Extraction of Fe(III) Ions through MDLM System Containing TOPO as Carrier

Ramazan DONAT[1*], Ömür DURMAZ[1]

ABSTRACT: In this study, the transport and mechanism of Fe(III) ions in acidic solution were investigated by using TOPO as carrier dissolved in kerosene with multi-drop membrane system. The parameters which are important in the transport of Fe(III) ions and their effects on the extraction process have been studied. These parameters are the effects of concentration of HCl solutions of donor phase, concentration of NaCl solutions of acceptor phase, concentration of TOPO solution of organic phase, transfer rate of organic phase, and temperature of the system. The optimum conditions for extraction of Fe(III) ions was conducted as 2.00 M of HCl and 100 mgL^{-1} Fe(III) ions for donor phase, 1.5×10^{-2} M of TOPO, 2.00 M NaCl of acceptor phase, 50 mLmin^{-1} of flux rate at 298.15 K. Over time, the reduction curves of the Fe(III) ions in the donor phase showed good agreement with the experimental data on the organic and acceptor phases. The activation energy was determined as 25.79 kJmol^{-1} and the extraction of Fe(III) ions was carried out by an intermediated-controlled process.

Keywords: Iron, MDLM system, Extraction, TOPO

[1] Ramazan DONAT (**Orcid ID:** 0000-0002-5701-5030), Ömür DURMAZ (**Orcid ID:** 0000-0002-5390-9352), Pamukkale University, Faculty of Science and Arts, Chemistry Department, 20070 Denizli, TURKEY

*Sorumlu Yazar: Ramazan DONAT, e-mail: rdonat@pau.edu.tr

INTRODUCTION

Iron, Fe(II) and Fe(III) ions are found in different rock and soil minerals and are the fourth most abundant element of the earth's crust (Bagheri, et al., 2000). Iron is one of the most indispensable trace elements for the human body can be found in many enzymes, proteins structure, and acts as cofactor for many cellular metabolism reactions. Iron helps to transport oxygen to all tissues by forming hemoglobin, and deficiencies and excesses in the human body result in various pathological disorders (Nandre et al., 2014).

Iron plays a role in photosynthesis and important growth nutrients for phytoplankton in the open ocean. Totally dissolved iron in natural water systems varies from 0.20 $nmolL^{-1}$ on the ocean surface to 400 $\mu molL^{-1}$ in polluted urban areas (Bagheri, et al, 2000). Unlikely to other fundamental trace elements the human body has capability to bank excess iron to use whenever required, whereas an excess exposure to iron becomes highly toxic because of the formation of reactive oxygen intermediates that result in peroxidative harm to vital cellular structures (Alguacil et al., 2010).

Precipitation as jarosite, goethite or hematite is a general method for the removal of Fe(III) ions from aqueous solutions, solvent extraction is also used for the same purpose (Pośpiech et al., 2005). Among them, membrane technologies especially liquid membranes show their importance (Alguacil and Alonso, 2000).

The separation technique that is still developing today is a technique based on liquid membranes. The liquid membrane emulsion technique is known as a double emulsion system. This technique provides a wide and potential range of applications due to its characteristics, such as ease of operation, relatively cheap and efficient operational costs (extraction and back-extraction stages in one stage) with high selectivity, and requires a fast extraction time (Hamzah et al., 2011). This technique has been used by many researchers in the separation (extraction) of various types of compounds and metals (Matsumoto, 1998; Djunaidi and Haris, 2003; Kargari et al., 2004; Othman et al., 2006; Gheorge et al., 2008; Kondo and Basuki, 2008; Praipruke et al., 2012). The extraction mechanism of the liquid membrane technique is that the molecule or ion to be extracted is initially in the external phase and diffuses to the internal phase through the membrane phase with the aid of the solute carrier molecule (chelating) in the membrane phase.

Fe(III) ions can be transported by using different organic carrier for liquid membrane systems such as organophosphorus acid derivatives of di-(2-ethylhexyl) phosphonic acid (PC-88A) and di-(2-ethylhexyl) phosphoric acid (D_2EHPA) (Jayachandran and Dhadke, 1997; Lupi and Pilone, 2000; Biswas and Begum, 2001). The neutral carriers used are methyl isobutyl ketone (MIBK), tributyl phosphate (TBP), trioctyl phosphine oxide (TOPO), and Cyanex 923 (Saji et al., 1999; Alguacil and Martinez, 2000; Gupta et al., 2001; Saji and Reddy, 2001; Fu et al., 2004,). Especially, TOPO is applied for supported liquid membrane system (Alguacil and Alonso, 2000).

