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Transportation and kinetic analysis of Zn(II) ions via MDLM system containing D2EHPA as carrier

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Abstract. In this study, a new method called as multi-dropped liquid membrane (MDLM) which is more practical and more effective than other liquid membrane techniques is applied for transport of Zn(II) has been studied. HCl as the stripping solution and D2EHPA dissolved in kerosene as the membrane solution, has been examined. The effects of stripping solution concentration, carrier concentration, temperature and pH in the feed phase on the transport of Zn(II) have also been investigated. As a result, the optimum transport conditions of Zn(II) were obtained, i.e., the concentration of HCl solution was 0.25 M, the concentration of D2EHPA was 8×10^{-3} M, and pH value in the donor phase was 5.00. Under the optimum conditions, the transport percentage of Zn(II) was up to >99% during the transport time of 80 min when the initial concentration of Zn(II) was 120 mgL^{-1}. The activation energy is calculated as 5.30 kcalmol^{-1}. The value of calculated activation energy indicates that the process is diffusionally controlled by Zn(II) ions. The experiments have demonstrated that D2EHPA derivative is a good carrier for Zn(II) transport through MDLM in the study.

Keywords: zinc; D2EHPA; membrane; MDLM; transport

1. Introduction

Heavy metals are the common metal pollutants introduced into the environment through industrial effluents. Heavy metals are non-degradable and hence their concentration continuously increases in the environment. Some of these metals are carcinogenic and pose a serious threat to biota and the environment. Nowadays attention is given not only to the removal of the pollutants from effluents, but also to recover them for reuse.

Recently, hydrometallurgical processes have been widely applied to produce metals and their compounds from low-grade ores. In particular, the selective recovery of these metals from such solutions is required for economic/environmental reasons and has a high-priority status in many governmental and industrial sites (Fouad 2008). There are many methods, which have been established commercially to recover precious metals from industrial waste such as solvent extraction, ion exchange, electrolysis, cementation, precipitation, and membrane separation (Othman *et al.* 2004). Electrolytic recovery, it is inadequate at lower concentrations and includes high cost and the formation of harmful gases. In ion exchange, similar to other membrane processes, electro dialysis membranes are susceptible to fouling and require regular replacement.

The fields of LM (liquid membrane) have appeared quite recently as a new prospective separation method. LM soon became very popular in various fields due to their good selectivity and efficiency achieved by the presence of a mobile and selectively acting agent (a carrier) (Religa *et al.* 2009). A suitable choice of the extractant decides the success of the extraction process (Guezzen and Didi 2002).

Several extractants were developed and their properties of extraction were evaluated for various metal ions. LM is currently undergoing a rapid expansion of the areas of both research and industrial separation techniques. The most popular application of LM concerns the removal and recovery of metal ions from waste water (Gill *et al.* 2000, Kulkarni *et al.* 2002).

There are three types of mass transfer mechanism in LM process namely, selective permeation, chemical reaction inside emulsion droplets and chemical reaction in membrane phase. In terms of metal extraction chemistry, it is basically identical to that found in solvent extraction, but the overall process is governed by kinetics rather than equilibrium parameters. However, little information concerning the liquid membrane LM transport of precious metals have been reported, since many transport systems have encountered different problems, for instances, slow extraction kinetics in stripping and deposition of metal species (Sastre *et al.* 2000). For the recovery and enrichment process of metal ions, the third mechanism should apply, which is the carrier species may be incorporated into the organic solvent in the membrane phase and gives rise to facilitate transport (Coelhoso *et al.* 1995, Bhowal and Datta 2001).

The zinc ion is one of the most useful of all the metals in different industries as it is always present in polluted waters, sewage and industrial waste (Boyadzihev and Lazarova 1995). Large amounts of zinc are added during

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industrial activities, such as mining, coal and waste combustion and steel processing (Wuana and Okieimen 2011). So, the extraction of zinc has been widely studied with different extractants.

In this study, a new method which is more practical and more effective than other techniques is applied. This method resembles the bulk liquid membrane system, but shows a little difference. Actually, it can be called as MDLM. The advantages of this technique are as follows: simple construction, lack of moving parts, lightweight and portable, flexible in operation, high membrane capacity, high separation factor than mixer-settler. And this new method reduces operation time, risk of contamination, amounts of reagents used, generated waste. This method can be applied to wastewater containing heavy metals by the enlargement of the donor and acceptor phase reactors (Donat and Durmaz 2015). Because of these attractive advantages, the current experimental studies can be a great alternative and economical process in order to remove the heavy metal ions caused by heavy metal industries.

The results of our investigation of the kinetics of Zn(II) ion transport through MDLM containing D2EHPA as a carrier, flowing over aqueous phases, are presented in this paper.

