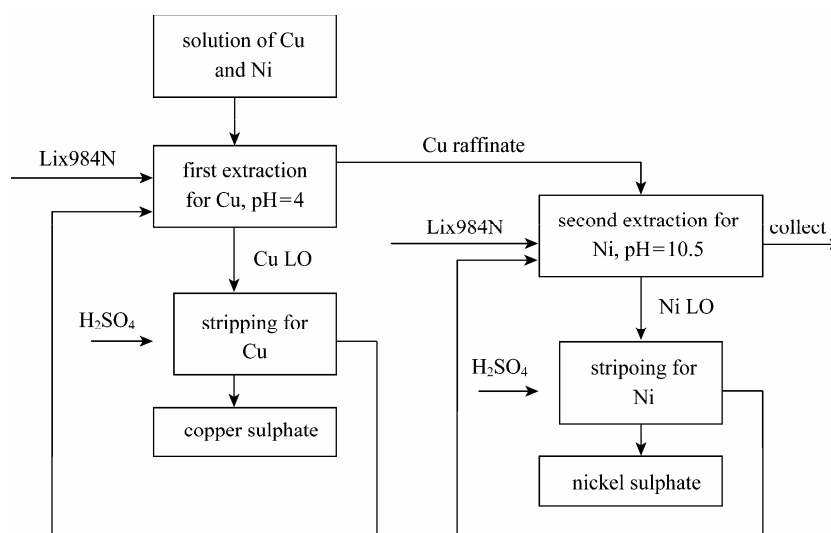


Figure 10 Flow sheet for separation of copper and nickel

Under the operation conditions of O/A ratio 1/2, concentration of H_2SO_4 $170 \text{ g}\cdot\text{L}^{-1}$, and stripping time of 8 min, the stripping efficiency of Cu^{2+} was higher than 99.1%. At O/A ratio of 1/2, concentration of H_2SO_4 $200 \text{ g}\cdot\text{L}^{-1}$, and stripping time of 8 min, the stripping efficiency of Cu^{2+} was higher than 99.3%.

3.3 Flow sheet for recovery of copper and nickel

A flow sheet for separating Cu^{2+} and Ni^{2+} was obtained and is shown in Fig. 10. The approximate separation steps are as follows. (1) The pH value of plating wastewater is adjusted to 4 and the extraction for Cu^{2+} is carried out. (2) The Cu loaded organic phase is stripped by $170 \text{ g}\cdot\text{L}^{-1}$ H_2SO_4 solution, forming CuSO_4 , and the organic solution from the first stripping returns to the first extraction solution. (3) The pH value of Cu raffinate from the first extraction is adjusted to 10.5 and the extraction for Ni^{2+} is carried out, then the Ni loaded organic phase is stripped by $200 \text{ g}\cdot\text{L}^{-1}$ H_2SO_4 solution, forming NiSO_4 . The organic solution from the second stripping returns to the second extraction solution.

4 CONCLUSIONS

Lix984N presents excellent extraction performance for the separation of Cu^{2+} and Ni^{2+} from sulphate medium when the solution is adjusted to appropriate pH value, and the optimal pH values for extracting Cu^{2+} and Ni^{2+} are 4 and 10.5, respectively.

The maximal extraction efficiency for Cu^{2+} and Ni^{2+} are 92.9% and 93.0%, respectively, by single-stage extraction at Lix984N concentration of 15% (by volume), phase ratio (A/O) of 1, extraction time of 120 and 240 s for Cu^{2+} and Ni^{2+} , respectively, and temperature range of 25–30 °C.

With the recovered Cu^{2+} and Ni^{2+} stripped in $170 \text{ g}\cdot\text{L}^{-1}$ and $200 \text{ g}\cdot\text{L}^{-1}$ H_2SO_4 medium, respectively, the stripping percentages of Cu^{2+} and Ni^{2+} are >99.1% and >99.3%, respectively, by a two-stage counter-current stripping at phase ratio (O/A) of 1/2, 8 min, and temperature range of 25–30 °C.

A flow sheet for separation of Cu^{2+} and Ni^{2+} is proposed, which can be applied for treating plating wastewater for recovering Cu^{2+} and Ni^{2+} . It is expected to reduce the environmental pollution and provide a resource of Cu^{2+} and Ni^{2+} .

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