Research Article

Transport of Zn (II) by TDDA-Polypropylene Supported Liquid Membranes and Recovery from Waste Discharge Liquor of Galvanizing Plant of Zn (II)

Hanif Ur Rehman,¹ Gul Akhtar,² Haroon Ur Rashid,¹ Nauman Ali,² Imtiaz Ahmad,² Saeed Ur Rehman,² Kamin Khan,¹ and Muhammad Arshad³

¹Department of Chemistry, Sarhad University of Science & Information Technology, Peshawar, Khyber Pakhtunkhwa, Pakistan

²Institute of Chemical Sciences, University of Peshawar, Peshawar, Khyber Pakhtunkhwa, Pakistan

³Chemistry Division, Directorate of Science, PINSTECH, Nilore, Islamabad, Pakistan

Correspondence should be addressed to Hanif Ur Rehman; chem.ics.edu.pk@gmail.com and Nauman Ali; nali75pk@upesh.edu.pk

Received 11 April 2017; Revised 30 July 2017; Accepted 13 August 2017; Published 2 November 2017

Academic Editor: Thijs A. Peters

Copyright © 2017 Hanif Ur Rehman et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The facilitated passage of Zn (II) across flat sheet supported liquid membrane saturated with TDDA (tri-n-dodecylamine) in xylene membrane phase has been investigated. The effect of acid and metal ion concentration in the feed solution, the carrier concentration in membrane phase, stripping agent concentration in stripping phase, and coions on the extraction of Zn (II) was investigated. The stoichiometry of the extracted species, that is, complex, was investigated on slope analysis method and it was found that the complex $(LH)_2 \cdot Zn(Cl_2)$ is responsible for transport of Zn (II). A mathematical model was developed for transport of Zn (II), and the predicted results strongly agree with experimental ones. The mechanism of transport was determined by coupled coion transport mechanism with H^+ and Cl^- coupled ions. The optimized SLM was effectively used for elimination of Zn (II) from waste discharge liquor of galvanizing plant of Zn (II).

1. Introduction

Over the past few decades, the prompt boost in the utilization of heavy metals has increased the flux of metallic ingredients into soils and natural water resources. The presence of even small amount of heavy metals in the environment is hazardous as the majority of them are harmful and persistent [1]. The zinc concentration in the earth crust is about 70 ppm. Zinc and its compounds have many applications and are used in galvanization, alloys, catalysts, wood preservation, vulcanization for rubber, photographic paper, ceramics, fertilizers, textiles, batteries, pigments and as dietary supplements and in medicines [2, 3].

About two billion people suffer from zinc deficiency in the developing countries and this thus causes various disorders in them. In minors, zinc deficiency is responsible for growth retardation, infection susceptibility, delayed sexual

maturation, and diarrhea. These disorders lead to the deaths of about 800,000 children throughout the world every year.

Excess of zinc in the human body has been associated with system dysfunction which in turn can affect growth and reproduction. The presence of free zinc ion in solution has been reported to be very toxic for vertebrates, invertebrates, and plants [4–6]. Due to its toxic effect, large scale applications, and increasing demand for pure zinc, it is necessary to remove and separate zinc from industrial effluents.

Traditional techniques of recovery for metal ions, such as adsorption [7, 8], solvent extraction [9–12], precipitation [13], and ion exchange [14], have normally low efficiency, require high capital and operating cost, and produce secondary pollution complications [15]. Among novel techniques suggested for transport of metal ions, supported liquid membrane is one of the promising methods. The technique comprises the applications of solvent extraction (high selectivity and

distribution coefficient) while overcoming usual extraction's shortcomings (loss of carrier due to emulsification and dispersion) [16–18].

Kanungo and Mohapatra [19] investigated the transport of Zn (II) through supported liquid membrane using bis(2,4,4-trimethylpentyl)phosphinic acid as a metal ion carrier. A model for the rate of transport of binary and ternary complex species has been discussed. The transport of Zn (II) via di-(2-ethylhexyl)phosphoric acid supported liquid membrane has been studied by Ata et al. [20]. The influence of pH of feed solution, carrier, and stripping agent concentration, temperature, and flow rate of feed and stripping solution on the transport of Zn (II) has been investigated. Wódzki and Szczepański found simultaneous recovery and bifurcation of Zn (II) and Cu (II) by means of two parallel BLMs. The two selective carriers, 5-nonylsalicylaldoxime and di-(2-ethylhexyl), were employed for transport of Zn (II) and Cu (II), respectively [21]. The selective removal of Zn (II) from other transition metals and transport across polymer inclusion membrane was investigated by Ulewicz and his coworkers [22]. It has been observed that transport selectivity of Zn (II) over Ni (II), Co (II), Cd (II), and Cu (II) decreases while increasing pH of the feed solution. Furthermore, it has been studied that Zn (II) can be selectively eliminated from dilute aqueous feed solution by solvent extraction. Kozłowska et al. studied the competitive transport of Zn (II), Cd (II), and Pb (II) through polymer inclusion membranes having organophosphorous acids as an ion carrier [23]. The nature of the extractants on cation efficiency and selectivity has been elaborated. Torz et al. reported the transport of Zn (II) from hydrochloric acid feed solution through hollow fiber modules using tributyl phosphate as a carrier [24]. It has been observed that the kinetics of the mass transfer process was restricted by the diffusion of species in the membrane openings. Lee et al. investigated the separation of zinc and copper by hollow fiber supported liquid membrane containing LIX 84 and PC-88A as mobile carriers. The influence of numerous operational factors on separation and permeation rate of Zn (II) and Cu (II) has been studied [25].

