Extraction of Cd^{2+} ions from MDLM System with TNOA carrier

TNOA taşıyıcısı ile MDLM Sisteminden Cd+2 iyonlarının ekstraksiyonu

Ramazan DONAT[1] ⓘ **, Melike İlknur EYİCE[1]** ⓘ

[1]*Pamukkale University, Faculty of Sciences Arts, Department of Chemistry, 20070 Denizli, Turkey*

Abstract

The extraction of Cd^{2+} ions via a new Multi-Dropped Liquid Membrane System: Extraction of Cd^{2+} ions from the solution phase was studied by using the multi-dropped liquid membrane system, which is different from other liquid membranes. The extraction of Cd^{2+} ions through multi-dropped liquid membrane containing tri-n-octyl amine in kerosene as mobile carrier and protons as counter ions in the acceptor phase (CH$_3$COONH$_4$) was investigated. Donor, acceptor, and the organic phase in the reduced concentration of Cd^{2+} model time dependence curves showed a good fit to experimental data obtained. The activation energy in the extraction mechanism of Cd^{2+} ions was calculated to be 17.07 kcal/mol. The value of this calculated activation energy indicates that the extraction of Cd^{2+} ions with the multi-dropped liquid membrane system is chemically controlled. The experimental results suggest the possibility of removing Cd^{2+} ions from aqueous solution in an extractor based on multi-dropped liquid membrane system.

Keywords: Cadmium, Extraction, MDLM, TNOA.

Öz

Cd^{+2} iyonlarının yeni bir Çok Damlacıklı Sıvı Membran Sistemi ile ekstraksiyonu: Cd^{+2} iyonlarının çözelti fazından ekstraksiyonu, diğer sıvı membran tiplerinlerinden farklı olan çok damlacıklı sıvı membran sistemi kullanılarak çalışılmıştır. Çok damlacıklı sıvı membran sisteminde kerozen içinde çözünmüş taşıyıcı tri-n-oktil amin ve aksptör faz olarak karşıt iyon olan protonlayıcı (CH$_3$COONH$_4$) içeren çözelti ile Cd^{+2} iyonlarının ekstraksiyonu incelenmiştir. Donör, akseptör ve organik fazdaki Cd^{+2} iyonlarının zamanla azalan konsantrasyon eğrileri elde edilen deneysel verilerle iyi bir uyum göstermiştir. Cd^{+2} iyonlarının ekstraksiyon mekanizmasına ait aktivasyon enerjisi, 17.07 kcal/mol olarak hesaplandı. Bu hesaplanan aktivasyon enerjisinin değeri çok damlaçıklı membran sistemi ile Cd^{+2} iyonlarının ekstraksiyonunun kimyasal kontrollü olduğunu göstermiştir. Deneysel sonuçlara göre çok damlaçıklı sıvı membran sistemine dayanan bir eksraktör ile sulu çözeltiden Cd^{+2} iyonlarının uzaklaştırılmasının mümkün olduğunu göstermektedir.

Anahtar Sözcükler: Kadmiyum, Ekstraksiyon, ÇDSM, TNOA.

I. INTRODUCTION

Cadmium that is a toxic element, normally presents in metallurgical and industrial wastewaters [1,2]. If Cadmium waste is directly discharged into the environment, it will certainly cause disturbances to various components of the environment, one of which living creatures including humans, which can lead to environmental pollution. It is characterized by the gradual form of order and the condition of the origin of the environment to worse condition, even though the Cd^{2+} in inorganic compounds can decompose into simple compounds, but remain toxic materials that can harm human life.

Cadmium in trace amounts is important industrially, as a toxicant, non-biological, an environmental pollutant and an occupational hazard in industry, also it is extremely toxic metal ion [3]. Interestingly, the small size of these heavy metals is

widespread and is common in our diet, the limit is very important because we can actually be healthy [4]. Cadmium unveils human health to fatal dangers by inciting cancer, mucous membrane destruction, kidney damage, diarrhea, vomiting, and bone damage and also testosterone and influence the generation of progesterone [5]. Hence, for environment and economy, removal of cadmium ions from industrial sources and waste waters is significant [6].

There are lots of waste water treatment methods such as solvent extraction, electro coagulation, activated carbon adsorption, ion exchange, etc. Mechanical separation of industrial waste water containing heavy metal ions is becoming increasingly important due to increased environmental protection. The general principles for the removal of heavy metal ions by chemical precipitation from industrial wastes are based on the low solubility of heavy metal hydroxides, salts, or sulphur, but the low dissolved metal ion concentration is a less efficient method [7]. In connection with this problem, heavy metal waste processing methods are effective, especially when their concentration in low waste. Solvent extraction is a commonly used technique, but requires a large number of organic solvents and metal extractants and becomes inefficient when the concentration of metal ions in the waste stream is low [8].Of all these techniques, liquid membrane (LM) has a great interest to researchers due to the removal and recovery of heavy metals from synthetic aqueous solutions or wastewater applications [9].

LM extraction is a method that can be used in the process of separation, purification, extraction, or the recovery process of the desired material. LM system is a method for the separation and purification of extracting metal ions by combining transportation and stripping in one step [10]. This method has advantages, such as the ability to be applied using a bit of organic solvents, even if the concentration of dissolved metal ions is low, the process takes place continuously [11]. Application of liquid membrane technique has recently become very popular in different fields due to their high efficiency and selectivity due to the presence of a mobile carrying agent (ligand). Selecting the transport agent appropriate for the metal ions determines the success of the extraction process. LM emulsions in various formulations make this technique a very useful process for different applications [12].

Several carrier ligands were synthesized by the researchers and the properties of these synthesized extractants were evaluated for the extraction of various metal ions [13]. LM is now rapidly expanding the fields of both research and industrial separation techniques [14]. Removal and recovery of heavy metal ions from waste water are the most popular applications among the applications of liquid membranes[13-16].

In this study, the optimum conditions for Cd^{2+} ion extraction from the chloride medium by multi-dropped liquid membrane (MDLM) system were examined. In our MDLM system, the effects of various parameters affecting the affinity of Cd^{2+} ions were investigated and optimum conditions were determined. Cadmium in the liquid synthetic solution of this research will be lowered its concentration, so that in accordance with the standard of environmental quality that is safe for the environment.

II. EXPERIMENTAL

2.1 Chemical and solutions

Analytical-grade inorganic chemicals: $CdCl_2.5H_2O$, NaCl, HCl, and CH_3COONH_4 were obtained from Merck firm, Germany. Commercial kerosene used as diluents was obtained from TÜPRAŞ Petroleum Company. The extractant of tri-n-octyl amine (TNOA) (purity>95%) is used without further purification [17].

