



Di(2-ethylhexyl)phosphoric acid-coconut oil supported liquid membrane for the separation of copper ions from copper plating wastewater

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Abstract

Permeation of Cu(II) from its aqueous solution through a supported liquid membrane (SLM) containing di(2-ethylhexyl)phosphoric acid (D2EHPA) carrier dissolved in coconut oil has been studied. The effects of Cu(II), pH (in feed), H₂SO₄ (stripping) and D2EHPA (in membrane) concentrations have been investigated. The stability of the D2EHPA-coconut oil has also been evaluated. High Cu(II) concentration in the feed leads to an increase in flux from 4.1×10^{-9} to 8.9×10^{-9} mol/(m²·s) within the Cu(II) concentration range 7.8×10^{-4} – 78.6×10^{-4} mol/L at pH of 4.0 in the feed and 12.4×10^{-4} mol/L D2EHPA in the membrane phase. Increase in H₂SO₄ concentration in strip solution leads to an increase in copper ions flux up to 0.25 mol/L H₂SO₄, providing a maximum flux of 7.4×10^{-9} mol/(m²·s). The optimum conditions for Cu(II) transport are, pH of feed 4.0, 0.25 mol/L H₂SO₄ in strip phase and 12.4×10^{-4} mol/L D2EHPA (membrane) in 0.5 μm pore size polytetrafluoroethylene (PTFE) membrane. It has been observed that Cu(II) flux across the membrane tends to increase with the concentration of copper ions. Application of the method developed to copper plating bath rinse solutions has been found to be successful in the recovery of Cu(II).

Key words: coconut oil; supported liquid membrane; copper; effluent treatment

Introduction

Efficient separation and recovery of metal ions from industrial wastes as well as from raw materials are gaining more and more importance because of the increasing demand for high purity products and also for environmental concerns (Saji *et al.*, 1999). Conventional methods for heavy metal removal include chemical precipitation, electrolytic recovery, electrodialysis, ion-exchange/chelation, solvent extraction and liquid membrane (LM) separation (Rorrer, 1998). Among these, LM has received considerable attention in the past three decades due to its characteristics such as ease of operation, energy and selectivity advantages and low cost operation factors (Alguacil, 2001; Gherrou and Kerdjoudj, 2002; Valenzuela *et al.*, 2002; Alguacil *et al.*, 2001; Venkateswaran and Palanivelu, 2007; Kocherginsky *et al.*, 2007).

Several studies dealt with the use of supported liquid membranes (SLMs) on Cu(II) separation from various aqueous media and using different extractants. There have been many studies on commercial extractants such as the crown ethers (Gherrou and Kerdjoudj, 2002), LIX series (Breembroek *et al.*, 1998; Yang and Fane, 1999; Hara and Bohrer, 1989; Gill *et al.*, 2000; Alguacil, 2001; Alguacil *et al.*, 2001; Valenzuela *et al.*, 2002; Molinari *et al.*, 2004; Nuri Ata, 2005) ACORGA

series (Szpakowska and Nagy, 1997; Alguacil *et al.*, 2002) and organophosphorus acid (Zhang and Gozzelino, 2003; Sarangi and Das, 2004; Molinari *et al.*, 2005; Yang *et al.*, 2001) as carriers and from thiourea derivatives (Gherrou *et al.*, 2001, 2002; Arous *et al.*, 2004). Among this LIX series have been most widely studied, and new extractants are introduced. A novel extractant LIX 984N (a mixture of 5-nonylsalicylaldoxime and 2-hydroxy-5-nonyl-acetophenone oxime) was reported for the liquid-liquid extraction of Cu(II) (Paugam and Buffle, 1998). Further, coupled uphill transport of Cu(II) across a bulk liquid membrane containing LIX 984N as carrier was also performed and the rate-limiting step was identified. Recently, Sengupta *et al.* (2006) found that LIX 984N-C could extract up to 80% Cu(II) from aqueous solutions at pH value of 1. Performance of LIX 984N-C was also compared with LIX 84 and LIX 84-I at different pH values. Their results indicated that the LIX 984N-C could open up new avenues for extraction of copper, not only from dilute solutions, but also from sulphuric acid leach solutions.

Of the salicylaldoximes derivatives used as membrane carriers, Acorga M5640 is the most efficient for Cu(II) transport across a FSSLM (Alguacil *et al.*, 2002). Several studies (Gherrou *et al.*, 2002; Sarangi and Das, 2004; Swain *et al.*, 2004) have suggested that D2EHPA is a highly effective extractant used for the separation of Cu(II).

