Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2015.1020508

57 (2016) 8549–8560
April

Taylor & Francis
Taylor & Francis Group

Selective removal of zinc using tri-ethanolamine-based supported liquid membrane

Khurshid Ali, Robila Nawaz*, Nauman Ali, Alia Khaliq, Rizwan Ullah[1]

Institute of Chemical Sciences, University of Peshawar, Peshawar 25120, Pakistan, email: alikhurshid74@yahoo.com (K. Ali), Tel. +9291 9216652; emails: robila29@yahoo.cm (R. Nawaz), nali75pk@hotmail.com (N. Ali), aliakhaliq81@yahoo.com (A. Khaliq), srizvi2007@hotmail.com (R. Ullah)

Received 23 June 2014; Accepted 5 February 2015

ABSTRACT

This work is a comprehensive study on the selective removal of Zn (II) from aqueous solution using a flat-sheet polypropylene-supported liquid membrane system. Tri-ethanolamine (TEA) dissolved in cyclohexanone was used as a carrier for extraction of zinc ions through supported liquid membrane. Different parameters affecting the zinc ion transport were studied. The experiments were performed at various operating conditions such as metal and acid concentration in feed phase, strip phase concentration, and carrier concentration, to find the best set of parameters that would yield the maximum extraction. The extraction time, flux value, the stoichiometry of the complex formed, and membrane stability was also investigated. The experiments were performed in co-transport mode. The optimized conditions obtained for zinc ion transport are as follows: 2.30×10^{-4} mol/dm^3 of Zn^{2+} ions and 1 M of HCl in feed solution, 50% TEA in cyclohexanone in membrane phase, and 0.7 M of NaOH in stripping phase. Under these optimum conditions, the membrane is stable for about 10 consecutive experiments. The extraction efficiency was found to be 87% in 120 min.

Keyword: Supported liquid membrane; Extraction; Zinc ion; Tri-ethanolamine; Membrane stability, and Extraction efficiency

1. Introduction

With the growing industrial development, the use of various metals has been tremendously increased in recent decades. The importance of these metals and environmental pollution problems demand to avoid the wastage and to remove and recover metals from industrial process wastewater.

Removing and recovering metals from aqueous solutions can be carried out, *inter alia*, by chemical precipitation, reverse osmosis, adsorption, ion exchange, and solvent extraction processes [1–4]. Due to the inherent limitations of these techniques including low efficiency, sensitive operating conditions, production of secondary sludge, and high operating cost, more efficient and cost-effective removal and recovery of metals is now under intensive investigation which mainly includes the removal of metals using liquid membrane which is one of the most promising techniques. Some of the important advantages of this technique over the traditional separation techniques are low capital and operating cost, low energy and solvent requirements, etc. [5–7].

---

*Corresponding author.

[1] Department of Chemistry, Abdul Wali Khan University, Mardan, 23200, Pakistan.

In membrane separation techniques, the membrane used is basically a thin film which is porous in nature and acts as a semipermeable barrier for allowing certain species to transport and others to retain on one side of the membrane. Membrane separation processes are dependent on molecular size, charge, and charge density of the species being permeated and other parameters. The extraction reagents are dissolved in an organic solvent and immobilized in microporous inert support (membrane) for removal of metal ions from a mixture [8,9].

Liquid membrane may be broadly classified into three types: (1) bulk liquid membrane (BLM), (2) emulsion liquid membrane (ELM), and (3) supported liquid membrane (SLM). The ELMs and BLMs are non-supported liquid membranes, while flat-sheet liquid membrane and hollow fiber are supported liquid membranes.

SLM has applications in both industries and analytical fields for separation, pre-concentration, treatment of wastewater, and hydrometallurgy [10,11]. Owing to its advantages over other separation techniques, SLM has become the subject of intensive studies in the arena of scientists.

In supported liquid membrane, usually an extractant or carrier, dissolved in organic liquid, is embedded in small pores of inert polymer support and is retained there by capillary forces. The organic layer is immiscible with the aqueous feed and strip solutions, thus separating these two aqueous phases. The organic liquid is generally an inert organic solvent to keep the viscosity at the optimum level and may also contain a modifier to avoid so-called third phase formation [12].

Extractants used in supported liquid membrane for extraction of metals are chelating substances or may be acids, which are commonly used in the hydrometallurgical process for separating and extraction of various metal ions such as Zn, Mn, Ni, Co, Cu, Fe, and Mo [13,14]. The extractants or carriers are usually tertiary amines and/or quaternary ammonium salts for example tri-ethanolamine (TEA), tri-octylamine, tri-dodecylamine, tri-iso-octylamine, and trioctylmethylammonium chloride (Aliquat 336), which are used to remove metal ions from acid solution through the liquid membrane [15].

Fig. 1(a) shows the mechanism of SLM-based separation of ions. In this case, metal A from the feed solution is selectively extracted from the carrier through an organic membrane. The carrier picks up specie "A", at the membrane–feed interface, diffuses across the membrane as a complex, and finally exchanges "A" with the charged specie "C" on the strip side of the membrane. In this case, "C" has the same charge as on "A". Thus, the carrier acts as a shuttle carrying "A" and "C" in the opposite directions. That is why the process is called facilitated coupled countertransport. The typical example of this process is the metal cation exchange with H^+ ions facilitated by acidic carrier. Basic carrier, for example amines, can be used to carry H^+ ions together with negatively charged ions, such as Cl^-, in the same direction. This process is called facilitated coupled co-transport as shown in Fig. 1(b) [8].

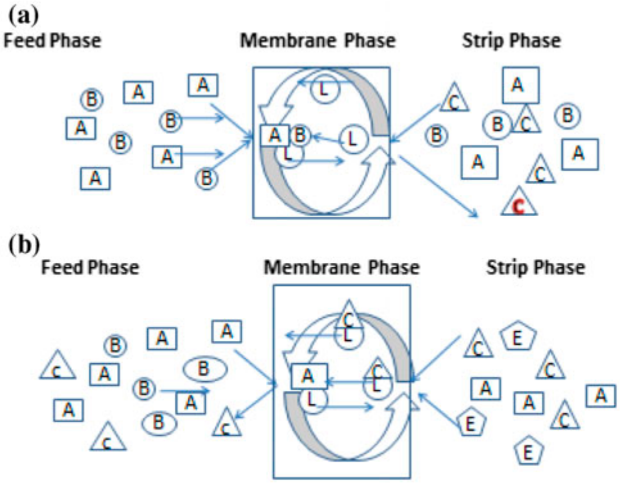

Fig. 1. Mechanism of metal ion transport through the SLM (a) facilitated coupled counter transport and (b) facilitated coupled co-transport.

Zinc makes up about 0.0075% of the earth crust, making it the 24th most abundant element. Soil contains 5–770 ppm of zinc. Seawater has only 30 ppb zinc [16]. It is the fourth most common element in use after iron, aluminum, and copper. It is extensively used in galvanizing, making alloys, other industrial and everyday used items [17,18].

Due to extensive use of zinc, a significant amount of zinc is being dumped in the lakes and rivers from various industrial wastewater which causes serious environmental problems.

In this study, extraction of zinc has been carried out using SLM based on TEA/cyclohexanone. After optimizing the extraction operational parameters, the technique has been successfully applied for extraction of zinc from dry battery wastewater.

2. Materials and methods

2.1. Chemicals

The TEA (Acros, Organics, 98%) in the cyclohexanone diluent (Merck, 99%) was used without further purification. The zinc chloride (98%), HCl (A.G., 35.4%), and NaOH (A.G., 99%) were obtained from Fluka company.