2.2 The experimental setup

All experimental studies were performed with the MDLM system (Figure 1). More detailed information on how the MDLM system works in the extraction of different metal ions can be seen in our previous work [18-20].
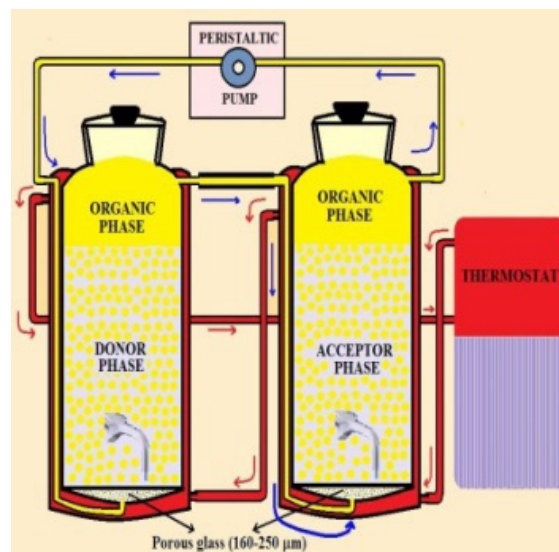

Figure 1. General diagram of MDLM System.

2.3 Determination concentration of Cd2+ ions with Uv-vis spectrophotometrically

Analyses of cadmium ions were made by taking samples from the donor and acceptor phases of the MDLM system

at intervals of 10 minutes. Cd^{2+} ions in aqueous phases determined by UV spectrophotometer (dithizone-λ= 600 nm) [21]. Cd^{2+} ions concentration at phases plotted against time and extraction kinetic graphs are drawn. The extraction of Cd^{2+} ions in MDLM system was investigated. The effects of temperature, concentration of the carrier, donor phase pH and acceptor phase concentration were studied to investigate the combined extraction and stripping process of Cd^{2+} using MDLM system.

2.4 Theoretical assessment of extraction of Cd2+ ions

The MDLM system consists of three membranes in contact with an external donor solution containing Cd^{2+} ions and a acceptor solution at the opposite interface (Figure 2): The co-transport involves various reactions and change (donor, organic and acceptor phases), which are described below.
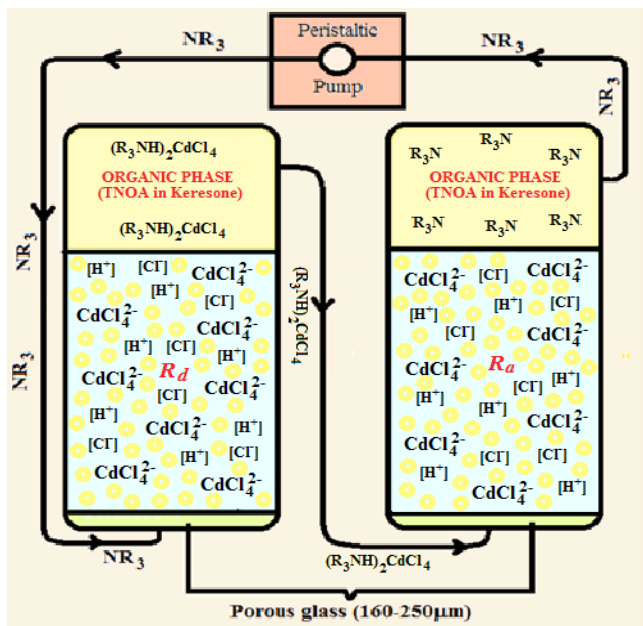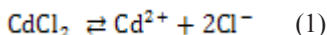

Figure 2. Extraction mechanism of Cd^{2+} through MDLM system.

a.   Reaction at the donor phase
In all of our studies, solutions of $CdCl_2.5H_2O$ prepared for the donor phase were used. The $CdCl_2$ compound forms Cd^{2+} ions when dissolved in water:

$$CdCl_2 \rightleftarrows Cd^{2+} + 2Cl^- \quad (1)$$

The reaction in Eq. 1 is very fast, the dissolved Cd^{2+} ions react with the $Cl-$ ions dissolved in the aqueous phase [22]:

$$2H^+ + Cd^{2+} + 4Cl^- \rightleftarrows H_2CdCl_4 \rightleftarrows CdCl_4^{2-} \quad (2)$$
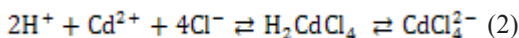
b.   Reaction of R_3N with HCl from donor solution at donor/organic interface
In the HCl solution, the carrier TNOA (R_3N) receives a proton with a positively charged species. The Cd^{2+} ions in HCl may also be extracted as $(R_3NH)_2CdCl_4$. All the general reactions on the donor side are given below. [23]:

$$2H^+_{aq} + CdCl^{2-}_{4aq} + 2R_3N_{org} \rightleftarrows (R_3NH)_2CdCl_{4org} \quad (3)$$
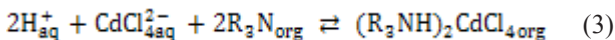
In the MDLM system, the transport time is very short in the equilibrium. Equation (2) is not rate limiting. The stoichiometric arrangement of $(R_3NH)_2CdCl_4$ is confirmed in literature [19]. It is possible to determine the K_d distribution ratios of Cd^{2+} ions at the interfaces [24]:

$$K_d = \frac{[(R_3NH)_2CdCl_{4(org)}]}{[Cd^{2+}]_i} \quad (4)$$

where $[(R_3NH)_2CdCl_{4(org)}]$ and $[Cd^{2+}]_i$ indicate Cd^{2+} concentrations in the organic and donor phase, respectively.

c.   Reaction at the acceptor phase
In the acceptor phase, reaction on the stripping side of the MDLM surface, in the presence of CH_3COONH_4 will be

$$(R_3NH)_2CdCl_{4org} + 2CH_3COOCl^-_{aq} + 2R_3N_{org} + CdCl^{2-}_{4aq} + 2CH_3COOH_{aq} \quad (5)$$
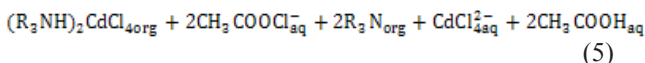
It shows that the extraction of Cd^{2+} ions according to the above reaction is carried out by transporting with proton. The most commonly used driving forces of concentration gradients of both H^+ and $Cl-$ ions [22].

For practical reasons, the donor (R_d), organic (R_m) and acceptor (R_a) symbols were used for the Cd^{2+} ions in the excess of MDLM system ($R_d = n_d/n_{do}$, $R_m=n_m/n_{do}$ and $R_a = n_a/n_{do}$, the sum of $R_d+R_m+R_a$ obviously being unity).