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Recently, Molinari *et al.* (2006) compared the transport, kinetic selectivity and stability in SLM operations using a new carrier, molecule 2-hydroxy-5-dodecylbenzaldehyde (2H5DBA) and D2EHPA in kerosene. Transport and stability tests were carried out to compare them in terms of flux at the optimal carrier concentration. 2H5DBA performance was less compared to D2EHPA.

Different types of acid solutions have previously been used as stripping phases in LM process with D2EHPA as a carrier. Nitric acid 1.0 mol/L (Gherrou *et al.*, 2002), 0.9 mol/L H₂SO₄ (Sarangi and Das, 2004; Swain *et al.*, 2004), 0.5 mol/L H₃PO₄ (Zhang and Gozzelino, 2003). It is clear that Cu(II) can be released from the carrier complex with strong mineral acids. Diluents like kerosene (Yang and Fane, 1999; Gherrou *et al.*, 2001; Sarangi and Das, 2004; Swain *et al.*, 2004; Nuri Ata, 2005), *n*-hexane (Valenzuela *et al.*, 2002), Iberfluid (Alguacil, 2001; Alguacil *et al.*, 2001), *n*-decanol (Zhang and Gozzelino, 2003), *n*-octane (Maria, 1996; Szpakowska and Nagy, 1997) and chloroform (Gherrou and Kerdjoudj, 2002; Gherrou and Kerdjoudj, 2002; Arous *et al.*, 2004) have been employed as diluent for D2EHPA, which are toxic, volatile in nature.

A common problem for SLMs is the loss of membrane solvent and/or carrier to the both aqueous phases, and as the result the SLM-based processes have not been exploited industrially. The polymer inclusion membrane (PIM) (prepared from cellulose triacetate (support), tris(2-*n*-butoxyethyl)phosphate (plasticizer), LIX[®] 84-I (carrier), and ethanol (additive)) transport of Cu(II) has been studied (de Gyves *et al.*, 2006). From the study, it was observed that besides the improvement in metal ion flux and reduction in metal accumulation in the membrane by the incorporation of the additive in the casting solution, an increase in membrane stability also attained. The characteristics of the organic phase diluent have a great influence on the performance of solvent extraction systems (Ritcey and Ashbrook, 1984) and the same effect has been observed in LM systems (Molinari *et al.*, 1992; Dozol *et al.*, 1993). To overcome the instability of SLMs, many attempts have been proposed by Teramoto *et al.* (2000) and reviewed by Kemperman *et al.* (1996).

Vegetable oils have created a great deal of interest as greener replacement for traditional volatile organic solvents. They basically have little or no vapour pressure, which makes them an ideal replacement for the volatile, conventional organic solvents used in solvent extraction and LM processes. From our lab the transport of dyes (Muthuraman and Palanivelu, 2006), phenols (Venkateswaran and Palanivelu, 2006) by SLM containing vegetable oil as the novel LM have been reported. In the present study coconut oil was used as the novel, stable diluent for the well-established extractant D2EHPA for Cu(II) recovery from aqueous solutions. The fundamental parameters governing the Cu(II) transport optimized and the stability of the D2EHPA-coconut oil was evaluated. The developed system was applied for the recovery of Cu(II) from the real copper plating wastewater.

1 Experimental

1.1 Chemicals and membranes

Carrier D2EHPA (M. wt. = 322.4 g/mol; $d^{20} = 0.97$ g/ml) was supplied by Venus Ethoxy ether (India) and diluent coconut oil, VVD (India) was used as received. The stock solution of Cu(II) was prepared by dissolving the required amount of hydrated copper sulphate (AR grade, Merck) in double distilled water. Sulphuric acid and all the other reagents used were of AR grade. Commercially available PTFE plain 1.0 μ m pore size membrane of thickness 10 μ m with porosity 85%, was obtained from PALL Pharma lab filtration, India. PTFE plain membrane of 0.5 μ m pore size, 18 μ m thickness with 85% porosity obtained from Millipore (India), India and 0.2 μ m (Sartorius, Germany) membrane of 25 μ m thickness were used for the studies.

1.2 Apparatus

The pH of the aqueous phase was measured with WTW (Germany) pH meter. The stirring speed of the aqueous solutions was measured with a digital tachometer (systems, India). The transport of Cu(II) from feed phase to strip phase was determined by analyzing the copper ion concentration by using Analytik Jena (Germany) flame atomic absorption spectrophotometer (APHA, 1998).