The membrane was microporous polypropylene film (Celgard 2400), with a thickness of 25 μm, porosity 41%, and pore size of 0.043 μm.

2.2. Analytical techniques

The atomic absorption spectrometer (Perkin Elmer model 400) was used for the measurement of concentration of zinc ions. The pH measurement was carried out by a NeoMet pH meter 200L. The viscosity measurement of TEA in cyclohexanone was determined by Brookfield Viscometer/Rheometer LVDV-III. The SEM analysis was carried out using Scanning Electron Microscope model JSM-5910 JEOL (Japan).

2.3. Membrane cell

Extraction experiments were performed at 25 ± 1℃ in the simple batch like permeater (cell). The cell was made of acrylic material having two compartments with flanges to clamp the membrane between these compartments. Each compartment had a volume capacity of 250 cm^3. The effective membrane contact area was 24.64 cm^2. Both the compartments had electrical stirrers to agitate the liquid.

2.4. Procedure

The carrier TEA was dissolved in cyclohexanone to get solutions of various concentrations (10–70%). The liquid membrane was prepared by soaking the polypropylene film for 24 h in a solution that was prepared by diluting TEA in cyclohexanone. For the extraction experiments, different concentrations of zinc $(9.8–19.6) \times 10^{-4}$ mol/dm^3 and HCl (0.1, 0.5, 1, 1.5, and 2 M) were used as feed solution, NaOH solutions (0.1, 0.3, 0.5, 0.7, 1, and 1.5 M) were used as stripping solution in strip phase. The feed and strip compartments of the cell were filled with their respective solutions which were separated by the membrane mounted in between the two compartments. The solutions in each compartment were stirred with an electric stirrer at a speed about 1,500 rpm. This was necessary to avoid concentration polarization at the membrane faces. Samples from the feed and the stripping solutions were taken after regular time intervals and analyzed by atomic absorption spectrophotometer.

2.5. Flux measurements

The flux was calculated using the following equation:

$$\text{Flux } (J) = \frac{\text{Change in the zinc ion concentration } \left(\frac{\text{mole}}{\text{dm}^3}\right) \times \text{volume of solution in strip or feed } (\text{dm}^3)}{\text{membrane area } (\text{m}^2) \times \Delta t} \tag{1}$$

where Δt represents the time interval (Fig. 2).

3. Theory

The chemistry of metal ion transfer through SLM is same as it is for liquid–liquid extraction. The extraction mechanism can be viewed as consisting of extraction by compound formation, ion-pair association, or solvation. In this study, the mechanism of extraction involves the ion-pair association. In this process, extractant makes an ion-pair complex, which is neutral and can be permeated through a hydrophobic membrane phase. The following possibility of protonation of TEA has been reported [19] in the acidic medium

$$\text{TEA} + \text{H}^+ \rightleftharpoons \text{TEAH}^+ \tag{2}$$

or in general form

$$\text{TEA} + n\text{H}^+ \rightleftharpoons [\text{TEAH}_n]^{n+} (I) \tag{3}$$

where “n” may be 1, 2, 3, or 4, as TEA molecule has one nitrogen and three oxygen atoms, and therefore,

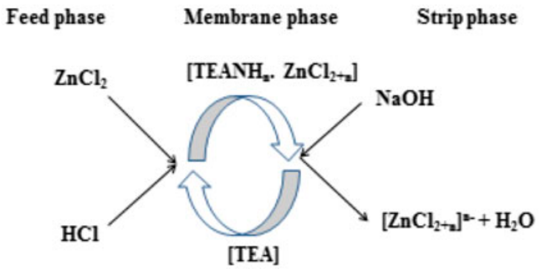

Fig. 2. Schematic representation of transport mechanism of zinc ions.

maximum protonation up to 4 can take place. Specie I will associate with a zinc ion in the anionic form associated with chloride.

$$\mathrm{Zn}^{2+} + 2\mathrm{Cl}^- \rightleftharpoons [\mathrm{ZnCl}_2] \tag{4a}$$

$$\mathrm{ZnCl}_2 + \mathrm{Cl}^- \rightleftharpoons [\mathrm{ZnCl}_3]^- \tag{4b}$$

or in general, depending upon the association number "n"

$$\mathrm{ZnCl}_2 + n\mathrm{Cl}^- \rightleftharpoons [\mathrm{ZnCl}_{2+n}]^{n-} \quad \text{(II)} \tag{4c}$$

Anionic species II will associate with a cationic complex of TEA, specie I at the feed–membrane interface.

$$[\mathrm{TEAH}_n]^{n+} + [\mathrm{ZnCl}_{2+n}]^{n-} \rightleftharpoons [\mathrm{TEAH}_n\,\mathrm{ZnCl}_{2+n}] \quad \text{(III)} \tag{5}$$

Specie III permeates through the membrane and releases zinc on the strip side at strip–membrane interface, due to reaction of protons with OH^- of the strip solution as follows:

$$[\mathrm{TEAH}_n\ \mathrm{ZnCl}_{2+n}] + n\mathrm{OH}^- \rightleftharpoons \mathrm{TEA} + [\mathrm{ZnCl}_{2+n}]^{n-} + n\mathrm{H}_2\mathrm{O} \tag{6}$$

The Zn–TEA complex is unstable in the basic medium as H^+ of the complex spontaneous reacts with OH^- ion, destroying the charge balance, equilibrium of the so-called complex, releasing thus TEA for further transport of zinc ions.

From the aforementioned discussion, the overall reaction can be written as

$$[\mathrm{ZnCl}_{2+n}]^{n-} + [\mathrm{TEAH}_n]^{n+} + n\mathrm{OH}^- \rightleftharpoons \mathrm{TEA} + [\mathrm{ZnCl}_{2+n}]^{n-} + n\mathrm{H}_2\mathrm{O} \tag{7}$$

For simplicity and specific mathematical purpose, Eq. (5) can be written as

$$[\mathrm{ZnCl}_{2+n}]^{n-} + [\mathrm{TEA}] + n[\mathrm{H}^+] \rightleftharpoons [\mathrm{TEAH}_n\ \mathrm{ZnCl}_{2+n}] \quad \text{(III)} \tag{8}$$

The equilibrium constant for reaction 8 can be written as

$$K_{\mathrm{Zn}} = \frac{[\mathrm{TEAH}_n\ \mathrm{ZnCl}_{2+n}]}{[(\mathrm{ZnCl}_{2+n})^{n-}][\mathrm{TEA}]\ [\mathrm{H}^+]^n} \tag{9}$$

If λ_{Zn} denotes the distribution coefficient of zinc ions for distribution between the membrane and aqueous phases,

$$\lambda_{\mathrm{Zn}} = \frac{[\mathrm{TEAH}_n\ \mathrm{ZnCl}_{2+n}]}{[(\mathrm{ZnCl}_{2+n})^{n-}]} \tag{10}$$

In light of Eqs. (10) and (9) can be written as

$$K_{\mathrm{Zn}} = \frac{\lambda_{\mathrm{Zn}}}{[\mathrm{TEA}]\ [\mathrm{H}^+]^n} \tag{11}$$

On rearranging Eq. (11), we obtain

$$\lambda_{\mathrm{Zn}} = K_{\mathrm{Zn}}[\mathrm{TEA}]\ [\mathrm{H}^+]^n \tag{12}$$

According to the Ficks' First Law, the rate of diffusion $\frac{\mathrm{d}n}{\mathrm{d}t}$ of metal ions across an area A known as diffusion flux and is given the symbol (J) [20].

$$J = \frac{\mathrm{d}n}{\mathrm{d}t} = -DA\frac{\mathrm{d}c}{\mathrm{d}x} \tag{13}$$

Where $\frac{\mathrm{d}c}{\mathrm{d}x}$ is the concentration gradient of the metal ions and dn is the amount of metal ions crossing the area A in time dt.