Transport of Cd^{2+} ions obeys the kinetics law of two consecutive irreversible first-order reactions according to the kinetic scheme [23].

$$C_D \xrightarrow{k_1} C_M \text{ (organic)} \xrightarrow{k_2} C_A \quad (6)$$
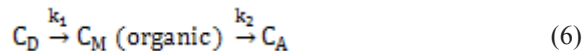
where the symbols of C_D, C_M, and C_A are Cd^{2+} ions in the donor, organic, and acceptor phases, respectively.

III. RESULTS and DISCUSSION

3.1 Kinetics of Cd2+ ions extraction

The change in the concentration of reduced Cd^{2+} ions in the donor, organic and acceptor phases over time is shown in Figure 3 (TNOA concentration in organic phase $7.0x10^{-3}$ mol/L, CH_3COONH_4 concentration in acceptor phase 0.50 M).

It can be noted that R_d gradually mono-folded over time, R_a followed a growing sigmoid type curve, and R_m represented maximum.
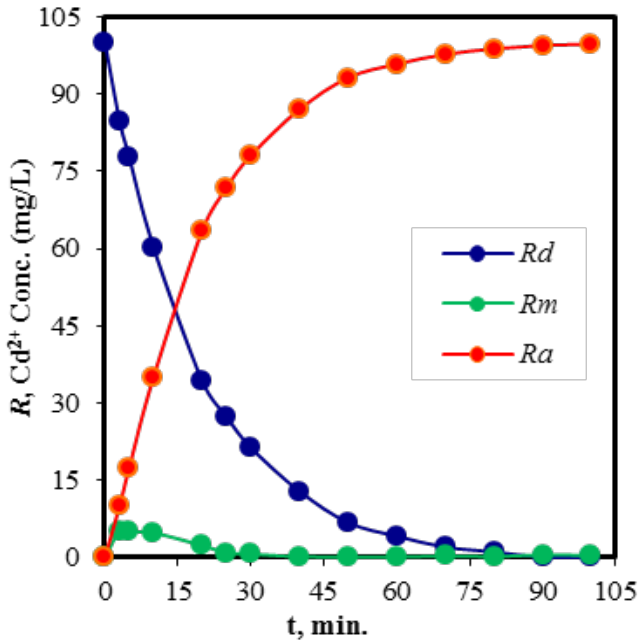

Figure 3. Change graph of Cd^{2+} ions over time in three phases (donor, organic, and acceptor).

These results show that the Cd^{2+} extraction proceeds according to the chemical kinetic laws of two successive irreversible first order reactions. This mechanism of some divalent ions has been used to define the extraction system through the MDLM system [25-27]. Irreversibility can be expected because R_m and R_d are tends to zero, whereas R_a tends to 99.72 mg/L. The extraction of Cd^{2+} ions from the donor phase to the acceptor phase seems to be almost complete. The above kinetic scheme may be defined in our MDLM system by the following equations

$$\frac{dR_d}{dt} = -k_1 R_d \equiv J_d \tag{7}$$

$$\frac{dR_m}{dt} = k_1 R_d - k_2 R_m \tag{8}$$

$$\frac{dR_a}{dt} = k_2 R_m \equiv J_a \tag{9}$$

where, k_1 and k_2 are the pseudo-first order rate constants of the interfacial reactions (3) and (5) and J is for flux of membrane. When $k_1 \neq k_2$, integrals of the differential equations (7)-(9), gives [23]:

$$R_d = \exp(-k_1 t) \tag{10}$$

$$R_m = \frac{k_1}{k_2 - k_1}\left[\exp(-k_1 t) - \exp(-k_2 t)\right] \tag{11}$$

$$R_a = 1 - \frac{1}{k_2 - k_1}\left[k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)\right] \tag{12}$$

According to Eq (11), the value of R_m in experimental studies increases at first, then decreases with time [23]. Furthermore R_m value has a maximum which allows for the calculation of maximum values of cadmium concentration in the organic phase and time, according to the following equations [28]:

$$t_{max} = \frac{\ln\left(\frac{k_1}{k_2}\right)}{k_1 - k_2} \tag{13}$$

R_m^{max} values at that time period [29].

$$R_m^{max} = \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_1 - k_2}} \tag{14}$$

When equations (13) and (14) are combined, the following equation can be obtained:

$$k_2 = \frac{\ln\left(\frac{1}{R_m^{max}}\right)}{t_{max}} \tag{15}$$

From eqs (7)-(9), the first-order time differentiation lead to the final form of the flux equations.

$$\frac{dR_d}{dt} = -k_1 \exp(-k_1 t) \tag{16}$$

$$\frac{dR_m}{dt} = \frac{k_1}{k_2 - k_1}\left[\exp(-k_1 t) - \exp(-k_2 t)\right] \tag{17}$$

$$\frac{dR_a}{dt} = \frac{k_1 k_2}{k_2 - k_1}\left[\exp(-k_1 t) - \exp(-k_2 t)\right] \tag{18}$$

The expression t_{max} for equation (13) replaces Eqs. (16-18), from which the maximum flows can be obtained [30].

$$\left[\frac{dR_d}{dt}\right]_{max} = -k_1 \left(\frac{k_1}{k_2}\right)^{\frac{k_1}{k_1 - k_2}} = J_d^{max} \tag{19}$$

$$\left[\frac{dR_m}{dt}\right]_{max} = 0 \tag{20}$$

$$\left[\frac{dR_a}{dt}\right]_{max} = k_2 \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_1 - k_2}} = J_a^{max} \tag{21}$$

$$-\left[\frac{dR_d}{dt}\right]_{max} = +\left[\frac{dR_a}{dt}\right]_{max} \, Þ \, -J_d^{max} = +J_a^{max} \tag{22}$$

Model curves of time depending of R_d, R_m, and R_a, calculated from Eqs (10)-(12) and it is also shown in Figure 3. Good agreement is obtained between experimental studies and model data.

