

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Special Issue 12, May 2016

Transportation of Pb(II) ions with D2EHPA as Carrier by MDLM System

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ABSTRACT: This study consists of the transportation of Pb(II) ions by MDLM system used D2EHPA as a carrier. In the experimental work, the effect of temperature (at pH of 7.00 in donor phase), concentration of acceptor phase (HNO₃) and organic ligand (D2EHPA) on the extraction of Pb(II) ions were investigated. Optimum conditions for Pb(II) transportation were as follows: pH of donor phase is 7.00, 0.30M HNO₃ as acceptor phase, and flux rate is 50mL/min. Pb(II) ion transportation is consecutive first order irreversible reaction and diffusion controlled process. The kinetic parameters were calculated for the interface reactions, assuming two consecutive, irreversible first-order reactions. The results show that D2EHPA derivative is a good carrier for Pb(II) transportation through MDLM in the study.

KEYWORDS: Lead; D2EHPA; MDLM; Transportation; Extraction; Liquid membrane.

I. INTRODUCTION

Many research groups have given attention to determination of heavy metals, especially some toxic metals like lead because of their toxicity and harmful effects on human beings [1,2]. Showing the special characteristics such as resistant to corrosion, conductivity and special reversible reactions between lead oxide and sulfuric acid makes the metal, lead, a raw material and used in storage batteries, cable sheaths, solder, radiation shielding, gasoline antiknock products, paint pigments [1]. These fields are not the only areas that lead is applied in industry. The others are as follows: pulp, paper, petrochemicals, refineries, printing, photographic materials, explosive manufacturing, ceramic, glass, oil, metal, phosphate fertilizer, electronics, wood production, combustion of fossil fuel, forest fires, mining activities, sewage waste water, automotive, coating, aeronautical, alloy, and steel industries [1,3-6].

The toxicity of lead is so high even in low concentrations that it is called as a cumulative poison because of their harmful effects on health and people is exposed it through air, water and food [2,7-10].

Lead has severe bad impacts even in trace concentrations on human body. After binding to with the -SH group in enzymes or proteins, lead(II) ions (Pb²⁺) act as an enzyme inhibitor. Lead steps into calcium metabolisms and deposits in bones. Since absorbed by the body through the skin and mucus membranes, organic lead compounds like tetramethyl lead are highly toxic [2]. Moreover, lead poisoning causes severe diseases such as anemia, encephalopathy, hepatitis, nephritic syndrome and severe damages in kidneys, liver, brain, reproductive system, central nervous system [1,2,9,11]. Particularly, in children lead can cause, raising hearing threshold, decreasing IQ levels, memory loss and encephalopathy at low levels in blood, even death at high levels in blood [9,12].

In the light of these information, it is obvious that the determination and removal of lead even in trace amounts from air, water and food is significantly inevitable for human health. Due to severe toxic effects of lead, it is necessary to eliminate lead from the environment for its safe removal. Various researchers have studied the extraction of lead by different techniques, like ion exchange [13], solvent extraction [14-16], cloud point methodology [17,18], and sorption [19-21]. However, these given processes have some shortcomings, incomplete metal ion removal, enhanced capital cost due to costly equipment and solvents and generation of toxic sludge [22,23].

Apart from these techniques, LM separation process is one of the promising techniques for extraction of metal ions [24,25]. There are several methods for the removal of lead from waste water, such as chemical precipitation,

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electrochemical reduction, ion exchange, activated carbon, adsorption, biosorption, LM system [1, 26-35]. Since conventional methods for metal recovery are ineffective at a very low concentration in ppm or ppb levels, among these separation techniques, LM system stands out [36]. Liquid membranes are important due to very high separation selectivity, relatively low process cost, cheap pretreatment, highly concentrated products because of the facilitated transport mechanism, rapid mass transfer on carriers [1].