1.3 Supported liquid membrane cell

Figure 1 depicts the schematic representation of the SLM used in the study. The organic LM phase was prepared by dissolving the required volume of D2EHPA in the coconut oil diluent to obtain carrier solutions of different concentrations. The PTFE support was impregnated with the carrier solution by immersion for 24 h, then leaving them to drip for 10 s before being placed in the flat sheet SLM (FSSLM) cell. Batch experiments were carried out with a two-compartment permeation cell, which consists of feed phase (150 ml) separated from a stripping phase chamber (150 ml) by a LM having an effective area of 15.2 cm². The feed and strip phases were stirred mechanically by a magnetic stirrer to avoid concentration polarization conditions at the membrane interfaces and in the bulk of the solutions. All the experiments were carried out at 27 \pm 1 $^{\circ}$ C.

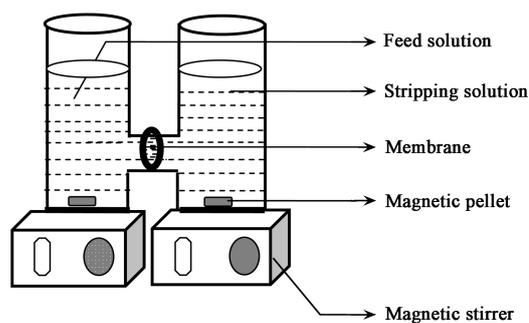


Fig. 1 Schematic representation of the SLM used in Cu(II) separation.

1.4 Transport measurements

The experiments on transport of copper from feed phase to strip phase through SLM was conducted for 7 h each or other wise stated. The Cu(II) transport from feed phase to the strip phase was measured by taking samples from the feed and strip solutions at regular time intervals and analyzed for the Cu(II) concentrations. The precision of multiple readings of the same sample was generally within 5% while that of the duplicated experiments ranged from 3% to 8%. The flux (J mol/(m²·s)) measures the number of moles diffusing per unit time and unit surface area, given by the equation.

$$J = -\frac{V}{A} \frac{dC}{dt} \quad (1)$$

where, V is the volume of feed solution (m³); A is the effective contact area of membrane (m²); C is the change in concentration of Cu(II) with time (mol/L); t is elapsed time (s).

2 Results and discussion

The application of coconut oil as novel, stable diluent with D2EHPA carrier for the permeation of Cu(II) through the SLM was investigated as a function of various experimental variables. The results are discussed here under.

2.1 Selection of support material

A blank experiment was performed to ensure the transport of Cu(II) with the plain PTFE support without D2EHPA carrier in coconut oil diluent, no Cu(II) transport was observed. Hence, the carrier D2EHPA (15.5×10^{-4} mol/L) was dissolved in diluent coconut oil (1:1 ratio) and used for the evaluation of polymeric support. Various membranes of pore sizes 0.2, 0.5 and 1.0 μ m was considered for the Cu(II) transport comparison studies. The transport studies were conducted with an initial Cu(II) concentration of 15.7×10^{-4} mol/L (100 mg/L) in the feed phase for 6 h. The results revealed that membrane with 0.5 and 1.0 μ m pore size was found to have more transport efficiency with J_{Cu} value of 5.9×10^{-9} mol/(m²·s) where as the 0.2 μ m pore size containing membrane has the J_{Cu} value was 2.2×10^{-10} mol/(m²·s) only. Thus the pore size characteristics of the polymeric support play an important role in the effective transport of Cu(II) species. There was no accumulation of Cu(II) in the membrane phase observed which is proved from the mass balance in feed and strip phases. Hence, further studies were carried out using PTFE membrane of 0.5 μ m pore size only.

2.2 Effect of feed phase pH

In flat sheet SLM system, the pH gradient between source and stripping phases is one of the important driving forces for the permeation of the metal ion. In order to assess the role of Cu(II) aqueous source phase pH, its variation in the range of 2.0–6.0 was carried out. Sulphuric acid was used to maintain the feed solution pH in the above range. Separation of Cu(II) was carried out from feed solution containing single metal ion of 7.8×10^{-4}