The multi-drop liquid membrane (MDLM) system is one of the liquid membrane techniques. In the recent years, the extraction of heavy metals by MDLM system has been the subject of many studies. Contribution in this regard has been made by many researchers who have extracted number of heavy metal ions, such as Th(IV) (Tavşan, 2012), Cu(II) (Donat et al. 2017, Eyice, 2013), Mo(VI) (Donat et al., 2015) U(VI) (Erden et al., 2015), Pb(II) (Durmaz and Donat, 2016), Cr(VI) (Tuncay, 2017), Cd(II) (Donat and Eyice, 2018), Zn(II) (Erden and Donat, 2018), Mn(II) (Donat et al., 2018) and Fe(III) (in this study). MDLM technique is the most popular membrane system and has been used with great success.

The present investigation covers the single extraction of Fe(III) ions over different

temperatures, pH of donor phase, concentrations of acceptor phase and organic carrier from a dilute aqueous solution across MDLM system with TOPO as organic carrier. This MDLM technique involves the extraction of Fe(III) ions across the organic membrane via their concentration gradient by a suitable carrier dissolved in a water immiscible organic diluent that is kerosene for this study.

MATERIALS AND METHODS

Chemicals and solutions used in the study

Refined kerosene (supplied by indigenously Turkish Petroleum Refineries Company) was used as diluent to obtain the desired concentrations of TOPO organic carrier. Iron(III) nitrate, TOPO, potassium thiocyanate, and all other chemicals were obtained from Merck.

Stock solution of 500 mgL^{-1} Fe(III) ions was prepared by $Fe(NO_3)_3.9H_2O$, and respectively and diluted to the required concentrations when necessary. 0.10 M KSCN

was prepared by dissolving 2.43 g in water and made up to 250 mL 7.50×10^{-3} M TOPO was diluted by kerosene from the stock solution. 2.00 M of HCl in donor phase and 2.00 M of NaCl solution in acceptor phase was applied.

Procedure

The MDLM system was designed by Pamukkale University academics Halil Cetişli and Ramazan Donat. The scheme of MDLM system is shown in Fig. 1. The porous glass was applied to the bottom of the reactor for a more homogeneous distribution of the droplets. The organic phase is circulated in both reactors with a peristaltic pump and forms multi droplets through the pores under both reactors. The organic phase passes from either phase as bubbles and mixes the donor and acceptor phase. 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(Donat et al., 2015; Erden et al., 2015).
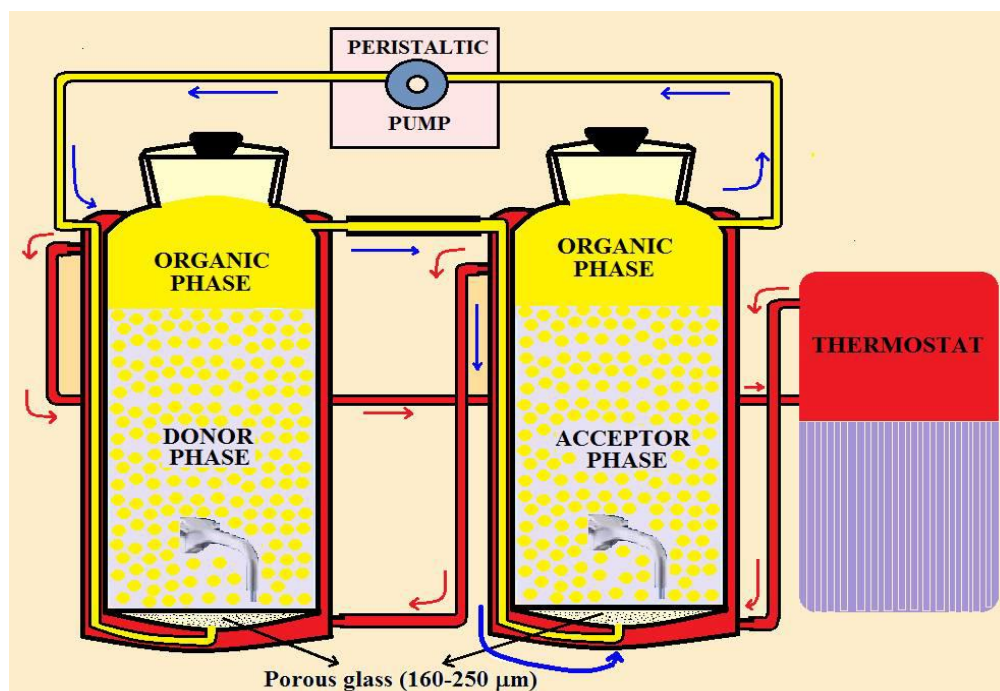

Figure 1. Picture of the measuring set with flowing MDLM.

CircuWCR P8 Wise model refrigerated bath circulator was used to keep the temperature constant of MDLM system. BT30-2J model peristaltic pump device was used to transport and flow the organic phase through the donor and acceptor phase.

Kinetic analysis

The kinetics of transport was investigated by the model used, where the reduced concentration were used. For practical reasons, the donor (C_d), organic (C_m) and acceptor (C_a) symbols were used for the Fe(III) ions in the excess of MDLM system ($C_o = C_d + C_m + C_a$ obviously being unity).