In this study, the process has much in common with facilitated transport since it employs a carrier agent. For the extraction of Pb(II) ions from various solutions, D2EHPA was selected as a carrier agent due to high lead removal capacity from the solutions based on the literature [36-41]. Our earlier work [42], involved a detailed investigation on the Mo(VI) transport from feed solution with buffer solution to stripping solution containing Na₂CO₃ solution via organic carrier as TNOA in kerosene. The effect of temperature, and different stripping phase concentrations on the transportation as well as information about a new method called as Multi-Dropped Liquid Membrane (MDLM) is reported. The advantages of this new technique are mentioned as: simple construction, lack of moving parts, lightweight and portable, flexible in operation, high membrane capacity, high separation factor than mixer-settler.

II. MATERIALS AND METHODS

Chemicals and solutions

Refined kerosene was supplied from TUPRAŞ A.Ş (Turkish Petroleum Refineries Company), Lead (II) nitrate, nitric acid, D2EHPA, PAR, and all other chemicals were purchased from Merck and were used directly as received from the manufacturer.

A Stock solution of Pb(II), 250 mg/L was prepared by dissolving 0.40 g Pb(NO₃)₂ in water and lower concentration of Pb(II) solutions was prepared by serial dilution of the stock solution. 1.00 × 10⁻³ M PAR was prepared by dissolving 2.15 × 10⁻² g PAR in ethanol and made up to 100 mL [43]. 7.50 × 10⁻³ M D2EHPA was prepared in kerosene. Buffer solution for pH of the feed solution was prepared by 1.00 M CH₃COONa and 1.00 M HCl solutions.

Experimental Procedure

Batch experiments were performed by a flowing MDLM technique. The scheme of the experimental setup is shown in Fig. 1 and Fig. 2. For more homogeneous dispersion of droplets, porous glass was fixed to the bottom of the reactor.

All the experiments were conducted by two reactors made of glass as shown in Fig. 1 and Fig. 2. The liquid membrane system consists of two reactors; 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, type of carrier, D2EHPA dissolved in kerosene is placed to 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 on 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. The 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 glass constitutes 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 [42].

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Fig. 1. Photograph of the running MDLM system for Pb(II) extraction.

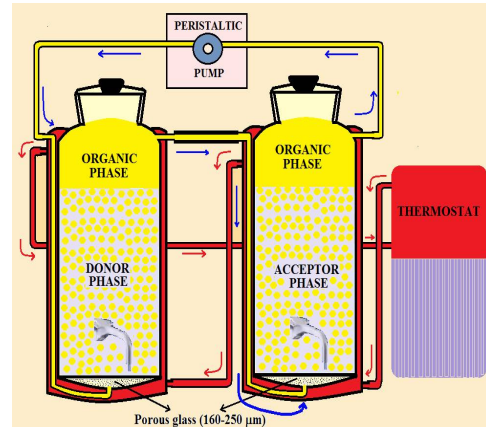


Fig. 2. Picture of the measuring set with flowing MDLM.

Samples were drawn from the first(donor phase) and second reactor(acceptor phase) in 10min time interval and analyzed by UV-vis spectrophotometer PAR method- $\lambda = 556\text{nm}$.

Analytical instruments

All absorbance measurements of Pb(II) ions in solutions were carried out by using Shimadzu UV-1201V model spectrophotometer with 1.00cm quartz cells. In our experimental study; in order to control temperature, Circu-WCR-P8 Wise model creosote device; to determine the concentration of Pb(II) ions in the solution, Shimadzu 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 model Microprocessor pH meter is used.

Data analysis

Pb(II) ion concentration in the membrane phase was established by the material balance. For practical reasons, dimensionless reduced concentrations of Pb(II) in the donor (R_d), organic (R_m), and acceptor phases (R_a) were used ($R_d = C_{dt}/C_o$, $R_m = C_{mt}/C_o$ and $R_a = C_{at}/C_o$, the sum of $R_d + R_m + R_a$ obviously being unity. When R_d , R_m , and R_a values are determined, the result suggests that the Pb(II) ion transport obeys the kinetic laws of two consecutive irreversible first-order reaction according to the kinetic scheme.



