Treatment of electroplating effluent through emulsion-free liquid membrane†

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Separation of dissolved heavy metals such as Cr(VI) and Cu(II) from electroplating effluents using a new technique of emulsion-free liquid membrane (EFLM) has been studied. Experimental results show that nearly 95% extraction is obtained resulting in stripping phase enrichment up to 50 times relative to feed. It is also found that emulsion-free liquid membranes are highly efficient and superior to other types of liquid membranes.

Electroplating effluent streams of plating industries containing heavy metals, contribute to water pollution in significant proportions. These metals being carcinogenic, their presence in effluent stream in significant concentration poses serious threat to biota and environment. Conventional treatment of these dilute streams is expensive and inefficient. Separation of dissolved metals from industrial aqueous effluents using liquid membrane process is highly beneficial owing to its higher degree of separation, efficiency and application potential1. Three types of liquid membranes, viz., (i) bulk liquid membrane (BLM), where a thin layer of organic membrane phase is in contact with two aqueous phases2, (ii) supported liquid membrane (SLM), which consists of a microporous polymer film with an organic solution held within the pores by capillary forces3, (iii) emulsion liquid membrane (ELM), which consists of a water-in-oil-in-water system4 have been extensively studied. Bulk and supported liquid membranes are losing out to emulsion liquid membranes due to lack of efficiency and low flux rates. Even though emulsion liquid membranes are highly efficient and a very attractive alternative to other types of membranes, it failed to succeed in industrial applications due to its low stability and de-emulsification problems.

To overcome these drawbacks, an emulsion-free liquid membrane (EFLM) is developed, which does not require surfactants to form stable membranes and therefore de-emulsification process is eliminated. Loss of expensive carrier is avoided by restricting all the membrane solution to the reactor. This system operates on continuous basis with very low breakage and leakage.

In the present investigation, experiments have been conducted with an EFLM system. Metal complexing carriers such as LIX 64 N and Alamine 336 have been used to extract two major pollutants, Cu and Cr from electroplating effluent.

**Principle of EFLM Process**

Schematically an EFLM system is shown in Fig. 1. It consists of a rectangular parallelepiped reactor with tapering bottom, containing membrane solution. Its upper part is divided into an extraction cell and a stripping cell by a specially made baffle plate and its lower part into extraction and stripping settlers, respectively. Settlers are separated from each other by an impermeable divider. The extraction cell and its settler are inter-

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communicating and so are the stripping cell and its settler. The organic membrane solution can flow freely through baffle while the feed solution and strip solution on either side of the baffle plate are completely separated. The feed solution containing the metal to be extracted and the stripping solution are fed into the extraction and stripping cells, respectively. Compressed air and the aqueous solution are sent through a jet, where aqueous feed and strip phase are atomized. The aqueous droplets (of size 1-6 μm) are subsequently dispersed in extraction and stripping cells, respectively. The metal complex formed by reaction with the carrier in the continuous membrane phase, in the extraction cell, driven by its own concentration gradient diffuses through the baffle plate into the stripping cell. In the stripping cell, complex in the continuous membrane phase will be stripped into aqueous stripping droplets. The carrier in original form will then diffuse back to the extraction cell due to concentration gradient. Here, extraction and stripping reactions are coupled within the reaction tank. Under steady state operation, the concentration of metal complex in continuous membrane phase will be very low throughout, much lower than the equilibrium value. Hence, the amount of carrier in the membrane solution can be maintained at very low value without affecting the efficiency of the process.

Meanwhile, aqueous drops in respective cells will sink under gravity in the membrane phase. As these two types of aqueous droplets come to settlers, they separate from the continuous membrane phase, and the raffinate and the concentrate are collected or recirculated depending on the process demands.

The degree of membrane leakage is an important parameter in assessing the stability and thereby the success of liquid membranes. In EFLM process "leakage" refer to leaking of feed phase from the extraction cell to the stripping cell and vice versa. In this system, leakage is very low as a specially designed baffle separates the two aqueous phases completely. Occlusion of external phase into the membrane phase is also completely eliminated in EFLM system.