Where C_o is initially concentration of Fe(III) ions. C_d, C_m and C_a indicate the Fe(III) ions concentrations in the donor, organic and acceptor phases at time (t>0).

Transport of Fe(III) ions obeys the kinetics law of two consecutive irreversible first-order reactions according to the kinetic scheme (Patel et al., 2009).

$$C_D \overset{k_1}{\to} C_M \overset{k_2}{\to} C_A \qquad (1)$$

where the symbols of C_D, C_M, and C_A are Fe(III) ions in the donor, organic, and acceptor phases, respectively (Donat et al., 2015).

The integrated forms of C_d, C_m and C_a are given in equilibrium (2-4).

$$C_d = C_o . e^{-k_1 t} \qquad (2)$$

$$C_m = C_o \left(\frac{k_1}{k_2 - k_1}\right)(e^{-k_1 t} - e^{-k_2 t}) \qquad (3)$$

$$C_a = C_o \left[1 - \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_2 - k_1}\right] \qquad (4)$$

According to Eq. (5), the value of C_m in experimental studies increases at first, then decreases with time. Furthermore C_m value has a maximum which allows for the calculation of maximum values of Fe(III) ions concentration in the organic phase and time, according to the following equations.

$$t_{\max} = \ln(k_1/k_2)/(k_1 - k_2) \qquad (5)$$

$C_B^{\max}$ values at that time period.

$$C_B^{\max} = C_o \left(\frac{k_2}{k_1}\right)^{\frac{k_2}{k_1 - k_2}} \qquad (6)$$

When equations (5) and (6) are combined, the following equation can be obtained:

$$k_2 = -\ln(C_m^{\max}/C_o)/t_{\max} \qquad (7)$$

By considering the first-order time differentiation of equations(2–4) at $t = t_{\max}$, one obtains (Patel et al., 2009);

$$\left(\frac{dC_d}{dt}\right)_{max} = -k_1 \left(\frac{k_1}{k_2}\right)^{-k_1/(k_1 - k_2)} \equiv J_d^{max} \qquad (8)$$

$$\left(\frac{dC_B}{dt}\right)_{max} = 0 \qquad (9)$$

$$\left(\frac{dC_a}{dt}\right)_{max} = -k_2 \left(\frac{k_1}{k_2}\right)^{-k_2/(k_1 - k_2)} \equiv J_a^{max} \qquad (10)$$

The maximum membrane input (J_d^{max}) and output (J_a^{max}) fluxes values are equal to each other but have reverse signs:

$$J_a^{max} = -J_d^{max} \qquad (11)$$

The process of achieving complex transition states requires energy supplied from outside the system. This energy is called the activation energy. In both endotherm and exothermic reactions, both have a positive activation energy, since the complex transition state has a higher energy level than the reactant.

The kinetics of extractions throughout the MDLM system is defined as a first order reaction in the metal ion concentration (Erden et al., 2015):

$$\ln(C_o/C_e) = kt \qquad (12)$$

where C_o is the initial concentration of Fe(III) ions and C_e is the Fe(III) ions concentration at a given time in the donor phase respectively. The k values were determined by the plots of $\ln(C_o/C_e)$ vs. time.

The activation energy values were obtained from the Arrhenius equation by using the membrane input or output flux values at the different temperature. The following arranged version of the equation.

$$ln \; \pm J_{d,a}^{max} = ln(A) - (E_a/\text{RT}) \qquad 13)$$

where J is the rate constant, A is the frequency factor, E_a is the activation energy, $R = 8.314 \, Jmol^{-1}K^{-1}$ is the gas constant, and T is the Kelvin temperature.

Determination of the percentage of extraction of Fe(III) ions successfully extracted into the organic phase, then measured the amount of Fe(III) ions still dissociated in the external phase using the spectrophotometer. To know the percentage of extraction of Fe(III) ions obtained in this research used equation (14) as follows:

$$E, \% = \frac{[Fe(III)]_{ini} - [Fe(III)]_{fin}}{[Fe(III)]_{ini}} x100 \qquad (14)$$

where E,% = percent extraction; $[Fe(III)]_{ini}$ = initial concentration of Fe(III) in the donor phase and $[Fe(III)]_{fin}$ = the final concentration of the Fe(III) ions in the acceptor phase (Donat et al., 2015; Erden et al., 2015).
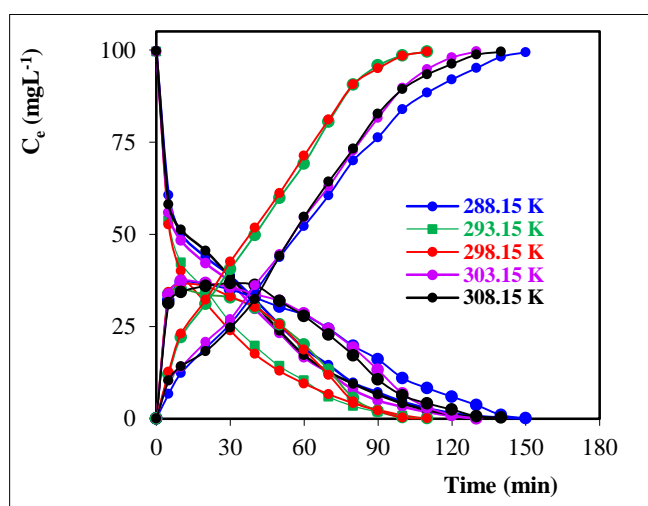
RESULTS AND DISCUSSION