In our previous papers [26–29], an effort was made to design a model for transport of Ag (I), Mn (II), Pb (II), and Tl (III), through SLM using various carriers and diluents, and successfully applied to industrial waste effluents.

The present work elaborates the extraction and separation of Zn (II) from aqueous acidic feed solution through flat sheet supported liquid membrane using TDDA as a mobile carrier. In SLM studies, the influence of several process parameters like acid concentration in the feed solution, Zn (II) concentration in the feed solution, the carrier concentration in membrane phase, and NaOH concentration in strip solution on the Zn (II) flux was investigated. Another aim of current work was to investigate the species formed during the transport of Zn (II) and mechanism of Zn (II) and further to establish the stoichiometry of the chemical reactions through SLM. Furthermore, this study was concentrated to ascertain the most optimum conditions for transport of Zn (II), especially for its large scale separation and recovery from industrially galvanizing waste effluents of Zn (II). No such

investigations have been done so far using TDDA SLM system for transport of Zn (II).

2. Theory

Transport of metal ion through SLM occurs by diffusion of metal-carrier complex via various basic steps. First, the metal ion diffuses across aqueous diffusion layer from aqueous bulk feed solution to membrane feed interface and the metal-carrier complex is prepared at feed membrane interface. The complex is then diffused through liquid membrane phase to strip membrane interface owing to the concentration gradient. The complex is finally dissociated at strip membrane interface, carrier returns back across liquid membrane phase, and metal ion diffuses through aqueous diffusion layer into bulk strip solution. The theoretical model of mass transfer of Zn (II) for this purpose is important for the diffusion of metal-carrier complex.

3. Experimental

3.1. Chemicals and Reagents. ZnCl_2 (97% BDH) in HCl (37% Merck) was used as feed in various concentration. NaOH (99–100% Merck) in distilled water in various concentrations was used as a stripping solution and TDDA ($\geq 95\%$ Merck) with diluent xylene (99.5%) to get the various composition of metal ion carrier. Double distilled and deionized water was used in all experiments. All other chemicals used were of analytical or better grade.

3.2. Analytical Instruments. Atomic absorption spectrometer of Perkin Elmer model 400 was used to measure the concentration of zinc (II) and other metal ions in feed and strip solutions. pH was determined through pH meter of Metrohm model 827. Viscosity determination of TDDA (in xylene) was performed via viscometer/rheometer of Brookfield LVDV-III.

3.3. Permeation Cell. The metal ion transport study was performed in two-compartment cell made of Perspex material as reported in our previous work [26]. Each half cell of the permeation cell had the volume capacity of 300 cm^3 and active membrane area was 23.79 cm^2 . Each half was equipped with synchronous motors, pH electrode, and sampling port. The stirring speed of 1500 rpm [26] was optimized for the similar type of permeation cell and carrier; therefore this stirring speed was used in all the permeation study. All the experiments were conducted at $25 \pm 0.5^\circ\text{C}$.

3.4. SLM Preparation. The microporous polypropylene thin coating of Celgard 2400 was applied as a solid support for a liquid organic carrier with an active pore size of $0.02\text{ }\mu\text{m}$, the thickness of $25\text{ }\mu\text{m}$, and porosity of 38%. The membrane was cut into rectangular pieces of $8 \times 6\text{ cm}$ and was soaked in the premeasured concentration of TDDA diluted with xylene in Petri dish for overnight. The membrane was then taken out from the organic solution. The excess amount of organic carrier and solvent were removed by allowing them to drain off the membrane for about five minutes.