The kinetics of extraction through MDLM is defined as the first order reaction in the metal ion concentration [29]:

$$\ln\left(\frac{C_o}{C_e}\right) = kt \qquad (23)$$

where k is the rate constant (min^{-1}), C_o is the initial concentration of Cd^{2+} ions in the donor phase (mg/L), C_e is concentration of Cd^{2+} ions at a given time in the donor phase (mg/L), t is the time extraction (min) and The k values were calculated from the plots of $\ln(C_o/C_e)$ vs. time [29]. In Figure 4, the graph of the extraction kinetics of Cd^{2+} ions is given.
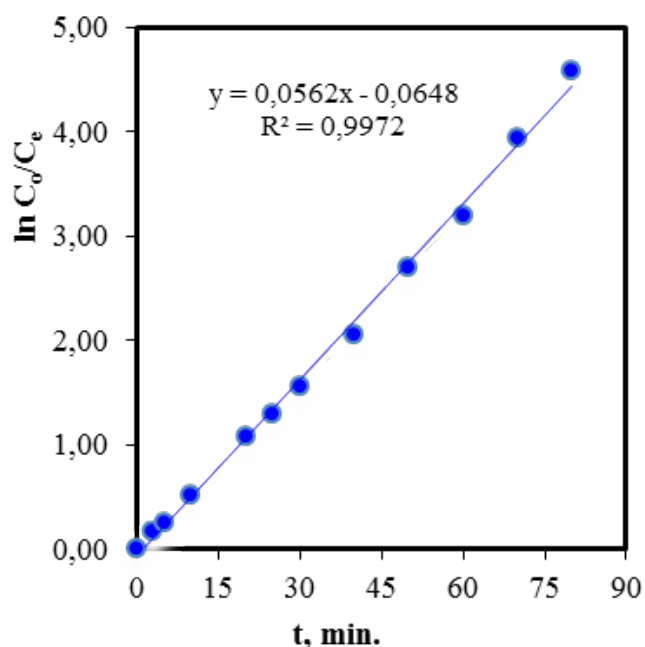

Figure 4. The graph of the extraction kinetics of Cd^{2+} ions for experiments.

The values of $t_{1/2}$, t_{max}, R_m^{max} J_d^{max}, and J_a^{max} for Cd^{2+} ions are calculated using the relevant equations and are given in Table 1. The value of k_1 is acquired by iteration from Eq. (10). This value is introduced as a constant value in Eqs. (11) and (12). An initial value of k_2 is obtained from Eq. (15) and introduced in Eqs. (11) and (12) and iterated [31].

It is used to calculate the percentage of metal ions recovered by Eq. (24):

$$E, \% = \frac{[Cd^{2+}]_{strip(t)}}{[Cd^{2+}]_{(o)}} \times 100 \qquad (24)$$

where $[Cd^{2+}]_{strip(t)}$ is the concentration of Cd^{2+} ions Cd^{2+} ions in the acceptor phase at elapsed time.

According to the graph, extraction efficiency yields of Cd^{2+} ions from donor phase to acceptor phase is 99.72%, respectively.

3.2 Effect of NaCl concentration in donor phase

Depending on the mechanism of the mass transfer process, the concentration difference between the donor phase and the acceptor phase is the driving force of the mass transfer process. In the salt concentration (0.2, 0.4, 0.6, 0.8, 100 M NaCl) effect of donor phase; the volume of donor and acceptor phase is 100 mL (0.5 M CH$_3$COONH$_4$), that of organic phase is 90 mL, concentration of TNOA in the organic phase is 7.0x10^{-3} mol/L, temperature is 298.15 K, the peristaltic pump transfer rate of the solution is fixed to 125 mL/min. This factor, as given in Figure 5 illustrates the effect of varying NaCl concentration in donor phase on the extraction of Cd^{2+} ions, depicting the decrease of Cd^{2+} ion concentration in the donor phase whereas an increase in its concentration in the acceptor phase with time. As shown in Figure 5, the recovery efficiencies of Cd^{2+} ions at different salt concentrations (0.20-1.0 M NaCl) from the donor phase to the acceptor phase are 99.26, 99.52, 99.18, 98.72 and 98.52%, respectively. Figure 5 shows the permeation of Cd^{2+} ions through membrane having five different NaCl concentrations with pH=2.50 HCl acid concentration in the donor phase.

The carrier of the amine derivative used to work in the donor/organic interface of Cd^{2+} for the extraction of organic phase from the donor phase requires first to be protonated. For this, it is necessary for the donor/organic phase interface to be acidic It can be seen that R_d decreases (Figure 5a) exponentially with time, accompanied by a simultaneous increase of R_a (Figure 5b), while R_m (Figure 5c) is present at its maximum level in ten minutes. In Figure 6, the graph of the extraction kinetics of Cd^{2+} ions is given. Kinetic data obtained by the calculations of continuous extraction of Cd^{2+} ions containing different concentrations of the salt with TNOA experiments are given in Table 2. The maximum R_m values were observed to be between 24.22 and 62.78 mg/L (Table 2). This clearly shows that the organic

Table 1. Comparison of the calculated kinetic parameters for the extraction of Cd^{2+} ions via MDLM.

k_1 (min^{-1})	k_2 (min^{-1})	k_2/k_1	$t_{1/2}$ (min)	$t_{max,}$ (min)	R_m^{max} (mg/L)	J_d^{max} (min)	J_a^{max} (min)
5.62	74.25	13.21	12.33	3.76	6.13	-4.55	4.55

phase and NaCl concentration play an important role in the extraction of Cd^{2+} ions. One of the other important factors is that the t_{max} values are found at the minimum level with increasing NaCl concentration. On the other hand by the use of 0.2-1.0 M NaCl k_2/k_1 ratio decreases. According to the results, it is clear that when the salt concentration is 0.4 M, extraction efficiency is extremely high. Results obtained above shows that, optimal salt concentration for the best Cd^{2+} ions extraction is determined as 0.40 M.
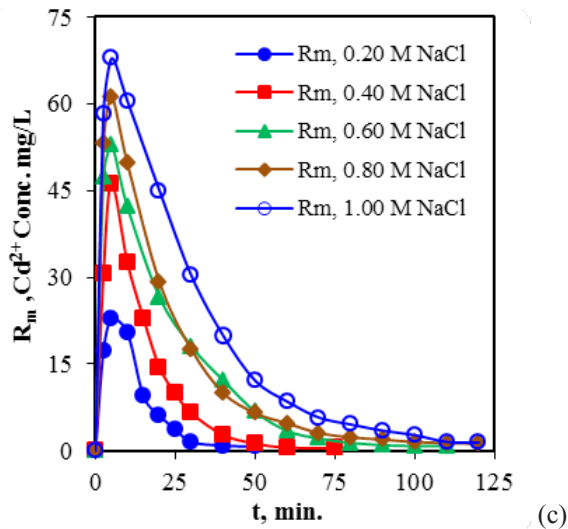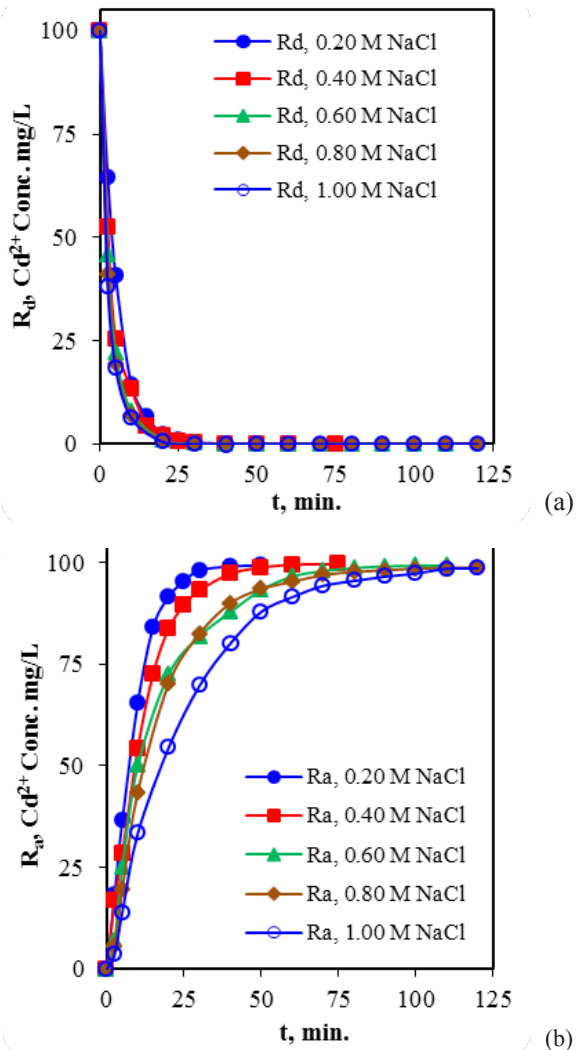

