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Extraction of copper from wastewater through supported liquid membrane using tri-ethanolamine as a carrier

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ABSTRACT

In the present work, the extraction of copper(II) ions through a tri-ethanolamine/cyclohexanone-based supported liquid membrane (SLM), has been investigated. The polypropylene (Celgard 2400) was used as a membrane. The various experimental parameters at room temperature including feed pH, feed, carrier, and strip phase concentration were optimized to acquire the optimum conditions for the extraction of copper(II) ions from waste water. Oxalic acid, sodium carbonate, sodium sulfate, nitric acid, and ethylene-di-amine-tetra-acetate (EDTA) were tested for best stripping reagent for SLM configuration. The extraction time, flux value, stoichiometry of the complex formed, and membrane stability was also investigated. The optimum experimental conditions for copper(II) extraction were 3.5 mol/L tri-ethanol amine (TEA) in the membrane phase as carrier, 1 mol/L hydrochloric acid and 3.17×10^{-3} mol/L copper(II) in the feed, and 0.03 mol/L EDTA in the strip solutions. Under these optimum conditions, the extraction time was found to be 120 min and membrane was stable for about 10 consecutive experiments. The transport efficiency of copper(II) ions was found to be 87% under the optimized conditions.

Keywords: Supported liquid membrane; Tri-ethanolamine; Copper(II); Stripping reagent; Transport efficiency

1. Introduction

Membrane technology has widely been used nowadays for the wastewater treatment and has many advantages over other conventional separation techniques. The energy efficiency, high separation capacity, and selectivity are a few important features of the membrane technology [1–5]. Supported liquid membrane (SLM) is a form of liquid membrane which shows great potential in the hydrometallurgy and wastewater treatment [6–8]. An SLM is made up of an extractant absorbed into the pores of a membrane acting as a support. Mass transport in this system occurs by extracting the metal ions from the aqueous feed phase and releasing it into the aqueous strip phase through the membrane [9,10]. Both of these steps occur in a single unit operation, which is an advantage of SLMs. SLMs are classified according to the different shapes and structures, i.e. flat sheet, tubular, hollow fibers, etc. [11]. The simplicity of operation, least amount of carrier or solvent consumption, high fluxes, and low-operating expenses are the major advantages of SLM over conventional solvent extraction techniques [12,13]. Nowadays SLM technique is

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being used for separation/recovery of metal ions from different hazardous sources.

The concentration of copper is about 50 ppm in the earth's crust [14]. It occurs largely in the form of minerals such as cuprite, azurite, and chalcocite. The main applications of copper are in plumbing, roofing, electrical wires, and industrial machinery. Copper is also used in making alloy such as brass and bronze to gain hardness [15]. Copper is also used in agriculture in the manufacturing of fungicides and nutritional supplements [16].

Copper is a vital component of the human body. It is an important constituent of many proteins, enzymes, and coenzymes. Copper deficiency in the body results in haematological deficiencies, anemia [17], neutropenia [18], thrombocytopenia [19], and skin depigmentation [19]. A high level of copper can cause severe toxicity. High copper consumption may cause kidney loss, pain in intestine, and the deposition of copper in the skin, liver, and brain [19].

The use of SLM technology in the removal of different heavy metal ions from industrial effluents [20] and in hydrometallurgy [21] is of great interest, because of their distinct characteristics. A significant work on copper extraction through liquid membrane using different extractants/carriers has been carried out.

Ren et al. [22] studied a hollow fiber liquid membrane technique for extraction of the copper metal ions from the waste water. Takahashi and Takeuchi [23] employed the hybrid type liquid membrane for the transportation study of copper. The LIX65N in kerosene was used as a carrier which extracted copper(II) from an aqueous sulfate feed into a strip solution containing dilute sulfuric acid. Alaguraj et al. [24] reported the removal of copper(II) ions through an emulsified liquid membrane. The extractant, Alamine, and span-80 (a surfactant) were used as a membrane phase, dissolved in kerosene. The LIX 984NC-based tubular SLM is also used for the extraction of copper ions [25]. The copper extraction was carried out through the hollow fibers containing Aliquat 336 dissolved in kerosene as a carrier and HCl as a stripping reagent [26]. Alguacil et al. [27] employed the MOC-55 TD in Iberfluid for the transport of copper(II) ions through facilitated SLM and they further studied the process using theoretical modeling of mass transfer of the copper ions.

The water reservoirs become contaminated due to different industrial effluents which may contain copper apart from other hazardous materials. Therefore, an efficient process is needed for the removal of copper from different industrial sources. It is necessary to develop the new transport system for the selective removal of copper from the aqueous solution.

The extraction of organic and inorganic compounds from aqueous solution by aliphatic amines and their salts in organic solvents, immiscible in water, is one of the most recent developments in separation technology. In the system, with nitrogen bearing basic extractants, the extraction involves the formation of ammonium salt. Higher the extent of the ion-pair association between alky-ammonium cation and metal ion, higher will be the extractability [28]. There are three classes of amines, i.e. primary, secondary, and tertiary amines. The tertiary amines are widely used in extraction process as compared to primary and secondary amines because the primary amines are highly water miscible and secondary amines are subjected to amide formation during regeneration [29]. High capacity and high selectivity are two important characteristics of tertiary amines for the distribution coefficient and separation factor [30]. Long-chain aliphatic tertiary amines are less soluble in water and are thermally stable [30].

Based on above facts, we aimed to study and develop low-cost amine-based carrier transport method for the removal and recovery of copper from the aqueous solution. The tri-ethanolamine is very efficient complexing agent and forms moderate complexes with most of the metal ions [31]. The solubility of the complex in the organic phase permits the effective transport of metal ions from feed to membrane phase. In our previous papers [32,33], we have carried out the extraction of manganese and zinc metal ions through tri-ethanolamine successfully. Therefore, in the present work we have selected the tri-ethanolamine for the transport of copper through SLM. EDTA was used as the stripping agent and Celgard 2400 as membrane phase. The effect of feed phase concentration, strip phase concentration and carrier concentration have been studied for optimum extraction of copper(II). The optimized conditions have been employed on industrial wastewater to remove copper (II) ions.

2. Experimental

2.1. Reagents

The $CuCl_2$ monohydrated (99.0%) was obtained from Fluka. The TEA (99%) carrier, cyclo-hexanone, EDTA (99%), H_2SO_4 (99%), oxalic acid (99%), formic acid (98%), HNO_3 (65%), and HCl (37%) were purchased from Merck Company. Double-distilled water was used for the preparation of solutions.

2.2. Membrane

The polypropylene film (Celgard 2400) was used as a solid support with thickness of 25 μm, porosity of 41%, and a mean pore diameter of 0.043 μm.

2.3. Permeator cell

The extraction experiments were carried out in permeator cell which consists of two parts, each with 250 cm^3 volume capacity and equipped with flanges to hold the membrane between the compartments of the cell and agitated with electrical stirrers (Fig. 1). The active membrane contact area with aqueous solution was 0.0016 m^2.

2.4. Instruments

The Perkin-Elmer model 400 atomic absorption spectrometer was used for determination of copper ion concentration in the feed and strip solutions. The digital pH meter Neo-Met model 200L was used for determination of pH. The viscosity measurement of tri-ethanolamine in cyclohexanone was carried out by Brookfield Viscometer/Rheometer LVDV-III. The scanning electron microscope model JSM-5910 JEOL (Japan) was used to carry out the SEM analysis.

2.5. Procedure

The SLM was prepared by soaking it, in a solution of tri-ethanolamine (in varied concentrations) in cyclohexanone, for 24 h during which the pores of the membrane are filled with carrier solution by capillary action. Afterward, the membrane was taken out of the carrier solution and allowed to drain off for 5 min to remove excess amount of carrier solution from the surface of the membrane. The membrane was tightly clamped in between the two compartments of the permeator cell, feed, and strip compartments, to be filled with feed and stripping solutions, respectively. The electric stirrer was used in each compartment to stir the solution at 1,500 rpm to avoid polarization of concentration. In the experiments, various copper(II) ions ($0.79–3.97 \times 10^{-3}$ mol/L) and EDTA (0.01–0.05 mol/L) concentrations were used as feed and strip solutions, respectively. After every 60 min, 1 mL of aliquot from the feed and the stripping solutions were withdrawn and analyzed by atomic absorption spectrophotometer.

2.6. Flux measurement

The flux per unit area was determined by the following equation:

$$\text{Flux (J)} = \frac{\text{Change in the copper ion concentration in time interval } \Delta t \ \left(\frac{\text{mol}}{\text{L}}\right) \times \text{Volume of solution in feed (L)}}{\text{Membrane area } (\text{m}^2) \times \Delta t \text{ (s)}} \quad (1)$$

where Δt represents the time interval (s).