3.5. SLM Transport Study. The membrane after preparation was placed in between the two compartments of the cell and screwed together to form a water tight seal. Both compartments of the cell were filled with 300 mL of predetermined concentration of feed and strip solutions. To avoid concentration polarization at feed and strip membrane interfaces,

the two solutions in feed and strip compartments were continuously stirred. Samples were collected after a specific time interval from both feed and strip solution and tested for metal ion concentration. For most of the experiments, the carrier concentration was 0.80 mol/dm³ in xylene.

The flux (J) was calculated as follows [26]:

$$\text{Flux} = \frac{\text{concentration of Zn}^{2+} \text{ mol/dm}^3 \times \text{solution volume in feed or strip (dm}^3\text{)}}{\text{effective membrane area (m}^2\text{)} \times \Delta t} \quad (1)$$

4. Results and Discussion

4.1. Reactions at Feed Membrane Interface. If tri-n-dodecylamine (TDDA) is represented by L, the following possibilities of reactions may take place. The tri-n-dodecylamine can be protonated to LH⁺ in acidic medium (HCl).

It is supposed that ZnCl₂ in feed solution in the presence of excess chloride ions due to HCl is converted to

The cationic (LH⁺)(org) and anionic species [Zn(Cl₂ + n)]ⁿ⁻_(aq) then interact at feed membrane interface and form the complex as

The subscript org represents organic phase and aq aqueous phase and n indicates the number of Cl⁻, H⁺, and L molecules associating with Zn (II) ions to form the neutral complex (LH)_n·Zn(Cl₂ + n)_(org).

To express the contribution of H⁺ and Cl⁻, (3) may be represented as

4.2. Reactions at Strip Membrane Interface. The neutral complex formed at feed membrane interface as per (3)/(4) is extractable in liquid organic phase and disperses from feed membrane interface to strip membrane interface. The

complex at strip membrane interface is dissociated owing to NaOH in the stripping phase as follows:

The free carrier molecule (L) diffuses back through the liquid membrane phase towards feed membrane interface and again forms the complex. As per Wilke-Chang, the diffusion coefficient of the forward moving complex (LH)_n·Zn(Cl₂ + n)_{org} should be noticeably lesser than the diffusion coefficient of the backward moving free carrier molecules [30]. Owing to this reason, the free carrier concentration at feed membrane interface will constantly be higher than the complex. Figure 1 represents the schematic transport mechanism of Zn (II) through supported liquid membrane.

The equilibrium constant K_{zn} of (4) for Zn (II) can be written as follows:

$$K_{zn} = \frac{[(LH)_n \cdot Zn(Cl_2 + n)]_{org}}{[L]_{org}^n \cdot [H^+]_{aq}^n \cdot [Zn^{2+}]_{aq} \cdot [Cl^-]_{aq}^n} \quad (7)$$

The distribution coefficient of Zn²⁺ (λ_{zn}) for distribution between the membrane and aqueous phases can be represented as follows:

$$\lambda_{zn} = \frac{[(LH)_n \cdot Zn(Cl_2 + n)]_{org}}{[Zn^{2+}]_{aq}} \quad (8)$$

$$K_{zn} = \frac{\lambda_{zn}}{[L]_{org}^n \cdot [H^+]_{aq}^n \cdot [Cl^-]_{aq}^n} \quad (9)$$

And on rearranging of (8),

$$\lambda_{zn} = K_{zn} \cdot [L]_{org}^n \cdot [H^+]_{aq}^n \cdot [Cl^-]_{aq}^n \quad (10)$$

Now considering the extraction constant, distribution coefficient, and laws of diffusion via the same path as [29], it can be indicated as:

$$\log J\eta = \frac{\log y + \log T + n \log [L]_{org} + n \log [H^+]_{aq} + n \log [Cl^-]_{aq} + \log C_f}{\ell} \quad (11)$$

$$\log J\eta = \text{constant} + n \log [L]_{org} + n \log [H^+]_{aq} + n \log [Cl^-]_{aq} + \log C_f \quad (12)$$

FIGURE 1: Transport mechanism of Zn (II) through supported liquid membrane.

Equation (11) shows that, at a constant temperature, the flux (J) of Zn (II) is directly proportional to the concentration of Cl^- , H^+ , L , and C_f . This equation can be used to find the number of H^+ related to L in the form of LH^+ . This can be determined by various methods: one method is to keep $[\text{Cl}^-]$, $[L]$, and C_f constant in (11) and plotting $\log J\eta$ against $\log[\text{H}^+]$; the slope of the curve will provide the “ n ” value for a number of H^+ ions in the complex. Likewise by drawing $\log J\eta$ versus $\log[L]$ and maintaining $[\text{Cl}^-]$, $[\text{H}^+]$, and C_f constant, the slope of the plot will give a number of moles (n) of TDDA contributing in complex formation of Zn (II).