Since solutions are stirred therefore, the metal ion concentration in feed and strip phases, C_f and C_s, respectively, is maintained at a uniform level. 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. At steady state, the rate of diffusion does not change with time as long as the concentrations of

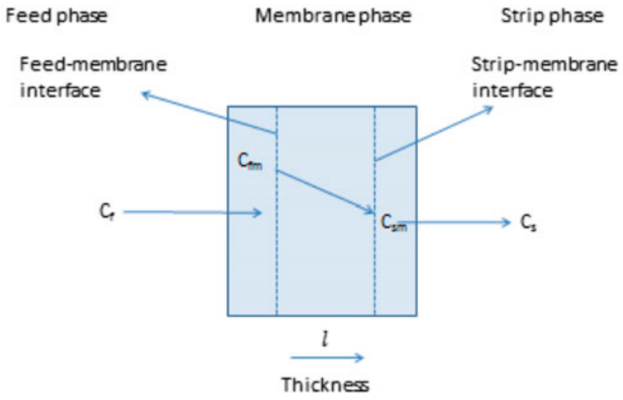

Fig. 3. Concentration gradient of zinc ions at the feed and strip sides of the membrane.

metal ions at membrane interfaces of feed and strip sides, C_{fm} and C_{sm}, respectively, remain constant. In order for there to be a steady state, the concentration gradient must be uniform across the membrane. In other words, the concentration within the membrane must fall linearly, as shown in Fig. 3. The concentration gradient is thus given by

$$-\frac{\mathrm{d}c}{\mathrm{d}x} = \frac{C_{fm} - C_{sm}}{l} \tag{14}$$

And by the Ficks' First Law, the rate of flow through the membrane is

$$\frac{\mathrm{d}n}{\mathrm{d}x} = DA\frac{C_{fm} - C_{sm}}{l} \tag{15}$$

The diffusion coefficient D is therefore calculated from the measurement of the rate of flow; the area A, thickness l, and concentration difference $C_{fm} - C_{sm}$ are readily determined.

Where, as mentioned earlier, D is the diffusion coefficient. Since the distribution coefficient of Zn^{2+} at the membrane surface of the feed side and strip side can be given by λ_f and λ_s, respectively, that is,

$$\lambda_f = \frac{C_{fm}}{C_f} \quad \text{and} \quad \lambda_s = \frac{C_{sm}}{C_s} \tag{16}$$

where C_f and C_s represent feed and strip concentration of Zn^{2+}, respectively.

From relations (16), we obtain

$$C_{fm} = \lambda_f C_f \quad \text{and} \quad C_{sm} = \lambda_s C_s \tag{17}$$

and with the help of Eq. (17), Eq. (15) becomes

$$J = DA\left(\frac{\lambda_f C_f - \lambda_s C_s}{l}\right) \tag{18}$$

As there is no extraction from the strip to the membrane phase, so $\lambda_s \rightarrow 0$ and as a result, λ_s Cs ≈ 0 and Eq. (18) transform to

$$J = DA\left(\frac{\lambda_f C_f}{l}\right) \tag{19}$$

In our case $\lambda_f = \lambda_{\mathrm{Zn}}$ as given by Eq. (12), thus Eq. (19) becomes

$$J = DA\ \frac{K_{\mathrm{Zn}}[\mathrm{TEA}]\ [\mathrm{H}^+]^n\ [\mathrm{ZnCl}_{2+n}]^{n-}C_f}{l} \tag{20}$$

According to Wilke-Chang relation

$$D = \frac{\acute{k}T}{\eta} \tag{21}$$

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

$$J = \frac{\acute{k}T}{\eta}A\frac{K_{\mathrm{Zn}}[\mathrm{TEA}]\ [\mathrm{H}^+]^n[\mathrm{ZnCl}_{2+n}]^{n-}C_f}{l} \tag{22}$$

Since $\acute{k}$, K_{Zn}, T, l and A are constants, combining all these as K (i.e. $K = \acute{k}K_{\mathrm{Zn}}T$, l, A), we obtain

$$J = \frac{K[\mathrm{TEA}]\ [\mathrm{H}^+]^n[\mathrm{ZnCl}_{2+n}]^{n-}C_f}{\eta} \tag{23}$$

However, if C_f does not change rapidly, then for a short interval of time, C_f may be taken nearly constant. Rearranging Eq. (23)

$$J\eta = K[\mathrm{TEA}]\ [\mathrm{H}^+]^n[\mathrm{ZnCl}_{2+n}]^{n-}C_f \tag{24}$$

Taking log of Eq. (24)

$$\begin{aligned} \log J\eta = {} & \log K + \log[\mathrm{TEA}] + n\log\ [\mathrm{H}^+] + \log[(\mathrm{ZnCl}_{2+n})^{n-}] \\ & + \log C_f \end{aligned} \tag{25}$$

Since a specially designed experiment was carried out by keeping K, TEA, $(\mathrm{ZnCl}_{2+n})^{n-}$, C_f as constants in order to study the effect of H^+ concentration on extraction of zinc ions, therefore, the terms involving these parameters in Eq. (26) can be collected in a single parameter as follows:

$$B = \log k + \log \mathrm{TEA} + \log[(\mathrm{ZnCl}_{2+n})^{n-}] + \log C_f \tag{26}$$

Thus, Eq. (25) becomes

$$\log J\eta = B + n\log\ [\mathrm{H}^+] \tag{27}$$

Eq. (27) can be used to determine the number of H+ ion "n" associated with TEA in the form $[\mathrm{TEAH}_n]^{n+}$. Eq. (27) is a straight line equation in which $\log J\eta$ can be plotted on y axis and log $[H^+]$ on x axis. The slope of this curve will give "n" which gives the number of protons associated with TEA.

4. Results and discussion

4.1. Effect of TEA concentration on the extraction of zinc

In this study, the extraction of zinc ion has been carried out through tertiary amine and TEA, as a carrier. Different concentrations of TEA in cyclohexanone diluent were employed to study the extraction of zinc metal ion. The concentration range of TEA was from 10 to 70%. Samples from feed and strip phases, in a single run of the experiment, were drawn simultaneously at different interval of time and analyzed for zinc ion by AAS. In this manner, seven different experiments were carried out with different concentrations of TEA as mention above. It was observed that with an increase in concentration of TEA, extraction of zinc ion increases as shown in Figs. 4 and 5. From the figures, it is clear that concentration of Zn^{2+} ions decreases in feed, while at the same time, it increases in strip phase with the passage of time. It can be carefully analyzed that the concentrations of TEA in the feed phase at any particular time supplement that of in the strip phase i.e. it exhibits an additive behavior.