Where C_d , C_m , and C_a are the Pb(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, respectively. The kinetic scheme Eq. (1) for consecutive irreversible reactions can be described by the following rate equations [44-47].

$$\frac{dR_d}{dt} = -k_1 R_d \equiv J_{a/m} \quad (2)$$

$$\frac{dR_m}{dt} = k_1 R_d - k_2 R_m \quad (3)$$

$$\frac{dR_a}{dt} = k_2 R_m \equiv J_{a/m} \quad (4)$$

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

$$R_d = \exp(-k_1 t) \quad (5)$$

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

$$R_a = 1 - \frac{1}{k_2 - k_1} [k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] \quad (7)$$

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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 is a maximum at time at which it occurs being obtained from $dR_m/dt=0$.

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

the value of R_m at that time being

$$R_m^{\max} = \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_1 - k_2}} \quad (9)$$

Combining Eqs. (8) and (9) the following relationship can be obtained:

$$k_2 = \frac{\ln\left(\frac{1}{R_m^{\max}}\right)}{t_{\max}} \quad (10)$$

First-order time differentiation of Eqs. (5)–(7) leads to the final form of the flux equations [48].

$$\frac{dR_d}{dt} = -k_1 \exp(-k_1 t) \quad (11)$$

$$\frac{dR_m}{dt} = \frac{k_1}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)] \quad (12)$$

$$\frac{dR_a}{dt} = \frac{k_1 k_2}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)] \quad (13)$$

By substituting the expression of t_{\max} given for Eq. (8) in Eqs. (11)–(13), maximum fluxes can be obtained [48].

$$\left[\frac{dR_d}{dt}\right]_{\max} = -k_1 \left(\frac{k_1}{k_2}\right)^{\frac{k_1}{k_1 - k_2}} = J_d^{\max} \quad (14)$$

$$\left[\frac{dR_m}{dt}\right]_{\max} = 0 \quad (15)$$

$$\left[\frac{dR_a}{dt}\right]_{\max} = k_2 \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_1 - k_2}} = J_a^{\max} \quad (16)$$

$$-\left[\frac{dR_d}{dt}\right]_{\max} = +\left[\frac{dR_a}{dt}\right]_{\max} \Rightarrow -J_d^{\max} = +J_a^{\max} \quad (17)$$

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 [47].

The activation energy values were obtained by Arrhenius equation by using the k_1 and k_2 values at different temperature [49]:

$$\ln(J) = \ln(A) - \frac{E_a}{R} \left(\frac{1}{T}\right) \quad (18)$$

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

$$\ln\left(\frac{C_o}{C_e}\right) = kt \quad (19)$$

Where C_e is the metal ion concentration at a given time in the feed phase, C_o is the initial concentration of metal ions in the feed phase, k is the rate constant (min^{-1}), and t is the time (min). The k values were calculated by the plots of $\ln(C_o/C_e)$ vs. time. The percentage of metal ions transported was calculated according to Eq. (20):

$$E, \% = \frac{[\text{Pb(II)}]_{\text{strip}(t)}}{[\text{Pb(II)}]_{(o)}} \times 100 \quad (20)$$

Where $[\text{Pb(II)}]_{\text{strip}(t)}$ is the metal concentration in the stripping phase at elapsed time.

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

In the extraction of Pb(II) ions by the MDLM system; 100mg/L Pb(II) solutions as donor phase, buffer solution for different pH values of donor phase and HNO₃ in different concentrations as acceptor phase and D2EHPA diluted by kerosene as organic phase are used [36,41]. In the experimental work, the effect of temperature in different pH values of donor phase, and different concentration of HNO₃, various concentrations D2EHPA, different pH values of the donor phase on the extraction of Pb(II) ions was investigated.