4.3. Effect of Carrier Concentration. The carrier in the liquid membrane phase of the supported liquid membrane has a critical role in the extraction of metal ions by SLM [26]. Various concentrations of carrier ranging from 0.157 mol/dm^3 to 1.103 mol/dm^3 were used in solvent xylene to observe the effect of carrier concentration on the transport of Zn (II) through SLM. During this study, the Zn (II) concentration in feed solution was kept at $7.385 \times 10^{-4} \text{ mol/dm}^3$ in 2.0 mol/dm^3 of HCl and the NaOH concentration in strip solution was fixed at 2.0 mol/dm^3 .

Figure 2 shows that with the increase of carrier concentration from 0.157 to 0.80 mol/dm^3 in xylene in the membrane phase has a significant effect on flux of Zn (II). It follows (11) where flux (J) is directly proportional to carrier concentration $[L]$. However, the flux is insignificant as the concentration of carrier increases beyond 0.80 mol/dm^3 . This reduction in transport of Zn (II) might be the result of enhanced friction of liquid membrane phase owing to high viscosity, as with the increase in carrier concentration, the viscosity of liquid membrane phase increases [29]. Hence 0.80 mol/dm^3 of tri-*n*-dodecylamine was considered the optimum carrier concentration and more investigations were performed with this concentration of carrier.

Finding the number (n) of tri-*n*-dodecylamine (L) taking part in complex $(\text{LH})_n \cdot \text{Zn}(\text{Cl}_2 + n)$ was determined by plotting $\log[\text{TDDA}]$ versus $\log J\eta$ as shown in Figure 3. The slope of the plot is 2.008 , and this indicates that two molecules of TDDA take part in the complex formation.

FIGURE 2: Effect of carrier concentration on transport of Zn (II) in the stripping phase. $[\text{HCl}]$ in feed solution = 2.0 mol/dm^3 , $[\text{TDDA}]$ in membrane phase = 0.157 mol/dm^3 to 1.103 mol/dm^3 , $[\text{NaOH}]$ in stripping solution = 2.0 mol/dm^3 , $[\text{Zn (II)}] = 7.385 \times 10^{-4} \text{ mol/dm}^3$, time = 5.0 h .

FIGURE 3: Plot of $\log[\text{TDDA}]$ versus $\log J\eta$ (same operating conditions as given in Figure 2).

In our previous study for the stability of membrane for such type of carrier, it has been observed that supported liquid membrane is quite stable for a period of 120 h with very minute flux variation in the metal ion flux and no indication of structural deformation of polypropylene membrane was investigated. Furthermore, the membrane was reused several times without leakage and metal ion flux decline [28].

4.4. Role of HCl Concentration in Feed Phase. The HCl performs an important part in the transportation of Zn (II) because it provides H^+ and Cl^- for the formation of complex $(\text{LH})_n \cdot \text{Zn}(\text{Cl}_2 + n)$ as per (4). The effect of HCl concentration on extraction Zn (II) was observed by varying the concentration of HCl in the range of 0.5 mol/dm^3 to 3.0 mol/dm^3 , while keeping the concentration of TDDA in the liquid membrane phase at 0.80 mol/dm^3 and concentration of NaOH on strip side at 2.0 mol/dm^3 . Figure 4 shows that as the concentration of HCl increases from 0.5 mol/dm^3 to 2.0 mol/dm^3 and the flux of Zn (II) increases. Thus, it can be concluded that with an increase of HCl concentration, the concentration of H^+ and Cl^- ions in feed solution also increases. This, in turn, increases the formation of the complex as per (4), which ultimately enhances the transport of Zn (II). Although, by further increasing the concentration of HCl beyond 2.0 mol/dm^3 , the transport of Zn (II) decreases and this may be due to the formation of $\text{H}_n \cdot \text{Zn}(\text{Cl}_2)_n$ type species due to the large quantity of H^+ and Cl^- in feed phase and reaction

FIGURE 4: Effect of HCl concentration in feed solution on flux (J) of Zn (II). [HCl] in feed solution = 0.50 mol/dm^3 to 3.0 mol/dm^3 , [TDDA] in membrane phase = 0.80 mol/dm^3 , [NaOH] in stripping solution = 2.0 mol/dm^3 , time = 5.0 h.

FIGURE 5: Plot of $\log[\text{HCl}]$ versus $\log J\eta$ (same operating conditions as given in Figure 4).

(4) is hindered in forward direction. This study shows that 2.0 mol/dm^3 of HCl is the most favorable concentration for transport of Zn (II), and further studies were carried out with this concentration of HCl to evaluate various parameters for subsequent studies.