Effect of temperature on extraction of Fe(III) ions

The MDLM system used throughout this extensive experimental part consisted of 100 mL of donor, organic and acceptor phase, 100 mgL^{-1} of Fe(III) ions and 2.00 M of HCl solution at donor phase, 2.00 M of NaCl solution as acceptor phase and $7.50x10^{-3}$ molL^{-1} of kerosene diluted TOPO as organic phase. The transfer rate of TOPO dissolved in kerosene from donor phase to acceptor phase was adjusted to 50 mLmin^{-1}. The batch experiment was accomplished at five different temperatures being adjusted by creosote device as 288.15, 293.15, 298.15, 303.15, and 308.15 K. Concentration of Fe(III) ions for donor, organic and acceptor phase solutions versus time plot is highlighted in Fig. 2. The change of $ln(C_o/C_e) \sim$ time plots is illustrated in Fig. 3.

The recovery efficiency of Fe(III) ions at five temperatures (288.15-308.15K) was obtained 99.94, 99.95, 99.95, 99.96 and 99.75%, respectively. Duration varied for different temperatures(288.15-308.15K) as 150, 110, 110, 130, and 140 min, respectively.
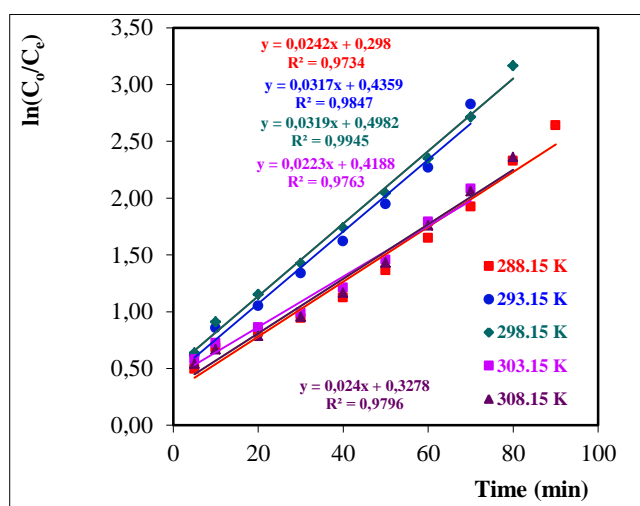

Figure 2. Concentrations of Fe(III) ions in the donor, acceptor, and organic phases versus time for the experiments carried out at different temperature.

Figure 3. Plots of $ln(C_o/C_e)$ vs. time t for the transport of Fe(III) ions through the MDLM system at five different temperatures.

Based on the data given in Table 1, reaction rate constant(k_1) differed for varying temperatures (288.15-308.15 K) as 2.42×10^{-2}, 3.17×10^{-2}, 3.19×10^{-2}, 2.23×10^{-2}, and 2.40×10^{-2} min^{-1}, respectively. k_1 (stands for the reaction rate constant of the reaction takes place at the interface of donor and organic phase) and k_2 (stands for the reaction rate constant of the reaction takes place at the interface of acceptor and organic phase) elevates due to temperature rise until the temperatures reached to 303.15 K. Moreover, half-life of the reaction and flux rates of donor and acceptor phases (J_d^{max} and J_a^{max})

likewise varied with k_1 and k_2 for rising temperature. The change of viscosity of three phases and the rise of mobility of Fe(III) ions may cause the discrepancy between the data based on 288.15-298.15 K and 303.15-308.15 K. Furthermore, less contact time of organic phase with donor and acceptor phases at higher temperatures may drive the extension of stripping time.

Comparative kinetic parameters of the stripping process of Fe(III) ions via MDLM system at five different temperatures is exhibited in Table 1.

Table 1. Kinetic parameters of the stripping process of Fe(III) ions via MDLM at five temperatures.

