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TECHNICAL NOTE

Selective Transport of Copper through Liquid Membranes Using LIX 860 as Mobile Carrier

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ABSTRACT

Copper has been selectively extracted from aqueous solutions containing metal ions (Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, and Zn^{2+}) by a liquid membrane technique. Experiments were carried out in a beaker equipped with a baffle, and the system was stirred by a variable-speed mixer equipped with a turbine impeller; the mixing speed was 300 rpm. A typical membrane formulation was 2.0% Span 80, 4.0% LIX 860, and 94.0% of commercial kerosene, all values being by weight. Copper was selectively separated and concentrated from both synthetic and natural aqueous mine solutions containing various metal ions.

INTRODUCTION

Recent years have witnessed a growing interest in the recovery of metal ions from their dilute aqueous solutions or wastewaters as a result of efficient methods developed to apply conventional liquid extraction, liquid membrane, or liquid pertraction techniques. An approach to this is the development of emulsion liquid membranes by Li (1) in 1968. Liquid membrane separation, combining the processes of extraction, diffusion, and stripping in a single step, has aroused much interest in recent years since it constitutes one of the cheapest separation techniques because of its relatively smaller inventory and low running costs. Thus, energy consumption is quite low and organic losses are often negligible under proper operating conditions (2, 3). The emulsion liquid membrane technique is a new and effective method for separation and concentration of mixtures, with potential applications in nuclear waste processing, hydrometallurgy, wastewater treatment, and biochemical/biomedical processes.

The present work is aimed at separating and concentrating copper from dilute aqueous copper mine solutions containing various metal ions (such as Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, Zn^{2+}, Ca^{2+}, Al^{3+} etc.) by using the commercial LIX 860 carrier.

EXPERIMENTAL

The liquid membrane phase was composed of a surfactant (sorbitan monooleate, commercially known as Span 80), a carrier (a mixture of 5-dodecyl-salicylaldoxime and a small amount of 5-nonylacetophenone oxime, known as LIX 860), and a solvent (a commercial kerosene). Span 80 is a surfactant for preparing stable emulsions. A commercial kerosene having a density of 830 kg/m^3 and a viscosity of 1.6 mPa·s at 20°C was used as the solvent. The internal phase was a sulfuric acid (concentration, 225 g/L). The external or feed phase (250 mL) was a synthetic mine solution consisting of 2.3000 g $CuSO_4$ (875 ppm Cu), 0.3850 g $CoSO_4{\cdot}7H_2O$ (57.5 ppm Co), 0.0300 g $NiSO_4{\cdot}6H_2O$ (4.0 ppm Ni), 9.0477 g $FeSO_4{\cdot}7H_2O$, 0.8786 g $Fe(NO_3)_3{\cdot}9H_2O$, 14.9750 g $MgSO_4{\cdot}7H_2O$ (1470 ppm Mg), and 2.7500 g $ZnSO_4{\cdot}7H_2O$ in 1 L of water or natural mine water. All chemicals used for the feed phase were a minimum of 99% purity and were purchased from Merck. The feed phase was adjusted to the desired pH with H_2SO_4. The internal aqueous solution (25 mL) was added dropwise to the membrane solution (25 mL), stirred at 1900 rpm for 20 minutes at ambient temperature, and passed through a burette in about 10 minutes. The volume ratio of the membrane phase to the internal phase was 1/1. A typical membrane formulation was 2.0% by weight of Span 80, 4.0% LIX 860 by weight (supplied by Henkel Corporation, Germany), and 94.0% of kerosene. The appropriate liquid membrane emulsion was added to a 600 mL-baffled beaker which contained the mine solution to be extracted. The two-phase system was stirred by a variable speed mixer (Ultra Turrax, IKA) equipped with a turbine-type Teflon impeller. The mixing speed was 300 rpm. The uptake of metal ions was monitored by removing samples of the feed solution periodically for analysis. Atomic absorption spectrophotometry was used for metal determinations. All aqueous solutions were prepared using 3 × deionized water. When the extraction was completed, the mixer was stopped and a sufficient time was allowed for the emulsion phase to separate from the aqueous phase. The emulsion was broken up by the addition of toluene and heating the mixture on a magnetic hot plate.

RESULTS AND DISCUSSION

Several experiments were performed for the selective separation and concentration of copper from a feed solution containing various metal ions (Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, and Zn^{2+}). The external or feed phase was a synthetic mine solution consisting of 875 ppm Cu, 57.5 ppm Co, 4.0 ppm Ni, 1938 ppm Fe, 573 ppm Zn, and 1470 ppm Mg, or natural mine water obtained from Black Sea Copper, Inc. The membrane formulation was 2.0% Span 80, 4.0% LIX 860, and 94.0% of commercial kerosene by weight. The internal phase was sulfuric acid, 225 g/L, as recommended by the manufacturer for quick stripping (4).