To investigate that how much hydrogen is taking part in complexation of Zn (II), $\log J\eta$ was plotted versus $\log[\text{HCl}]$ (Figure 5). The slope of this plot was approximately 2.0, indicating that two hydrogens take part in a complex of Zn (II) transport. As the transport study concluded that two molecules of TDDA and H^+ are involved in the complex formation of Zn (II), the complex formed during this extraction study may be $(\text{LH})_n \cdot \text{Zn}(\text{Cl}_2 + n)$.

4.5. Influence of Feed Concentration. To study the capability of this SLM for metal ion transport, various concentrations of Zn (II) from $3.692 \times 10^{-4} \text{ mol/dm}^3$ to $18.463 \times 10^{-4} \text{ mol/dm}^3$ were used in the feed solution. During this particular study, the concentrations of the carrier, stripping phase, and HCl in feed solution were kept at 0.80 mol/dm^3 , 2.0 mol/dm^3 , and 2.0 mol/dm^3 , respectively.

Figure 6 shows that as Zn (II) concentration in feed solution rises, the transport of Zn (II) also increases; this is as per (11), where flux (J) is directly proportional to feed concentration (C_f). Such type behavior has already been studied in our previous study [27, 28]. This study shows that up to $18.463 \times 10^{-4} \text{ mol/dm}^3$ no saturation of carrier with metal ion takes place.

FIGURE 6: Effect of Zn (II) concentration in feed solution on its flux. [Zn(II)] in feed = $3.692 \times 10^{-4} \text{ mol/dm}^3$ to $18.463 \times 10^{-4} \text{ mol/dm}^3$, [HCl] in feed = 2.0 mol/dm^3 , [NaOH] in stripping solution = 2.0 mol/dm^3 , [TDDA] in membrane phase = 0.80 mol/dm^3 , time = 5.0 h.

FIGURE 7: Effect of NaOH concentration in strip solution on the flux of Zn (II). [NaOH] in stripping solution 0.05 mol/dm^3 to 2.5 mol/dm^3 , [HCl] in feed solution = 2.0 mol/dm^3 , [TDDA] in membrane phase = 0.80 mol/dm^3 , time = 5.0 h.

4.6. Influence of Stripping Phase Concentration. The stripping agent dissociates the complex $(\text{LH})_n \cdot \text{Zn}(\text{Cl}_2 + n)$ at strip membrane interface and releases Zn (II) in strip solution. To investigate the effect of NaOH on the transport of Zn (II), numerous concentrations of NaOH in the range of 0.05 mol/dm^3 to 2.5 mol/dm^3 were used, while keeping the TDDA concentration at 0.80 mol/dm^3 and HCl concentration in feed solution at 2.0 mol/dm^3 .

Figure 7 shows that as the concentration of NaOH rises from 0.05 mol/dm^3 to 0.1 mol/dm^3 , the flux of Zn (II) decreases and, beyond this concentration of NaOH, the flux of Zn (II) increases. The decrease in transport of Zn (II) at a lower concentration of NaOH can be explained that it forms a precipitate of $\text{Zn}(\text{OH})_2$ which is insoluble and blocks the pores of polypropylene membrane and transport of Zn (II) is restricted [31]. The SEM (Figure 8(b)) indicates the blocked SLM at a lower concentration of NaOH. More increase in the concentration of NaOH increases the transportation of Zn (II), as the precipitate of $\text{Zn}(\text{OH})_2$ is soluble in excess of NaOH and more OH^- are available that enhance the decomposition of the complex at strip membrane interface as per (5).

(a) SEM of the membrane before Zn (II) transport

(b) SEM of membrane at 0.1 mol/dm^3 of NaOH ([HCl] in feed solution = 2.0 mol/dm^3 , [TDDA] in membrane phase = 0.80 mol/dm^3 , [Zn (II)] = $7.385 \times 10^{-4} \text{ mol/dm}^3$).

FIGURE 8

FIGURE 9: Variation in Zn (II) concentration in feed and strip solution against time (waste discharge liquor of galvanizing plant). Initial Zn (II) conc. in feed = $5.16 \times 10^{-4} \text{ mol/dm}^3$, [HCl] in feed = 2.0 mol/dm^3 , [NaOH] in stripping solution = 2.0 mol/dm^3 , [TDDA] in membrane phase = 0.80 mol/dm^3 .