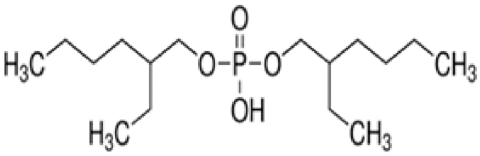


Fig. 1 Chemical structure of D2EHPA

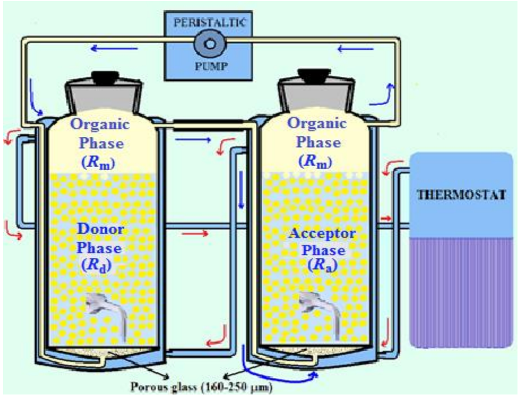


Fig. 2 Schema of the measuring set with flowing MDLM system

2. Experimental

2.1 Chemicals and solutions

LM is composed of an extractant, and a diluent. The mobile carrier or extractant is D2EHPA which is purchased from Merck, Germany. D2EHPA is an organophosphorus compound with the formula $(C_8H_{17}O)_2PO_2H$ (Fig. 1) D2EHPA has been shown to be an effective extractant and extensively used in hydrometallurgical processes for the separation and purification of divalent transition metals such as copper, cobalt, manganese, and zinc (Flett and Spink 1976, Sekine and Hasegawa 1977, Sato *et al.* 1978). Commercial kerosene (TUPRAS Oil Company, Turkey) was used as diluents. Commercial kerosene is a complex mixture of aliphatic origin and also contains aromatic, about 15% (w/w) (Kumbasar 2010). $ZnCl_2.2H_2O$, HCl, D2EHPA and all other chemicals were purchased from Merck and were used directly as received from the manufacturer.

2.2 Experimental procedure

Batch experiments were performed by a flowing MDLM technique. This method resembles the bulk liquid membrane system, but shows a little difference. The scheme of the experimental setup is shown in Fig. 2. For more homogeneous dispersion of droplets, porous glass was applied to the bottom of the reactor. The liquid membrane system consists of two reactors made of glass; one with target metal ions down and organic ligand in kerosene up, the other one with stripping phase down and organic ligands in kerosene up. In both reactors, there are two phases as indicated in Fig. 2 and they are immiscible. In reactor (left) 1, carrier ligand, D2EHPA dissolved in kerosene is placed in the upper part of the tube due to its lower density, donor phase and organic (membrane) phase are immiscible and there is a thin layer at the interface of two phases. The same situation happens in the reactor (right) 2 between stripping phase and organic phase. Donor and acceptor phases are in the base of the porous glass for more homogeneous dispersion of droplets. Organic phase is circled in both reactors by the help of peristaltic pump and forms multi droplets via pores at the bottom of the both reactors. The organic phase passes from either phase as bubbles and mixes the donor and acceptor phase. Porous glasses constitute the organic phase in the form of multiple bubbles. Transportation rate of the two phases of the organic phase can be adjusted by the peristaltic pump. The organic ligands carry target metals from donor phase to stripping phase, leave it there and then turn back to donor phase again in order to re-carry the target metals.

The system is tied up to thermostat (Circu-WCR-P8 Wise model creosote device) to fix the ambient temperature and peristaltic pump to fix the transportation rate. By the help of peristaltic pump, organic extractant passes through both aqueous phases (donor and acceptor) in the form of multi droplets. Samples were drawn from the first reactor (donor phase) to the second reactor (acceptor phase) in 10 minutes time interval and analysed by UV-vis spectrophotometer.

2.3 Analytical instruments

All absorbance measurements of Zn(II) ions in solutions were carried out by using Shimazdu UV-1201V Model spectrophotometer with 1.00 cm quartz cells. In the current experimental study; in order to control temperature, Circu-WCR-P8 Wise model creosote device; to determine the concentration of Zn(II) ions in the solution, Shimazdu UV-1201V model spectrophotometer; in order to carry the organic phase from one reactor to the other and provide compressive force, BT30-2J (YZ1515X titled) peristaltic pump device and finally; for the determination of pH changes of the solution, WTW Microprocessor pH meter is used.

2.4 Data analysis

Zn(II) ion concentration in the membrane phase was established from the material balance. For practical reasons, dimensionless reduced concentrations of Zn(II) in the donor (R_d), organic (R_m), and acceptor phases (R_a) were used ($R_\mathrm{d}=n_\mathrm{d}/n_\mathrm{do}$, $R_\mathrm{m}=n_\mathrm{m}/n_\mathrm{do}$ and $R_\mathrm{a}=n_\mathrm{a}/n_\mathrm{do}$, the sum of $R_\mathrm{d}+R_\mathrm{m}+R_\mathrm{a}$ obviously being unity) (León and Guzmán 2005). When R_d, R_m, and R_a values are determined, the result suggests that the Zn(II) ion transport obeys the kinetic laws of two consecutive irreversible first-order reaction according to the kinetic scheme (Mehta *et al.* 2010).

$$C_\mathrm{d} \xrightarrow{k_1} C_\mathrm{m} \xrightarrow{k_2} C_\mathrm{a} \tag{1}$$

where C_d, C_m, and C_a are the Zn(II) concentrations in donor, membrane and acceptor phases. k_1 and k_2 are pseudo-first-order apparent rate constants of the extraction and reextraction(stripping), respectively. The kinetic scheme Eq. (1) for consecutive irreversible reactions can be described by the following rate equations (Szpakowska and Nagy 1999, Alpoguz *et al.* 2006, Saf *et al.* 2006).