III. RESULTS AND DISCUSSION

Effect of temperature (at pH=7.00)

The experiment is carried out at 288.15, 293.15, and 298.15K. Other parameters keep constant. The concentration of target metal ions [Pb(II)] in the donor phase is 100mg/L. The volumes of feed, organic and stripping solutions were 100mL. pH of the donor phase is 7.00, concentration of D2EHPA 7.50×10^{-3} M, the transfer rate of the peristaltic pump is fixed to 50mL/min. Pb(II) concentration in the feed, membrane phase and stripping solution against time graph is given in Fig. 3.

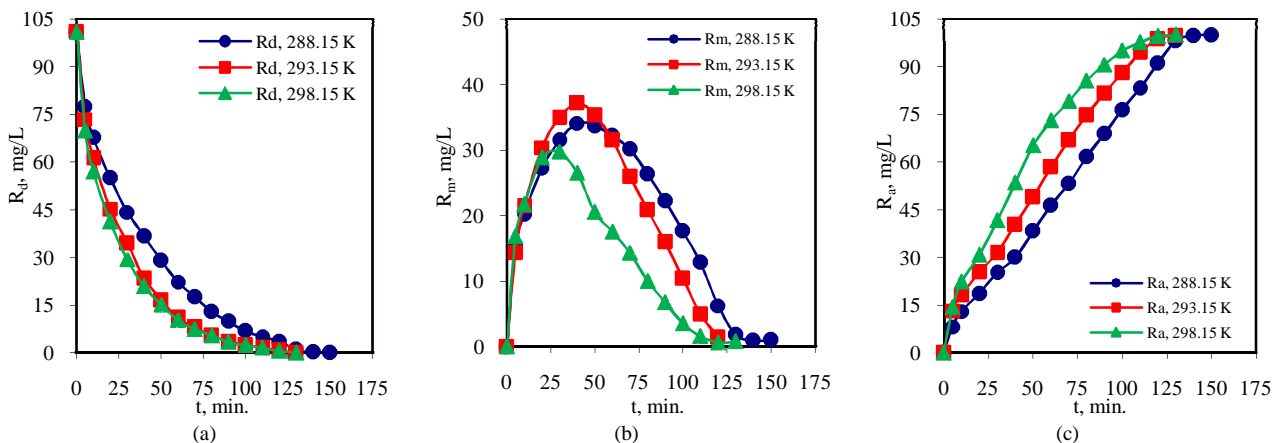


Fig. 3. Concentrations of Pb(II) ions versus time graphs for the continuous extraction studies through the kerosene-based MDLM of (a) donor, (b) organic, and (c) acceptor phase at different temperatures.

Pb(II) extraction and stripping processes obey consecutive first order reaction kinetics and reaction rate constants assume different values at different ambient temperature at pH of 7.00 of donor phase. Hence, the plots of $\ln(C_0/C_e)$ vs time graph are given in Fig.4.

Transportation efficiency of Pb(II) ions in different temperatures (288.15-298.15K) from donor phase to acceptor phase is 98.83, 98.77, and 98.72%, respectively. As it is seen, the results are very close to each other. Extraction time for different temperatures (288.15-298.15K) is 150, 130, and 130 min, respectively. Transportation efficiency is not enough to determine the optimum temperature for the extraction of Pb(II) ions. So it is better to compare the results in Table 1.

As shown in Table 1, in continuous system with D2EHPA, reaction rate constants varying temperatures (288.15-298.15K) are 0.0264, 0.0365, and 0.0362 min^{-1} , respectively.

By the increase of ambient temperature, transportation efficiency of Pb(II) ions from donor phase to organic phase and organic phase to acceptor phase rises. When the data in Table 1 is analyzed, t_{\max} and R_m^{\max} values from low temperature to high temperature varies. According to these results, since high yield of Pb(II) ions transportation and retrieval can be achieved at any temperatures, it is better to study at 298.15K to reduce the cost of the extraction.