5. Recovery of Zinc (II) from Waste Discharge/Effluent of Galvanizing Plant

The objective of this work was to design and develop SLM for recovery of Zn (II) from industrial waste effluents. The polypropylene as supported liquid membrane, TDDA as a carrier, was utilized for extraction of Zn (II) from waste discharge liquor of galvanizing plant. To check and assess the efficiency of SLM system, samples of galvanized industrial waste were collected from the different locations of the drain carrying the galvanizing industrial effluent. The effluent samples were analyzed using the aforementioned method as described in Experimental and the percent extraction and recovery of the Zn(II) metal ions were determined using atomic absorption spectrophotometry method. The data obtained is provided in Figure 9 which indicates approximately the complete extraction and recovery of Zn (II) after

210 minutes. This shows the suitability and effectiveness of this SLM for recovery of Zn (II).

6. Recovery and Transport of Zn(II) from Galvanizing Plant Waste

The present SLM was designed for the transport of Zn(II) metal ions and applied to zinc industrial effluents of galvanizing plants because zinc is one of the industrial important metals because of its applications and its use for protection, passivation, and decoration of some heavy elements. The data in Table 2 show that TDDA-polypropylene SLM system has significant transport efficiency for Zn(II) metal ions, that is, about 99.8%, while other metal ions like Co, Cu, Cd, Mn, Cr, and Fe show very little or more precisely negligible amount of transport that is 0.0 to 0.72% or in average 0.08% for Co, 0.23% for Cu, 0.15% for Cd, 0.36% for Mn, 0.06% for Cr, and 0.28% for Fe. This much smaller amount of transport may be attributed to experimental error. If error factor is taken into account then TDDA-polypropylene SLM system is highly selective for transport of Zn(II) metal ions only. The data are represented in Tables 1 and 2.

7. Conclusions

The flux ($J_{\text{Zn(II)}}$) got increased by increasing carrier concentration up to 0.80 mol/dm^3 , and, further increasing the carrier concentration, the transport of Zn (II) was found to decrease. The Zn(II) ions transport was increased by increasing HCl concentration in feed solution up to 2.0 mol/dm^3 and then decreased using a higher concentration of HCl. The slope analysis studies of $\log J_{\eta}$ of Zn (II) versus $\log[\text{TDDA}]$ and $\log[\text{HCl}]$ showed that 2.0 mole of each tri-n-dodecylamine and hydrogen are involved in the transport of Zn (II). The maximum transport of Zn (II) was achieved at 0.80 mol/dm^3 of TDDA in membrane phase and 2.0 mol/dm^3 of HCl and NaOH in feed and strip solution, respectively. It was also found to be coupled coion extraction pathway, as H^+ , Cl^- , and Zn (II) travel in the same direction. Two moles of hydrogen

TABLE I: Analysis of galvanizing plants waste.

Metal ions	Zinc galvanizing plant-I			Zinc galvanizing plant-II			Zinc galvanizing plant-III			Zinc galvanizing plant-IV		
	Original concentration of actual sample BT (mg/L)	Concentration of actual sample after transport AT (mg/L)	Original concentration of actual sample BT (mg/L)	Concentration of actual sample after transport AT (mg/L)	Original concentration of actual sample BT (mg/L)	Concentration of actual sample after transport AT (mg/L)	Original concentration of actual sample BT (mg/L)	Concentration of actual sample after transport AT (mg/L)	Original concentration of actual sample BT (mg/L)	Concentration of actual sample after transport AT (mg/L)	Original concentration of actual sample BT (mg/L)	Concentration of actual sample after transport AT (mg/L)
Zn	170 ± 0.57	1.0 ± 0.28	130 ± 0.36	0.2 ± 0.05	150 ± 0.64	3.0 ± 0.05	191 ± 0.1	1.20 ± 0.1				
Co	4.66 ± 0.01	4.65 ± 0.011	1.364 ± 0.001	—	9.04 ± 0.5	9.03 ± 0.005	7.05 ± 0.01	7.04 ± 0.001				
Cu	3.86 ± 0.01	3.71 ± 0.015	—	—	5.86 ± 0.01	5.84 ± 0.005	13.3 ± 0.005	13.29 ± 0.32				
Cd	9.990 ± 0.012	9.979 ± 0.006	116.4 ± 0.15	116.168 ± 0.03	11.5 ± 0.003	11.48 ± 0.01	22.0 ± 0.06	21.97 ± 0.01				
Mn	2.850 ± 0.001	2.836 ± 0.0005	6.26 ± 0.01	6.24 ± 0.005	1.56 ± 0.01	1.55 ± 0.002	4.033 ± 0.01	4.032 ± 0.0005				
Cr	—	—	37.48 ± 0.011	37.43 ± 0.01	21.70 ± 0.01	21.70 ± 0.01	7.51 ± 0.006	7.50 ± 0.006				
Fe	16.84 ± 0.005	16.718 ± 0.001	13.2 ± 0.004	13.18 ± 0.01	5.835 ± 0.001	5.820 ± 0.01	3.14 ± 0.01	3.139 ± 0.0005				

BT, before transport; AT, after transport; galvanizing plants I & II, Industrial State Peshawar, Pakistan; galvanizing plants III & IV, Industrial State Rawalpindi, Pakistan.