mol/L of Cu(II) and 0.5 mol/L H₂SO₄ as stripping reagent. The extractant concentration in membrane phase was 15.5×10^{-4} mol/L. The amount of Cu(II) transport from feed phase to strip phase at various pH values are shown in Fig.2. There was no extraction of Cu(II) below pH 2.0. The transport of Cu(II) starts at the pH of 2.0 and increased with increasing pH up to 4.0 and then remains constant thereafter up to pH 5.0 and decreases further. The decrease in transport beyond pH 5.0 can be attributed to hydroxide formation, which can be explained on the basis of the solubility product constant (K_{sp}): in fact, considering that initial feed concentration is equal to $C_{Cu^{2+}} = 50$ mg/L (7.8×10^{-4} mol/L) and that $K_{sp}(Cu(OH)_2) = C_{Cu^{2+}} \times C_{OH^-}^2 = 10^{-20}$, at 25°C (Mahan and Myers, 1987), maximum feed admissible pH to avoid precipitation is approximately 5.0. In order to ensure all the Cu(II) in aqueous phase are dissolved form, further studies were carried out at feed pH of 4.0.

2.3 Effect of strip solution concentration

The stripping reaction at the membrane–strip solution side plays a vital role in the transfer of metal ion from feed side to strip side. If the metal complex is not completely stripped, the membrane phase becomes saturated with the complex and the permeation rate may therefore decrease (Sarangi and Das, 2004). In the present study H₂SO₄ was used as the stripping agent. Fig.3 shows the effect of strip solution (H₂SO₄) concentration (0.05–0.50 mol/L) on

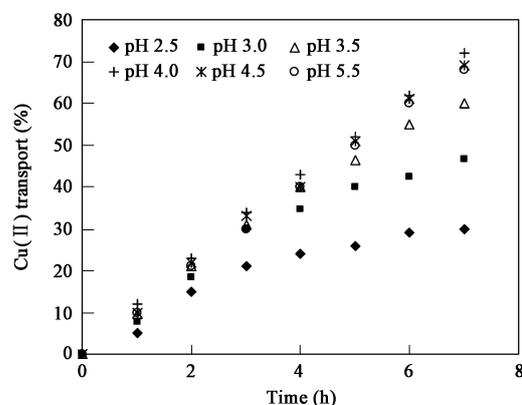


Fig. 2 Amount of Cu(II) transport from feed phase to strip phase at various pH.

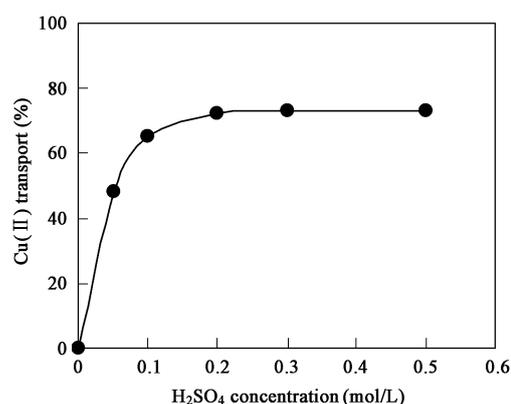


Fig. 3 Effect of strip solution (H₂SO₄) concentration.

the transport of Cu(II) through the SLM. It is seen that with increase in concentration of H_2SO_4 the percentage of Cu(II) transport increased and tends to take a maximum at 0.2 mol/L, and above 0.2 mol/L it has no effect on the transport rate. In deed, the decrease in efficiency below 0.2 mol/L H_2SO_4 solution may be due to the decrease of the driving force for diffusion of Cu-D2EHPA complex through the SLM owing to an increase of metal complexes concentration at the membrane–strip interface. This is the lowest concentration of acid used for the stripping of Cu(II) from its D2EHPA complex when comparing with the earlier works.

From the above results, 0.25 mol/L H_2SO_4 was chosen as the stripping reagent for the further studies.

2.4 Influence of D2EHPA concentration

The organic phase carrier concentration had a significant effect on the metal ion transport across the membrane. It is generally expected to increase with the carrier concentration unless other factors, such as viscosity impede the transport process (Shailesh *et al.*, 2006). In the present study, the effect of D2EHPA concentration variation on Cu(II) transport at feed pH 4.0 and 0.25 mol/L H_2SO_4 stripping phase was studied. The flux of Cu(II) through the membrane as a function of D2EHPA concentration is shown in Fig.4. The results show a linear increase in the flux from 3.1×10^{-4} mol/L to 12.4×10^{-4} mol/L ($J = 7.2 \times 10^{-9}$ mol/(m²·s)), which indicate a diffusion controlled transport of copper. This observation also suggested that there was no aggregation of ligand molecules. This may be explained keeping in view the increasing availability and formation of extractable complex with Cu(II) and hence its extraction into membrane (organic) phase, at the feed solution membrane. Increase in D2EHPA concentration will lead to more Cu-D2EHPA complex formation and hence increase in its concentration gradient within the membrane along the membrane thickness, but the viscosity of the organic phase also increases (Bukhari *et al.*, 2006) beyond 12.4×10^{-4} mol/L resulting in to decrease in its diffusion through membrane phase, leads to low flux value. The maximum flux value obtained is known as limiting flux J_{lim} of Cu(II), which can be explained by assuming that diffusion in the organic membrane is negligible compared with that for aqueous diffusion and the permeation process