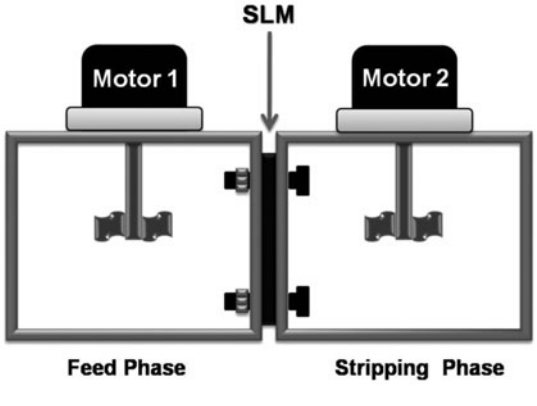

Fig. 1. View of permeator cell.

2.7. Percentage Extraction efficiency

The percentage extraction efficiency was calculated using following equation:

$$\%\ \text{Extraction efficiency} = 100\left(\frac{C}{C_o}\right) \quad (2)$$

where C is the metal ions concentration in the strip side after the completion of extraction process, and C_o is the initial concentration of metal ions in the feed side.

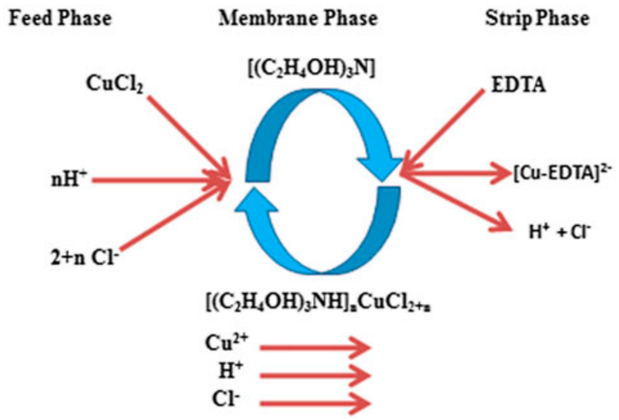

Fig. 2. Transport mechanism of Cu(II) ions through SLM.

3. Theory

3.1. *Proposed mechanism of copper(II) ions transport through SLM*

The extraction chemistry of metal ion through SLM is similar to that of liquid–liquid extraction. In this process, the ion-pair association mechanism is involved in the extraction of copper(II) ion as shown in Fig. 2. During the process the carrier makes a neutral ion-pair complex with the metal ions as shown in the proceeding discussion. This complex is transported through hydrophobic membrane phase. In acidic medium, the protonation of TEA molecule takes place [34], which is as follows:

$$(C_2H_4OH)_3N + nH^+ \rightleftharpoons [(C_2H_4OH)_3NH_n]^{n+} \text{ (a)} \tag{3}$$

where "*n*" may possibly be 1, 2, 3, or 4, maximum protonation up to 4 can take place in TEA molecule as it has one nitrogen and three oxygen atoms. The value of "*n*" will be determined experimentally. Specie (a) will associate with a copper(II) ion in the anionic form of the copper chloride (b).

$$Cu^{2+} + 2Cl^- \rightleftharpoons [CuCl_2] \tag{4a}$$

$$CuCl_2 + Cl^- \rightleftharpoons [CuCl_3]^- \tag{4b}$$

Or in general, depending upon the association number "*n*":

$$CuCl_2 + nCl^- \rightleftharpoons [CuCl_{2+n}]^{n-} \text{ (b)} \tag{4c}$$

At the feed–membrane interface, anionic species (b) will associate with cationic specie (a) of tri-ethanolamine.

$$\begin{aligned}&[(C_2H_4OH)_3NH_n]^{n+}\\&\quad + [CuCl_{2+n}]^{n-} \rightleftharpoons \left[(C_2H_4OH)_3NH_nCuCl_{2+n}\right] \text{ (c)}\end{aligned} \tag{5}$$

Or Eq. (5), can be written as:

$$\begin{aligned}&[CuCl_{2+n}]^{n-} + [(C_2H_4OH)_3N]\\&\quad + n[H^+] \rightleftharpoons \left[(C_2H_4OH)_3NH_nCuCl_{2+n}\right] \text{ (c)}\end{aligned} \tag{6}$$

Specie (c) is permeated through the membrane phase and discharges copper(II) ions at strip–membrane interface due to reaction of copper(II) ions with EDTA of the strip solution. This experiment has been carried out at pH 10, at which the EDTA is in the form of $(EDTA)^{4-}$, which associates with the copper ion very effectively as Cu $(EDTA)^{2-}$ as follows:

$$\begin{aligned}&\left[(C_2H_4OH)_3NH_nCuCl_{2+n}\right] + EDTA \rightleftharpoons (C_2H_4OH)_3N\\&\quad + [Cu\text{–}EDTA]^{2-} + (n+4)H^+ + (2+n)Cl^-\end{aligned} \tag{7}$$

It may be noted that each molecule of EDTA releases four H^+ ions.

It can also be noted from Eq. (7) that Cu-TEA complex, $\left[(C_2H_4OH)_3NH_nCuCl_{2+n}\right]$, becomes unstable in the basic medium, as a result it decomposes into TEA molecules, which remains in the membrane phase, while copper is released into the strip phase as copper-EDTA complex, $[CuEDTA]^{2-}$.

From Eq. (6) the equilibrium constant for copper (II) ion for feed and membrane phase can be given as:

$$K_{Cu} = \frac{\left[(C_2H_4OH)_3NH_nCuCl_{2+n}\right]}{[(CuCl_{2+n})^{n-}][(C_2H_4OH)_3N][H^+]^n} \tag{8}$$

The distribution coefficient of copper(II) ions for between the membrane and the aqueous phase is denoted by λ_{Cu} and can be given as:

$$\lambda_{Cu} = \frac{\left[(C_2H_4OH)_3NH_nCuCl_{2+n}\right]}{\left[(CuCl_{2+n})^{n-}\right]} \tag{9}$$

In the light of Eq. (9), Eq. (8), can be written as:

$$K_{Cu} = \frac{\lambda_{Cu}}{[(C_2H_4OH)_3N][H^+]^n} \tag{10}$$

On rearranging Eq. (10), we obtain:

$$\lambda_{\mathrm{Cu}} = K_{\mathrm{Cu}}[(\mathrm{C_2H_4OH})_3\mathrm{N}][\mathrm{H}^+]^n \tag{11}$$

The Fick's First Law is given as below [35]:

$$J = \frac{\mathrm{d}n}{\mathrm{d}t} = -DA\frac{\mathrm{d}c}{\mathrm{d}x} \tag{12}$$

where J is the rate of diffusion of solute across an area A, known as diffusion flux.

where $\mathrm{d}c/\mathrm{d}x$, is the concentration gradient of the metal ions and $\mathrm{d}n$ is the amount of metal ions crossing the area A in time interval $\mathrm{d}t$.

Since solutions are stirred therefore, the metal ion concentration in feed and strip phases, C_{f} and C_{s}, respectively, are maintained at a uniform level throughout the bulk, i.e. there is no concentration gradient in the feed and strip phases. The two solutions are separated by a membrane of thickness "l", as shown schematically in Fig. 3. The membrane contains pores filled with extractant dissolved in diluent which is responsible for the transport of metal ions. The concentration of the metal ions falls linearly within the membrane constituting a concentration gradient, as shown in Fig. 3. Which is given as follows:

$$-\frac{\mathrm{d}c}{\mathrm{d}x} = \frac{C_{\mathrm{fm}} - C_{\mathrm{sm}}}{l} \tag{13}$$

According to the Fick's First Law, the rate of flow through the membrane is:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = DA\frac{C_{\mathrm{fm}} - C_{\mathrm{sm}}}{l} \tag{14}$$

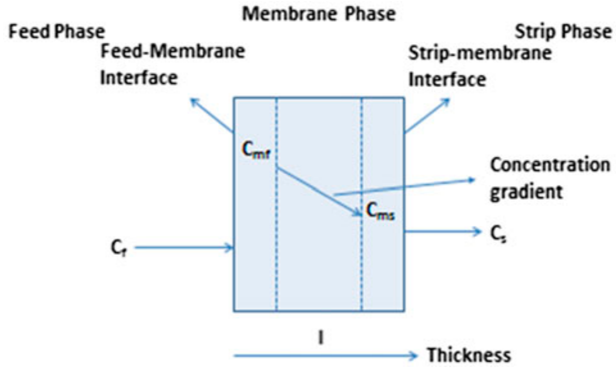

Fig. 3. Concentration gradient of copper(II) ions at the feed and strip sides of the membrane.

Since the concentration gradient, $\mathrm{d}c/\mathrm{d}x$, is negative which cancels out the negative sign in Eq. (12), and hence in Eq. (14):

The diffusion coefficient D can be readily calculated from the measurement of the rate of flow, $\mathrm{d}n/\mathrm{d}t$; the area A, thickness l, and the concentration difference $C_{\mathrm{fm}} - C_{\mathrm{sm}}$, where C_{fm} and C_{sm} are concentrations of metal ions at the membrane interfaces of feed and strip sides, respectively.