Figure 5. Time evolution of (a) donor R_d, (b) acceptor R_a, and (c) organic R_m phase for Cd^{2+} extraction through MDLM on different NaCl concentrations in donor phase.
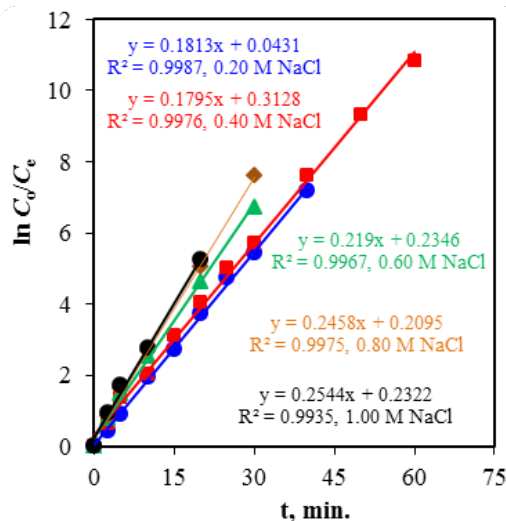

Figure 6. The graph of the extraction kinetics of Cd^{2+} ions for experiments performed at different NaCl concentrations (0.2-1.0 M NaCl).

Table 2. Effect of NaCl concentration (0.2-1.0 M) on kinetic parameters for extraction of Cd^{2+} ions through MDLM system

NaCl (M)	k_1 (min^{-1})	k_2 (min^{-1})	k_2/k_1	$t_{1/2}$ (min)	t_{max} (min)	R_m^{max} (mg/L)	J_d^{max} (min)
0.20	0.180	0.379	2.104	3.743	24.226	-0.092	0.092
0.40	0.179	0.081	0.450	8.091	52.046	-0.042	0.042
0.60	0.219	0.080	0.363	7.26	56.109	-0.045	0.045
0.80	0.246	0.064	0.262	7.383	62.150	-0.040	0.040
1.00	0.254	0.064	0.253	7.231	62.776	-0.040	0.040

Dingsheng and Ming (2004), similarly they studied on cadmium, used TOE as a carrier in xylene and 0.50 M CH$_3$COONH$_4$ as acceptor phase. Cd^{2+} ions transferred from donor phase (0.10 M HCl + 8.90x10^{-4} M Cd^{2+}) in the presence of 0.4 M NaCl with a yield of over 98% by the bulk liquid membrane system [24].

According to the results obtained, our liquid membrane system with the increasing amount of salt concentration or without NaCl in the donor phase is much more advantageous than other membrane systems. We use ten times less TNOA ligand concentration to achieve the same extraction efficiency of Cd^{2+} ions compared to other liquid membrane techniques.

3.3 Effect of Temperature

Examination of the effect of ambient temperature on the extraction process indicated that TNOA concentration was 7.00x10^{-3} M, initial Cd^{2+} ions concentration 100 mg/L and the peristaltic pump transfer rate of the solution fixed to 125 mL/min. At five different temperatures (288.15, 293.15, 298.15, 303.15 and 308.15 K), the change in Cd^{2+} ions concentration over time was investigated. The data obtained at different temperatures were used to plot the concentrations of Cd^{2+} ions in the donor, organic and acceptor phases versus time graphs as shown in Figure 7. It can be seen that the value of R_d decreases exponentially with time, accompanied by a simultaneous increase in R_a, whereas the value of R_m is presented at the maximum level in 5.86-25.55 minutes. For the related temperature, extraction yields of Cd^{2+} ions from donor phase to acceptor phase were found as 87.06, 91.45, 99.52, and 99.14%, respectively. It is clear that high extraction efficiency (>87.06%) of Cd^{2+} ion extraction can be achieved at the temperature 288.15-303.15 K and 7.00x10^{-3} M TNOA in kerosene.