is controlled by the diffusion in the stagnant film of the aqueous feed phase (Alguacil, 2001). Also, it can be assumed that diffusion coefficients of loaded and free carrier forms decrease with increase in their concentration and that increasing the number of carrier molecules enhances the transport; specific equilibrium between these factors results in near maximum flux when the feed phase copper ions concentration was 23.61×10^{-4} mol/L. Thus;

$$P_{lim} = \frac{D_{aq}}{d_{aq}} \quad (2)$$

the aqueous diffusion layer thickness was calculated assuming the value of $D_{aq} = 10^{-9}$ m²/s for the aqueous diffusion coefficient of Cu^{2+} (Alguacil, 2001) and P_{lim} at the corresponding time is 0.35 m/s, calculated as described earlier (Alguacil *et al.*, 2002). The value of d_{aq} is 2.85×10^{-8} m, this value being the minimum thickness of the stagnant aqueous diffusion layer within the present experimental condition.

For further experiments, 12.4×10^{-4} mol/L D2EHPA was chosen as the carrier solution.

2.5 Influence of stirring speed

In order to achieve effective permeation of Cu(II) in a SLM system, it is necessary to explore the effect of stirring speed on the transport flux. Diffusional resistances encountered during the transport of a metal ion across a SLM are of two types: (1) the resistance due to the liquid boundary layer and (2) that due to the membrane. Indeed, in many cases the magnitude of the boundary layer resistance is comparable to or even greater than the membrane resistance (Bohrer, 1983). In the present investigations, stirring of the source and receiving phases was carried out from 200 to 800 r/min and the results are depicted in Fig.5. The flux value increased from 200 to 400 r/min, and beyond that no appreciable increase was observed. This indicates that the aqueous boundary layer thickness (d_{aq}) diminishes continuously with increasing stirring speed and that the boundary layer is a minimum above 400 r/min for the difference ($C_{Cub} - C_{Cui, tot}$) and the flux remains constant in the range 400 to 600 r/min. At high concentrations of C_{Cu} this difference is indistinguishable with respect to C_{Cub} , as the carrier concentration reaches saturation. Therefore, the appearance of a plateau region does not necessarily mean the elimination of the aqueous diffusion layer, although the resistance due to it

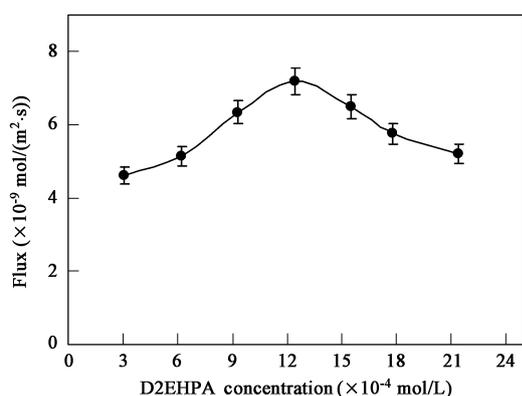


Fig. 4 Effect of D2EHPA concentrations in membrane phase.

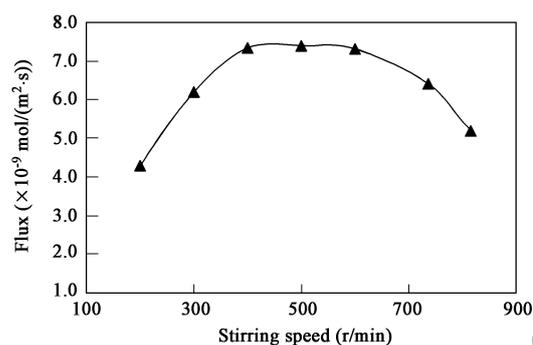


Fig. 5 Influence of stirring speed.

is minimized. Further, a slight decrease in permeability at 600 r/min could be due to the high turbulence caused by stirring, resulting in displacement of carrier from the membrane pore.