$$\frac{\mathrm{d}R_\mathrm{d}}{\mathrm{d}t} = -k_1 R_\mathrm{d} \equiv J_\mathrm{d/o} \tag{2}$$

$$\frac{\mathrm{d}R_\mathrm{m}}{\mathrm{d}t} = k_1 R_\mathrm{d} - k_2 R_\mathrm{m} \tag{3}$$

$$\frac{\mathrm{d}R_\mathrm{a}}{\mathrm{d}t} = k_2 R_\mathrm{m} \equiv J_\mathrm{a/m} \tag{4}$$

where J represents the flux rate. When $k_1 \neq k_2$, integrating Eqs. (3)-(5) gives the following expressions

$$R_\mathrm{d} = \exp(-k_1 t) \tag{5}$$

$$R_m = \frac{k_1}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \tag{6}$$

$$R_\mathrm{a} = 1 - \frac{1}{k_2 - k_1}[k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] \tag{7}$$

where k_1 and k_2 values are the apparent extraction and reextraction rate constants, respectively.

These equations show that the time dependence of R_d is monoexponential and the time dependence of both R_m and R_a is biexponential. R_m has a maximum value at the time which it occurs that being obtained from $\mathrm{d}R_\mathrm{m}/\mathrm{d}t=0$ (León and Guzmán 2005).

$$t_\mathrm{max} = \frac{ln\left(\frac{k_1}{k_2}\right)}{k_1 - k_2} \tag{8}$$

the value of R_m at that time being

$$R_\mathrm{m}^\mathrm{max} = \left(\frac{k_1}{k_2}\right)^{\frac{k2}{k1-k2}} \tag{9}$$

Combining Eqs. (8) and (9) the following relationship can be obtained (Donat and Durmaz 2015)

$$k_2 = \frac{ln\left(\frac{1}{R_\mathrm{m}^\mathrm{max}}\right)}{t_\mathrm{max}} \tag{10}$$

First-order time differentiation of Eqs. (5)-(7) leads to the final form of the flux equations (He *et al.* 2000).

$$\frac{\mathrm{d}R_\mathrm{d}}{\mathrm{d}t} = -k_1 \exp(-k_1 t) \tag{11}$$

$$\frac{\mathrm{d}R_\mathrm{m}}{\mathrm{d}t} = \frac{k_1}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \tag{12}$$

$$\frac{\mathrm{d}R_\mathrm{a}}{\mathrm{d}t} = \frac{k_1 k_2}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \tag{13}$$

By substituting the expression of t_max given for Eq. (8) in Eqs. (11)-(13), maximum fluxes can be obtained (He *et al.* 2000).

$$\left[\frac{\mathrm{d}R_\mathrm{d}}{\mathrm{d}t}\right]_\mathrm{max} = -k_1 \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_1 - k_2}} = = J_\mathrm{d}^\mathrm{max} \tag{14}$$

$$\left[\frac{\mathrm{d}R_\mathrm{m}}{\mathrm{d}t}\right]_\mathrm{max} = 0 \tag{15}$$

$$\left[\frac{\mathrm{d}R_\mathrm{a}}{\mathrm{d}t}\right]_\mathrm{max} = k_2 \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_1 - k_2}} = J_\mathrm{a}^\mathrm{max} \tag{16}$$

$$-\left[\frac{\mathrm{d}R_\mathrm{d}}{\mathrm{d}t}\right]_\mathrm{max} = + \left[\frac{\mathrm{d}R_\mathrm{a}}{\mathrm{d}t}\right]_\mathrm{max} \Rightarrow \; -J_\mathrm{d}^\mathrm{max} = +J_\mathrm{a}^\mathrm{max} \tag{17}$$

The kinetic parameters k_1 and k_2 were obtained by fitting Eqs. (5)-(7) to the experimentally obtained data. The observed experimental results reveal that R_d decreases exponentially with time, accompanied by a simultaneous increase of R_a, whereas R_m presents a maximum at intermediate times (Alpoguz *et al.* 2010).

The actual numeric analysis was carried out by non-linear curve fitting using Sigma-Plot software program. The activation energy values were obtained from the Arrhenius equation by using the k_1 and k_2 values at different temperatures (Yilmaz *et al.* 2008).

$$\ln(J) = \ln(A) - \frac{E_\mathrm{a}}{R}\left(\frac{1}{T}\right) \tag{18}$$

The kinetics of the transport across MDLM was described as a first-order reaction in metal ion concentration

$$\ln(J) = \ln(A) - \frac{E_\mathrm{a}}{R}\left(\frac{1}{T}\right) \tag{19}$$

where C is Zn(II) ion concentration at a given time in the feed phase, C_o is the initial concentration of Zn(II) ion in the feed phase, k is the rate constant (min^{-1}), and t is the time transport (min). The k values were calculated from the plots of $\ln(C_\mathrm{o}/C)$ vs. time (Kozlowski 2014).

In the extraction experiment, the extraction efficiency, E is expressed as

$$E = \frac{n_\mathrm{o}}{n_\mathrm{d0}} = \frac{n_\mathrm{d0} - n_\mathrm{d}}{n_\mathrm{d0}} \tag{20}$$

where n_o is the molar quantity of the analyte in the organic phase after extraction.