TABLE 2: Percent transport of metal ions from galvanizing plants waste.

Metal ions	Percent transport of metal ions from waste of zinc galvanizing plants			
	Zinc galvanizing plant-I (% transport)	Zinc galvanizing plant-II (% transport)	Zinc galvanizing plant-III (% transport)	Zinc galvanizing plant-IV (% transport)
Zn	98.50	99.33	98	99.37
Co	0.2	00	0.011	0.14
Cu	0.38	00	0.5	0.07
Cd	0.11	0.19	0.17	0.13
Mn	0.49	0.31	0.64	0.02
Cr	00	0.13	00	0.13
Fe	0.72	0.15	0.25	0.03

and TDDA interact with one mole of Zn (II) producing a complex $(LH)_n \cdot Zn(Cl_2 + n)$, that is responsible for transport of Zn (II). This SLM system was effectively used for removal of Zn (II) to the waste discharge liquor of galvanizing plant of zinc.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

The authors acknowledge Sarhad University of Science and Information Technology, Peshawar, KPK, Pakistan, for providing financial assistance to accomplish this work.

References

- [1] R. A. Wuana and F. E. Okieimen, "Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation," *ISRN Ecology*, vol. 2011, Article ID 402647, 20 pages, 2011.
- [2] D. W. Thomas, *Metals and Their Compounds in the Environment*, Edited by E. Merian, Wiley, Weinheim, Germany, 1991.
- [3] ATSDR (Agency for Toxic Substances and Disease Registry), *Toxicological Profile for Zinc*, Public Health Service, U.S. Department of Health and Human Services, Atlanta, Ga, USA, 2005.
- [4] A. S. Prasad, "Zinc deficiency," *The British Medical Journal*, vol. 326, no. 7386, pp. 409-410, 2003.
- [5] K. M. Hambidge and N. F. Krebs, "Zinc deficiency: a special challenge," *Journal of Nutrition*, vol. 137, no. 4, pp. 1101-1105, 2007.
- [6] G. J. Fosmire, "Zinc toxicity," *American Journal of Clinical Nutrition*, vol. 51, no. 2, pp. 225-227, 1990.
- [7] L. Monser and N. Adhoum, "Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater," *Separation and Purification Technology*, vol. 26, no. 2-3, pp. 137-146, 2002.
- [8] S. Liang, X. Guo, and Q. Tian, "Adsorption of Pb^{2+} and Zn^{2+} from aqueous solutions by sulfured orange peel," *Desalination*, vol. 275, no. 1-3, pp. 212-216, 2011.
- [9] F. J. Alguacil and S. Martínez, "Solvent extraction of Zn(II) by cyanex 923 and its application to a solid-supported liquid membrane system," *Journal of Chemical Technology and Biotechnology*, vol. 76, no. 3, pp. 298-302, 2001.
- [10] K. C. Sole, T. L. Ferguson, and J. B. Hiskey, "Solvent extraction of silver by cyanex 272, cyanex 302 and cyanex 301," *Solvent Extraction and Ion Exchange*, vol. 12, no. 5, pp. 1033-1050, 1994.
- [11] P. M. Cole and K. C. Sole, "Zinc solvent extraction in the process industries," *Mineral Processing and Extractive Metallurgy Review*, vol. 24, no. 2, pp. 91-137, 2003.
- [12] M. S. Lee and S.-H. Nam, "Solvent extraction of zinc from strong hydrochloric acid solution with Alamine336," *Bulletin of the Korean Chemical Society*, vol. 30, no. 7, pp. 1526-1530, 2009.
- [13] F. M. Pang, S. P. Teng, T. T. Teng, and A. K. M. Omar, "Heavy metals removal by hydroxide precipitation and coagulation-flocculation methods from aqueous solutions," *Water Quality Research Journal of Canada*, vol. 44, pp. 1-9, 2009.
- [14] S. V. Plokhov, I. G. Matasova, V. A. Utkin, and V. Y. Vodzinskii, "Specific features of ion-exchange zinc(II) extraction from washing water of zinc plating," *Russian Journal of Applied Chemistry*, vol. 75, no. 6, pp. 950-953, 2002.
- [15] K. H. Park, P. K. Parhi, and N.-H. Kang, "Studies on the removal of low content copper from the sea nodule leach liquor using the cationic resin TP 207," *Separation Science and Technology*, vol. 47, no. 10, pp. 1531-1541, 2012.
- [16] J. D. Gyves and E. R. San Miguel, "Metal ion separations by supported liquid membranes," *Industrial and Engineering Chemistry Research*, vol. 38, no. 6, pp. 2182-2202, 1999.
- [17] V. V. Prasad, D. J. Yogesh, D. S. Ajay et al., "Simultaneous extraction of neodymium and uranium using hollow fiber supported liquid membrane," *Separation Science and Technology*, vol. 49, no. 10, pp. 1509-1520, 2014.
- [18] B. Mokhtari and K. Pourabdollah, "Inclusion separation of alkali metals in emulsion liquid membranes by nanobaskets of calix[4]crown-3," *Brazilian Journal of Chemical Engineering*, vol. 29, no. 4, pp. 783-793, 2012.
- [19] S. B. Kanungo and R. Mohapatra, "Coupled transport of Zn (II) through a supported liquid membrane containing bis (2,4,4-trimethyl pentyl) phosphinic acid in kerosene. 1. A model for the rate process involving binary and ternary complex species," *Journal of Membrane Science*, vol. 105, pp. 217-226, 1995.
- [20] O. N. Ata, A. V. Beşe, S. Çolak, B. Dönmez, and A. Çakıcı, "Effect of parameters on the transport of zinc ion through supported liquid membrane," *Chemical Engineering and Processing: Process Intensification*, vol. 43, no. 7, pp. 895-903, 2004.
- [21] R. Wódzki and P. Szczepański, "Simultaneous recovery and separation of Zn^{2+} and Cu^{2+} in hybrid membrane systems,"