Temp. (K)	$k_1 \cdot 10^2$ (min^{-1})	$k_2 \cdot 10^2$ (min^{-1})	$t_{1/2}$ (min)	C_m^{max} (mgL^{-1})	$J_d^{max} \cdot 10^3$ (min	$J_a^{max} \cdot 10^3$ (min
288.15	2.42	7.20	28.63	13.00	39.01	-13.93
293.15	3.17	7.82	21.86	12.20	38.35	-17.12
298.15	3.19	12.51	21.72	8.00	36.56	-19.98
303.15	2.23	9.80	31.07	10.00	37.35	-14.42
308.15	2.40	3.33	28.87	30.00	36.69	-10.31

Based on the literature, a process of which activation energy is less than 20 kJmol^{-1} is referred as diffusion-controlled, between 20 kJmol^{-1} and 50 kJmol^{-1} as intermediated-controlled, and more than 50 kJmol^{-1} as chemical reaction-controlled (Chang et al., 2011). Eq. (13) is used for the determination of activation energy. The activation energy of the transportation process by the help of maximum output rates (J_a^{max}) and input (J_d^{max}) and whether

the transportation is diffusion controlled or chemically controlled (Lazarova Z, Boyadzhiev, 1993; Kobya et al., 1997). Activation energy was found out by the slope of J_a^{max} versus $1/T$ plot that is given in Fig. 4. The activation energy for transportation of Fe(III) ions was calculated as 25.79 kJmol^{-1} and this transportation process was found to be intermediate-control process (Erden et al., 2015).
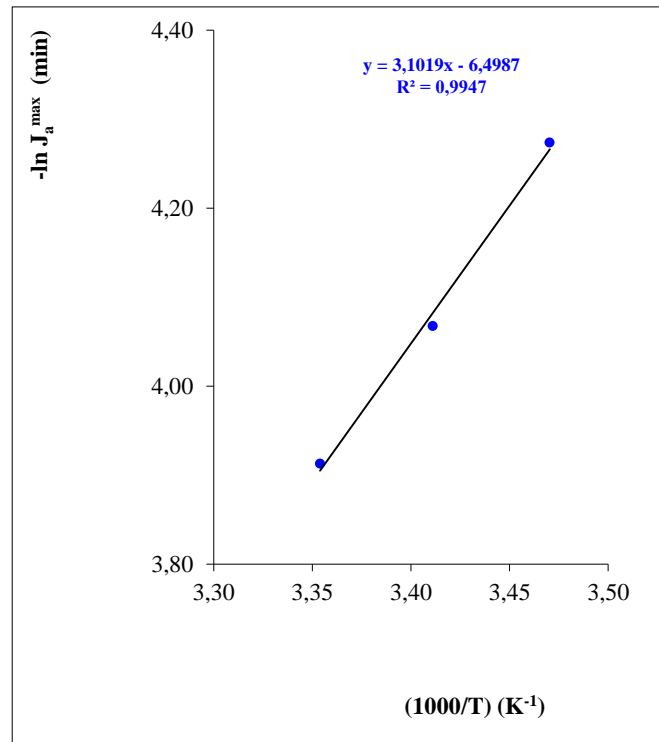
Figure 4. Maximum output rates versus 1/T graph.

The effect of HCl concentration in the donor phase

The extraction behavior of Fe(III) ions by TOPO across MDLM system was investigated through different concentrations (0.50, 1.00, 1.50, 2.00, 2.50, and 3.00 M) of HCl solution of donor phase at 298.15 K. The extraction was performed through the concentration of acceptor phase as 2.00 M NaCl, concentration of TOPO as 7.50×10^{-3} M, the volume of feed, organic and stripping solutions as 100 mL and the transfer rate of the peristaltic pump fixed as 50 mLmin^{-1}.

Fe(III) concentration of feed, membrane and acceptor phase solutions against time plot is reported in Fig. 5. Data based on different HCl concentration of donor phase are applied to plot concentrations of Fe(III) ions versus time graphs

by the help of each concentration of Fe(III) ions in the donor, organic and acceptor phase.

According to the Eq. (14), extraction efficiency of Fe(III) ions for different HCl concentrations is over 99% and extraction time for different HCl concentrations (0.50-3.00 M) is 160, 140, 130, 110, 100, and 90 min, respectively. The extraction and stripping of the Fe(III) ions treatments conforms to the successive first-order reaction kinetics according to the change of ln (C_o/C_e) with the time plots plotted in Figure 6.