This has been shown in Fig. 6 wherein the two curves show the said additive behavior which is clear from their mirror image nature. By a careful observation, it can be analyzed that a decreasing trend in the concentration of zinc in the feed side is observed, however, the concentration goes to a minimum value at 50% TEA where after, it increases for 60 and 70% concentration which is an indication of smaller transport of zinc toward the strip side. This might be due to the increase in the viscosity of organic phase of the membrane (Fig. 7), which hampers the movement of complex through the membrane. This fact can conversely observe from the feed side where the

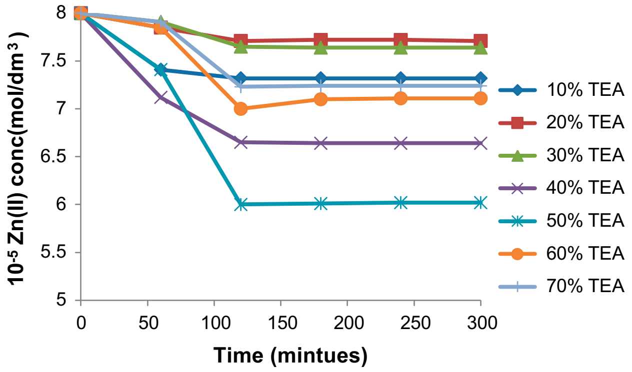

Fig. 4. Variation in Zn^{2+} ion concentration with time in the feed solution at various concentrations of TEA (Zn^{2+} ions conc. = 8×10^{-5} mol/dm^3, HCl conc. = 1 M, NaOH conc. = 1 M, and TEA conc. = 10–70%).

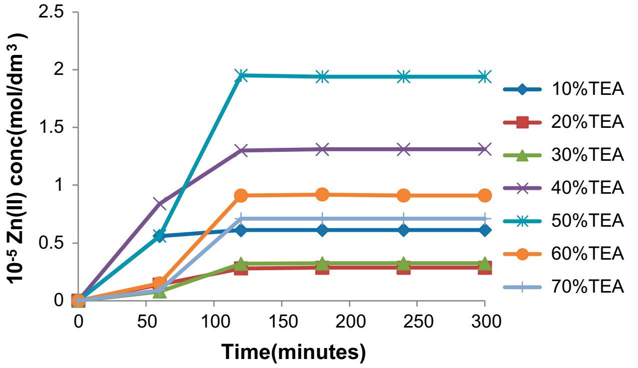

Fig. 5. Variation in Zn^{2+} ion concentration with time in strip solution at various concentrations of TEA (Zn^{2+} ions conc. = 8×10^{-5} mol/dm^3, HCl conc. = 1 M, NaOH conc. = 1 M, and TEA conc. = 10–70%).

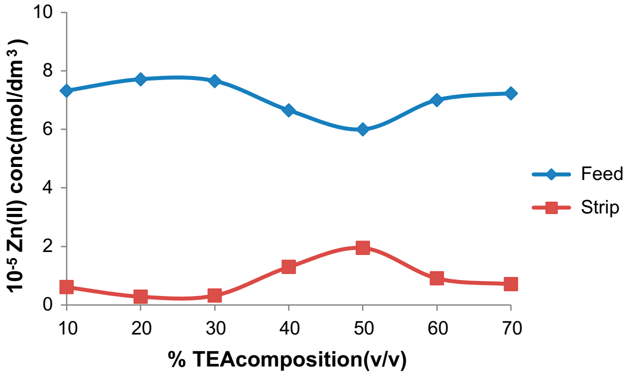

Fig. 6. Concentration of zinc ions vs. TEA composition.

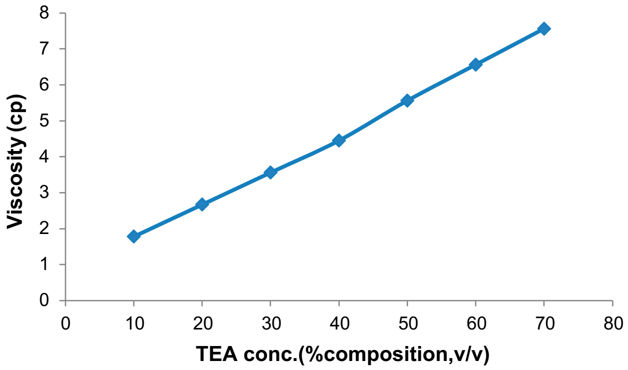

Fig. 7. Viscosity of TEA–cyclohexanone solutions.

concentration of zinc increases with the increase of TEA concentration, reaches a maximum at 50% concentration of TEA, and then decreases afterward. So 50% TEA concentration was an optimum condition for zinc extraction.

4.1.1. Flux study

The flux of zinc ions was calculated using Eq. (1) and represented in Fig. 8. It can be observed that flux decreases from 10 to 20% TEA concentration and then slightly increases up to 30% and then increases rapidly and goes up to a maximum value of 50%, where the value of flux was observed as 3.58×10^{-11} mol/m^2 s. Then, there is a steep decrease from 60 and 70% TEA concentration. This decrease in flux, as mentioned earlier, is due to increase in viscosity of TEA solution which hampers the transport of zinc ions due to restricted movement of metal–TEA ion complex.

4.2. Effect of NaOH concentration on the extraction of zinc

The stripping agents in the stripping phase play an important role in transport of metal ions through the organic membrane phase to the stripping phase. The membrane phase becomes saturated with the complex if the metal complex is not properly stripped off. Otherwise, this will adversely affect the permeation rate. In this work, NaOH has been used as a strippent reagent for the extraction of zinc. The concentration range of NaOH from 0.1 to 2 M has been studied.

As indicated in Figs. 9 and 10, increasing the concentration of NaOH, the extraction as well as flux value increases with time. Consequently, maximum extraction was noted at 0.7 M NaOH. On further increase in NaOH concentration, the extraction was decreased abruptly. This could be because at higher concentration of NaOH, precipitation of ZnO at strip–membrane interface may be formed due to excess amount of OH$^-$ ions. This precipitate gets penetrated into the membrane pores and affects the transport of zinc due to clogging of pores [21]. Therefore, 0.7 M NaOH was an optimum condition for zinc extraction. At the strip-membrane interface, the complex immediately dissociates and releases Zn^{+2} and Cl$^-$ ions along with H$^+$ ions which spontaneously react with OH$^-$ to form H$_2$O into the strip solution.

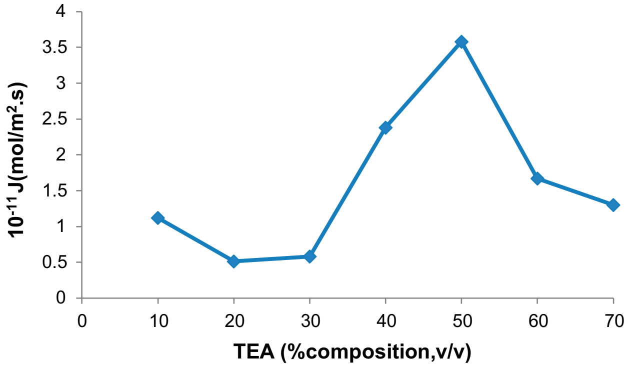

Fig. 8. Effect of TEA concentration on flux (Zn^{2+} ions conc. = 8×10^{-5} mol/dm^3, HCl conc. = 1 M, NaOH conc. = 1 M, and TEA conc. = 10–70%).