Hence, a stirring speed of 500 r/min was maintained throughout the subsequent SLM investigations.

2.6 Effect of Cu(II) ion concentration in feed phase

The influence of the initial Cu(II) concentration on the transport of Cu(II) by D2EHPA-coconut oil LM was investigated. Variation of Cu(II) concentration in the feed was studied from 7.8×10^{-4} – 78.7×10^{-4} mol/L (50–500 mg/L), when the receiving phase contained a negligible concentration of Cu(II). The results of Cu(II) transport flux through the membrane as a function of Cu(II) concentration is shown in Fig.6. The result shows that the cation flux initially increased sharply from 4.1×10^{-9} to 9.2×10^{-9} mol/(m²·s) at the initial feed concentration of 23.61×10^{-4} mol/L and beyond this became independent of the initial concentration, ranging from 31.4×10^{-4} to 78.7×10^{-4} mol/L. At lower Cu(II) concentrations, the initial flux is strong function of the initial Cu(II) concentration in the source phase; thus, the permeation process is controlled by diffusion of Cu(II) species in the lower range of concentrations (Alguacil, 2001; Fatima *et al.*, 1999).

$$J \propto C_{(\text{Cu})\text{feed}} \quad (3)$$

Hence, there should be an increase in flux with an increase in metal concentration. Evidently, this is true up to 31.4×10^{-4} mol/L concentration of Cu(II), beyond which J became constant, probably due to membrane saturation and lower effective membrane area in the SLM and secondly due to maximisation as a result of saturation of membrane pores with metal carrier species and build-up

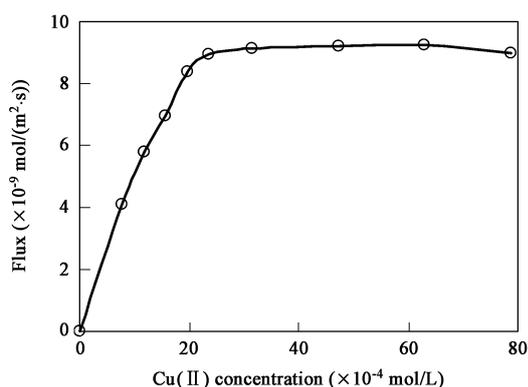


Fig. 6 Effect of initial Cu(II) concentration on the transport flux.

of the carrier layer on the membrane interface (Alguacil, 2001), enhancing the retention of the separating constituent on the entry side and thus causing the permeability flux to be constant.

The summary of the experiments conducted on the optimization of SLM transport of Cu(II) by D2EHPA is presented in Table 1.

2.7 Feed to strip ratio

In order to increase the enrichment of Cu(II) concentration in the strip phase the same strip solution was reused for further repetition of the transport studies. On continuous repetition of the procedure up to five runs at the optimal conditions, without change of strip solution the average flux for five runs was 6.5×10^{-9} mol/(m²·s), where as the flux obtained during fresh strip solution was 5.8×10^{-9} mol/(m²·s). At the end of the fifth run the Cu(II) concentration in the feed phase was below 1.5×10^{-6} mol/L (0.1 mg/L). Thus a concentration factor of five can be achieved easily. It shows that the D2EHPA-coconut oil LM has efficiency of uphill transport and achieves a concentration factor > 5.

2.8 Studies on LM stability

In order to evaluate the LM loss, ten consecutive transport studies were carried out with out changing the membrane; where as the feed Cu(II) 15.7×10^{-4} mol/L at pH 4.0 and stripping solutions (0.25 mol/L H₂SO₄) were replaced for each run. In these studies the Cu(II) transport flux was the same as the first run indicating the stability of the LM for 110 h. The average flux value for these ten studies is 6.4×10^{-9} mol/(m²·s). This longer lifetime of the membrane was related to the stability of the D2EHPA-coconut oil LM with the PTFE membrane.