For six different concentrations of HCl solution (0.50-3.00 M) in donor phase, k_1 is 1.69×10^{-2}, 2.01×10^{-2}, 2.16×10^{-2}, 3.16×10^{-2}, 3.47×10^{-2}, and 3.89×10^{-2} min^{-1}, respectively. Increasing concentration also elevated the k_1 values.
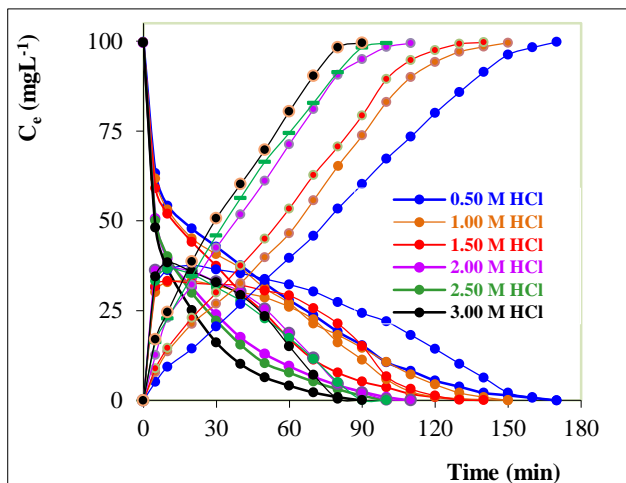
Figure 5. Graph of change of extraction of Fe(III) ions from different HCl concentration in donor phase against time.
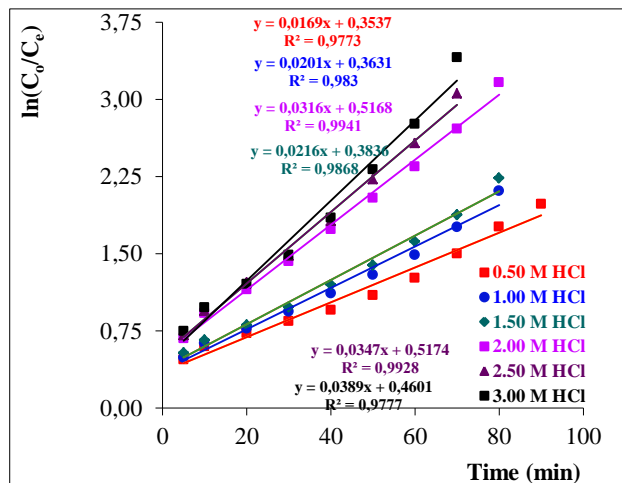

Figure 6. $\ln(C_o/C_e)$ versus time plots for the single extraction studies of Fe(III) ions through MDLM system at different HCl concentrations of donor phase.

According to these results, the transport and recovery of higher Fe(III) ions can be obtained effectively at any HCl concentration.

Alguacil et al., 2000, extracted Fe(III) ions by using different concentrations (0.20, 0.80, and 2.00 M) of HCl solution in the donor phase and rising HCl concentration increased the retrieval of Fe(III) ions. Highest extraction was observed at 2.00 M HCl solution and at the interface of the donor and organic phase, the reaction given below occurred.

$$H^+_{(aq)} + FeCl^-_{4(aq)} + 2L_{(org)} \rightleftarrows HFeCl_4.L_{2(org)} \quad (15)$$
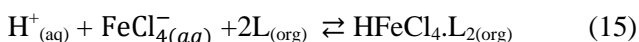
Mechanism of the extraction is illustrated in Fig. 7.

The effect of NaCl concentration in the acceptor phase

The stripping process of the transportation of Fe(III) ions plays an important role to complete the extraction. The NaCl in the stripping solution functioned as a back-extractant.

The effect of the acceptor phase concentration on the extraction of Fe(III) ions was carried out by changing the NaCl concentration from 0.50 to 3.50 M. The other parameters are kept constant during experiments.
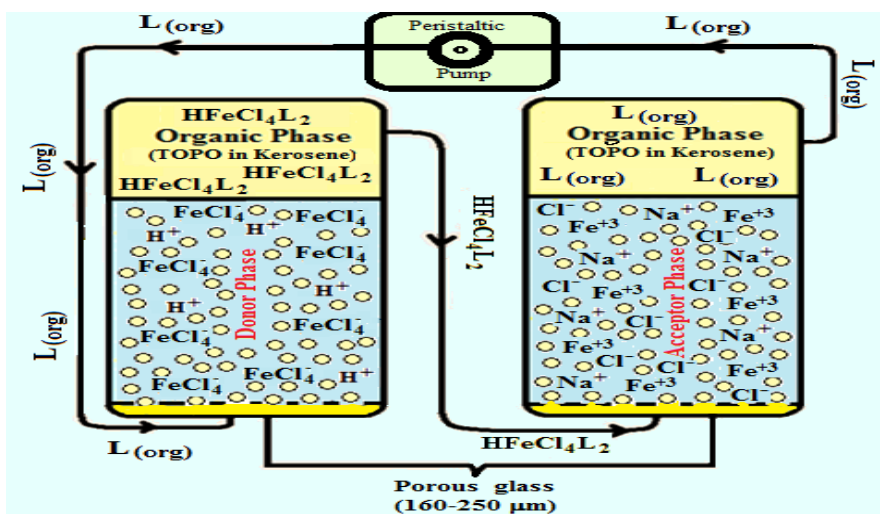

