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Removal of Cu (II) using emulsion liquid membrane

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Abstract: This is a study on the removal of copper (II) ions from a feed solution using an emulsified liquid membrane (ELM). The membrane was prepared by dissolving the extractant Alamine, used as a mobile carrier, and Span-80, a surfactant, in kerosene. The ELM allowed an efficient metal transport from the feed solution towards the strip liquor, in experiments carried out in a batch-type stirred tank at 30 ^{0}C. The experimental results indicated that the significant variables on copper transport through the membrane were the extractant concentration, the surfactant concentration, initial copper concentration and the pH of the feed, strip solution. Concentration of H_2SO_4 as stripping agent affected only the initial metal extraction rate but not the extraction extent. The surfactant concentration range employed in this study adequately stabilized the membrane. However, it did not produce any positive effect on metal extraction. It was observed that the use of an excessively high content of surfactant produced lower metal transport extraction since it gave rise to a higher interfacial resistance. The experimental results reported show the potential for removal of Cu (II) from the synthetic solution using an extractor based on emulsified liquid membranes. Copper in the aqueous phase was determined by Atomic absorption spectrophotometer.
Keywords: Emulsion liquid membrane; Copper (II); Surfactant; Carrier.

1. Introduction

The emergence of bulk liquid membrane and supported liquid membrane has not met with much success in industrial applications since they in common suffered from low flux rates, low selectivity and high operating costs. Bulk liquid membranes possess much higher selectivity than polymeric membranes, thereby reducing staging requirements markedly. However, bulk liquid membranes have not been able to overcome the high costs associated with achieving sufficient mass transfer area to make significant impact as a good separation process. Problems associated with polymeric membranes such as low selectivity, low mechanical strength, low flux rates due to high diffusional resistance and short life span have restricted the use of supported liquid membrane as a potential industrial separation process. Thus, mass transfer area, efficiency and economic viability have become necessary requirements in the application of liquid membranes in any large-scale operation.

Emulsion liquid membrane (ELM) developed by N.N.Li [1], overcome the problem encountered in achieving large mass transfer area at low cost.ELM offers a mass transfer area of 3000–6000 m^2 / m^3 of equipment volume compared to 10-20 m^2 / m^3 and 100-200 m^2 / m^3 in the case of BLM and SLM respectively. This large mass transfer area is achieved in small sized equipment without the need for mechanical support. Thus, ELM is an attractive alternative for the separation of mixtures in an efficient manner and has made significant impact in the field of separation engineering.

Emulsion liquid membrane in different formulations renders it an extremely versatile process useful for different applications. This includes waste water treatment[1-6], minerals recovery[2,7-15], hydrocarbon separation[16] and a number of biochemical and biomedical applications[17].

Studies on the removal of dissolved metals using emulsion liquid membranes are of great interest because of the higher efficiency of separation, and a potential for a various applications. Extraction of metals from hydrometallurgical solutions[18-19] and industrial effluents[20-21] continues to be an important topic of research. Investigations have been conducted on the removal of copper[22-23], chromium[24] and zinc[25] using ELM. Studies on the removal of heavy metals like mercury, cadmium, nickel, cobalt, etc. have been reported in the literature. Attempts have also been made to extract rare earth metals like vanadium[26], tungsten[27] and removal of radioactive elements like uranium and products of uranium from nuclear wastes[28] , using liquid membrane technique.

Even though studies have been conducted on different aspects of liquid membranes, and their applications[29,30] , most of the studies dealt with the transport of only one metal from a mixture. However, in industrial systems it is common to have more than one extractable species which needs to be removed simultaneously in one step. This is possible when a carrier is capable of forming complex with these permeants. Simultaneous removal of metal species eliminates successive processing for each species. This reduces the processing cost and makes treatment process more efficient, compact and realistic. The present study deals with the extraction of copper ions from a synthetic solution using the commercially available Alamine extractant dissolved in commercial kerosene, using a batch surfactant membrane contactor.

2. Experimental

2.1. Reagents

The liquid membrane phase is composed of a surfactant, a carrier, and a diluent. The non-ionic surfactant used for stabilizing the emulsion is sorbitan monooleate which is a product of Fluka and commercially known as Span 80. The mobile carrier is Alamine336 which is purchased from Sigma–Aldrich Company. Commercial kerosene (density 830 kg/m^3 and viscosity 1.6mPa.s at 20 ˚C) was used as diluent. Commercial kerosene is a complex mixture of aliphatic origin and also contains aromatics about 15% w/w. Sulphuric acid, ammonia, sodium carbonate, and sodium hydroxide were of A.R. grade (Merck, Germany), that were used directly as received from the manufacturer.