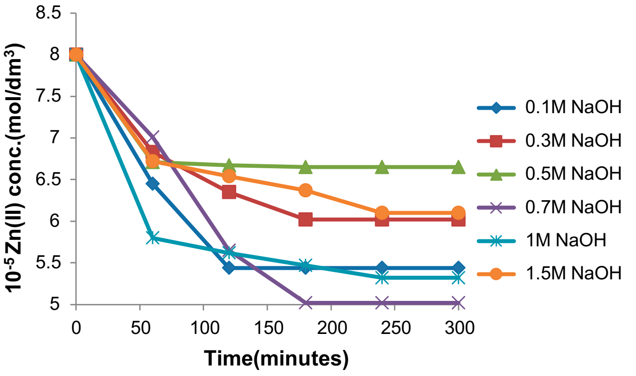

Fig. 9. Variation in Zn^{2+} ion concentration with time in the feed solution at various concentrations of NaOH (Zn^{2+} ions conc. = 8.0×10^{-5} mol/dm^3, HCl conc. = 1 M, NaOH conc. = 0.1–1.5 M, and TEA conc. = 50%).

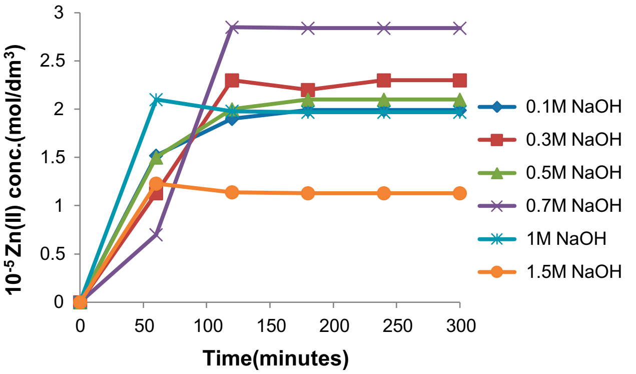

Fig. 10. Variation in Zn^{2+} ion concentration with time in strip solution at various concentrations of NaOH (Zn^{2+} ions conc. = 8.0×10^{-5} mol/dm^3, HCl conc. = 1 M, NaOH conc. = 0.1–1.5 M, and TEA conc. = 50%).

$$[\mathrm{TEAH}_n\ \mathrm{ZnCl}_{2+n}] + n\mathrm{OH}^- \rightleftharpoons \mathrm{TEA} + [\mathrm{ZnCl}_{2+n}]^{n-} + n\mathrm{H}_2\mathrm{O} \qquad (6)$$

This reaction was established by monitoring the pH value of the strip solution which was decreased,

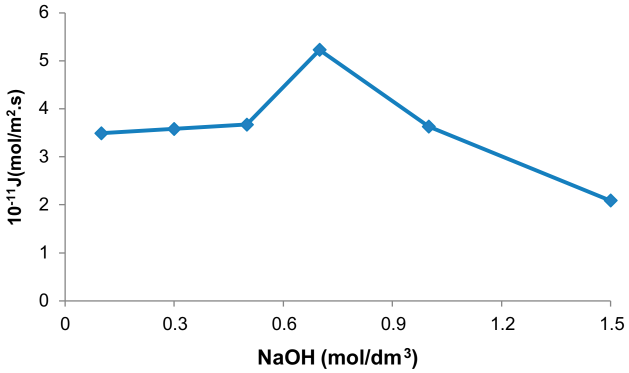

Fig. 11. Effect of NaOH concentration on flux (Zn^{2+} ions conc. = 8.0×10^{-5} mol/dm^3, HCl conc. = 1 M, NaOH conc. = 0.1–1.5 M, and TEA conc. = 50%).

showing the consumption of the OH^- ions in the above reaction.

The flux value increases gradually from 0.1 to 0.5 and then becomes maximum at 0.7 M NaOH, where after the decreasing, trend can be seen (Fig. 11) up to 1.5 M NaOH concentration.

4.2.1. SEM analysis

The SEM images of the membrane before and after the extraction are given in Fig. 12(a) and (b). It can be observed that before the extraction, the membrane was smooth with cracks therein whose approximated length ranges from 0.2 to 6 μm and width of the crack is 0.025 μm in average. A careful examination of the SEM image after the extraction shows a material deposition on the membrane with larger dimension of the cracks. This deposition can be of ZnO which may have been deposited after a number of consistent use of the membrane [22].

4.3. Effect of HCl concentration on the extraction of zinc

Figs. 13 and 14 indicate the effect of HCl concentration, in the feed side, on extraction of zinc ions. The concentration of HCl in the range of 0.1–2 M was studied while keeping the concentration of TEA at 50% in cyclohexanone and NaOH at 0.7 M in stripping phase. It was observed that the extraction of zinc ion increases with the increase in HCl concentration, it reaches at its maximum value at 1 M HCl where after the extraction decreases. The Cl^-/Zn^{2+} ratio would have significant effect on extraction efficiency: Fewer amounts of Cl^- result in the formation of $ZnCl^+$, while excess of Cl^- leads to the formation of $ZnCl_3^-$or $ZnCl_4^{2-}$ [21]. At very high concentration, common ion effect causes the reaction to go in reverse direction and inhibits the formation of Zn–TEA complex. So, 1 M HCl concentration was an optimum condition for the extraction of zinc ions.

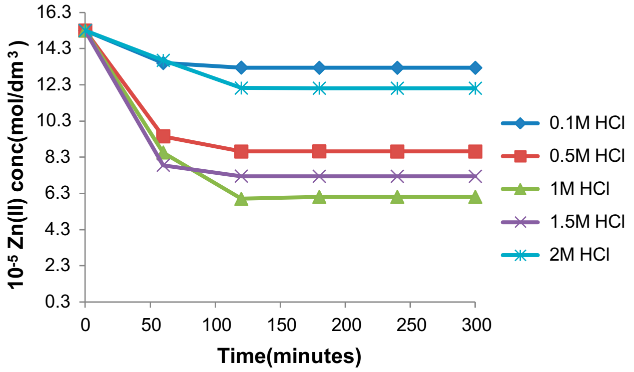

Fig. 13. Variation in Zn^{2+} ion concentration with time in the feed solution at various concentrations of HCl (Zn^{2+} ions cons. = 15.3×10^{-5} mol/dm^3, HCl conc. = 0.1–2 M, NaOH conc. = 0.7 M, and TEA conc. = 50%).

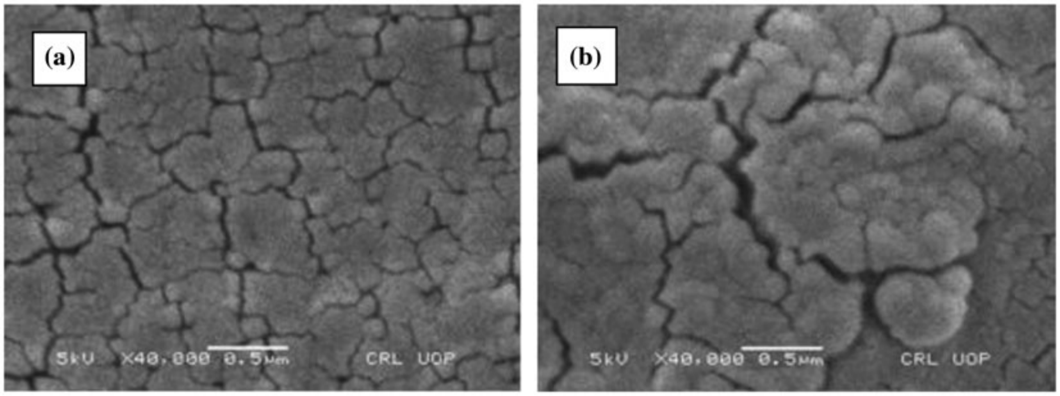

Fig. 12. SEM analysis (a) before extraction and (b) after extraction.

