Heavy metal removal using liquid membrane

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Experiments have been conducted to obtain the optimum conditions of hydrogen ion concentration of feed and strip phases and concentration of the carrier ALAMINE 336, in the extraction of Cr(VI) and Hg(II) using two different types of liquid membranes—bulk liquid membrane and emulsion liquid membrane. Experiments have also been carried out to find the effect of metal loading and the effect of extraction time on metal flux.

In recent years, increasing attention has been placed on removal of toxic materials from industrial wastewaters, not only for pollution control, but also to enable reuse of the water and in some cases, the toxic materials themselves. Most of the wastewaters result from cooling and rinsing operations in the industry and many of these waters are contaminated with heavy metals. Heavy metals are not biodegradable hence, their concentration continuously increases in the environment. These metals besides being carcinogenic, pose serious threat to biota and environment. Conventional treatment of these dilute effluents is generally expensive and the metals removed are usually not recovered, which also represents a major reuse opportunity. Hence, wastewater treatment awaits the development of a highly efficient, cost effective, energy saving-novel technology like "Liquid Membrane Technology".

Liquid membranes with different formulations render an extremely versatile process, especially for the removal of heavy metals from wastewaters down to very low levels. They are ideally suited for wastewater treatment applications since, they have the potential for the removal of toxic substances (organic, inorganic, etc) down to very low levels. Both molecular and ionic species (anions, cations and complexions) have been extracted successfully by properly constituted liquid membranes. Liquid membranes (LM) possess a number of advantages over solvent extraction methods for the recovery of valuable metals from dilute aqueous solution and hence, are used in hydrometallurgical processes. This process is successfully employed in industrial-scale of operations, for the separation of metals from industrial aqueous effluents. Apart from these, LM's are used for a variety of oil well control problems in petroleum industry, and also in many chemical industries in controlling several chemical reactions. Liquid membranes are especially well suited for biomedical and biochemical applications, such as oxygenation of blood, preparation of artificial blood cells, removal of toxins from blood, emergency treatment of drug overdose, preparation of artificial kidney, encapsulation of enzymes and in several controlled release systems.

In the present work, experiments have been conducted with different liquid membrane (LM) formulations like bulk liquid membranes (BLM) and emulsion liquid membranes (ELM) to determine the optimum operating conditions. Effects of carrier concentration, hydrogen ion concentration, metal loading, etc. over metal flux and efficiency were investigated.

**Experimental Procedure**

The complexing agent used in these studies was ALAMINE 336, a commercial solvent extraction agent (Henkel Corporation, USA) and distilled kerosene was used as a diluent. SPAN 80 was used as a surfactant in the preparation of ELM. These studies were performed to determine the performance of liquid membrane system in simultaneous removal of chromium and mercury from effluent streams, and also to evaluate the effects of amount of carrier present in the membrane phase, pH of feed and strip phases, metal loading in strip phase, etc. All the chemicals used in these studies were AR grade and experiments were carried out
at room temperature. Similar kinds of experiments were conducted with both the types of liquid membranes. The pH of the feed solution was varied from 0 to 7 and the pH of the strip solution was varied from 0 to 12. The pH was adjusted with conc. H$_2$SO$_4$ and NaOH. Concentration of carrier ALAMINE 336 in the membrane solution was varied over 0-100% (v/v). All the above experiments were conducted at a metal concentration of 1000 ppm each of Cr and Hg.

Metal concentration in the strip phase was varied in the range 0-25,000 ppm to study the effect of metal loading. These experiments were conducted at optimized conditions of pH of feed and strip solutions, and carrier concentration obtained from the above experiments. Experimental procedures for each type of liquid membrane studied, are discussed below.

**Bulk liquid membrane**—Experiments were conducted in a cell as shown in Fig. 1. Aqueous feed containing the synthetic feed solution of Cr and Hg (equal metal concentration) and strip solution were placed separately in two different compartments. The membrane solution containing ALAMINE 336 diluted with distilled kerosene was placed above, in contact with the two aqueous phases. A four-flat-blade glass turbine of 4 cm diameter was used as impeller. Membrane phase and aqueous phases were stirred separately (200 rpm.) using a variable speed stirrer.

**Emulsion liquid membrane**—In these studies, experiments were conducted in a 1 L stirred glass vessel with four baffle plates of 1 cm width. A four-flat-blade glass turbine of 4 cm diameter was used as impeller. First an emulsion was prepared by mixing an organic membrane phase (50 mL) containing 5% (v/v) surfactant SPAN 80, carrier ALAMINE 336 and diluent with an aqueous stripping phase (50 mL) at 1000 rpm. Later, the emulsion was dispersed in 500 mL of continuous phase (feed phase) containing 1000 ppm each of Cr and Hg, at 400 rpm to form globules encapsulating droplets of stripping phase.