**Experimental Procedure**

Extraction experiments were conducted in a rectangular reactor (30 × 16 × 16 cm) made of perspex. 2.5 L of membrane solution was placed in the reactor. Experiments were conducted separately for Cu(II) and Cr(VI). LIX 64N (10% v/v) was used as a carrier for Cu extraction and Alamine 336 (2% v/v) for Cr. Distilled kerosene was used as the diluent. 1000 mg/L each of Cu (as CuSO₄·5H₂O) and Cr (as K₂Cr₂O₇) were used for extraction experiments. Pulse setting pumps with a common shaft were used to pump both feed and strip solutions with flow rates of 1000 and 100 mL/h, respectively. Compressed air at 1 kg/cm² (400 L/min) was fed along with feed and strip solutions through a jet to atomize the aqueous phases inside the reactor. Treated feed and enriched strip solutions were removed continuously from the extraction and stripping settlers at a predetermined flow rate. Samples removed at regular intervals were analysed using Atomic Absorption Spectrophotometer (model 904, GBC).

**Results and Discussions**

The success of extracting a metal from the feed phase and concentrating it in the stripping phase depends on the low metal concentration in the membrane phase. This is possible only if the strength of the acid/base in the feed and strip phase is sufficient to maintain a high rate for extraction and stripping reaction. Since the driving force for the extraction and stripping is the pH gradient, it is necessary to maintain the feed and strip phase at a pH, where maximum extraction and stripping is possible. Experimental results of
Cu and Cr extraction, showing the effect of pH of the aqueous solution on metal extraction and stripping are presented in Figs 2 and 3, respectively. The extraction reaction between copper and LIX 64N (a hydroxy oxime) can be represented as follows:

\[ 2RH_{(org)} + Cu^{2+}_{(aq)} \rightarrow R_2Cu_{(org)} + 2H^{+}_{(aq)} \]

From the stoichiometry, it is seen that Cu\(^{2+}\) is exchanged for H\(^+\) during the stripping process. Hence, the stripping phase should be more acidic compared to the feed phase for copper extraction. As it can be seen from the Fig. 2, Cu extraction increases with increase in pH with a maximum around pH 7. Similarly from the stripping experiments it was found that maximum stripping occurs at pH 1.5. Hence, the best extraction and stripping pH was found to be 7 and 1.5, respectively.

Similarly, the effects of pH of the aqueous feed solution on Cr extraction is presented in Fig. 3. In coupled transport of chromium, Alamine 336 (mixture of tertiary amine (R\(_3\)N)) is used as the complexing agent to extract dichromate and hydrogen ions from aqueous solutions as follows:

\[ 2H^{+}_{(aq)} + Cr_2O_7^{2-}_{(aq)} + 2R_3N_{(org)} \rightarrow (R_2NH)_2Cr_2O_7_{(org)} \]

Hence, extraction of Cr strongly depends on the hydrogen ion concentration in the aqueous solution. It was observed that extraction is high in acidic range, being maximum at pH 1.0. A small decrease in extraction rate was observed at pH below 1.0. This was essentially because at very low pH, bisulphate ions in the aqueous phase can displace the metal ion from metal-carrier complex decreasing the total extraction.

From the literature, it is observed that chromium can be stripped easily from the membrane solution using an aqueous phase containing inorganic salts such as Na\(_2\)CO\(_3\). The stripping reaction between the chromium complex and Na\(_2\)CO\(_3\) can be represented as follows:

\[ (R_2NH)_2Cr_2O_7_{(org)} + 2Na^+ + CO_3^{2-}_{(aq)} \rightarrow 2R_2N_{(org)} + H_2O_{(aq)} + CO_2 + 2Na^+ + Cr_2O_7^{2-}_{(aq)} \]