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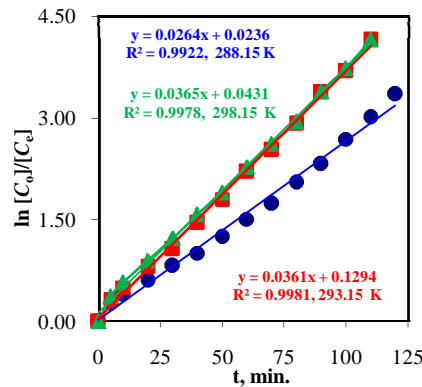
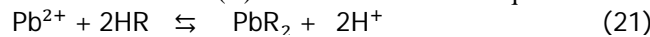


Fig. 4. $\ln(C_o/C_c)$ versus time graphs for the continuous extraction studies for the transportation of Pb(II) ions through the kerosene-based MDLM at different temperatures.

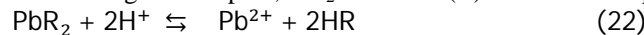
Table 1. Comparison of kinetic parameters for the transportation of Pb(II) ions through the kerosene-based MDLM at different temperature.

Temp. (K)	$k_1 \times 10^2$ (min ⁻¹)	$k_2 \times 10^2$ (min ⁻¹)	k_2/k_1	t_{max} (min)	R_m^{max} (mg/L)	$J_d^{max} \times 10^2$ (min)	$J_a^{max} \times 10^2$ (min)
288.15	2.64	2.94	1.11	35.88	35.14	-1.024	1.024
293.15	3.65	4.09	1.12	25.85	35.03	-1.421	1.421
298.15	3.62	5.22	1.44	22.87	30.53	-1.582	1.582

In MDLM system, the transport mechanism of Pb(II) ions involves various equilibrium reactions as follows:



At the interface of the feed and membrane phase, reaction 21 occurs. Here HR indicates D2EHPA in kerosene and the PbR_2 metal-ligand complex. The metal-ligand complex, PbR_2 carries Pb(II) ions to the stripping phase.



At the interface of the membrane and stripping phase, reaction 22 occurs. The metal complex combines with the hydronium ions at the interface of membrane-stripping phase and Pb(II) ions stripped by HNO_3 over there. Carrier ligand, D2EHPA, returns to the interface of the feed and membrane phase [1,36].

Mechanism of the extraction is figured out in the following scheme. Summary of the mechanism of Pb(II) extraction via MDLM system is illustrated in Fig. 5.

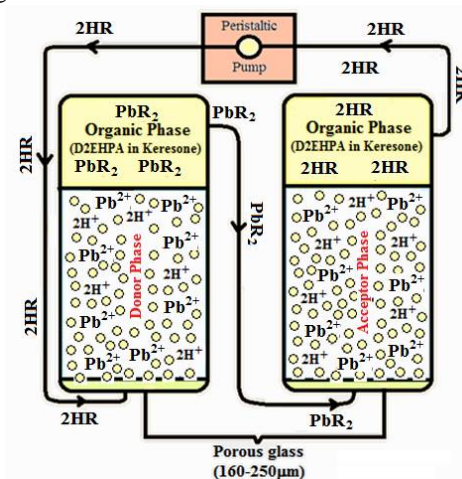


Fig. 5. Scheme of the transportation of Pb(II) ions through MDLM system.

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Temperature is one of the most significant parameters on the transport of Pb(II) ions to understand the kinetics of the extraction. Pb(II) ion transport is consecutive first order irreversible reaction and the calculation of the activation energy of the process by the help of the input and output transport rate constants can be difficult. As it is mentioned in the literature [50], activation energy can be calculated by the help of maximum input (J_d^{\max}) and output rates (J_a^{\max}) by using the Eq. (18). Maximum output rates versus $1/T$ graph is shown in Fig.6. The activation energy is calculated by using the slope of the line of the graph as 7.41 kcal/mol.