2.2. Optimization Experiments

Experiments were conducted to find the effect of different process conditions on the performance of the system and to obtain best conditions for maximum separation and concentration. Experiments are conducted to find the effect of

1. pH of the feed phase
2. pH of the strip phase
3. Carrier concentration
4. Surfactant concentration
5. Treat ratio, and
6. Stirring speed

2.3. Extraction Experiments

2.3.1. Preparation of the Reactor

A major problem encountered during stirring was that the emulsion phase had a strong tendency to deposit on the walls of the vessel and even on the metallic parts namely baffles and impeller rod. Under certain conditions, like stirring at high r.p.m. virtually all the material was lost by deposition. To overcome this problem the following technique was adopted. The glass beaker was thoroughly cleaned before starting and very thin coat of 10 % aqueous solution of polyvinyl alcohol was applied on the walls. On slight heating, this coating hardened into a thin layer on the glass impeller. The metallic parts on the other hand were given a very high degree of buffing.

2.3.2. Experimental Procedure

All the experiments were conducted in a stirred baffled vessel as shown in Fig. The water-in-oil emulsion, prepared by mixing 50 cm^3 of organic solution containing surfactant, mobile carrier and diluent, was mixed with 25 cm^3 aqueous solution of internal phase and agitated for 15 minutes. The emulsion thus prepared was dispersed in a 1L vessel containing a known amount of feed solution. The vessel was equipped with a four-bladed turbine agitator. Samples were drawn from the external aqueous phase and the metal concentration was analyzed by atomic absorption spectrophotometer. All the experiments were conducted at a temperature of 303°K and the initial concentrations of each metal in Phase I and Phase III were 1000 ppm and 0 ppm respectively.

3. Results and Discussions

3.1. Effect of pH on Feed

For any extraction process, pH of the feed is an important parameter which governs the efficiency of the separation process. Extraction of metal from external phase and concentrating it in the encapsulated internal phase depends on the strength of the acid/base in these two phases. Effect of pH in the feed phase on extraction of copper is presented in Fig.2. As can be seen, extraction of copper increases with decrease in the acidity and is found to be maximum in the basic range pH=8.0 TO 10.0.

3.2. Effect of pH of Strip Phase

The effect of pH on stripping is presented in the Fig.3. As can be seen from the plot, copper stripping is maximum in the acidic range pH=1.0 to 2.0. Here stripping phase is H_2SO_4.

3.3. Effect of Carrier Concentration

Effect of carrier concentration in the membrane phase on extraction is presented in Fig.4. Change in the metal concentration in the external phase is plotted against extraction time at different carrier concentration. As can be seen from figure extraction was found to be maximum at 4 % of Carrier (Alamine) at the given experimental conditions. Higher values of carrier resulted in a decrease of extraction due to increase in the viscosity of the membrane phase.

3.4. Effect of Treat Ratio

For most extraction processes, a high ($V_{external}/V_{emulsion}$) ratio is desirable to minimize equipment size, and cost of chemicals. The effect of this ratio on metal extraction is shown in Fig.5. Although the overall percentage extraction of metal decreases with increase in the ratio, the effect is not very large. Even at 6/1 ratio 95 % of copper in the external phase is removed in 15 min. At a very high ratio of 25/1, 75% extraction was obtained at the end of 15 min. Compared to the amount of feed treated, enrichment factor achieved, reduction in equipment size and the cost of chemicals, this reduction in overall extraction is negligible.

However, in all further experiments a ratio of 6/1 is maintained for nearly complete extraction of metal from aqueous feed solutions.

3.5. Effect of Surfactant Concentration

Experiments were conducted to find the effect of surfactant (SPAN 80) on the stability of the emulsion. Surfactant concentration was varied from 1 - 5 % (v/v). Stable emulsions were formed at a concentration of 5 %. Hence, all the experiments were conducted at a surfactant concentration of 5 % (v/v).