The distribution coefficient of Cu(II) ions at the membrane interfaces of the feed and strip side can be given by λ_{f} and λ_{s}, respectively, i.e.

$$\lambda_{\mathrm{f}} = \frac{C_{\mathrm{fm}}}{C_{\mathrm{f}}} \text{ and } \lambda_{\mathrm{s}} = \frac{C_{\mathrm{sm}}}{C_{\mathrm{s}}} \tag{15}$$

where C_{f} and C_{s} represent feed and strip phase concentration of Cu(II) ions, respectively.

From Eq. (15) we can write:

$$C_{\mathrm{fm}} = \lambda_{\mathrm{f}}C_{\mathrm{f}} \text{ and } C_{\mathrm{sm}} = \lambda_{\mathrm{s}}C_{\mathrm{s}} \tag{16}$$

And with the help of Eq. (16), Eq. (14) becomes

$$J = DA\left(\frac{\lambda_{\mathrm{f}}C_{\mathrm{f}} - \lambda_{\mathrm{s}}C_{\mathrm{s}}}{l}\right) \tag{17}$$

As there is no extraction from the strip to the membrane phase, i.e. there is no back extraction, so $\lambda_{\mathrm{s}} \rightarrow 0$ and as a result, $\lambda_{\mathrm{s}}\ C_{\mathrm{s}} \approx 0$ and Eq. (17), converts to

$$J = DA\left(\frac{\lambda_{\mathrm{f}}C_{\mathrm{f}}}{l}\right) \tag{18}$$

In our case $\lambda_{\mathrm{f}} = \lambda_{\mathrm{Cu}}$, as given by Eq. (11), thus Eq. (18) may be written as:

$$J = DA\frac{K_{\mathrm{Cu}}[(\mathrm{C_2H_4OH})_3\mathrm{N}][\mathrm{H}^+]^n C_{\mathrm{f}}}{l} \tag{19}$$

According to Wilke–Chang relation:

$$D = \frac{\acute{k}T}{\eta} \tag{20}$$

where T is the absolute temperature, η is the viscosity, and $\acute{k}$ is constant and so

$$J = \frac{\acute{k}T}{\eta}A\frac{K_{\mathrm{Cu}}[(\mathrm{C_2H_4OH})_3\mathrm{N}][\mathrm{H}^+]^n C_{\mathrm{f}}}{l} \tag{21}$$

Since $\acute{k}$, K_{Cu}, T, l, and A are constants, and if C_{f} does not change rapidly, then C_{f} can be taken approximately constant for a short interval of time, combining all these as $\check{K}$ (i.e. $\check{K} = \acute{k}K_{\mathrm{Cu}}T\ C_{\mathrm{f}}A/l$) we obtain:

$$J = \frac{\check{K}[(\mathrm{C_2H_4OH})_3\mathrm{N}][\mathrm{H}^+]^n}{\eta} \tag{22}$$

Readjusting Eq. (22):

$$J\eta = \check{K}[(\mathrm{C_2H_4OH})_3\mathrm{N}][\mathrm{H}^+]^n \tag{23}$$

Taking log of Eq. (23):

$$\log J\eta = \log \check{K} + \log[(\mathrm{C_2H_4OH})_3\mathrm{N}] + n \log[\mathrm{H}^+] \tag{24}$$

Since a specially designed experiment was carried out by keeping K, $[(\mathrm{C_2H_4OH})_3\mathrm{N}]$, C_{f} as constants in order to study the effect of H^+ concentration on extraction of copper ions, therefore, the terms involving these parameters in Eq. (24) can be collected in a single parameter as follows:

$$L = \log \check{K} + \log[(\mathrm{C_2H_4OH})_3\mathrm{N}] \tag{25}$$

Hence Eq. (25), becomes:

$$\log J\eta = L + n \log[H^+] \tag{26}$$

From the above Eq. (25) the stoichiometry of the Cu-TEA complex formation can be determined by calculating the number of H^+ ion "n" associated with the TEA molecule in the form of $[(\mathrm{C_2H_4OH})_3\mathrm{NH}_n]^{n+}$. Eq. (25) is a straight line equation in which log $J\eta$ vs. log[H^+] can be plotted, from the slope of this curve we can calculate the number of protons "n" associated with the TEA carrier.

4. Result and discussion

4.1. The effect of TEA carrier concentration on copper(II) extraction

The effect of TEA concentration on the extraction of copper has been graphically represented in Fig. 4. The concentration of TEA has been studied in the range from 1 to 4 mol/L. The transport of Cu(II) ions increases with the increase in the concentration of TEA. From the figure, it is clear that with the passage of time, the concentration of Cu(II) ions decreases in feed (Fig. 4(a)), while at the same time it increases in strip phase (Fig. 4(b)). It can be carefully analyzed that at any particular time, the concentration of copper ions in the feed phase supplements that of in the strip phase, i.e. it shows an additive behavior. It can be further noted that with the increase in TEA concentration the extraction of copper increases, reaches at maximum at 3.5 mol/L of TEA, beyond that it decreases. The initial increase in the transport of copper with the increasing TEA concentration corresponds to the high transport ability of the carrier which enhances the rate of formation of Cu-TEA complex and facilitates the transport of copper(II) ion and hence the distribution coefficient value of copper(II) ion at the feed–membrane interface increases with increase in the concentration of TEA. The decline in the extraction of copper (II) ion beyond 3.5 mol/L concentration of TEA is due to the high viscosity of TEA which renders the complex difficult to diffuse in the membrane phase [35]. Thus, the optimum extraction value was obtained at 3.5 mol/L of TEA.

Fig. 5 indicates the influence of TEA concentration on the flux value of Cu(II) ion extraction. The flux per unit area of copper ions was calculated using Eq. (1). There is a gradual increase in the flux value with increasing concentration of TEA, and it reaches to a maximum value of 2.84×10^{-4} mol/m^2 s at 3.5 mol/L TEA. As discuss previously, this tumble in flux value attributed to the increase in TEA solution viscosity, which impedes the transport of copper(II) ions due to the limited movement of Cu-TEA complex ion towards the strip side.

4.2. The effect of concentration of Cu(II) ion on extraction

In the case of EDTA strippent, the extraction of copper(II) ions is being strongly affected by its own concentration. In the experiment, 1 mol/L HCl in the feed and 0.03 mol/L EDTA in strip solution at pH 10 were employed. The copper concentration was varied from 0.79 to 3.97×10^{-3} mol/L. The variation in copper(II) ion concentration with respect to time both for the feed and strip solutions have been represented in Fig. 6. With the passage of time, the copper(II) ion concentration in the feed decreases and increases in strip phase. It can be noted from Fig. 6 that the extraction becomes maximum at 3.17×10^{-3} mol/L of copper ion concentration beyond which it decreases. This could be attributed to the following reason. As mentioned in Eq. (7) with the associated discussion, copper forms a complex with EDTA which is present in the strip side and plays the role of strippent.

$$\mathrm{Cu}^{2+} + \mathrm{EDTA} \rightarrow \mathrm{Cu{-}EDTA}^{2-} \tag{27}$$

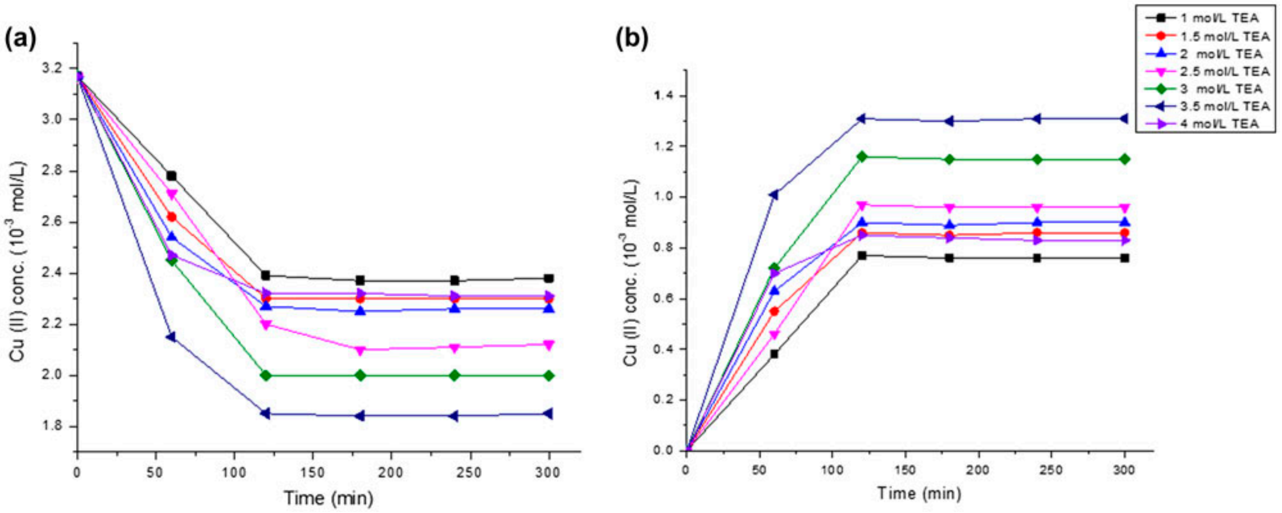

Fig. 4. Variation in Cu(II) ion concentration with time in feed (a) and strip (b) solutions at various concentrations of TEA ($[Cu^{2+}] = 3.17 \times 10^{-3}$ mol/L, [HCl] = 1 mol/L, [EDTA] = 0.02 mol/L, [TEA] = 1–4 mol/L, pH 10).