Figure 7. Diagram of transport mechanism of Fe(III) ions in MDLM system

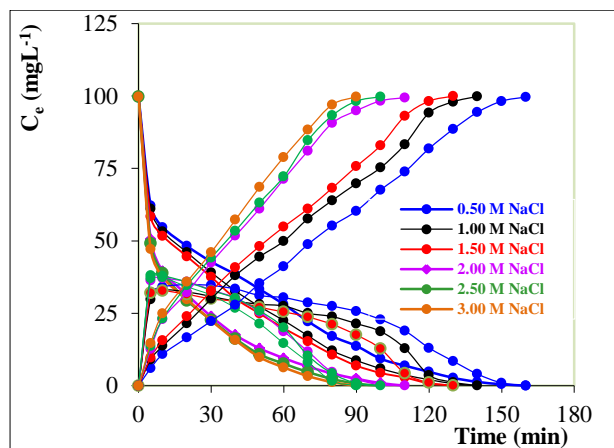Fig. 8 shows the kinetic profiles of each phase at different NaCl concentrations. Extraction efficiency of Fe(III) ions at different acceptor phase concentration (0.50, 1.00, 1.50, 2.00, 2.50 and 3.00 M NaCl) is 99.96, 99.98, 99.90, 99.95, 99.97, and 99.95%, respectively.
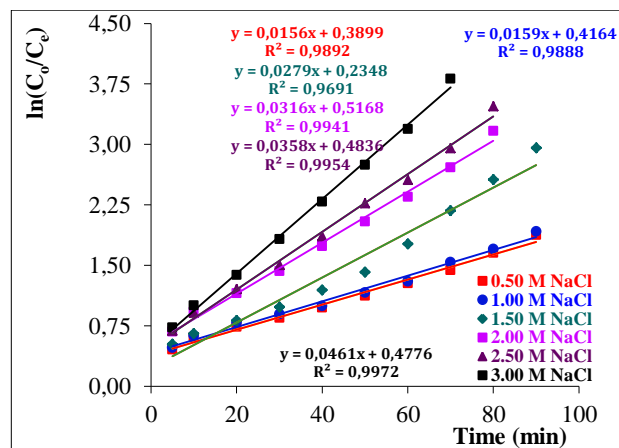

Figure 8. Time evolution of donor, organic acceptor phase for Fe(III) extraction through MDLM on different NaCl concentrations in acceptor phase.

Figure 9. The graph of the extraction kinetics of Fe(III) ions for experiments performed at different NaCl concentrations (0.5-3.0 M).

$\ln(C_o/C_e)$ vs time plots are illustrated in Fig. 9. When the concentration of NaCl was 0.50-3.50, by changing transfer time (from 0 to 90 min) measured the natural logarithm of the ratio of initial concentration (C_o) to given time concentration (C_e) of Fe(III) the kinetic curve can be obtained (see Fig. 9)(Erden et al.,2015). $\ln C_o/C_e \sim t$ curve line is a good straight line respectively, this shows that the concentration of chlorine ions in the stripping solution don't interfere.

Time of extraction for different receiving phase concentration (0.50-3.00 M NaCl) is 170, 150, 140, 110, 100, and 90 min, respectively. It can be concluded that the rise of NaCl concentration in the acceptor phase accelerates rate of Fe(III) ions extraction marginally. Hereby, best results are obtained at 2.00 M NaCl in the acceptor phase.

The effect of the concentration of TOPO on Fe(III) transport

To analysis the effect of the TOPO carrier concentration in the organic solution of the pseudo-emulsion phase, several experiments were performed using Comesaña et al., 2011)

donor phase of 100 mgL^{-1} Fe(III) in 2.0 molL^{-1} HCl and strip solutions of 2.00 M NaCl and organic solutions of TOPO carrier (3.75×10^{-3}, 7.50×10^{-3}, 1.125×10^{-2}, and 1.50×10^{-2} molL^{-1}) in kerosene. The effect of the concentration of TOPO in the organic phase on the extraction of Fe(III) ions is shown in Figure 10. Furthermore, $\ln(C_o/C_e)$ vs time plots are illustrated in Fig.11.

According to Figure 11, the extraction and eluation of Fe(III) in the different acceptor phase concentration processes conforms to the successive first order reaction kinetics. Extraction efficiency of Fe(III) ions at different extractant concentration (3.75×10^{-3}, 7.50×10^{-3}, 1.125×10^{-2}, and 1.50×10^{-2} molL^{-1}) is 99.95, 99.98, 99.96, and %99.97, respectively. Time of extraction for different TOPO concentration in kerosene (3.75×10^{-3}- 1.50×10^{-2} molL^{-1}) is 140, 100, 90, and 80 min, respectively. For four different concentrations of TOPO solution (3.75×10^{-3}-1.50×10^{-2} molL^{-1}) in donor phase, k_1 is 1.72×10^{-2}, 3.49×10^{-2}, 3.41×10^{-2}, and 3.85×10^{-2} min^{-1}, respectively. When the concentration of TOPO was $>3.75 \times 10^{-3}$ the transport of Fe(III) would decrease with transfer time.
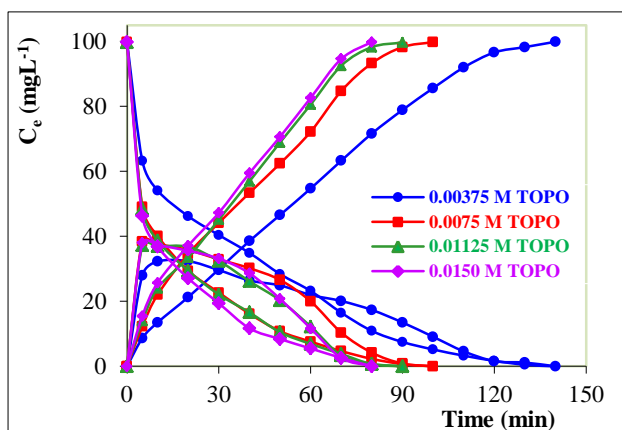
Figure 10. The effect of TOPO concentration in the organic phase on the percent extraction of Fe(III) ions.