The solubility of the D2EHPA-coconut oil with the aqueous phase was evaluated by transport experiments with and without the aqueous solutions presaturated with the organic membrane phase. It is apparent that in the range 0–8 h, there was no change in the flux value of 7.2×10^{-9} mol/(m²·s) with the presaturated aqueous solutions and the experiments without the presaturated aqueous solution. This might be explained by the non-solubility of D2EHPA-coconut oil with the aqueous phase and also the low solubility of the carrier D2EHPA in water (< 0.01%). During similar studies for the transport of Cu(II) through LIX 984N (Yang and Fane, 1999) found the initial loss of membrane liquid in the case of non-presaturated aqueous solutions due to the solubility effect. However, subsequently, the flux values reached similar non-presaturated and presaturated aqueous solution studies. Yang and Fane

Table 1 Summary of optimum conditions for transport of Cu(II) by D2EHPA

Sl. No.	Parameter	Range studied	Optimum value chosen
1	SLM pore size (μm)	0.2–1.0	0.5
2	Feed phase pH	2.0–6.0	4.0
3	Stripping reagent (H ₂ SO ₄) concentration (mol/L)	0.05–0.50	0.25
4	Effect of D2EHPA concentration (mol/L)	3.1 – 21.38×10^{-4}	12.4×10^{-4}
5	Effect of stirring speed (r/min)	200–800	500
6	Effect of initial copper feed concentration (mol/L)	7.8 – 78.7×10^{-4}	23.61×10^{-4}

(1999) reported that due to the solubility of LM in the aqueous phases the Cu(II) transfer rate decreased gradually with time. They suggested that the slight decrease in transport efficiency could be increased by re-impregnation of the membrane substrate. This regeneration technique can also adopt for stabilizing the SLMs.

2.9 Transport mechanism

The extractant (D2EHPA) is dissolved in the membrane phase as a dimer form in non-polar solvents (Wieczorec *et al.*, 1997), which reacts at the donor phase-membrane interface with the Cu(II) cation by ion exchange of protons. The formed neutral complex diffuses across the membrane and reacts with the protons at the membrane-acceptor interface releasing the Cu(II) cation. The copper ions are stripped from the membrane phase and concentrated in the stripping phase. The regenerated carrier molecule starts the next cycle. The driving force for the mass transfer is an excess of protons in the acceptor solution compared to the donor solution. The plot of $\log C_{Cu}$ versus $\log C_{D2EHPA}$ is shown in Fig.7. The slope value one reveals that one molecule of D2EHPA involved in the transport of the one molecule of Cu(II) through the D2EHPA-coconut oil liquid membrane. The following stoichiometric equation can be arrived:



2.10 Transport kinetics

The concentration time profile of Cu(II) transport was studied over a time period of 11 h under optimum conditions. Fig.8 shows the concentration profile of Cu(II) in the feed and strip solution as a function of time. Cu(II) gets transported into the stripping solution with the increase in time. The SLM transport of Cu(II) follows the first order kinetics, as evident from straight line of Fig.9. The developed D2EHPA-coconut oil SLM system had the mass

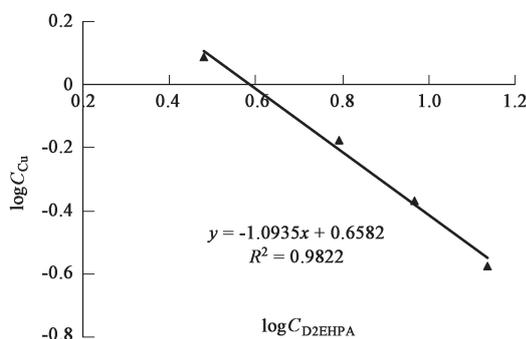


Fig. 7 Stoichiometry plot for the transport of Cu(II) through D2EHPA-coconut oil LM.

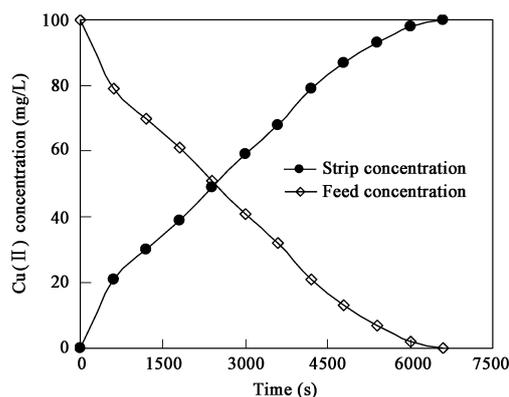


Fig. 8 Concentration profile of Cu(II) in the feed and strip solution as a function of time.