2.5 Studies of D2EHPA as a carrier ligand in the continuous extraction studies

For flux measurement, the feed and stripping solutions were filled in their respective cell compartments with membrane in the mid-position. The system worked continuously except being stopped for sampling. Samples from feed and stripping solutions were taken after regular time intervals and analysed spectrophotometrically (Shar and Bhanger 2001). Zn(II) ions concentration at phases plotted against time and extraction kinetic graphs are drawn. The extraction of Zn(II) in MDLM system was investigated. The effects of temperature, carrier concentration, pH of donor phase and acceptor phase concentration were studied to investigate the combined extraction and stripping process of Zn(II) using MDLM system.

3. Results and discussion

3.1 Effect of D2EHPA concentration on transport of Zn(II)

A series of transportation experiments where performed to investigate the influence of the carrier concentration in the organic phase. D2EHPA concentration in the organic phase also plays a significant role in the transport of Zn(II). The effect of the concentration of D2EHPA on the transport flux of Zn(II) was studied in different D2EHPA concentration (4.00×10^{-3}, 6.00×10^{-3} and 8.00×10^{-3} M). In all the experiments, the feed solution in the extraction side of the membrane consisted of a 120 mgL^{-1} Zn(II) solution, at pH 5.00 adjusted with HCl solution. The acceptor stripping solution consisted of a 1.50 M HCl solution. To investigate the effect of concentration of carrier ligand in an organic phase; the temperature is 298.15 K, the volume of donor, acceptor, and organic phase solution is 125 mL, and the peristaltic pump transfer rate of the organic solution is fixed to 65 mLmin^{-1}. Data of different D2EHPA concentrations are used to plot concentrations of ions versus time graphs as shown in Fig. 3. The graph of the extraction kinetics of Zn(II) ions for carrier concentration study is shown in Fig. 4.

For the studied three different D2EHPA concentration (4.00×10^{-3}, 6.00×10^{-3} and 8.00×10^{-3} M) transport yields of Zn(II) ions from donor phase to acceptor phase are found 99.62 99.81, and 99.91% respectively. High extraction efficiency (99.90%) of Zn(II) ions transportation evidently achieved by the organic phase with 8.00×10^{-3} M D2EHPA in kerosene. By increasing the concentration of carrier in the membrane phase from 4.00×10^{-3} M to 8.00×10^{-3} M, the transport flux of Zn(II) increased, however, the increasing of the transport flux of Zn(II) was not obvious when the concentration of D2EHPA increased to 8.00×10^{-3} M from 8.00×10^{-3} M. The extraction percentage increased with the increase in the concentration of extractant, because there would be enough molecules of extractant in the membrane to complex with the zinc ions and carries these metal ions from one side of the membrane to the other side. However, it will be expected that at a very high content of extractant in the organic phase, the values of extraction time decreases (Al-Hemiri and Mahmoud 2010). This could be due to the reaching of high organic phase viscosity values when increasing the carrier concentration. The extraction of Zn(II) ions to organic phase is much higher when the metal cation is more interacted with organophosphorus compounds according to the electrostatic interactions (Fig. 5).

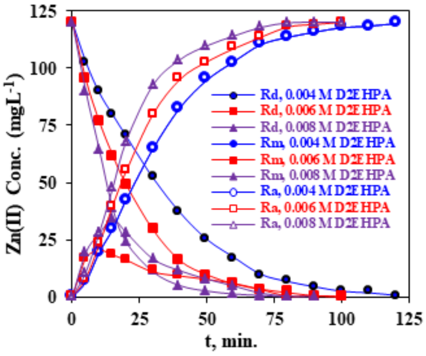


Fig. 3 Concentrations of Zn(II) ions in the donor (R_d), acceptor (R_a), and organic (R_m), phases versus time for the experiments carried out at different carrier ligand concentrations

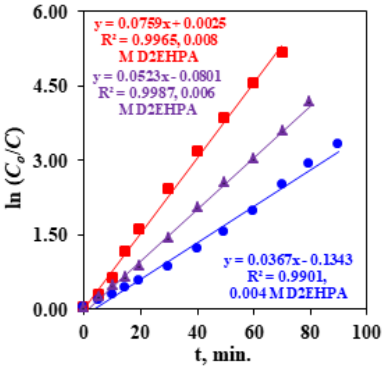


Fig. 4 The graph of extraction kinetics of Zn(II) ions for experiments carried out at different D2EHPA concentrations

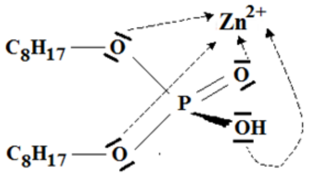


Fig. 5 Electrostatic interactions between D2EHPA and Zn(II)

The scheme of the reaction mechanism of the extraction process of Zn(II) ions from donor phase to organic phase and from the organic phase to acceptor phase is shown in Fig. 6. It is clear that the presence of the proton gradient drives the whole transport process to completion without any back leakage of Zn(II) ions.