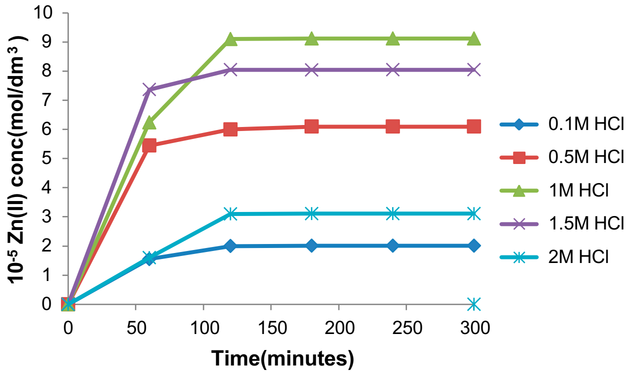

Fig. 14. Variation in Zn^{2+} ion concentration with time in strip solution at various concentrations of HCl (Zn^{2+} ions conc. = 15.3×10^{-5} mol/dm^3, HCl conc. = 0.1–2 M, NaOH conc. = 0.7 M, and TEA conc. = 50%).

Fig. 15 shows the pH change of the feed solution with time during a single extraction experiment. The increase in pH is slow at the beginning and rises almost steeply between the 90th and 120th minutes of the experiment. Initially, the protons of feed solution were utilized by carrier (TEA) molecules to convert it into a charged species by protonation at the feed–membrane interface. Further increase in pH may be attributed to the transport of H^+ ion from the feed to the membrane phase and ultimately to the strip phase.

Fig. 16 reveals the flux of Zn^{2+} with the concentration of HCl. The flux increases as the concentration of HCl increases and goes to a maximum at 1 M HCl and then, it decreases. The highest flux value of 3.20×10^{-7} mol/m^2 s was noticed at 1 M HCl. The decrease in the flux beyond 1 M HCl is due to the excess amount of H^+ concentration which suppresses the extraction in forward direction.

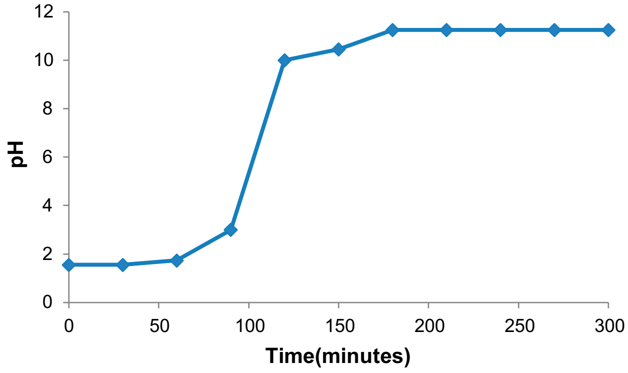

Fig. 15. Variation in pH of feed solution with time (Zn^{2+} ions conc. = 15.3×10^{-5} mol/dm^3, HCl conc. = 1 M, NaOH conc. = 0.7 M, and TEA conc. = 50%).

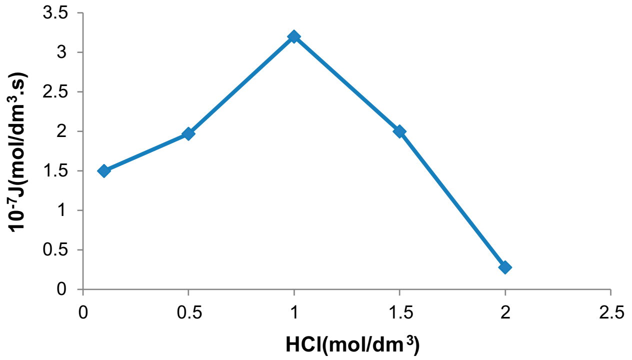

Fig. 16. Effect of HCl concentration on flux (Zn^{2+} ions conc. = 15.3×10^{-5} mol/dm^3, HCl conc. = 0.1–2 M, NaOH conc. = 0.7 M, and TEA conc. = 50%).

4.3.1. Determination of "n"

The number of H^+ ion "n" associated with TEA in the form of $[TEAH_n]^{n+}$ can be determined using Eq. (27) which is a straight line equation where $\log J\eta$ can be plotted on y axis and log $[H^+]$ on x axis. The slope of this curve will give "n" which gives the number of protons associated with TEA.

$$\log J\eta = B + n \log\,[H^+] \tag{27}$$

Fig. 17 shows $\log J\eta$ vs. log $[H^+]$. The first three values of the data from Fig. 15 were taken from this plot because these were showing an increasing trend in the flux with increase in H^+ ion concentration. The slope of the curve is showing a value of 1.098 which can be safely taken as 1. Thus, the complex $[TEAH_n]^{n+}$ can be assumed to be like $[TEAH]^+$, and analogously by intuition, we can say

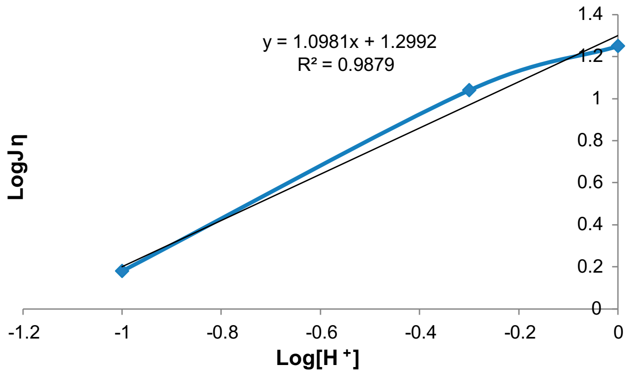

Fig. 17. Plot of log $J\eta$ vs. log $[H^+]$.

that the zinc-chloride anionic complex has the form $[\mathrm{ZnCl}_{2+1}]^-$. The zinc–TEA complex thus acquires the form $[\mathrm{TEAH}_n\ \mathrm{ZnCl}_{2+n}]$. Thus, in light aforementioned discussion, Eq. (5) can be written as

$$[\mathrm{TEAH}]^+ + [\mathrm{ZnCl}_{2+1}]^- \rightleftharpoons [\mathrm{TEAH\ ZnCl}_{2+1}] \tag{28}$$

Thus, Eq. (28) predicts the stoichiometry of the complex.

4.4. Effect of zinc metal concentration on the extraction of zinc

In order to investigate the effect of zinc ion concentration on the extraction, 0.77–3.84 × 10^{-4} mol/dm^3 concentrations of zinc were employed. During this study, the other parameters such as concentration of HCl in feed solution, NaOH in stripping solution, and TEA in membrane phase were kept at optimum levels, i.e. 1 M, 0.7 M, and 50%, respectively. Figs. 18 and 19 show the change in the zinc ion concentration with time in the feed and strip phases, respectively. It can be noted from Fig. 18 that maximum extraction was obtained with a zinc concentration of 2.30 × 10^{-4} mol/dm^3. A decrease in the extraction can be observed from the same figure by further increases in zinc ion concentration. This could be attributed to the following reason: As the concentration of metal ions increases, the requirement of HCl, to make zinc–chloride complex, also increases, whereas we have kept HCl concentration at a constant level which is insufficient to cater for the zinc-chloride complex [23].