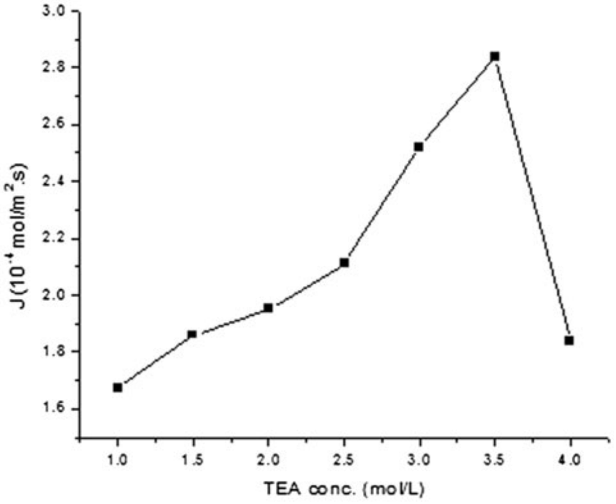

Fig. 5. Effect of TEA concentration on flux ($[Cu^{2+}] = 3.17 \times 10^{-3}$ mol/L, [HCl] = 1 mol/L, [EDTA] = 0.02 mol/L, [TEA] = 1–4 mol/L, pH 10).

EDTA has a strong affinity for the formation of such complex with copper this is true up to 3.17×10^{-3} mol/L copper(II) concentration, in the present case, with the further increase in copper(II) concentration the neutral Cu_2–EDTA complex is formed which is insoluble in aqueous medium and results in the formation of precipitate [36].

$$Cu^{2+} + Cu\text{–}EDTA^{2-} \rightarrow Cu_2\text{–}EDTA \qquad (28)$$

The deposition over the surface of the membrane might have clogged the membrane pores and thus, altered the extraction.

Fig. 7 shows the effect of Cu(II) ion concentration on the flux. The flux exhibits the maximum value of 3.28×10^{-4} mol/m^2 s at 3.17×10^{-3} mol/L of copper ion concentration beyond which it shows a decreasing trend. The decrease in the flux value is attributed to the aforementioned reason.

4.3. The effect of concentration of HCl on copper(II) extraction

The effect of HCl concentration on the copper transport from feed to strip phase is shown in Fig. 8(a) and (b). The Cu(II) ions transportation is affected by the presence of HCl in which the Cu(II) ions are converted into $CuCl_2$ but an excess amount of HCl leads to the formation of $[CuCl_n]^{2-n}$ complex, while the H^+ ions protonate the TEA molecules. The $[CuCl_n]^{2-n}$ complex ions associate with the protonated TEA molecules at feed–membrane interface and thus further process of transportation is carried out. A limited chloride ions concentration also have synergetic effect on the transport of copper. The Cl^-/Cu^{2+} ratio possibly affect the efficiency of extraction. Insufficient amount of Cl^- ions leads to the formation of $CuCl^+$, while with the excess of Cl^- ions, $CuCl_3^{3-}$ or $CuCl_4^{2-}$ were mainly formed [37] in these complexes Cl^-/Cu^{2+} ratio increases which helps the copper ions transportation. Further increase in the chloride ions

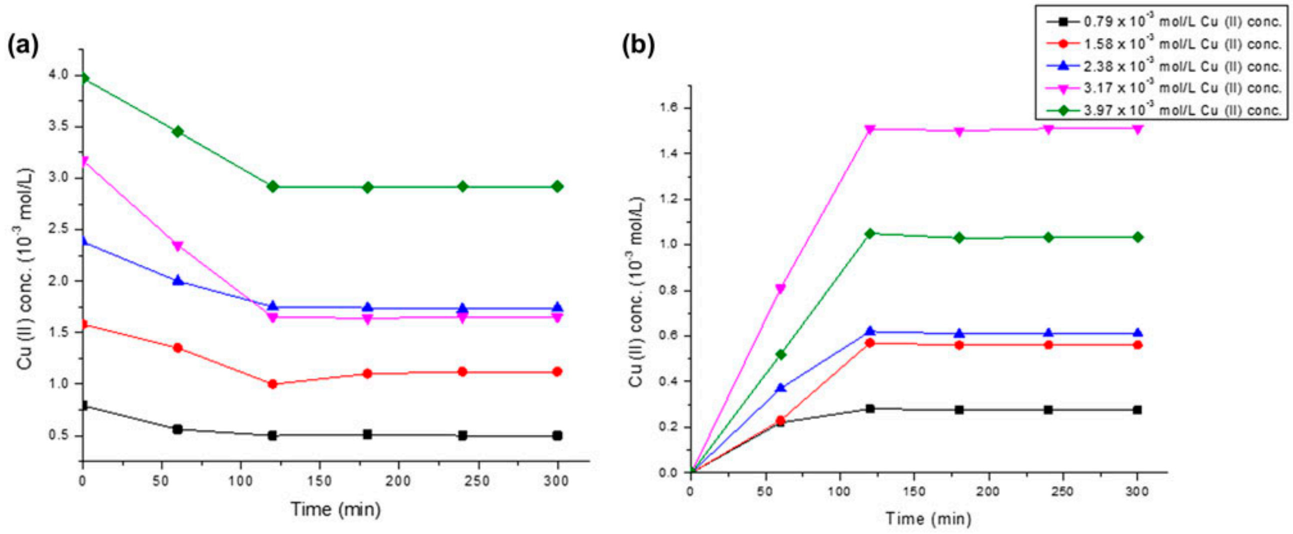

Fig. 6. Variation in Cu(II) ion concentration with time in feed (a) and strip (b) solutions at various concentrations of Cu (II) ions ($[Cu^{2+}] = 0.79–3.97 \times 10^{-3}$ mol/L, [HCl] = 1 mol/L, [EDTA] = 0.03 mol/L, [TEA] = 3.5 mol/L, pH 10).

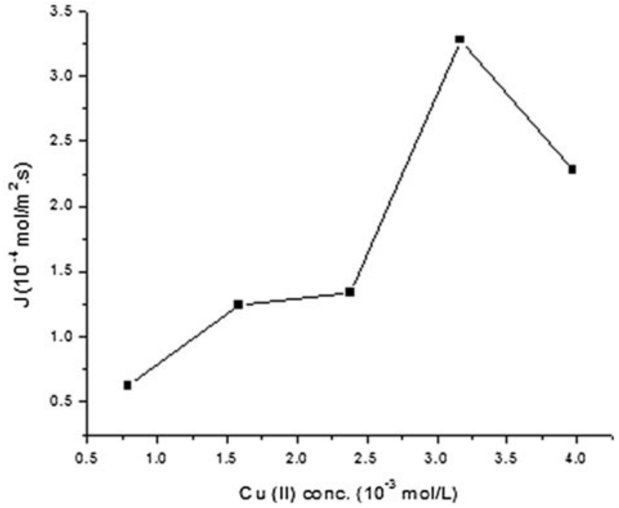

Fig. 7. Effect of Cu(II) ion concentration on flux ($[Cu^{2+}] = 0.79–3.97 \times 10^{-3}$ mol/L, [HCl] = 1 mol/L, [EDTA] = 0.03 mol/L, [TEA] = 3.5 mol/L, pH 10).

concentration inhibits the formation of $[CuCl_n]^{2-n}$ complex due to common ion effect.

Fig. 9 illustrates the effect of HCl concentration on the flux of copper ions through the membrane. As can be noted from the figure, the flux value increases as the concentration of HCl increases and gives a highest flux value of 2.80×10^{-4} mol/m^2 s at 1 mol/L HCl and then it gradually drops down. The decrease in the flux beyond 1 mol/L HCl is due to the excess amount of H^+ concentration which suppresses the extraction. If the amounts of protons increase beyond 1 mol/L HCl, there may be difficulties in dissociating MCl_4^{2-} from H_2MCl_4 in the feed phase [38]. The result causes the decrease of flux.

The pH change of the feed solution, with respect to time, is shown in Fig. 10. During a particular extraction experiment the pH almost remains constant at the beginning and rises gradually and then an abrupt increase is observed between the 80th and 120th minutes of the experiment. The initially increase in the pH may be attributed to the reason that the protons are reacting with carrier (TEA) molecules at the feed–membrane interface to convert it into a charged species by protonation. Since protons are transferred towards the strip side, which results in the further increase in pH.