The D2EHPA molecule, usually exists as a dimer in nonpolar media (i.e., most aromatic and aliphatic solvents) (Peppard *et al.* 1958), and monomeric is highly polar media (i.e., alcohols, carboxylic acids, and water) (Vandegrift and Horwitz 1979). The D2EHPA dimer consists of two D2EHPA monomers, joined by hydrogen bonds between

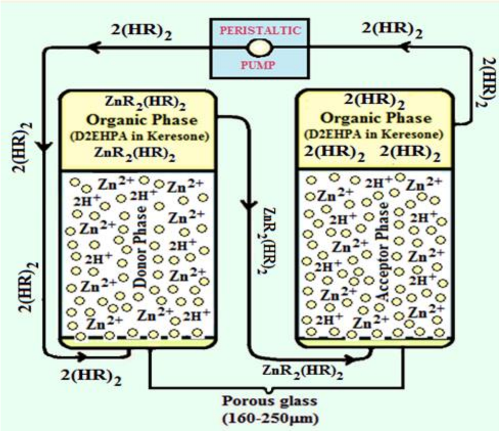


Fig. 6 Mechanism of facilitated counter-coupled transport of Zn(II) through kerosene-based MDLM [$(HR)_2$: dimeric D2EHPA; $ZnR_2(HR)_2$: Zn-D2EHPA complex]

Table 1 Comparison of kinetic parameters for the transportation of Zn(II) ions through the kerosene-based MDLM at different concentrations of D2EHPA

D2EHPA (M)	$k_1.10^2$ min^{-1}	$k_2.10^2$ min^{-1}	t_{max} (min)	R_m^{max} mgL^{-1}	$J_d^{max}.10^2$ min.	$J_a^{max}.10^2$ min.
0.004	3.67	26,22	8,72	12.22	-2.66	2.66
0.006	5.23	16.10	10.34	22.73	-3.04	3.04
0.008	7.59	10.68	11.05	36.92	-3.28	3.28

adjacent P=O and P-OH groups, as shown in Fig. 6.

Huang and Juang (1986) have shown that the extracted species (in kerosene at low metal loadings) have one associated D2EHPA monomer (i.e., n=1.50). Li *et al.* (1986) have demonstrated that as the organic phase becomes more fully loaded, viscosity incerases, suggesting the formation metal extractant polymers. In general, the composition of the extracted species was found to be $ZnR_2.HR$ (i.e., n=1.5) for aliphatic diluents, and $ZnR_2.(HR)_2$ (n=2.00) for aromatic diluents. Sato *et al.* (1978) found that the dominant species was $ZnR_2.(HR)_2$, while Grimm and Kolarik (1974) and Sastre and Muhammed (1984) concluded that the extracted species was a mixture of $ZnR_2.HR$ and $ZnR_2.(HR)_2$.

Mellah and Benarchour (2006) proposed a specific reaction equation for Zn(II) when extracting it using D2EHPA written as Eq. (21) based on the assumptions that extractant molecules exist as dimers in the solvent (kerosene in their work). They obtained a slope of 1.7152 and 1.7153 for 0.10 M and 0.20 M of D2EHPA, respectively.

$$\mathrm{Zn}^{2+}_{(\mathrm{aq})} + 1.5(\mathrm{H_2R_2})_{(\mathrm{org})} \xrightarrow{k_{(\mathrm{eq})}} \mathrm{Zn\ R_2(HR)_{org}} + 2\mathrm{H}^{+}_{(\mathrm{aq})} \quad (21)$$

Since the general reaction equation is applicable for Zn(II) and shown by Baba and Adekola (2011) as well, a slope of approximately 2 would be evident from the lg D_{eq} versus pH plot.

According to Fig. 4, the reaction rate constants of extraction experiments are calculated as: 3.67×10^{-2}, 5.23×10^{-2}, and 7.59×10^{-2} min^{-1} for concentrations of 4.00×10^{-3}, 6.00×10^{-3} and 8.00×10^{-3} M respectively. The above studies show that by increasing organic phase concentrations, the extraction efficiency increases the Zn(II) ions accumulate in the organic phase, the acceptor phase transition takes shorter and re-uptake yields slightly increase. Kinetic data obtained by the calculation of continuous extraction of Zn(II) ions for experiments carried out at different concentration of D2EHPA carriers are given in Table 1.

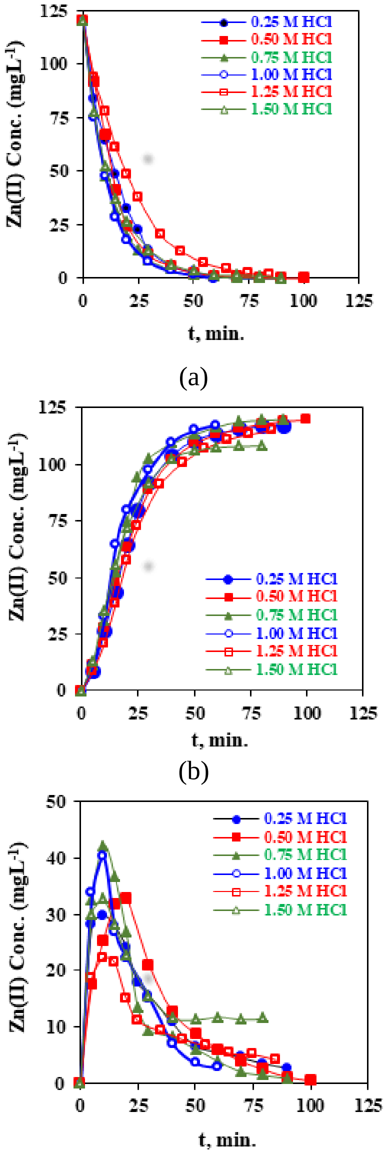
As it is seen, the transport rate, k_1, t_{max}, and R_m^{max} increase and k_2 decrease with an increase in carrier concentration. According to Table 1; k_2 values decrease with an increase in carrier concentration in the organic phase from 4.00×10^{-3}-8.00×10^{-3} M.