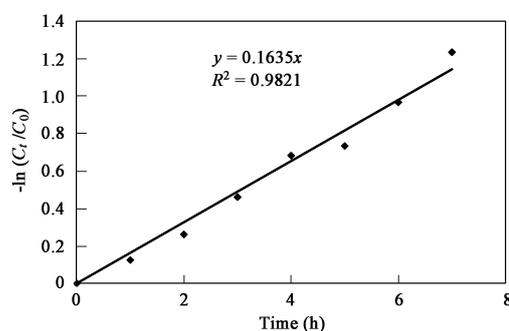


Fig. 9 Kinetic plot for transport of Cu(II) by SLM.

transfer coefficient (k) of 2.9×10^{-4} m/s, which was calculated from Eq.(5) as described earlier (Yang *et al.*, 2003).

$$\ln(C_t/C_i) = -(Ak/V)t \quad (5)$$

where, C_i is the initial Cu(II) concentration, C_t is the concentration of Cu(II) as a function of time t , V is the volume of the source solution and A is the membrane area. The comparison of mass transfer coefficients (k) for different SLM system is presented in Table 2. Among the carrier diluents presented in Table 2, the present system D2EHPA-coconut oil has the highest mass transfer rate. The mass transfer coefficient in SLM depends on the operating conditions however, for comparing the efficiency of different SLMs the results of k can be used as reported earlier (Yang *et al.*, 2003).

3 Separation of Cu(II) from industrial wastewater

The developed SLM was tested for its applicability to remove and recover Cu(II) from plating bath rinse solution kindly supplied by a copper plating industry

Table 2 Mass transfer coefficient (k) for different SLM system

Sl. No.	Carrier	Diluent	k (m/s)	Reference
1	LIX 984	Kerosene	6.0×10^{-6}	Nuri Ata, 2005
2	Acorga M 5640	Iberfluid	3.7×10^{-5}	Alguacil <i>et al.</i> , 2002
3	D2EHPA	Kerosene	2.0×10^{-6}	Molinari <i>et al.</i> , 2006
4	D2EHPA	Coconut oil	2.9×10^{-4}	This work

Table 3 Characteristics of electroplating bath rinse water

SI. No.	Parameter	Value	SI. No.	Parameter	Value
1	pH	4.2	6	Copper (II) (mg/L)	174
2	Conductivity (mS/cm)	35.9	7	Nickel (mg/L)	0.2
3	Total hardness (mg/L)	13375	8	Chromium (VI) (mg/L)	6.7
4	Chloride (mg/L)	7747	9	Cadmium (mg/L)	0.1
5	Sulphate (mg/L)	3050	10	Zinc (mg/L)	0.4

located in Chennai, India. The general characteristics of the wastewater are presented in Table 3. The wastewater was slightly acidic in nature with Cu(II) value of 174 mg/L. Other heavy metals like Ni, Cr(VI), Cd and Zn were present at 0.2, 6.7, 0.1, and 0.4 mg/L, respectively. The Cu(II) transport studies were carried out at feed copper concentration of 174 mg/L at pH 4.0, 12.4×10^{-4} mol/L D2EHPA-coconut oil in the PTFE membrane as SLM and 0.25 mol/L H_2SO_4 in the strip phase. The feed and strip solution were 150 ml each, stirred at 500 r/min by a magnetic stirrer. Samples were drawn at regular time intervals from feed and strip phase and analysed for Cu(II) concentration. The average flux for the transport of Cu(II) from the real wastewater is 9.1×10^{-9} mol/(m²·s). After 15 h of continuous operating time almost all copper ions were transported to the strip solution and the feed concentration was below 5.0×10^{-3} mg/L. The stripped solution was tested for the presence of other metals and found to below detection limits which confirm the selectivity of the system for Cu(II). In industrial level application large membrane area will be required to treat high volume of wastewater. This large membrane area cost in industrial application may be compensated by higher flux value of Cu(II) transport, which reduces the operating cost and time.

4 Conclusions

The recovery of Cu(II) using D2EHPA carrier in coconut oil has been effectively carried out through a flat sheet SLM. Cu(II) transport is influenced by a series of variables of the feed phase (pH, Cu(II) concentration) and the membrane phase (membrane pore size, D2EHPA concentration). The extracted Cu(II) was stripped from the membrane phase using low strength H_2SO_4 as stripping solution. Cu(II) permeation is independent of D2EHPA at higher carrier concentrations above 12.4×10^{-4} mol/L, indicating the transport process is controlled by the diffusion in the aqueous stagnant film. The stability of the D2EHPA-coconut oil LM was found to be stable for 110 h with up hill transport ability. Thus the application of coconut oil as novel, stable diluent for the separation of Cu(II) is proved. The developed system has the selectivity to separate Cu(II) from plating wastewater in the presence of other heavy metal ions.

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