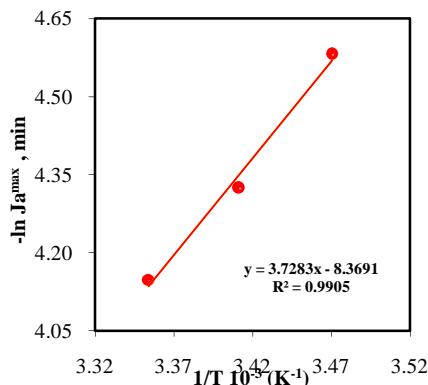


Fig. 6. Maximum output rates versus $1/T$ graph.

According to the literature since the temperature has a strong effect on rate constants, for diffusion controlled process the activation energy values are quite low, but for chemically controlled process it is very high [51,52]. Thus, for any process activation energy (E_a) values obtained are accepted as the rate-controlling step that assigns process whether diffusion controlled or chemically controlled. As mentioned in the literature, activation energy is less than 10kcal/mol for the diffusion controlled processes [51]. In this study, since the activation energy is found as 7.41 kcal/mol, this process is diffusion controlled process. According to these results, transportation of Pb(II) ions achieved successfully by using MDLM system.

Effect of concentration of acceptor phase

The experiment is carried out by changing the concentration of acceptor phase (HNO_3) as 0.10, 0.20, 0.23, 0.30, and 0.40M HNO_3 and the other parameters like temperature (298.15K) keep constant. 100mg/L Pb(II) ions are used as target metals to be transported to the acceptor phase by 7.50×10^{-3} M D2EHPA as an organic ligand in kerosene. The volumes of feed, organic and stripping solutions were 100mL. pH of the donor phase is 7.00, the transfer rate of the peristaltic pump is fixed to 50mL/min. Pb(II) concentration in feed, membrane phase and stripping solution against time graph is given in Fig. 7.

Data obtained by using different acceptor phase concentration are used to plot concentrations of Pb(II) ions versus time graphs as shown in Fig.7. To plot the graph, concentration of Pb(II) ion in the donor, organic and acceptor phase is used.

Benomar et al., (2011), studied on the extraction of Pb(II) ions by a BLM system and used DEHPA as extractant. Optimum conditions for the extraction is obtained at pH of 4.70 of donor phase (occurred by 0.08M acetate buffer solution), 0.07M DEHPA (in kerosene) concentration and 0.23M HNO_3 as acceptor phase. Extraction yield is 93.8% [41].

According to the Eq. (20), transportation efficiency of Pb(II) ions in different acceptor phase concentrations ($[\text{HNO}_3] = 0.10\text{--}0.40\text{M}$) from donor phase to acceptor phase is 98.88, 98.65, 98.77, 98.79, and 98.82%, respectively.

According to these results, high yield of Pb(II) ions' transportation and retrieval can be achieved efficiently at any concentration of acceptor phase. Extraction duration ($[\text{HNO}_3] = 0.10\text{--}0.40\text{M}$) is 150, 140, 130, 120, and 110 min. Also flux rates increased with the rise of the concentration of the acceptor phase.