Stripping experiments were conducted using different % (w/w) of Na\(_2\)CO\(_3\) and the results are presented in Fig. 4. Stripping is maximum with about 5% of Na\(_2\)CO\(_3\). On further increase of the salt concentration, stripping of chromium dramatically decreases. Stripping decreases from 91 to 79% on increasing Na\(_2\)CO\(_3\) concentration from 5 to 10%. This behaviour can be attributed to the formation of more water molecules with the increase of % Na\(_2\)CO\(_3\) which dilutes the stripping phase. Further, an increase in Na\(^+\) concentration may decrease the mobility of the metal ions in the stripping and also change the equilibrium value due to the formation of undesired by-products. Hence, for chromium stripping, 5% Na\(_2\)CO\(_3\) (w/w) is recommended.

Lower carrier concentrations can be employed in a liquid membrane system because the metal transport mechanism is not governed by an equilibrium situation. In other words, the carrier in the liquid membrane will not get saturated with metal but merely acts as "carrier" to transfer metal ion from one side of the membrane to the other side. In any case the amount of the carrier present in the membrane should not be less than the minimum required for extraction. The effect of carrier concentration on extraction for copper and chromium are presented in Figs 5 and 6, respectively. From the Fig. 5, it is observed that extraction of copper reaches its maximum at 10% (v/v) of LIX 64N concentration and any further increase (up to 15%) does not have appreciable effect on the extraction. Similarly, chromium extraction also reaches its maximum value around 2% (v/v) of Alamine 336 concentration as shown in Fig. 6. Hence, further increase in carrier concentration of LIX 64N (>15%) for copper extraction and Alamine 336 (>5%) for chromium extraction is found to decrease the flux across the membrane.
phase due to increase in viscosity of the membrane phase. Therefore, in all experiments, concentrations of LIX 64N and Alamine 336 were maintained at 10 and 2%, respectively.

The EFLM experiments were conducted at the optimized pH and the extraction and stripping curves for Cu and Cr, obtained under these conditions are presented in Figs 7 and 8. From the plot, it can be observed that almost 100% extraction is achieved in the first few minutes after which it slightly decreases to attain a steady value. This may be due to the fact that at the beginning of the experiment, membrane solution can load the metal to an extent (0.4 g/L copper(II) and 0.6 g/L chromium (VI) on one volume per cent of the carrier in the membrane phase) hence, reaction will be almost instantaneous. Once extraction cell is loaded with metal complex, facilitated transport mechanism prevails and the complex diffuses to the stripping cell due to concentration gradient. After stripping, unchanged carrier diffuses back to the extraction cell for the next cycle. Similarly from stripping curves it is observed that stripping rate rapidly increases and reaches a steady value both for copper and chromium.

As presented in Fig. 7, nearly 95% of copper is removed from feed droplets enriching the stripping phase up to 40 g/L. At steady state, separation factor $\phi = 40$ ($\phi =$ conc. of stripping phase/conc. of feed phase) is achieved in less than 8 s of total residence time of both feed and strip droplets in the reactor. Similarly from the extraction and stripping data for chromium presented in Fig. 8, it is observed that 95% of chromium is extracted enriching the stripping phase up to 50 g/L ($\phi = 50$). Since EFLM attains steady state in a few minutes, perturbations in feed and strip phase flow rates if any, can be effectively compensated.

**Conclusions**

This investigation shows that emulsion-free liquid membrane is likely to become a versatile and effective tool for a variety of industrial applications. This system is very simple and easy to operate with nearly 100% efficiency. EFLM system is studied for two different systems, copper and chromium using LIX 64N and Alamine 336 as carriers, respectively. Experiments were conducted to get the optimized conditions of feed, strip and membrane phases for these two systems. Separation factors up to 50 are obtained in few minutes both for copper and chromium separation. It also appears that emulsion-free liquid membranes are more efficient and superior to any other type of liquid membrane. This process is ideally suited for a variety of hydrometallurgical, petroleum, nuclear and other industrial applications.

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