Temperature is an effective parameter on the extraction of Cd^{2+} ions as it is seen in Table 3. It is well understood from the kinetic values of the Table 3 that the transport speed changes in direct proportion to the temperature. The kinetic values of k_1 and k_2 were calculated by using Eqs. (10)-(12). The k_1, k_2, k_2/k_1, R_m^{max}, t_{max}, J_d^{max}, and J_a^{max} values calculated at different temperatures are presented in Table 3 respectively. With increasing temperature, the maximum membrane input (J_d^{max}) and output (J_a^{max}) velocities increase the effect of temperature on the transport speed. Changes in t_{max} and R_m^{max} values with temperature indicate that it is an important factor in liquid membrane transport. The shortening of the t_{max} values calculated in Table 3 by increasing the temperature shows that the carrier ligands and Cd^{2+} ion form a complex in a short time and reach very fast equilibrium.
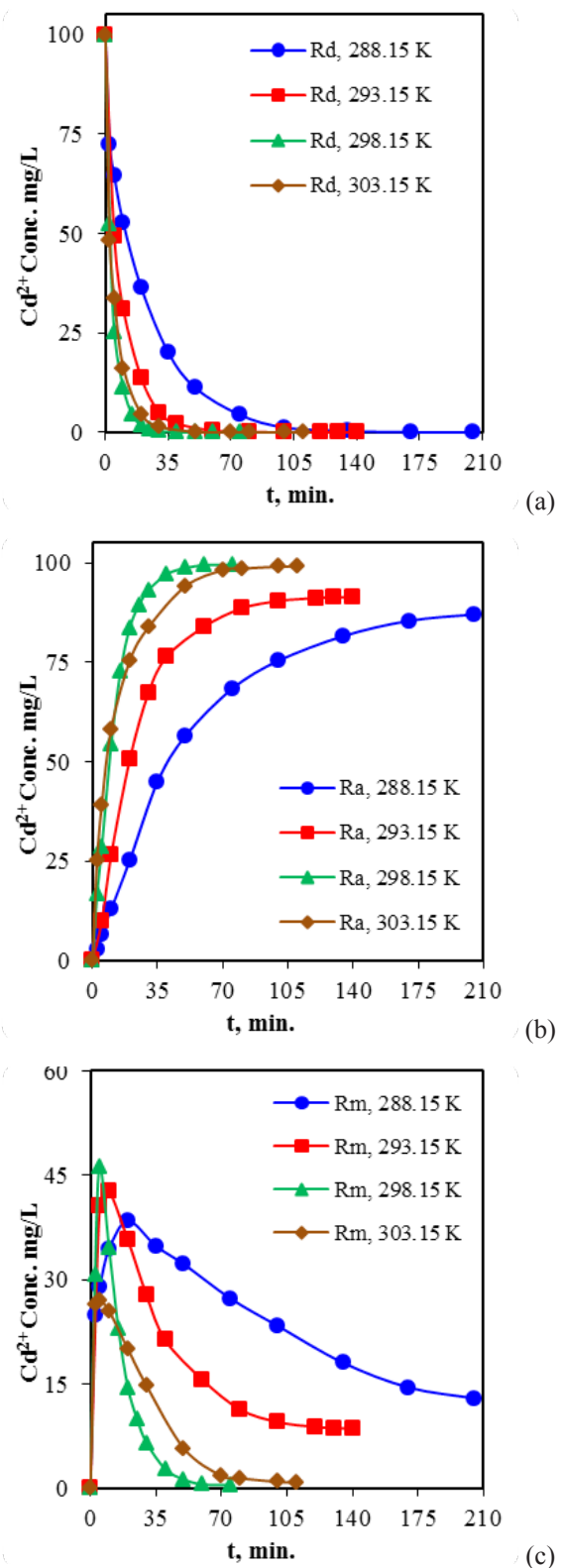

Figure 7. Concentration of Cd^{2+} ions versus time graphs for extraction studies through MDLM system of donor (R_d), acceptor (R_a), and organic (R_m), phases at different temperatures (288.15-308.15 K).

Plot of change $\ln(C_o/C_e)$ versus time is made by using reactive concentration at different temperatures (Figure 8).
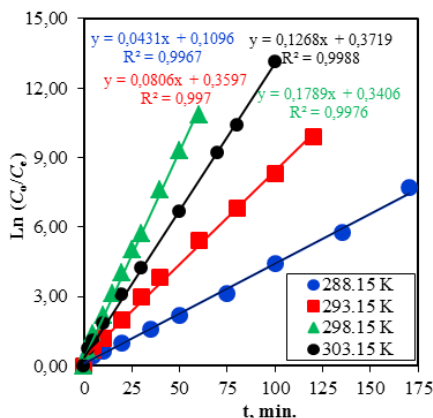

Figure 8. The graph of the extraction kinetics of Cd^{2+} ions for experiments carried out at different temperatures (288.15-303.15 K).

According to Figure 8 and Table 3, the reaction speed constants of extraction experiments were calculated as: 4.31x10^{-2}, 8.06x10^{-2}, 17.89x10^{-2}, and 12.68x10^{-2} min^{-1} for temperatures of 288.15-303.15 K, with k_1(298.15 K)>k_1(303.15 K) >k_1(293.15 K)>k_1 (288.15K), respectively.

For ideal studies; the reaction rate (or extraction) is desired to be neither fast nor slow. In order to calculate the kinetic data, it is supposed to occur at average reaction rate. Experimental results suggest that the extraction of Cd^{2+} ions could emerge at average rate and optimum study temperature is determined to be 298.15 K for extraction of Cd^{2+}.

The temperature on the kinetic parameters obtained for extraction of Cd^{2+} ions is very effective as given in Table 3. Since the common extraction of Cd^{2+} ions is in the form of irreversible first order reactions, it is not appropriate to calculate the activation energy of the transport process based on the membrane input and output rate constants. For this reason, it is better to calculate the activation energy (Eq 25) from the maximum membrane input (J_d^{max}) and maximum membrane output (J_a^{max}) velocities [32]. The activation energy of the process is calculated by the help of the input and output extraction rate constants via equation below;

$$\ln J = \ln(A) - \frac{E_a}{RT} \qquad (25)$$

where A is the frequency factor, R is the universal gas constant (8.314 J/molK), T is thermodynamic temperature and J is the flux rate. Therefore, it is more convenient to calculate the activation energy using the following Arrhenius equation [28]. Activation energy (E_a) values are calculated from the slope of the line obtained by plotting 1/T versus maximum membrane exit velocities in Figure 9. The activation energy for the TNOA carrier was found to be 17.07 kcal/mol and with the curves obtained from the graphs drawn in Figure 9. The activation energy (E_a) values for diffusion controlled processes are quite low, and for chemically controlled processes it is quite high [32,33]. Thus, the activation energy (E_a) values obtained for any process are the rate-control step that determines that the process is a chemical or diffusion reaction. As stated in the literature, activation energy values in diffusion controlled processes are less than 10 kcal/mol [33]. For TNOA carriers in this study, the activation energy values found in the transport of Cd^{2+} ion are greater than 10 kcal/mol. Since the activation energy is greater than 10 kcal/mol in the present study shows that the extraction of Cd^{2+} ions by MDLM system is a chemically-controlled process.
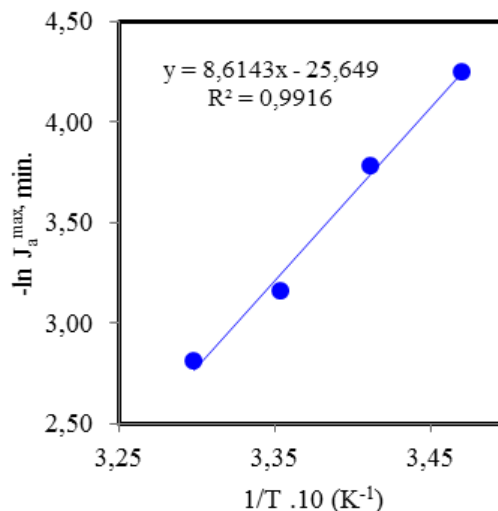

Figure 9. The Arrhenius graphic of extraction of Cd^{2+} ions by TNOA carrier at different temperatures (288.15-308.15 K).