4.3.1. Determination of "n"

Eq. (25) can be used to determine the number of H^+ ion "n" associated with TEA in the form of $[(C_2H_4OH)_3NH_n]^{n+}$. This equation is a straight line equation where $\log J\eta$ can be plotted on the y axis and $\log[H^+]$ on the x axis. The value of "n" can be determined from the slope of the curve.

$$\log J\eta = L + n \log[H^+] \qquad (29)$$

Fig. 11 shows the plot of $\log J\eta$ vs. $\log[H^+]$. The plot shows an increasing trend in the flux with increase in H^+ ion concentration. The slope of the curve gives a value of 1. Thus, one H^+ ion is associated with the complex $[(C_2H_4OH)_3NH_n]^{n+}$ that is, the complex has

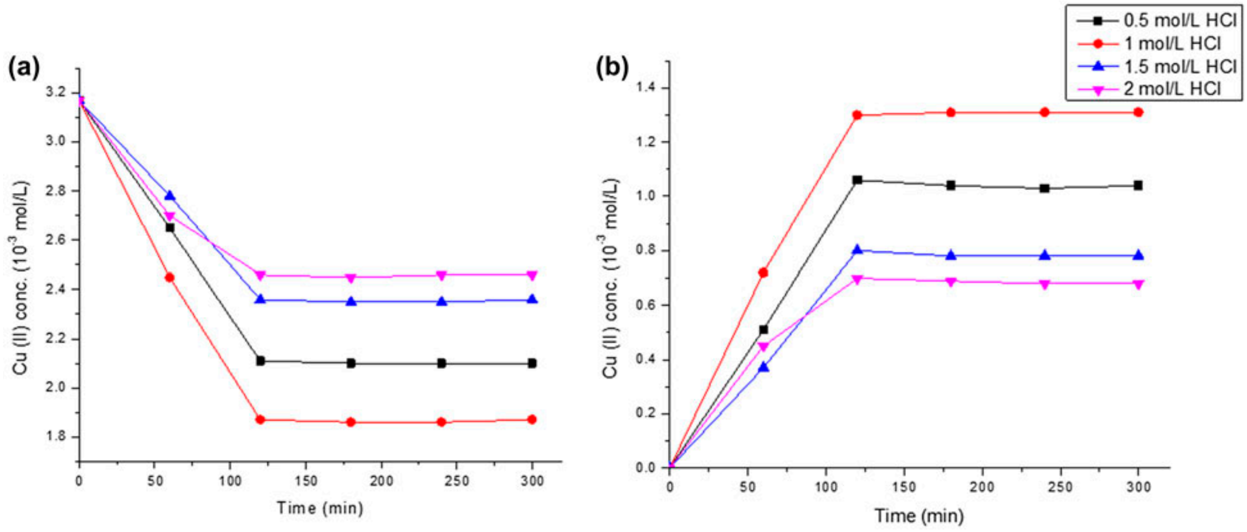

Fig. 8. Variation in Cu(II) ion concentration with time in feed (a) and strip (b) solutions at various concentrations of HCl ($[Cu^{2+}] = 3.17 \times 10^{-3}$ mol/L, [HCl] = 0.5–3 mol/L, [EDTA] = 0.03 mol/L, [TEA] = 3.5 mol/L, pH 10).

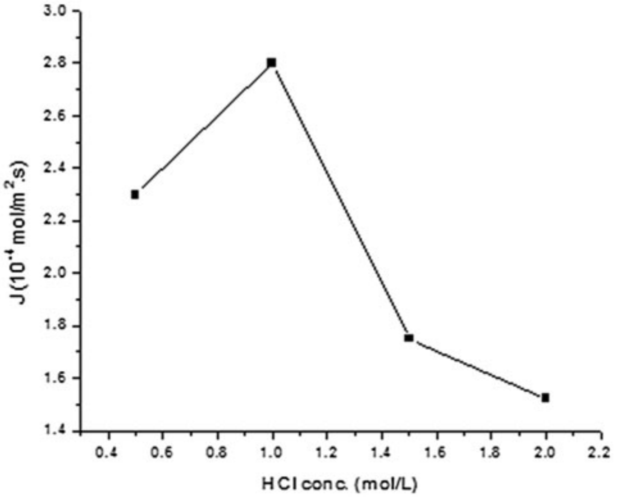

Fig. 9. Effect of HCl concentration on flux of copper ions ($[Cu^{2+}] = 3.17 \times 10^{-3}$ mol/L, [HCl] = 0.5–2 mol/L, [EDTA] = 0.03 mol/L, [TEA] = 3.5 mol/L, pH 10).

the form like $[(C_2H_4OH)_3NH]^+$ and further we can say that the copper chloride anionic complex has the form of $[CuCl_{2+1}]^-$. The copper-TEA complex, thus attain the form $\left[(C_2H_4OH)_3NHCuCl_{2+1}\right]$. Hence, in the light of this discussion Eq. (5), can be written as:

$$[(C_2H_4OH)_3NH]^+ + [CuCl_{2+1}]^- \rightleftharpoons \left[(C_2H_4OH)_3NHCuCl_{2+1}\right] \tag{30}$$

Which predicts the stoichiometry of the complex formation.

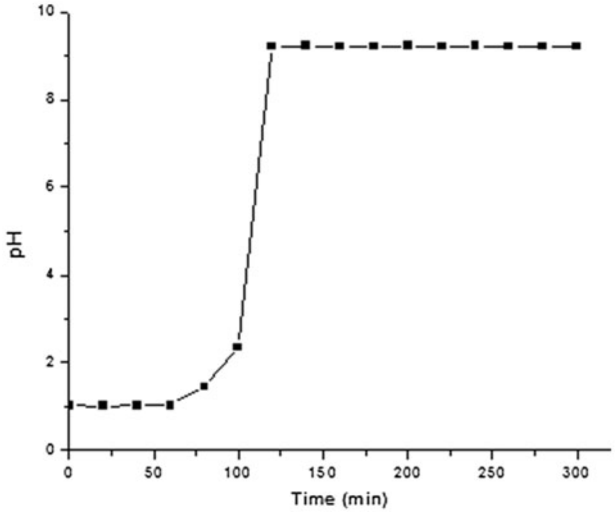

Fig. 10. Variation in pH of feed solution with time ($[Cu^{2+}] = 3.17 \times 10^{-3}$ mol/L, [HCl] = 1 mol/L, [EDTA] = 0.03 mol/L, [TEA] = 3.5 mol/L, pH 10).

4.4. The effect of nature and concentration of stripping reagents on the copper(II) extraction

Effectiveness of various stripping reagents such as, sodium carbonate, nitric acid, oxalic acid, sodium sulfate, and EDTA, were studied for the extraction of copper(II) ions and it was noticed that the EDTA is a best stripping agent among all these reagents as shown in Fig. 12. The formation of Cu-EDTA^{2-} complex ion depends on the concentration of the EDTA and pH of the strip solution. It has been

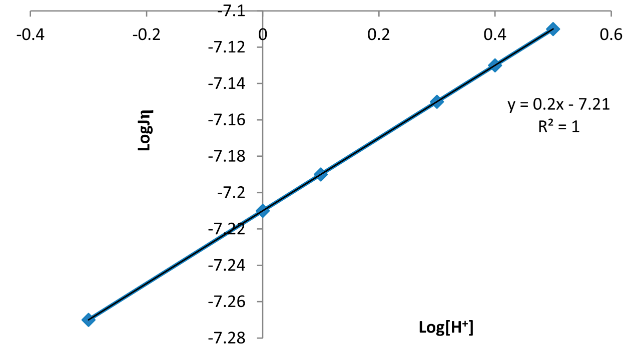

Fig. 11. The plot of log $J\eta$ vs. log[H^+].

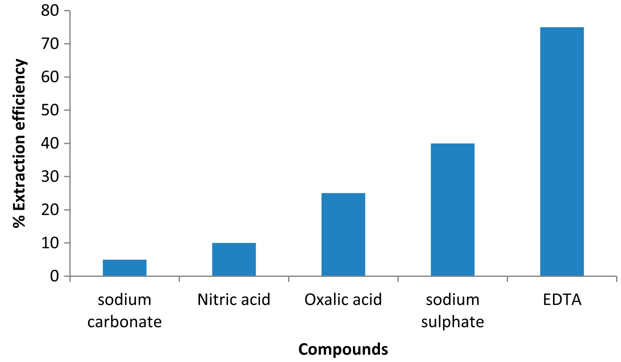

Fig. 12. Effect of different stripping reagents on the extraction of copper(II).

observed that the pH has a high influence on the extraction process. Good extraction is achieved at alkaline medium (pH 10) because in alkaline solution, the formation of Cu-EDTA^{2-} takes place while in acidic medium, the precipitates of Cu_2-EDTA complex is occur [39]. Thus, the stripping solution should be kept constant at pH 10 using ammonia buffer solution.