The flux was also maximum at this concentration and gives the value of 3.51 × 10^{-11} mol/m^2 s as shown in Fig. 20. There was a decrease in the flux beyond the aforementioned concentration of zinc ion due to the reason mentioned above.

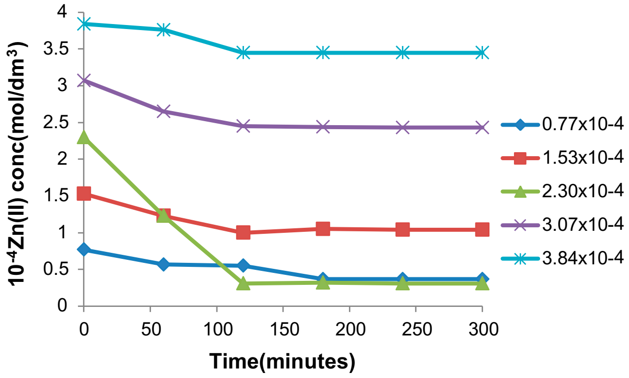

Fig. 18. Variation in Zn^{2+} ion concentration with time in the feed solution at various concentrations of zinc metal solution (Zn^{2+} ions conc. = 0.77 − 3.84 × 10^{-4} mol/dm^3, HCl conc. = 1 M, NaOH conc. = 0.7 M, and TEA conc. = 50%).

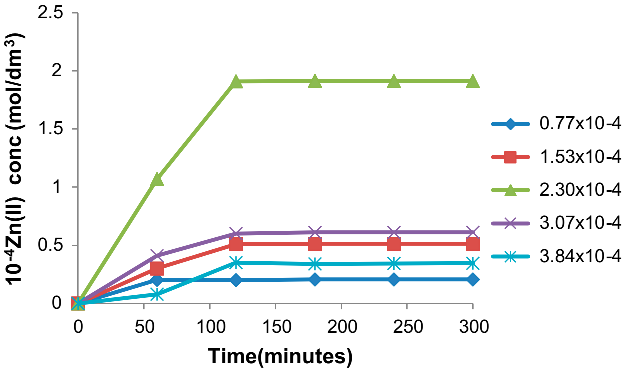

Fig. 19. Variation in Zn^{2+} ion concentration with time in strip solution at various concentrations of zinc metal solution (Zn^{2+} ions conc. = 7.72 × 10^{-6}–1.52 × 10^{-4} mol/dm^3, HCl conc. = 1 M, NaOH conc. = 0.7 M, and TEA conc. = 50%).

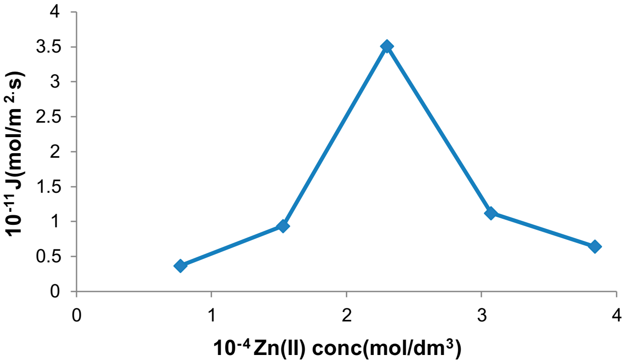

Fig. 20. Effect of Zn^{2+} ion concentration on flux (Zn^{2+} ions conc. = 7.72 × 10^{-6}–1.52 × 10^{-4} mol/dm^3, HCl conc. = 1 M, NaOH conc. = 0.7 M, and TEA conc. = 50%).

4.5. Extraction time

Fig. 21 shows the extraction of zinc against time at optimum conditions of the extraction of zinc ion. It can be noted that the extraction reaches to its maximum level (87%) at 120th minutes where after there is no increases in extraction and it remains constant as indicated by Fig. 21.

4.6. Membrane Stability

The stability of polypropylene–TEA–cyclohexanone SLM was studied for 10 d by carrying out 10 independent extraction experiments at optimum conditions for

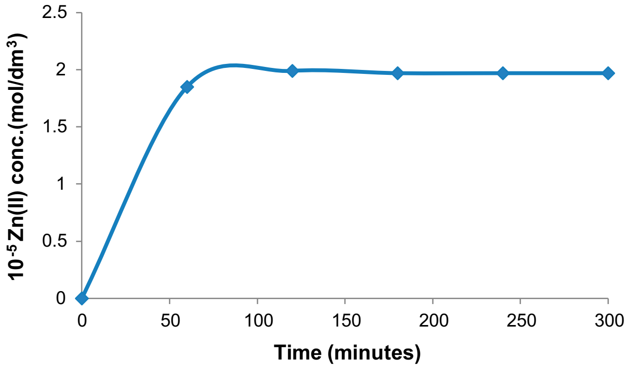

Fig. 21. Variation in Zn^{2+} ion concentration with time in strip phase (Zn^{2+} ions conc. = 2.30×10^{-4} mol/dm^{3,} HCl conc. = 1 M in feed phase, NaOH conc. = 0.7 M in strip phase, and TEA conc. = 50% membrane phase).

extraction. These optimum conditions were zinc ion concentration in the feed at 2.30×10^{-4} mol/dm^3, 1 M HCl, 50% TEA concentration in cyclohexanone, 0.7 M NaOH concentration in stripping phase, and at the stirring speed of 1,500 rpm. Each experiment was of 5 h duration using the same membrane impregnated only once, while fresh solutions were added into the feed and strip compartments for every experiment. As seen in Fig. 22, the extraction was not affected and remained at 87% during all the experiments. This shows that despite all deteriorating factors of membrane, what so ever, the efficiency has not decreased during these experiments.

4.7. Extraction of Zn (II) ion from dry battery waste

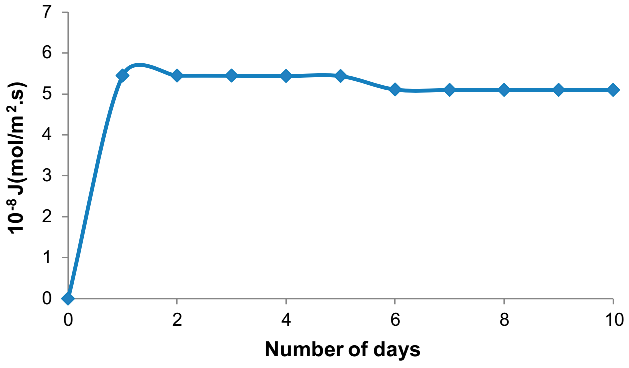

Fig. 22. Flux vs. time for stability study of SLM (Zn^{2+} ions conc. = 2.30×10^{-4} mol/dm^3, HCl conc. = 1 M, NaOH conc. = 0.7 M, and TEA conc. = 50%).

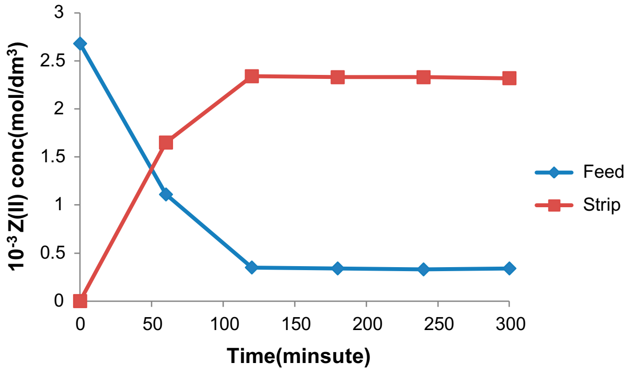

Fig. 23. Variation in Zn^{2+} ion concentration in the feed and strip solution vs. time (dry battery waste solution). (Zn^{2+} ions conc. = 2.68×10^{-3} mol/dm^3, HCl conc. = 1 M, NaOH conc. = 0.7 M, and TEA conc. = 50%).