Table 3. Comparison of kinetic parameters for the extraction of Cd^{2+} ions through MDLM system at different temperatures (288.15-303.15 K).

Temp. (K)	k_1 (min^{-1})	k_2 (min^{-1})	k_2/k_1	$t_{1/2}$ (min)	t_{max}, (min)	R_m^{max} (mgL^{-1})	J_d^{max} (min)
288.15	0.043	0.035	0.822	25.55	40.45	-0.014	0.014
293.15	0.081	0.050	0.619	15.62	45.88	-0.023	0.023
298.15	0.180	0.082	0.459	8.05	51.65	-0.042	0.042
303.15	0.127	0.223	1.762	5.863	26.98	-0.060	0.060

Table 4. Selected extractants used in different liquid membranes for Cd^{2+} ions transport.

Membrane System	Donor phase	Carrier Ligand	Organic Diluent Solvent	Stripping Agent	Extraction of Cd^{2+}, %	Reference
ELM	HCl + KI	TOA+ Span 80	oxylene	NaOH	95	[34]
ELM	HCl, KI	TIOA-Span 80	Dimethyl benzene	NaOH	95.8	[35]
SLM	pH:8 tricine + triethanol amine	Lasalocid (X537A)	nitrophenyl octyl ether	pH:2.0 HCl	95	[36]
SLM	pH:4, NaCl	TBP	cyclohexane	EDTA	85.4	[37]
SLM	HCl and H_3PO_4	Cyanex 23	xylene	Water	86	[38]
SDHLM	HCl+ NaCl	TNOA/Octanol	Kerosene	CH_3COONH_4	93.8	[39]
SLM	HCl+ NaCl	TNOA/Octanol	Kerosene	CH_3COONH_4	84.6	[39]
PIM	pH: 4.5 $NaNO_3$ + HNO_3	D2EHPA	CTA/$CHCl_3$	HNO_3	97.5	[40]
		Aliquat 336	CT A/$CHCl_3$	$HClO_4$	91.8	[40]
	pH: 7.5 NaCl+HCl					
SLM	pH:7.5 NaOH	D2EHPA	Kerosene		85	[41]
		PC-88A	Kerosene	H_2SO_4	83.4	
		Cyanex 272	Kerosene		82.2	
HLM	pH:3.0 KI, CH_3COOH	TIOA	Kerosene	pH:13 NaOH	91	[42]
SLM	HCl	CYPHOS IL101	Cumene	NH_4OH	83	[43]
MDLM	HCl+NaCl	TNOA	Kerosene	CH_3COONH_4	99.52	In this work

The transport of Cd^{2+} ions from different donor and acceptor phase solutions by using different carriers is reported in previous investigations(Table 4).

Table 4 shows that the extraction efficiency of cadmium ions with MDLM system is higher than other studies.

IV. CONCLUSION

As can be seen from the results, the decrease in Cd^{2+} concentration in the feed phase a corresponding increase in the stripping phase is observed. The extraction of Cd^{2+} ions through MDLM can be analysed in the formalism of

two consecutive irreversible first-order reactions, considering extraction and stripping reaction. MDLM process using TNOA to extract Cd^{2+} from aqueous solution was investigated, from which the following consequences can be concluded;

Effect of temperature and NaCl concentration in the donor phase were determined experimentally.

Cd^{2+} was extracted with an extraction efficiency of about >98.0%. Approximately 99.0% Cd^{2+} has been recovered when optimised MDLM system was applied for the removal Cd^{2+} from industrial contaminated water with cadmium

The activation energy value was calculated to be 17.07 kcal/mol for extraction. The value of calculated activation energy indicates that the process is chemically-controlled by Cd^{2+} ions.

The MDLM System can be used as a Cd^{2+} dropping system in liquid waste.

To summarize the results briefly, efficient outcomes can be obtained using the carrier ligands and the experimental setup of liquid membrane system.

Acknowledgment

V. REFERENCES

[1] Urtiaga, A.M, Alonso, A., Ortiz, I., Daoud, J.A., El-Reefy, S.A., Perez de Ortiz, S., Gallego, T. (2000). Comparison of liquid membrane processes for the removal of cadmium from wet phosphoric acid. *J. Membrane Sci.*, 164, 229-240.

[2] Safarzadeh, M.S., Bafghi, M.S., Moradkhani, D., Ilkhchi, M.O. (2010). A review on hydrometallurgical extractan drecovery of cadmium from various resources. *Miner. Engineer.*, 20, 211-220.

[3] Ullah, M.R., Enamul Hague, M. (2010). Spectrophotometric determination of toxic elements (cadmium) in aqueous media. *J. Chem. Engineer. IEB.*, 25, 1-12.

[4] Hutton, M., Symon, C. (1986). The Quantities of Cadmium, Lead, Mercury and Arsenic Entering the U.K. Environment from Human Activities. *Sci. Total Environ.*, 57,129-150, 1986.

[5] Agreda, D., Garcia-Diaz, I., Lopez, F.A., Alguacil, F.J. (2011) Supported liquid membranes. *Revista de Metalurgia*, 47, 146-168.

[6] Dalali, N., Yavarizadeh, H., Agrawal, Y.K. (2012). Separation of zinc and cadmium from nickel and cobalt by facilitated transport bulk liquid membranes using trioctyl methyl ammonium chloride as carrier. *J. Ind. Eng. Chem.*, 18, 1001-1005.

[7] Harrison, R.M., (1997). Pollution, Causes, Efect sand Control. 3rd ed., Berlin, Springer.

[8] Mohamed, Y.T., Ibrahim, A.H. (2012). Extraction of copper from waste solution using liquid emulsion membrane. *J. Environ. Prot.*, 3(1), 129-134.

[9] Ochromowicz, K., Apostoluk, K. (2010) Modelling of carrier mediated transport of chromium(III) in the supported liquid membrane system with D2EHPA. *Sep. Purif. Technol.*, 72(1), 112–117.

[10] Prayitno & Budiyono, M.E. (2001). Penurunan kadar tembaga dalam air limbah dengan proses ekstraksi membran cair. Prosiding P3TM-BATAN Yogyakarta.

[11] Mulder, M. (1996). Basic Principles of Membrane Technology. 2nd ed.Netherlands, Kluwer Academic Publisher.

[12] Alaguraj, M., Palanivelu, K., Velan, M. (2009). Removal of Cu(II) using emulsion liquid membrane. *Int. J. Chem. Tech. Res.*, 1(3), 722-726.

[13] Guezzen, B., Didi, M.A. (2012) Removal of Zn(II) from Aqueous Acetate Solution Using Di (2-Ethylhexyl) Phosphoric Acid and Tributylphosphate. *Int. J. Chem.*, 4(3), 32-41.