3.6. Effect of Initial Metal Concentration in the Feed Solution

The effect of initial metal concentration in the feed solution on extraction time is presented in Fig 6. As can be seen from the figure, the degree of copper removal decreases with an increase in the initial concentration of copper in the feed. When the initial concentration is very high, the internal droplets in the emulsion globule at the periphery will get saturated fast and the metal-carrier complex has to diffuse through the membrane phase to the inner region of the drop to release the metal to internal phase. Hence, the mass transfer resistance in the membrane phase becomes important. Whereas, when the metal concentration in the feed phase is less, external mass transfer is rate controlling.

3.7. Effect of initial metal concentration in the stripping phase

The effect of initial metal concentration in inner phase on extraction rate is an important factor which determines the practical application of emulsion liquid membranes. In an emulsion liquid membrane process, most of the emulsion phase after the process is recycled to the extraction unit without demulsification. Hence, the emulsion globule is loaded with metal both in the membrane as well as in the internal phase. This emulsion globule which is preloaded with metal is brought in contact with fresh feed solution in the next cycle. The effect of initial concentration of the metal in the stripping phase is presented in Fig 7. As can be seen from the figure, the extraction rate decreased with an increase in the initial concentration of metal in the stripping phase.

Conclusions

In this investigation application of emulsion liquid membranes to metal separation is studied. Experiments were conducted with Copper metal feed systems. Experiments were also conducted to optimize pH of the feed solution and it was found that copper can be extracted at pH 8.0.The optimum concentration of carrier for this system was found to be 4% (Alamine336). For stable emulsion formation a surfactant concentration of 5 % (v/v) (SPAN80) is found to be adequate. From experiments on treat ratio the optimum value is found to be 6: 1 (feed: emulsion) in the range studied. This model may be applied to similar bi-metallic and multi component feed systems containing more than two metals involving different types of carrier and interfacial reactions which may be encountered in waste water treatment and hydrometallurgical applications.