Table 1
Analysis of dry battery waste solution

S. No.	Metal ion	Concentration of metal ions	
		Before extraction	After extraction
1	Zn	2.68×10^{-3}	2.34×10^{-3}
2	Co	0.00	0.00
3	Ni	0.00	0.00
4	Mn	7.28×10^{-3}	0.00

One of the major applications of zinc is its use in zinc–carbon dry battery [17]. The optimized conditions were used for recovery of zinc from discharged zinccarbon dry battery. The carbon black powder from inside the heavy duty 1.5 V, size D, power flash zinccarbon dry battery was digested in acid for 4 h at room temperature and filtered through Whatman®-41 filter paper to remove the residue (carbon powder). This solution was analyzed for zinc, cobalt, nickel, and manganese ions by AAS. However, only zinc and manganese ions were found to be present in the solution. A known volume of 250 cm^3 of the filtrate was taken as the feed solution; the extraction experiment was carried out keeping all other conditions at the optimum level as mentioned before. The study shows that almost 87% zinc ions were recovered (Fig. 23), however, no Mn ions were detected in the strip phase, showing selective behavior of TEA for zinc ions (Table 1).

5. Conclusions

In the present work, SLM, containing Celgard 2400 as a support, TEA as carrier, and cyclohexanone as solvent, in the separation of zinc (II) from their aqueous acidic solution, have been investigated. The influence of various parameters on the transport of zinc (II) has been studied to optimize the process. The maximum extraction was obtained at 50% TEA concentration with a flux value of 3.58×10^{-11} mol/m^2 s. In feed phase, 2.30×10^{-4} mol/dm^3 of zinc ions and 1 M HCl were the optimum conditions for the extraction of zinc ions. The maximum flux value of 3.51×10^{-11} mol/m^2 s was noticed at 2.30×10^{-4} mol/dm^3 of zinc ion concentration, while 3.20×10^{-7} mol/m^2 s of flux was observed at 1 M HCl. While in case of strip phase, the 0.7 M NaOH concentration gives the highest value of flux, that is, 5.23×10^{-7} mol/m^2 s. Under these optimum conditions, the maximum extraction of zinc ions was achieved and gives 87% of extraction efficiency. The extraction time for zinc ion transport has been studied. The maximum extraction was found at 120 min. The stoichiometry of Zn–TEA complex [TEAH $ZnCl_{2+1}$] was evaluated through equilibrium slope method, and it was found that 1:1 mol ratio of TEA and H^+ ion was involved in the complex formation. The stability of SLM under optimum conditions was investigated, and it was concluded that the membrane was stable for up to 10 extraction experiments. This SLM was applied to recover Zn (II) from the dry battery wastewater, and about 87% zinc ions were extracted. The whole study was replicated thrice with relative standard deviation of ±2%.

Acknowledgment

One of the authors (Robila Nawaz) is greatly thankful to the Higher Education Commission (HEC) of Pakistan for the financial support.

References

[1] P. Parhi, Supported liquid membrane principle and its practices: A short review, J. Chem. 2013 (2012) 1–11.
[2] K.P. Lee, T.C. Arnot, D. Mattia, A review of reverse osmosis membrane materials for desalination—Development to date and future potential, J. Membr. Sci. 370 (2011) 1–22.
[3] S. Liang, X. Guo, Q. Tian, Adsorption of Pb^{2+} and Zn^{2+} from aqueous solutions by sulfured orange peel, Desalination 275 (2011) 212–216.
[4] P. Parhi, K.-H. Park, H.-I. Kim, J.-T. Park, Recovery of molybdenum from the sea nodule leach liquor by solvent extraction using Alamine 304-I, Hydrometallurgy 105 (2011) 195–200.
[5] T.A. Kurniawan, G. Chan, W.-H. Lo, S. Babel, Physico–chemical treatment techniques for wastewater laden with heavy metals, Chem. Eng. J. 118 (2006) 83–98.
[6] S. Ahluwalia, D. Goyal, Removal of heavy metals by waste tea leaves from aqueous solution, Eng. Life Sci. 5 (2005) 158–162.
[7] K. Ochromowicz, W. Apostoluk, Modelling of carrier mediated transport of chromium(III) in the supported liquid membrane system with D2EHPA, Sep. Purif. Technol. 72 (2010) 112–117.
[8] N. Kocherginsky, Q. Yang, L. Seelam, Recent advances in supported liquid membrane technology, Sep. Purif. Technol. 53 (2007) 171–177.
[9] R.A. Bartsch, J.D. Way, Chemical separations with liquid membranes: An overview, in: ACS Symposium Series, ACS Publication, Washington, DC, 1996.
[10] P. Kittisupakorn, W. Weerachaipichaskul, P. Thitiyasook, Modeling and simulation of copper-ion extraction with hollow fiber supported liquid membrane, J. Ind. Eng. Chem. 13 (2007) 903–910.
[11] B. Swain, K. Sarangi, R. Prasad Das, Separation of cadmium and zinc by supported liquid membrane using TOPS-99 as mobile carrier, Sep. Sci. Technol. 39 (2005) 2171–2188.
[12] A. Gabelman, S.-T. Hwang, Hollow fiber membrane contactors, J. Membr. Sci. 159 (1999) 61–106.
[13] 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 (2012) 629–634.
[14] B. Li, F. Liu, J. Wang, C. Ling, L. Li, P. Hou, A. Li, Z. Bai, Efficient separation and high selectivity for nickel from cobalt-solution by a novel chelating resin: Batch, column and competition investigation, Chem. Eng. J. 195–196 (2012) 31–39.
[15] S. Azzoug, O. Arous, H. Kerdjoudj, Metallic ions extraction and transport in supported liquid membrane using organo-phosphoric compounds as mobile carriers, J. Environ. Chem. Eng. 2 (2014) 154–162.
[16] C. Yang, R. Guo, R. Liu, Q. Yue, X. Ren, Z. Wu, Geostatistical analysis of the horizontal distribution of soil zinc in Guangdong, in: Agro-Geoinformatics (Agro-Geoinformatics), 2012 First International Conference on, IEEE, Shanghai, 2012, pp. 1–4.
[17] E. John, "Zinc" Nature's Building Blocks: An A–Z Guide to the Elements, Oxford University Press, Oxford, 2001, pp. 499–505.
[18] B.K. Prasad, A.K. Patwardhan, A.H. Yegneswaran, Dry sliding wear characteristics of some zinc-aluminium alloys: A comparative study with a conventional bearing bronze at a slow speed, Wear 199 (1996) 142–151.
[19] M. Waqar 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.
[20] 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.
[21] K. Chakrabarty, P. Saha, A.K. Ghoshal, Simultaneous separation of mercury and lignosulfonate from aqueous solution using supported liquid membrane, J. Membr. Sci. 346 (2010) 37–44.
[22] 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.
[23] K.K. Bhatluri, M.S. Manna, P. Saha, A.K. Ghoshal, Supported liquid membrane-based simultaneous separation of cadmium and lead from wastewater, J. Membr. Sci. 459 (2014) 256–263.