The effect of EDTA concentration on the Cu(II) ion extraction is shown in Fig. 13. The study was conducted at pH 10 in the strip side keeping other parameters at constant level such as 1 mol/L HCl concentration and 3.17 × 10^{-3} mol/L Cu(II) ions in the feed phase and 3.5 mol/L TEA in membrane phase. The concentration of EDTA was investigated in the range of 0.01–0.05 mol/L. From the curves in (Fig. 13), it can be observed that the extraction of Cu(II) ion increases with the increase in the concentration of EDTA up to 0.03 mol/L, and then decreases gradually. Beyond 0.03 mol/L EDTA, the extraction abruptly falls, which might be due to overcrowding of EDTA molecules at strip–membrane interface, which blocks the membrane. Below 0.03 mol/L, fewer EDTA molecules were available to form a Cu-EDTA^{2-}complex ion [39] and hence extraction of copper is dependent upon the concentration of EDTA. The optimum concentration of EDTA is 0.03 mol/L.

$$\left[(C_2H_4OH)_3NH_nCuCl_{2+n}\right] + \text{EDTA} \rightleftharpoons (C_2H_4OH)_3N + [\text{Cu–EDTA}]^{2-} + (n+4)H^+ + (2+n)Cl^- \tag{31}$$

The flux profile of copper ions is displayed in Fig. 14. Initially, the flux value increases somewhat rapidly up

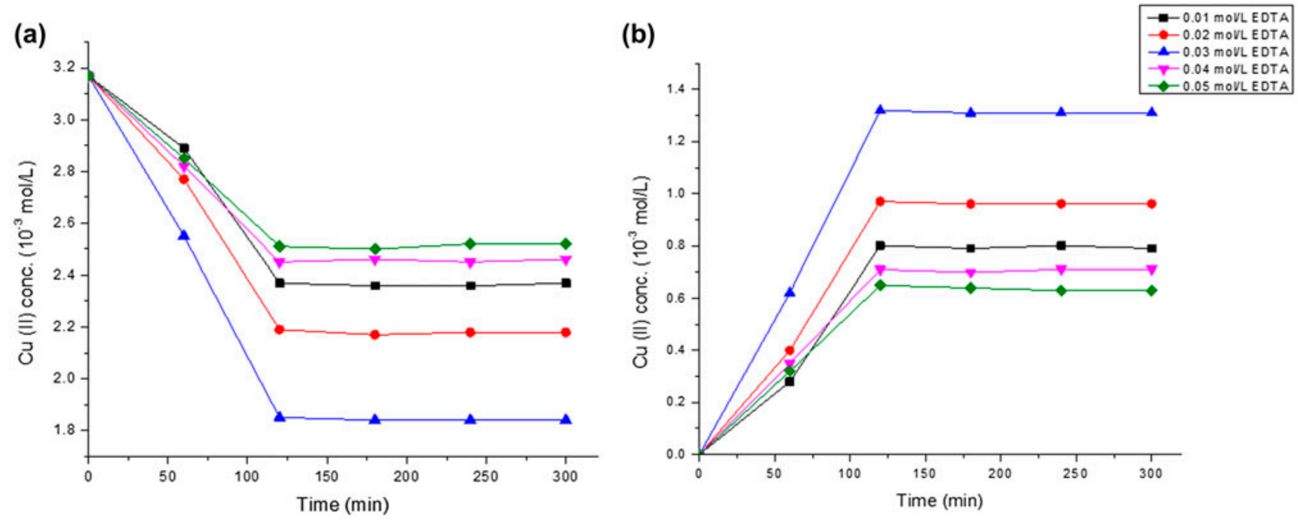

Fig. 13. Variation in Cu(II) ion concentration with time in feed (a) and strip (b) solutions at various concentrations of EDTA ([Cu^{2+}] = 3.17×10^{-3} mol/L, [HCl] = 1 mol/L, [EDTA] = 0.01-0.05 mol/L, [TEA] = 3.5 mol/L, pH 10).

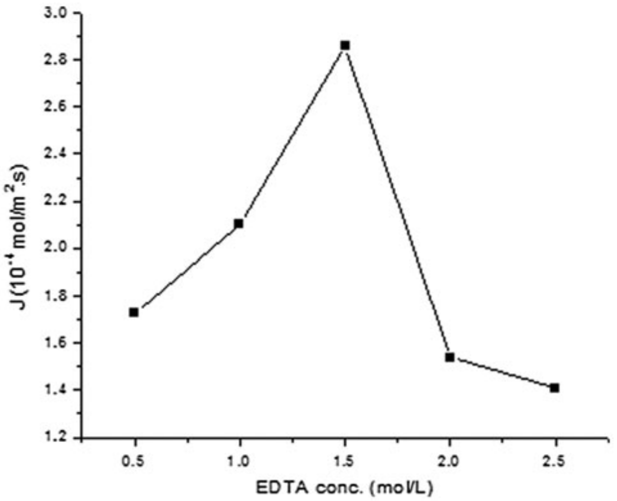

Fig. 14. Effect of EDTA concentration on flux ($[Cu^{2+}] = 3.17 \times 10^{-3}$ mol/L, [HCl] = 1 mol/L, [EDTA] = 0.01–0.05 mol/L, [TEA] = 3.5 mol/L, pH 10).

to 0.03 mol/L, where after, it decreases with concentration. From the profile the maximum value of flux can be noted which is 0.03 mol/L of EDTA.

4.5. SEM analysis

The membrane is an important part of the SLM technique and influences the transport of metal ions. The surface morphology of the membrane, Celgard 2400, was evaluated by scanning electron microscope images (SEM). The SEM images of the membrane before and after the extraction are given in Fig. 15(a) and (b). The porous cracks or grooves in the membrane can be seen before the extraction while some deposits can be seen after the experiment along with the pores and cracks. Fig. 15(c) shows the cross-sectional image of the membrane, from which the thickness of the membrane can be calculated and it is found to be 20.36 μm.

4.6. Extraction time

Fig. 16 shows the effect of extraction time on copper ions. At optimum conditions, the extraction of copper(II) ions increases with time and after 120 min about 87% of copper(II) ion has been extracted. The concentration of copper(II) ions become independent of the time after 120 min and further transport of copper ions to strip phase did not occur.

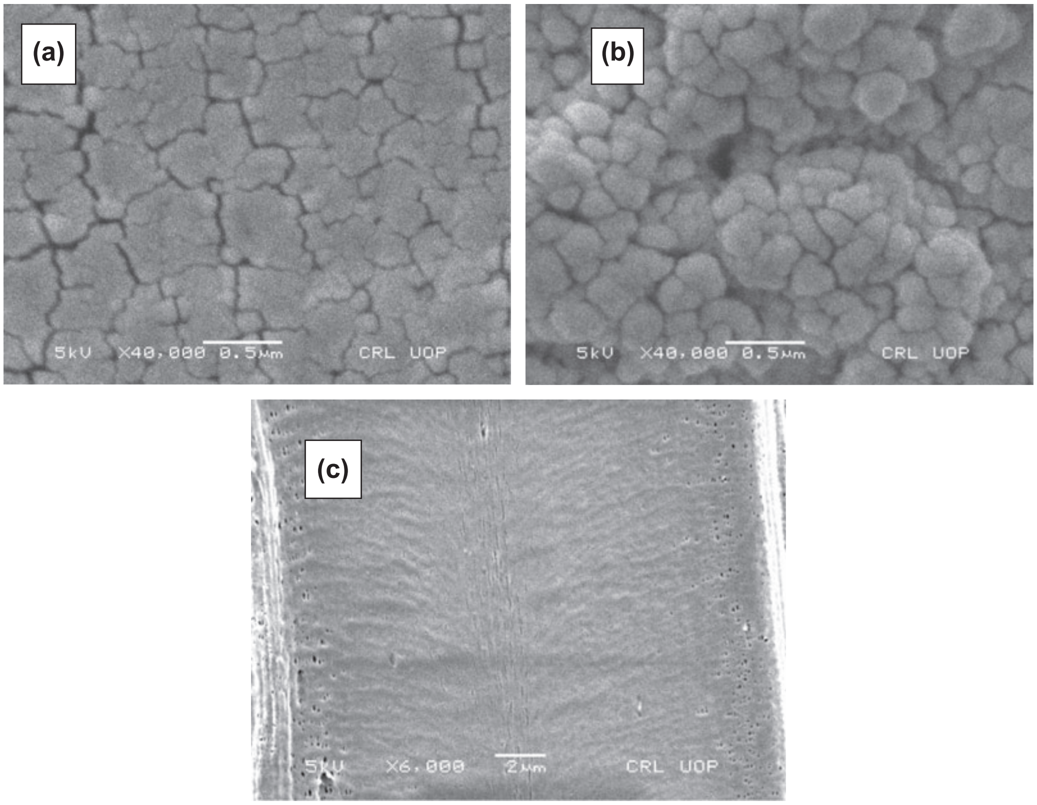

Fig. 15. SEM images of membrane: (a) before extraction, (b) after extraction, and (c) cross section image.