[14] Saad, H., Ammar, H., Attia, G., Affat, A-K.D. (2012). Extraction of metal ions mixture cadmium, iron, zinc and copper from aqueous solutions using emulsion liquid membrane technique, FNCES'12 / November 7 – 8.

[15] Ashraf, M., Chaudry, S., Ahmad, M., Malik, T. (1998). Supported liquid membrane technique applicability for removal of chromium from tannery wastes. *Waste Manage.*, 17, 211-218.

[16] Gill, J.S., Singh, H., Gupta, C.K. (2000). Studies on supported liquid membranes for simultaneous separation of Fe(III), Cu(II) and Ni(II) from dilute feed. Hydrometallurgy, 55, 113-116.

[17] Xinfang, L., Dingsheng, H., Ming, M. (2007). Transfer and separation of Cd(II) chloride species from Fe(III) by a hybrid liquid membrane containing tri-n-octylamine–secondary octylalcohol–kerosene. Chem. Engineer. J., 133(1-3), 265-272.

[18] Donat, R., Durmaz, O., Cetisli, H. (2015). Transportation and kinetic analysis of Mo(VI) ions through a MDLM system containing TNOA as carrier. *J. Hazard. Mater.*, 294, 17-26.

[19] Erden, K.E., Donat, R., Aytas, S. (2015). Simultaneous extraction and stripping of uranium ions via multi-dropped liquid membrane system. *Russ. J. Appl. Chem.*, 88, 1902-1912.

[20] Donat, R., Durmaz, O., Cetişli, H. (2017). The kinetic analysis of optimization and selective transportation of Cu (II) ions with TNOA as carrier by MDLM system. *Chinese J. Chem. Eng.*, 25(4), 415-425.

[21] Saltzman, B.E. (1953). Micro determination of Cadmium with Dithizone. Journal of Analytical Chemistry, 25, 493-496, 1953.

[22] Dingsheng, H., Ming, M., Zhenhua, Z. (2000). Transport of cadmium ions through a liquid membrane containing amine extractants as carriers. *J. Membrane Sci.*, 169(1), 53-59.

[23] Dingsheng, H., Ming, M. (2000). Kinetics of Cadmium(II) Transport through a Liquid Membrane Containing Tricapryl Amine in Xylene. J. Sep. Sci. Technol., 35(10), 1573-1585.

[24] Dingsheng, H., Xinfang, L., Ming, M. (2004). Transfer of Cd (II) Chloride Species by a Tri-n-octylamine-Secondary Octyl Alcohol-Kerosene Multimembrane Hybrid System. *Solvent Extr. Ion Exc.*, 22(3), 491-510.

[25] Szpakowska, M., Nagy. O.B. (1991). Membrane material effect on copper coupled transport through liquid membranes. *J. Membrane Sci.,* 64, 129-143.

[26] Szpakowska, M. (1994). Kinetics of coupled transport of Cu(II) ions through liquid membranes composed of technical solvents and paraffin mixtures. *J. Membrane Sci.*, 92, 267-273.

[27] He, D., Ma M., Zhao, Z. (2000). Transport of cadmium ions through a liquid membrane containing amine extractants as carriers. *J. Membrane Sci.*, 169, 53-59.

[28] León, G., Guzmán, M.A. (2004). Facilitated transport of cobalt through bulk liquid membranes containing diethlhexyl phosphoric acid. *Desalination*, 162, 211-215.

[29] Othman, N., Goto, M., Mat, H. (2004). Liquid membrane technology for precious metals recovery from industrial waste". Regional Symposium on Membrane Science and Technology, Johor Bahru, Johor, Malaysia, 21-25.

[30] Religa, P., Gawroński, R., Gierycz, P. (2009). Kinetics of Chromium(III) Transport Through a Liquid Membrane Containing DNNSA as a Carrier. *Int. J. Mol. Sci.* 10(3), 964-975.

[31] León, G., Guzmán, M.A. (2005). Kinetic study of the effect of carrier and stripping agent concentrations on the facilitated transport of cobalt through bulk liquid membranes. Desalination, 184(1–3), 79-87.

[32] Kobya, M., Topçu, N., Demircioglu, N. (1997). Kinetic analysis of coupled transport of thio cyanate ions through liquid membranes at different temperatures. *J. Membrane Sci.*, 130, 7-15.

[33] Lazarova, Z., Boyadzhiev, L. (1993). Kinetic aspects of copper(II) transport across liquid membrane containing LIX-860 as a carrier. *J. Membrane Sci.*, 78, 239-245.

[34] Li, Q., Liu, Q., Li, K., Tong, S. (1997) Separation study of cadmium through an emulsion liquid membrane. *Talanta,* 44, 657-662.

[35] Li, QM., Liu, Q., Zhang, QF., Wei, XJ., Guo, ZJ. (1998) Separation study of cadmium through an emulsion liquid membrane using triisooctylamine as mobile carrier. *Talanta*, 46, 927–932.

[36] Aouad, N., Miquel-Mercier, G., Blenvenue, E., Tronel-Peyroz, E., Jeminet, G., Juillard, J., Seta, P. (1998). Lasalocid (X537A) as a selective carrier for Cd(II) in supported liquid membranes. *J. Membrane Sci.*, 139, (1998) 167-174.

[37] Nowier, H.G. El-Said, N., Aly, H.F. (2000). Carrier-mediated transport of toxic elements through liquid membranes Transport of Cd(II) from high salinity chloride medium through supported liquid membrane containing TBP/cyclohexane. *J. Membrane Sci.*, 177, 41–47.

[38] Alguacil, F.J., Navarro, P. (2001). Permeation of cadmium through a supported liquid membrane impregnated with CYANEX 923. *Hydrometallurgy*, 61, 137–142.

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

[40] Ounissa K.S., Mansouri, L., Tingry, S., Seta, P., Benamor, M. (2008). Facilitated, Cd(II) transportacross CTA polymer inclusion membrane using anion (Aliquat 336) and cation (D2EHPA) metal carriers. *J. Membrane Sci.*, 310, 438-445.

[41] Parhi, P.K., Das, N.N., Sarangi, K. (2009). Extraction of Cadmium from dilute solution using supported liquid membrane. *J. Hazard Mater.*, 172, 773-779.

[42] Mortaheb, H.R., Zolfaghari, A., Mokhtarani, B., Amini, M.H. (2010). Study on removal of cadmium by hybrid liquid membrane process. *J. Hazard Mater.*, 177, 660-667.

[43] Comesana, A., Rodriguez-Monsakve, J., Cerpa, A., Alguacil, F.J. (2011). Non-dispersive solventextraction with stripdispersion (NDSXSD) pertraction of Cd(II) in HCl medium using ionic liquid CYPHOS IL101. *Chem. Engineer J.*, 175, 228-232.