It had been reported that in controlled conditions, k_1 increases with increasing carrier concentration, showing small and fractional exponent value. This obviously can be assumed from Eqs. (5)-(7) that the reduced dimensionless concentration is related to the carrier concentration (Alpoguz *et al.* 2006) Further increase in carrier concentration caused a slight decrease in k_2. Thus, k_2 determines the transport rate. According to the data obtained, extraction of Zn(II) ions take place at a moderate rate. A concentration of 8.00×10^{-3} M of D2EHPA was chosen as the optimum concentration of carrier. Under the conditions, the transport percentage of Zn(II) was 99.91% in 80 min.

3.2 Effect of HCl concentration on transport of Zn(II)

The stripping reaction in the acceptor phase plays a vital role in the transport of metal ions from the donor phase to the stripping phase. Thus, the effect of the concentration of HCl solution in the acceptor phase on the transport flux of Zn(II) was studied. All the other parameters, such as pH value, initial concentration of Zn(II) in the donor phase, and the peristaltic pump transfer rate kept constant, the concentration of D2EHPA was adjusted to 8.00×10^{-3} M, respectively. The effect of the concentration of HCl solution in the acceptor phase on the transport flux of Zn(II) is shown in Fig. 7.

For the experiments carried out by different initial acceptor phase (0.25-1.50 M HCl), transport yields of Zn(II) ions from donor phase to acceptor phase were found as 99.55, 99.81, 99.84 99.92, 97.33, and 90.03%, respectively. In Fig. 7, high yield of Zn(II) ions transportation can be achieved by different HCl concentrations of acceptor phases. It indicates that with increasing the acid concentration in the acceptor phase, the transport flux of Zn(II) increases. It can be seen that the effective concentration of HCl solution for transport is 0.25 to 1.00 M, of Zn(II). Increasing the concentration of HCl solution from 0.25 M to 1.25 M has no significant effect on the transport flux of Zn(II) because the concentration of Zn(II) complex and the concentration of organic solution. However, at a condition of 1.25 and 1.50 M of HCl solution, the transport flux is lower than 1.00 M, because of higher acidity resulting in the receding of complexation ability of D2EHPA. Considering controlling acidity as well as increasing transport flux, 0.25 M was chosen as the optimum concentration of HCl solution in the acceptor phase during the following experiments.



(a)

(b)

(c)

Fig. 7 Concentrations of Zn(II) ions in the (a) donor, (b) acceptor, and (c) organic phases versus time for the experiments carried out at different acceptor phase concentrations

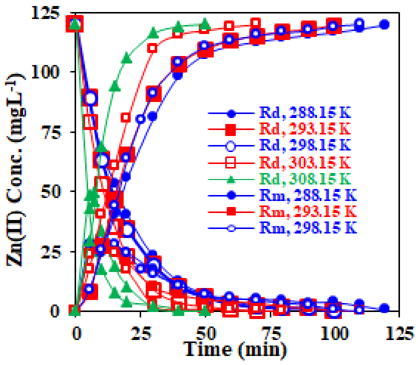


Fig. 8 Concentrations of Zn(II) ions versus time graphs for the continuous extraction studies through the kerosene based liquid membrane of donor (R_d), acceptor (R_a), and organic (R_m), phases at different temperatures(288.15-308.15 K)

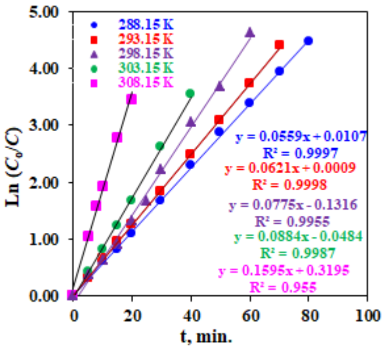


Fig. 9 The graph of extraction kinetics of Zn(II) ions for experiments carried out at different temperatures

Table 2 Comparison of kinetic parameters for the transportation of Zn(II) ions through the kerosene-based MDLM at different temperatures

Temp. (K)	$k_1.10^2$ min^{-1}	$k_2.10^2$ min^{-1}	t_{max} (min)	R_m^{max} mgL^{-1}	$J_d^{max}.10^2$ min.	$J_a^{max}.10^2$ min.
288.15	5.59	10.32	12.96	33.40	-2.71	2.71
293.15	6.21	12.12	11.31	32.30	-3.08	3.08
298.15	7.75	14.91	9.14	32.53	-3.82	3.82
303.15	8.84	16.33	8.19	31.49	-4.28	4.28
308.15	15.95	11.18	7.45	50.54	-4.86	4.86

3.3 Effect of temperature

The study of effect of ambient temperature on the extraction process indicated that D2EHPA concentration was 8.00x10^{-3} M, initial Zn(II) ions concentration 120 mgL^{-1} and the peristaltic pump transfer rate of the solution fixed to 62 mLmin^{-1}. For five different temperatures (288.15, 293.15, 298.15, 303.15, 308.15 K), variation of Zn(II) ions concentration by time was investigated.