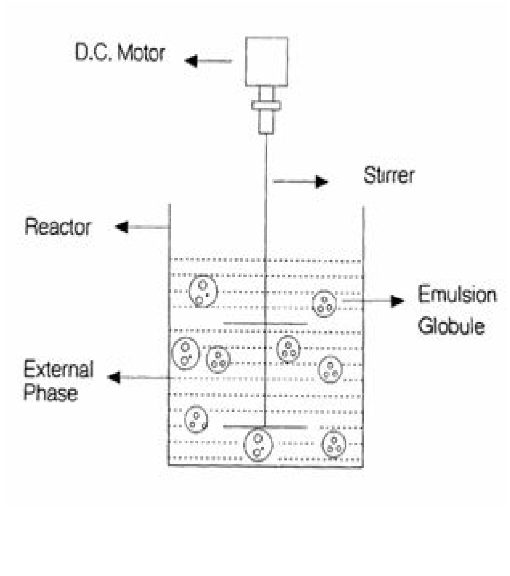

Figure 1: Experimental set up for emulsion liquid membrane process

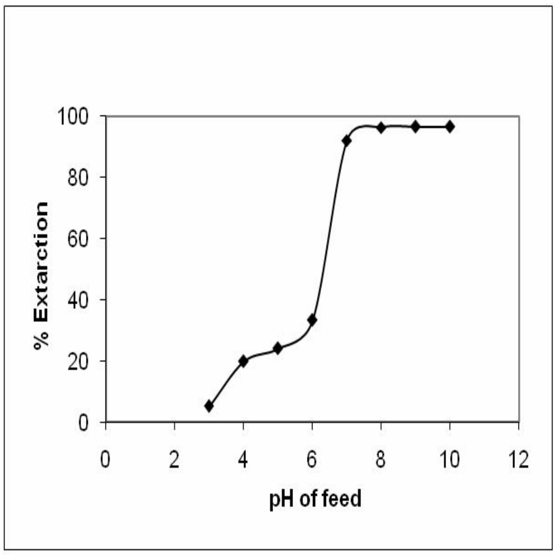

Fig.2: Effect of pH on Feed

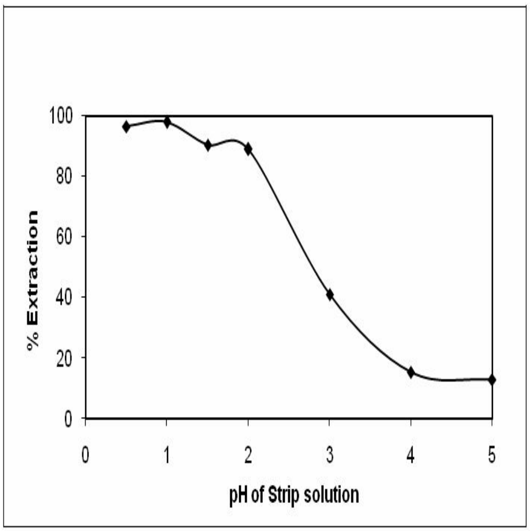

Fig.3: Effect of pH of Strip phase

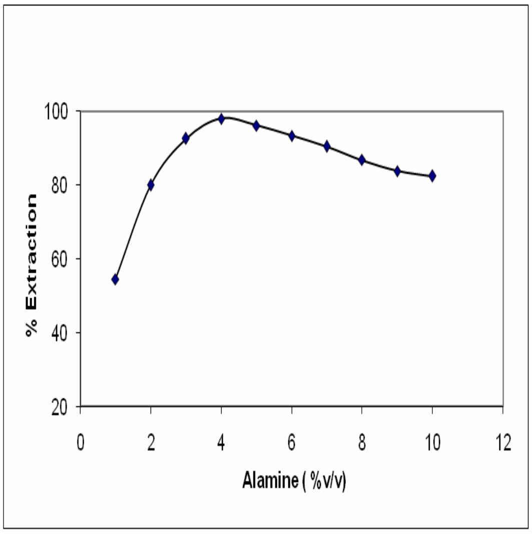

Fig.4: Effect of Carrier Concentration

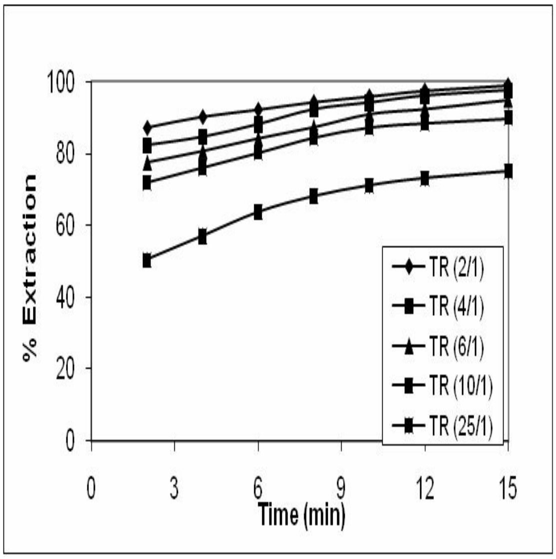

Figure 5: Effect of treat ratio on copper extraction

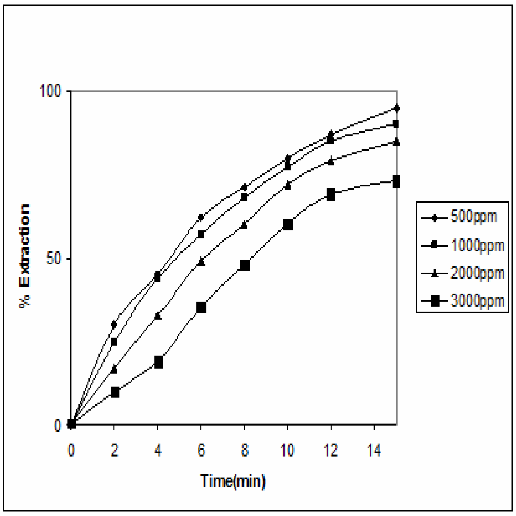

Figure.6: Effect of initial metal concentration in the feed solution.

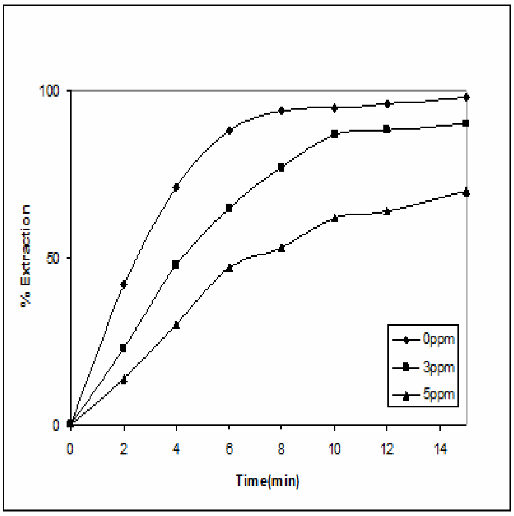

Figure.7: Effect of initial metal concentration in the stripping phase

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