Figure 1 shows the selective separation of copper from the feed mixture containing various metal ions. It is evident from Fig. 1 that the copper concentration in the feed mixture decreases exponentially while the concentrations of the other ions remains almost constant over time. After 40 minutes, the internal aqueous phase consisted of 3425 ppm Cu, 6.25 ppm Co, 0.75 ppm Ni, 469 ppm Fe, 111 ppm Zn, and 241 ppm Mg.

A natural mine solution from Black Sea Copper, Inc., Turkey, which contains ions of Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, Zn^{2+}, Ca^{2+}, Al^{3+}, Mn^{4+}, and Cd^{2+}, was also investigated. Initial concentrations in

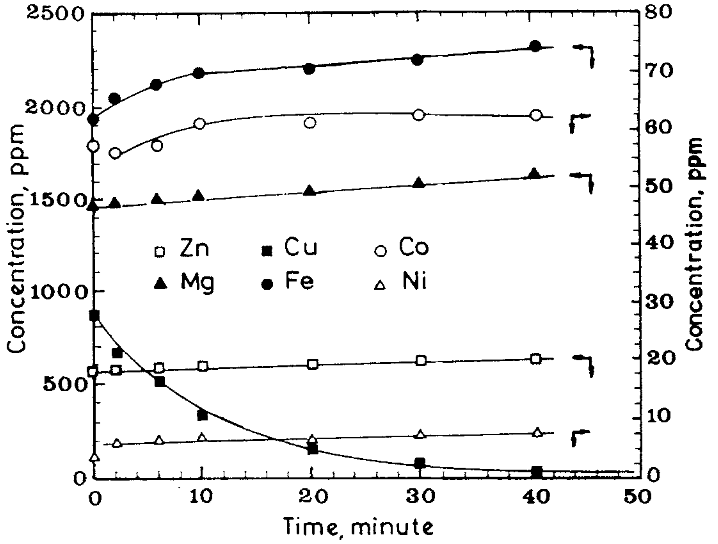

FIG. 1 The variation of metal ions' concentration in the feed phase with time in a synthetic mine water.

the feed are 175 ppm Cu, 25 ppm Co, 1.38 ppm Ni, 149 ppm Zn, and 150 ppm Fe. The selective separation of copper is shown in Fig. 2, which shows that the decrease of the copper concentration in the feed phase is similar to that given in Fig. 1, while the concentration of the other metal ions remains constant, and thus the internal phase consists of 496 ppm Cu, 3.5 ppm Co, 0.37 ppm Ni, 37.0 ppm Zn, and 190 ppm Mg. However, a strange behavior was observed for iron; that is, the iron concentration drastically increased with time, as indicated in Fig. 2. It may be argued that the increase in iron concentration was caused by a possible dissolution of the stainless steel baffle which was placed in the acidic mine water (pH 2). On the other hand, the iron concentration in the synthetic mine water exhibited a similar behavior, although it was moderate, as shown in Fig. 1. In fact, the higher iron concentration and less acidic nature of the synthetic mine water (pH 4.5) may be partly responsible for this type of behavior. Therefore, the baffle in the vessel should be coated, preferably using PTFE, to eliminate any possible contamination.

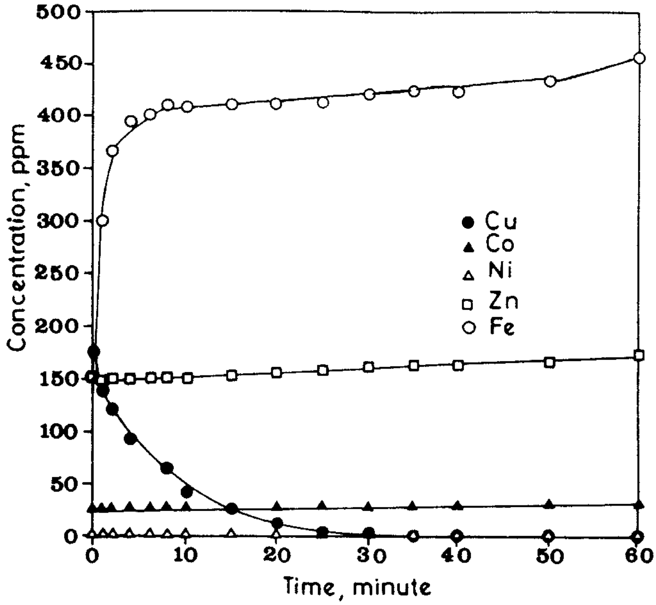

FIG. 2 The variation of metal ions' concentration in the feed phase with time in a natural mine water.

CONCLUSIONS

The results of liquid membrane extraction of copper from synthetic and natural mine solutions show that separation and concentration of copper is possible using LIX 860 as carrier. Enrichment factors of 5 or more are not difficult to achieve in a single step by properly manipulating the feed/strip volume ratios. Under our conditions, the emulsion liquid membranes are reasonably effective and selective for the separation of copper from aqueous mixtures containing the metal ions considered. This could be a significant development in such environmental technologies as wastewater treatment.

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