Data obtained at different temperatures were used to plot concentrations of Zn(II) ions in the donor, organic and acceptor phases versus time graphs as shown in Fig. 8. For the related temperature, transport yields of Zn(II) ions from donor phase to acceptor phase were found as 99.64, 99.73, 99.82, 99.85 and 99.90%, respectively. It is clear that high extraction efficiency (>99.60%) of Zn(II) ion transportation can be achieved at the temperature 288.15-303.15 K and 8.00×10^{-3} M D2EHPA in kerosene.

Zn(II) extraction and stripping processes obey consecutive first order reaction kinetics and reaction rate constants assume different values at different temperatures. Therefore, the plots of change ln(C_o/C) vs time are created using reactive concentrations at different temperatures (Fig. 9). Kinetic data obtained by the calculation of continuous extraction of Zn(II) ions for experiments carried out at different temperatures are given in Table 2.

According to Fig. 9 and Table 2, the reaction speed constants of extraction experiments were calculated as: 5.59×10^{-2}, 6.21×10^{-2}, 7.75×10^{-2}, 8.84×10^{-2}, and 15.95×10^{-2} min^{-1} for temperatures of 288.15-308.15K, with k_1 (308.15 K)>k_1 (303.15 K)>k_1 (298.15 K)>k_1 (293.15 K)>k_1 (288.15 K), respectively. In ideal studies; the reaction rate (or transport) is desired to be neither fast nor slow. In order to calculate the kinetic data, it is supposed to occur at an average reaction rate. Experimental results suggest that the transport of Zn(II) ions could emerge at an average rate and optimum study temperature is determined to be 298.15 K for extraction of Zn(II).

Temperature is very effective on the kinetic parameters of Zn(II) ion transport. Because Zn(II) ion transport is in irreversible reactions of consecutive first order, it is not very suitable to calculate the activation energy of the process according to the input and output transport rate constants. Therefore, calculation of the activation energy using the following Arrhenius equation seems more appropriate (Kobya *et al.* 1997). The activation energy (E_a) is calculated from the slope of the graph in Fig. 10.

From the slope of the Arrhenius graphic, the activation energy is calculated as 5.30 kcalmol^{-1}. Since there is a very strong effect of temperature on rate constants, activation energy of diffusion-controlled processes are quite low, but it is very high for chemically-controlled process (Kobya *et al.* 1997, Lazarova and Boyadziev 1993). Thus, activation energy values for any processes define the rate-controlling step to determine whether its occurrence is a diffusion process or a chemical reaction. In diffusion-controlled processes, the activation energy values are smaller than 10 kcalmol^{-1} (Michel *et al.* 2013). The fact that activation energy is smaller than 10 kcalmol^{-1} in the present study shows that the transport of Zn(II) ions by MDLM system is a diffusion-controlled process.

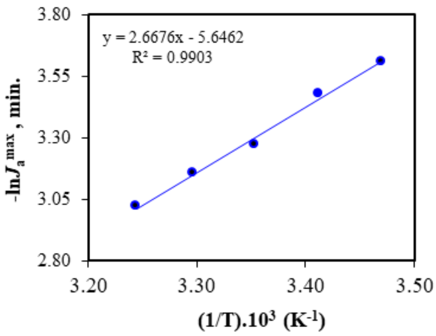


Fig. 10 The Arrhenius graphic of transport of Zn(II) ions by D2EHPA carrier at different temperatures (288.15-308.15 K)

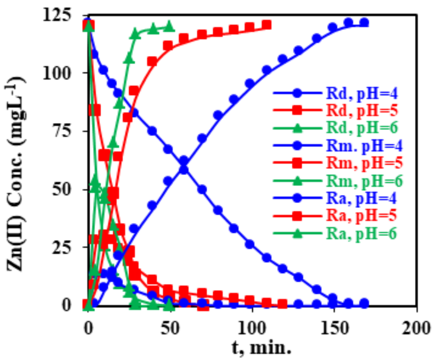


Fig. 11 Concentrations of Zn(II) ions versus time graphs for the continuous extraction studies through the kerosene based liquid membrane of donor (R_d), acceptor (R_a), and organic (R_m), phases at different pH values (4.00, 5.00, and 6.00)

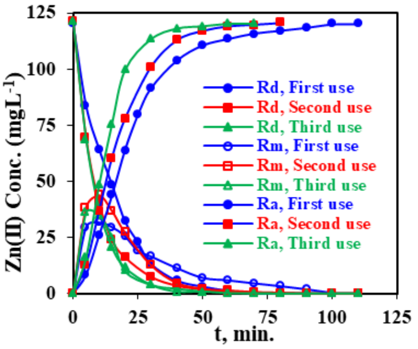


Fig. 12 Concentrations of Zn(II) ions versus time graphs for the continuous extraction studies through the kerosene based liquid membrane of donor (R_d), acceptor (R_a), and organic (R_m), phases for experiments of reusing organic phase solution(first, second, and third use)