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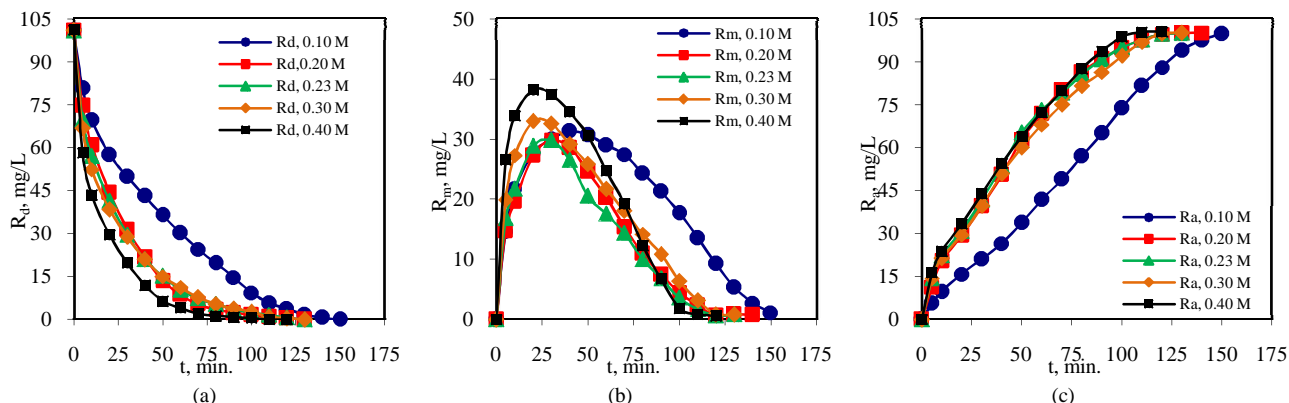


Fig.7. Concentrations of Pb(II) ions versus time graphs for the continuous extraction studies through the kerosene-based MDLM of (a) donor, (b) organic, and (c) acceptor phase at different acceptor phase concentrations.

Pb(II) extraction and stripping processes obey consecutive first order reaction kinetics and reaction rate constants assume different values at different concentration of acceptor phase. Therefore, the plots of change $\ln(C_o/C_e)$ vs time are created using reactive concentrations at different acceptor phase concentration (Fig.8).

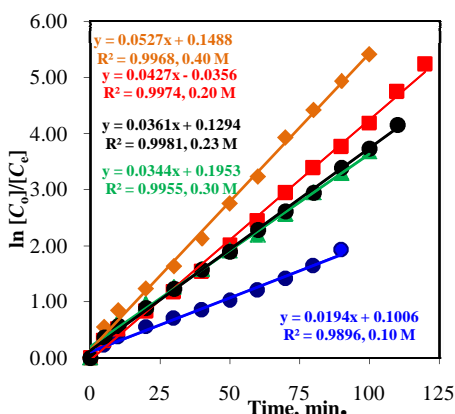


Fig.8. $\ln(C_o/C_e)$ versus time graphs for the continuous extraction studies for the transportation of Pb(II) ions through the kerosene-based MDLM at acceptor phase concentration.

For ideal kinetic studies, reaction rate (or the transportation together) should not be too high or too low. In order to calculate the kinetic data, reaction must take place at a moderate speed. According to the data obtained, extraction of Pb(II) ions best takes place at 0.30 M HNO_3 as acceptor phase and transportation efficiency is more than 98% which is better than literature [41].

IV. CONCLUSION

MDLM using D2EHPA dissolving in kerosene as the extractant is applied successfully for the transportation of Pb(II) ions from donor phase to acceptor phase. Optimum conditions of this extraction are as follows: pH of donor phase is 7.00, 0.30 M HNO_3 as acceptor phase, and flux rate is 50 mL/min. Pb(II) ion transport is consecutive first order irreversible reaction. Since activation energy is found as 7.41 kcal/mol, this process is called as diffusion controlled system. This study shows that MDLM method is more practical and more effective than other techniques and somehow resembles the BLM system but shows a little difference. The advantages of this technique are as follows: simple construction, lack of moving parts, lightweight and portable, flexible in operation, high membrane capacity, high

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separation factor than mixer-settler. Additionally, since this method reduces operation time, risk of contamination, amounts of reagents used, generated waste, it is more economical than other techniques.

ACKNOWLEDGEMENTS

This research project was financially supported by Pamukkale University as a Scientific Research Project (Project No: BAP 2012FBE077)

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