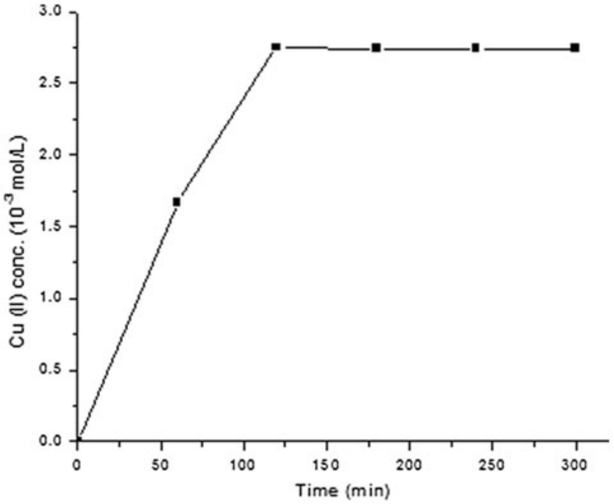

Fig. 16. Variation in Cu(II) ion concentration with time ([Cu^{2+}] = 3.17×10^{-3} mol/L, [HCl] = 1 mol/L, [EDTA] = 0.03 mol/L, [TEA] = 3.5 mol/L, pH 10).

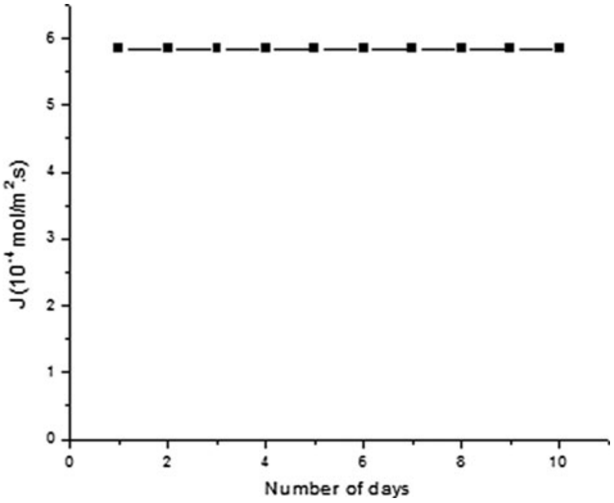

Fig. 17. Stability of SLM, flux vs. time ([Cu^{2+}] = 3.17 × 10^{-3} mol/L, [HCl] = 1 mol/L, [EDTA] = 0.03 mol/L, [TEA] = 3.5 mol/L, pH 10).

5. Membrane stability

Low stability of membrane is one of the main drawbacks of the SLM technique. The porous materials are used as supports for SLMs in which the carrier molecules are embedded in membrane pores. After prolonged use, the performance of membrane decreases. This happens due to loss of membrane solvent or carrier, formation of emulsion, chemical degradation, etc. [40,41]. To study the long term membrane stability, the extraction experiments were carried out consistently for 10 d (one experimental run per day) under the optimum conditions. For all these experiments the membrane was impregnated only once, while changing the feed and strip solutions after each run. The cell was kept filled with distilled water, between the successive experiments, in order to prevent the dryness of the membrane. The optimum experimental conditions were as follows; feed Cu(II) ion concentration was at 3.17 × 10^{-3} mol/L and 1 mol/L HCl, the TEA, and EDTA concentrations were kept constant at 3.5 mol/L in cyclohexanone and 1 mol/L, respectively, and the stirring speed was at 1,500 rpm. The result reveals (Fig. 17) that the efficiency of the membrane has not decreased during these experiments and hence, during all the experiments, the extraction of the copper(II) ion was not affected and stayed at 87%.

6. Extraction of copper(II) from industrial wastewater

The optimized experimental conditions were used for the removal of copper from match industrial wastewater. The wastewater sample was analyzed for different metal ions, the result is shown in Table 1 (column 2 and 3). The wastewater was filtered with Whattman filter paper; 80 mL of filtrate was diluted up to 250 mL with distilled water and taken as the feed solution. The extraction experiment was performed at optimum conditions as mentioned in Section 5. Analysis of wastewater was carried out through AAS and result is shown in Figs. 18 and 19

Table 1
Analysis of match industry wastewater

		Concentration of metals (mol/L)		
S. No.	Metal ion	Before extraction (feed phase)	After extraction (strip phase)	% Recovery
1	Cu	1.50 × 10^{-4}	1.31 × 10^{-4}	87.33
2	Cd	4.45 × 10^{-6}	0.45 × 10^{-6}	10.11
3	Pb	6.82 × 10^{-5}	1.25 × 10^{-6}	1.83
4	Zn	3.18 × 10^{-5}	1.10 × 10^{-6}	3.45

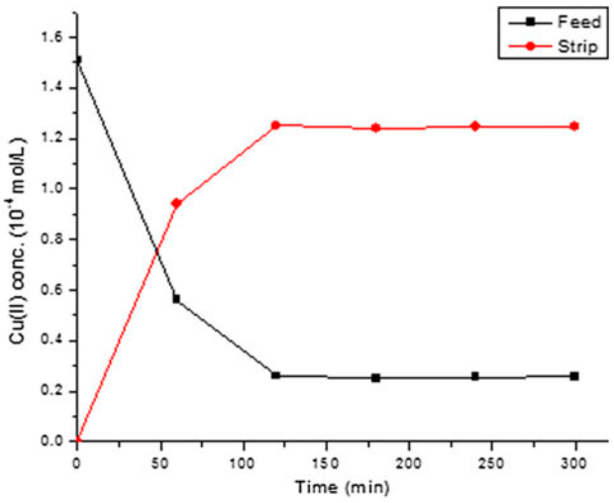

Fig. 18. Variation in Cu(II) ion concentration in feed and strip solution vs. time (match industry waste solution in feed) ($[Cu^{2+}] = 1.50 \times 10^{-4}$ mol/L, [HCl] = 1 mol/L, [EDTA] = 0.03 mol/L, [TEA] = 3.5 mol/L, pH 10).

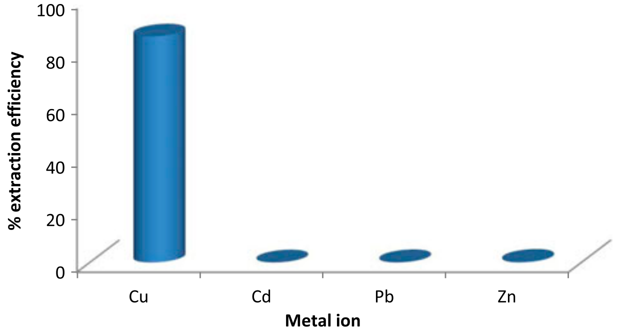

Fig. 19. % Extraction efficiency of different metal ions from match industrial waste water.

and the data are reproduced in Table 1. The study demonstrated that about 87% copper(II) ions were recovered. The results also reveal that a little extraction of other ions also takes place.

7. Conclusion

The flat-sheet SLM technique based on TEA-cyclohexanone has been employed for the transport of Cu (II) ions. The important parameters have been investigated to achieve the best set of the operating conditions for maximum separation of copper(II) ions from aqueous solution through SLM. The maximum extraction was obtained at 3.5 mol/L TEA concentration with a flux value of 2.84×10^{-4} mol/m^2 s. In the feed phase, 3.17×10^{-3} mol/L of copper(II) ions concentration exhibited the highest extraction with flux value of 3.28×10^{-4} mol/m^2 s, while 1 mol/L HCl has delivered the flux value of 2.80×10^{-4} mol/m^2 s for copper(II) ions. Thus, 3.17×10^{-3} mol/L of copper(II) ions concentration and 1 mol/L HCl are the optimum conditions for the extraction of copper(II) ions. Whereas in strip phase, 0.03 mol/L of EDTA concentration gives the highest value of flux of copper(II) ions, i.e. 2.86×10^{-4} mol/m^2 s. Under these optimum experimental conditions, the maximum extraction efficiency of (87%) copper(II) ion was achieved. The extraction time for copper(II) ion transport has also been studied. The maximum extraction was found at 120 min. The equilibrium slope method was used to calculate the stoichiometry of Cu-TEA complex $[(C_2H_4OH)_3NHCuCl_{2+1}]$ and it was found that 1:1 mol ratio of TEA and H$^+$ ion was involved in the Cu-TEA complex formation. The stability of SLM was also investigated under optimum experimental conditions and the result reveals that the membrane was quite stable for up to 10 extraction experiments. These optimized conditions were applied to recover Cu(II) ions from the match industry wastewater and about 87% copper(II) ions were extracted. The whole study was replicated thrice with relative standard deviation of ±2.

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References

[1] S. Jana, M.K. Purkait, K. Mohanty, Polymer enhanced ultrafiltration of mercury using chitosan impregnated ceramic membrane, Desalin. Water Treat. 37 (2012) 321–330.

[2] A. Surucu, V. Eyupoglu, O. Tutkun, Selective separation of cobalt and nickel by flat sheet supported liquid membrane using Alamine 300 as carrier, J. Ind. Eng. Chem. 18(2) (2012) 629–634.