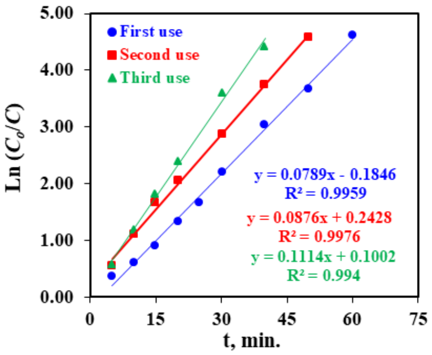


Fig. 13 The graph of extraction kinetics of Zn(II) ions for experiments of reusing organic phase solution

3.4 Effect of pH in the feed phase

Based on the mechanism of the mass transfer process, the concentration difference between feed phase and acceptor phase is the driving power of mass transfer process. So in donor phase the lower the H$^+$ concentration is, the stronger the driving power of the mass transfer process will be. Stronger power will promote the transport flux of Zn(II).

The effect of pH in the donor phase on the transport of Zn(II) was studied in a pH range of 4.00 to 6.00. Initial concentration of Zn(II) in the donor feed phase was 120 mgL^{-1}. Concentration of HCl solution was 0.25 M, the volume ratio of the organic solution to stripping solution was 1.00, the concentration of D2EHPA was 0.8×10^{-3} M in the acceptor. The results are shown in Fig. 11. The optimum pH value of the donor phase must be 5 to achieve a high efficiency of interphase transport and elution of Zn(II) ions.

3.5 The reuse of membrane solution

The reuse of membrane solution was studied under the optimal conditions. From the Fig. 12, we can know the organic phase solution in MDLM can be reused many times before the re-extraction with the strong acid (0.75 M HCl) after every experiment. Organic phase solution in MDLM can be reused many times and the tendency of transport

Table 3 Maximum stripping efficiency of various membrane system for stripping of Zn(II) ions reported in the literaturess

Type of extractant	Feed solution	Method	Surfactant	Stripping solution	Diluent	Recovery (%)	References
D2EHPA	$ZnSO_4$	SLM	-	H_2SO_4	Kerosene	99.00	Dingsheng *et al.* (2006)
D2EHPA	$ZnCl_2$	ELM		HCl	Kerosene	89.24	Ata and Çolak (2005)
PC-88A	Zn^{+2}/Cu^{+2}	SLM	Span-80	H_2SO_4	Kerosene	99.32	Valenzuela *et al* .(2005)
D2EHPA	$ZnSO_4$	PIM	DBSNa, CPCl	Na_2SO_4	-	89.60	Ulewicz and Walkowiak, (2003)
Ditizone	$ZnSO_4$	ELM	$CH_3(CH_2)_nOSO_3Na$	H_2SO_4	CCl_4	87.40	Al-Hemiri and Mahmoud (2010)
D2EHPA and TBP	$Zn(CH_3COO)_2$	CSE	-		$CHCl_3$	69.52	Guezzen and Didi (2002)
D2EHPA	$ZnCl_2$	MDLM	-	HCl	Kerosene	99.90	In this study

percentage changes was stable with MDLM in 3 experiments. Fig. 13 shows the extraction kinetic graphs of the reusing experiments.

As shown in Fig. 13, in a continuous system with D2EHPA organic ligand reaction rate constants varying reusing organic phase solution. (First, second and third use) are 7.89×10^{-2}, 8.76×10^{-2}, and 11.14×10^{-2} min^{-1}, respectively. R^2 values obtained by using the least squares method are very close to 1. That means that data obtained during the transportation are consistent with each other and have a linear relationship between the variables.

Transport in ELM (Emulsion Liquid Membrane), SLM (Supported Liquid Membrane), PIM (polymer inclusion membrane) and conventional solvent extraction (CSE) are accomplished by a carrier that is essentially a complexing agent or an ion-exchanger. The types of carriers used in SLM, ELM, and CSE research as reported in the literature along with the target Zn(II) ions, stripping solution, surfactant, or organic solutes, and recovery yields are summarized in Table 3. As shown in Table 3, the recovery of Zn (II) ions by the MDLM system is higher than other methods.

4. Conclusions

MDLM process using D2EHPA to extract Zn(II) from aqueous solution was investigated, from which the following consequences can be concluded:

- The optimum conditions were determined experimentally.
- Under optimum conditions, Zn(II) was extracted with an extraction efficiency of about 99.91%.
- The activation energy value was calculated to be 5.30 kcalmol^{-1} for extraction. The value of calculated activation energy indicates that the process is diffusionally-controlled by Zn(II) ions.
- To summarize the results briefly, efficient outcomes can be obtained using the carrier ligands and the experimental setup of liquid membrane system.
- Organic phase solution in MDLM can be reused many times.
- By investigating suitable donor, extractant, working conditions and selecting the acceptor solution, the liquid membrane system that we used in our experimental studies can be a great alternative and economical process in order to remove the heavy metal ions caused by heavy metal industries.

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