- Separation and Purification Technology*, vol. 41, no. 3, pp. 289–297, 2005.
- [22] M. Ulewicz, W. Walkowiak, J. Gega, and B. Pospiech, “Zinc (II) selective removal from other transition metal by solvent extraction and transport through polymer inclusion membranes with D2EHPA,” *Ars Separatoria Acta*, vol. 2, pp. 47–55, 2003.
- [23] J. Kozłowska, C. A. Kozłowski, and J. J. Koziol, “Transport of Zn(II), Cd(II), and Pb(II) across CTA plasticized membranes containing organophosphorous acids as an ion carriers,” *Separation and Purification Technology*, vol. 57, no. 3, pp. 430–434, 2007.
- [24] M. Torz, K. Alejski, and J. Szymanowski, “Modelling of zinc (II) extraction from model hydrochloric acid solutions in hollow fiber modules,” *Physicochemical Problems of Mineral Processing*, vol. 37, pp. 97–105, 2003.
- [25] J.-C. Lee, J. Jeong, B.-S. Kim, M. S. Kim, and M. Kobayashi, “Separation of copper and zinc ions by hollow fiber supported liquid membrane containing LIX84 and PC-88A,” *Materials Transactions*, vol. 45, no. 6, pp. 1915–1919, 2004.
- [26] S. U. Rehman, G. Akhtar, M. A. Chaudry, N. Bukhari, Najee-bullah, and 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,” *Journal of Membrane Science*, vol. 366, no. 1–2, pp. 125–131, 2011.
- [27] S. U. Rehman, G. Akhtar, and M. A. Chaudry, “Coupled transport of Tl^{3+} through triethanolamine-xylene-polypropylene supported liquid membranes,” *Journal of Industrial and Engineering Chemistry*, vol. 18, no. 1, pp. 492–498, 2012.
- [28] S. U. Rehman, G. Akhtar, M. A. Chaudry, K. Ali, and N. Ullah, “Transport of Ag^+ through tri-n-dodecylamine supported liquid membranes,” *Journal of Membrane Science*, vol. 389, pp. 287–293, 2012.
- [29] S. Ur Rehman, G. Akhtar, and M. A. Chaudry, “Coupled transport of Pb^{2+} through tri-n-octylamine-xylene-polypropylene supported liquid membranes,” *Canadian Journal of Chemical Engineering*, vol. 91, no. 6, pp. 1140–1152, 2013.
- [30] S. A. Ansari, P. K. Mohapatra, and V. K. Manchanda, “Recovery of actinides and lanthanides from high-level waste using hollow-fiber supported liquid membrane with TODGA as the carrier,” *Industrial and Engineering Chemistry Research*, vol. 48, no. 18, pp. 8605–8612, 2009.
- [31] F. Holleman, A. E. Wiberg, and N. Wiberg, *Zink, Lehrbuch der Anorganischen Chemie*, Walter de Gruyter, Berlin, Germany, 91th–100th edition, 1985.