[3] A.L. Dahi, K. Fatyeyeva, D. Langevin, C. Chappey, S.P. Rogalsky, O.P. Tarasyuk, A. Benamor, S. Marais, Supported ionic liquid membranes for water and volatile organic compounds separation: Sorption and permeation properties, J. Membr. Sci. 458 (2014) 164–178.

[4] S.K. Shukla, V. Kumar, M.C. Bansal, Treatment of combined bleaching effluent by membrane filtration technology for system closure in paper industry, Desalin. Water Treat. 13(1–3) (2010) 464–470.

[5] A. Bottino, G. Capannelli, A. Comite, C. Costa, J.I. Calvo, R. Saelee, Novel polytetrafluoroethylene tubular membranes for membrane distillation, Desalin. Water Treat. 53(6) (2015) 1559–1564.

[6] S.P. Barik, K.H. Park, P.K. Parhi, D.J. Kim, C.W. Nam, Separation and recovery of molybdenum from acidic solution using LIX 973 N, Sep. Sci. Technol. 49(5) (2014) 647–655.

[7] D.N. Ambare, S.A. Ansari, M. Anitha, P. Kandwal, D.K. Singh, H. Singh, P.K. Mohapatra, Non-dispersive solvent extraction of neodymium using a hollow fiber contactor: Mass transfer and modeling studies, Sep. Sci. Technol. 446 (2013) 106–112.

[8] S.S. Kumar, S.C. Tripathi, P.M. Gandhi, D.K. Singh, Studies on transport of anionic complex of plutonium from nitric acid medium across Aliquat 336/n-paraffin liquid membrane, Sep. Sci. Technol. 48(7) (2013) 1015–1022.

[9] S. Dixit, R. Chinchale, S. Govalkar, S. Mukhopadhyay, K.T. Shenoy, H. Rao, S.K. Ghosh, A mathematical model for size and number scale up of hollow fiber modules for the recovery of uranium from acidic nuclear waste using the DLM technique, Sep. Sci. Technol. 48(16) (2013) 2444–2453.

[10] A.P. de los Ríos, F.J. Hernández-Fernández, L.J. Lozano, S. Sánchez-Segado, A. Ginestá-Anzola, C. Godínez, F. Tomás-Alonso, On the selective separation of metal ions from hydrochloride aqueous solution by pertraction through supported ionic liquid membranes, J. Membr. Sci. 444(1) (2013) 469–481.

[11] J.E. Ferguson, The heavy metal elements: Chemistry, in: R. Maxwell (Ed.), Environmental Impact and Health Effects, Pergamon Press, Oxford, 1990.

[12] N.L. Nemerow, Liquid Waste of Industry, Theory, Practices and Treatment, Addison-Wesley, London, 1971.

[13] R.E. Burch, H.K.J. Hahn, J.F. Sullivan, Newer aspects of the roles of zinc, manganese and copper in human nutrition, Clin. Chem. 21 (1975) 501–520.

[14] A.K. Bhattacharya, S.N. Mandal, S.K. Das, Adsorption of Zn(II) from aqueous solution by using different adsorbents, Chem. Eng. J. 123 (2006) 43–51.

[15] T.P. Martin, G.A. Davies, The extraction of copper from dilute aqueous solutions using a liquid membrane process, Hydrometallurgy 2(4) (1977) 315–334.

[16] W. Zhang, C. Cui, Z. Hao, Transport study of Cu(II) through hollow fiber supported liquid membrane, Chin. J. Chem. Eng. 18(1) (2010) 48–54.

[17] W. Harless, E. Crowell, J. Abraham, Anemia and neutropenia associated with copper deficiency of unclear etiology, Am. J. Hematol. 81 (2006) 546–549.

[18] S.B. Goldhaber, Trace element risk assessment: Essentiality vs. toxicity, Regul. Toxicol. Pharmacol. 38(2) (2003) 232–242.

[19] Y. Loubières, A. Lassence, M. Bernier, A. Vieillard-Baron, J.M. Schmitt, B. Page, F. Jardin, Acute, fatal, oral chromic acid poisoning, J. Toxicol.: Clin. Toxicol. 37 (1999) 333–336.

[20] G. Müller, K. Janošková, T. Bakalár, J. Cakl, H. Jiránková, Removal of Zn(II) from aqueous solutions using Lewatit S1468, Desalin. Water Treat. 37 (2012) 146–151.

[21] Z. Ren, W. Zhang, H. Meng, J. Liu, S. Wang, Extraction separation of Cu(II) and Co(II) from sulfuric solutions by hollow fiber renewal liquid membrane, J. Membr. Sci. 365 (2010) 260–268.

[22] Z. Ren, W. Zhang, Y. Liu, Y. Dai, C. Cui, New liquid membrane technology for simultaneous extraction and stripping of copper(II) from wastewater, Chem. Eng. Sci. 62 (2007) 6090–6101.

[23] K. Takahashi, H. Takeuchi, Transport of copper through a supported liquid membrane, J. Chem. Eng. Jpn. 18(3) (1985) 205–211.

[24] M. Alaguraj, K. Palanivelu, M. Velan, Removal of Cu (II) using emulsion liquid membrane, Int. J. Chem. Tech. Res. 1 (2009) 722–726.

[25] S. Makaka, M. Aziz, A. Nesbitt, Copper recovery in a bench-scale carrier facilitated tubular supported liquid membrane system, J. Min. Metall.Sect. B 46 (2010) 67–73.

[26] S.H. Lin, R.S. Juang, Simultaneous extraction and stripping of EDTA-chelated metallic anions with Aliquat 336 in hollow fiber contactors, Chem. Eng. Sci. 57 (2002) 143–152.

[27] F.J. Alguacil, M. Alonso, A.M. Sastre, Modelling of mass transfer in facilitated supported liquid membrane transport of copper(II) using MOC-55 TD in Iberfluid, J. Membr. Sci. 184 (2001) 117–122.

[28] A.S. Kertes, C.J. King, Extraction chemistry of fermentation product carboxylic acids, Biotechnol. Bioeng. 28 (1986) 269–282.

[29] N.L. Ricker, Recovery of Carboxylic Acids and Related Organic Chemicals from Wastewaters by Solvent Extraction, PhD Thesis, Univ. of California at Berkeley, USA, 1978.

[30] J.F. Kennedy, J.M.S. Cabral, Recovery Processes for Biological Materials, Wiely & Sons, New York, NY, 1993.

[31] N.Z. Shaban, A.E. Ali, M.S. Masoud, Effect of cadmium and zinc ethanolamine complexes on rat brain monoamine oxidase-B activity in vitro, J. Inorg. Biochem. 95 (2003) 141–148.

[32] S. Rehman, G. Akhtar, M.A. Chaudry, N. Bukhari, N. Najeebullah, N. Ali, Mn(VII) ions transport by triethanolamine cyclohexanone based supported liquid membrane and recovery of Mn(II) ions from discharged zinc carbon dry battery cell, J. Membr. Sci. 366 (2011) 125–131.

[33] K. Ali, R. Nawaz, N. Ali, A. Khaliq, R. Ullah, Selective removal of zinc using tri-ethanolamine based supported liquid membrane, Desalin. Water. Treat. (2015) 1–12.

[34] M.W. Ashraf, M.A. Iqbal, Removal of cadmium(II) from aqueous waste effluents by using supported liquid membrane technology, Sci. J. Environ. Sci. 1 (2012) 30–39.

[35] S. Rehman, G. Akhtar, M.A. Chaudry, K. Ali, N. Ullah, Transport of Ag^+ through tri-n-dodecylamine supported liquid membranes, J. Membr. Sci. 389 (2012) 287–293.

[36] O. Gyliene, J. Aikaite, Formation of binuclear EDTA and Cu(II) complexes in aqueous solutions, Pol. J. Chem. 77(1) (2003) 99–104.

[37] K. Chakrabarty, P. Saha, A.K. Ghoshal, Separation of mercury from its aqueous solution through supported liquid membrane using environmentally benign diluent, J. Membr. Sci. 350 (2010) 395–401.

[38] S. Gu, Y. Yu, D. He, M. Ma, Comparison of transport and separation of Cd(II) between strip dispersion hybrid liquid membrane (SDHLM) and supported liquid membrane (SLM) using tri-*n*-octylamine as carrier, Sep. Purif. Technol. 51 (2006) 277–284.

[39] O. Gylienė, J.J. Aikaitė, O. Nivinskienė, Recovery of EDTA from complex solution using Cu(II) as precipitant and Cu(II) subsequent removal by electrolysis, J. Hazard. Mater. 116 (2004) 119–124.

[40] A.M. Neplenbroek, D. Bargeman, C.A. Smolders, Supported liquid membranes: Instability effects, J. Membr. Sci. 67 (1997) 121–132.

[41] F.F. Zha, A.G. Fane, C.J.D. Fell, Instability mechanisms of supported liquid membranes in phenol transport process, J. Membr. Sci. 107 (1995) 59–74.