Samples were collected at regular time intervals and were analysed for chromium and mercury, using Atomic Absorption Spectrophotometer (model 904, GBC). Experiments were done such that the membrane area generated in both the types of liquid membrane is equal (20 cm$^2$). By measuring the change in metal concentration in feed phase, the metal flux across the membrane was calculated from

$$\text{Flux} = \frac{\text{(change in concentration)} \times \text{(volume)}}{\text{(membrane area)} \times \text{(time)}}$$

**Results and Discussion**

The results of experiments conducted in these two types of liquid membranes, with ALAMINE 336 as carrier are presented in Fig. 3. The metal flux was calculated using the above equation.
flux through the membrane depends on the concentration of carrier in the liquid membrane as shown. There are two factors that cause the observed dependence on carrier concentration. As the concentration of carrier in the membrane is increased, the concentration gradient of the metal-carrier complex across the membrane increases as well. However, the viscosity of the organic solution also increases with increasing carrier concentration. Since the effective diffusivity is inversely proportional to the viscosity of the solution, the increased viscosity results in lower flux. If the carrier concentration is low, this results in a higher flux. At a carrier concentration of 28% (v/v), the flux increase due to the increasing concentration gradient is just sufficient to overcome the flux decrease due to the increasing viscosity, and hence at this carrier concentration, the flux reaches its maximum value and subsequently decreases with further increase in carrier concentration. All the experiments were therefore carried out with the membrane phase corresponding to this optimum composition.

The results of extraction experiments are presented in Fig. 4 showing the percentage of metal extracted by the membrane phase as a function of pH of the feed solution. It is observed from the figure that no chromium is extracted at pH higher than 7 and mercury extraction is also very less at pH higher than 7. As the pH of the aqueous feed phase decreases, extraction of metals increases, reaches its maximum value and subsequently decreases with further decrease in pH. Extraction is maximum in the pH range 1.5-3.5. There are some evidences that at pH lower than 1.5, bisulphate ions can displace metal ion from metal-carrier complex, reducing the extraction rate. The extraction data indicate that chromium and mercury are extracted nearly complete from feed solution at pH 2.0. In all the subsequent experiments pH of the feed solution is maintained at pH 2.0.

Similarly, the percentage of metal stripped is plotted as a function of pH of the stripping phase
as shown in Fig. 5. From this plot it is evident that metal stripping is negligible in acidic phase. Stripping is less than 10% till pH 7 and stripping rate increases suddenly on further increase of pH. It reaches its maximum value and does not vary much with further increase in pH. Stripping is observed to be maximum around pH 9.0, which is the optimum pH of the stripping phase.

From the above three sets of experiments it is clear that the efficiency of the liquid membrane systems for simultaneous removal of chromium and mercury is maximum for the systems containing 28% (v/v) carrier ALAMINE 336, feed pH 2.0 and strip solution pH 9.0. Hence, all other experiments are carried out at these optimum conditions.

Efficiency of these liquid membranes is also checked with respect to the capacity to transport metal against large concentration gradients as shown in Fig. 6 and ability to extract metals down to low levels, though unaffected by very high flux rates for prolonged time intervals, as shown in Fig. 7.

Fig. 6 clearly shows that the metals can be transported against large concentration gradients with liquid membrane systems. As it can be seen from this figure, metal flux is fairly independent of the metal concentration in the product solution. The decrease of metal flux is only about 8% as metal concentration in product solution is increased in the range 0-25000 ppm. In these experiments a concentration factor of 14,300 was achieved which proves the efficiency of these liquid membranes in uphill transport beyond any doubt. The variation of metal flux during extraction process as a function of time is shown in Fig. 7. As it can be seen from the plot, the variation in the value of metal flux for both Cr and Hg is less than 5% at the end of 5 h of extraction. These two experiments proved that this liquid membrane is efficient and effective for commercial exploitation of this technology.

Conclusions

Liquid membranes are effective and versatile tools for performing a large variety of separations. They are ideally suited for the removal of metal ions from wastewater. Best results are obtained in simultaneous removal of chromium and mercury using 28 vol % of carrier Alamime 336, and maintaining pH of the feed and strip phases at 2.0 and 9.0, respectively. Metal fluxes in these membranes are fairly independent of concentration of metal present in the feed and strip solutions and are very high for long periods. Hence, this can be used effectively and efficiently for prolonged periods. In addition liquid membranes are ideally suited for a variety of industrial, petroleum, biomedical and biochemical applications.

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