Figure 11. Plots of $\ln(C_o/C_e)$ vs. time t for the transport of Fe(III)) ions through the MDLM system at different carrier concentrations.

Extraction efficiency of Fe(III) ions rises with increasing TOPO concentration. However, some deviations were observed in k_1 values. This may be caused by decreasing the complexation amount of Fe(III) ions with TOPO in the donor phase as passing through or stripping of Fe(III) ions could be slowed down the reaction in the acceptor phase. Thus, 3.75×10^{-3} M TOPO concentration for the next parameter was chosen as the most suitable carrier concentration.

We can conclude that the carrier concentration in the organic phase has very important effect on the transport of Fe(III) ions from MDLM system, especially at transport times and flux rates.

CONCLUSION

Based on the results of the research that has been done, some conclusions can be drawn:

MDLM technology can be used to extract Fe(III) ions in solution.

The optimum condition that is obtained to extract Fe(III) ions from the feed solution to obtain >99% efficiency are hydrochloric acid concentrations in 2.00 M donor phase, the concentration of TOPO in the organic phase 1.5×10^{-2} M, NaCl concentrations in 2.00 M acceptor phase, 50 mLmin^{-1} of flux rate at 298.15 K.

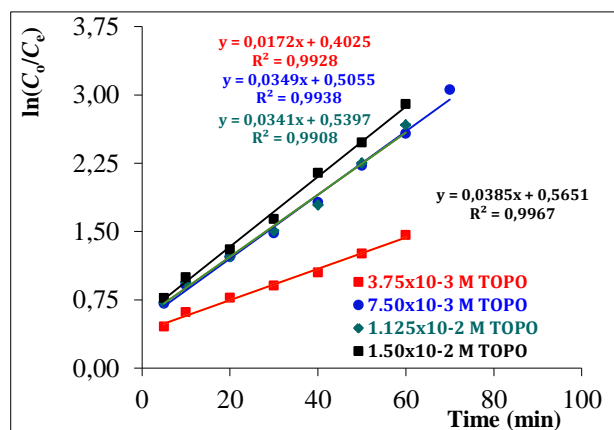As a result; The TOPO ligand has been found to be an effective carrier ligand for the transport and recovery of Fe(III) ions. In addition, in the separation and purification of heavy metals, it has been determined that the system is more economical, modular and simple compared to other methods, and it can be used to recover metal ions in optimal conditions in a short time.

REFERENCE

Alguacil, FJ, Alonso M, 2000. Iron(III) transport using a supported liquid membrane containing Cyanex 921. Hydrometallurgy, 58:81–88.

Alguacil FJ, Martinez S, 2000. Permeation of iron(III) by an immobilised liquid membrane using Cyanex 923 as mobile carrier. Journal of Membrane Science, 176: 249–255.

Alguacil FJ, Alonso M, Lopez FA, Lopez-Delgado A, Padilla I, Tayibi H, 2010. Pseudo-emulsion based hollow fiber with strip dispersion pertraction of iron(III) using (PJMTH+)$_2$(SO$_4$$^{2-}$) ionic liquid as carrier. Chemical Engineering Journal, 157:366–372.

Bagheri H, Gholami A, Najafi A, 2000. Simultaneous preconcentration and speciation of iron(II) and iron(III) in water samples by 2-mercaptobenzimidazole-silica gel sorbent and flow injection analysis system. Analytica Chimica Acta, 424:233–242.

Balkaya T, 2017. Çok Damlacıklı Sıvı Membran ile Dikromat iyonu ekstraksiyonunun incelenmesi, Pamukkale Üniversitesi Fen Bilimleri Enstitüsü, Yüksek Lisans Tezi (Basılmış).

Basuki KT, 2008. Mathematical modeling for the extraction of uranium and molybdenum with emulsion liquid membrane, including industrial application and cost evaluation of the uranium recovery. Jurnal Forum Nuklir, 2(1):63-87.

Biswas RK, Begum DA, 2001. Kinetics of stripping of Fe^{3+}-D2EHP complexes from D2EHPA-kerosene phase by aqueous HCl-Cl^- phase using the single drop technique. Hydrometallurgy, 60:81–97.

Chang SH, Teng TT, Norli I, 2011. Cu(II) transport through soybean oil-based bulk liquid membrane: Kinetic study". Chemical Engineering Journal, 173:352–360.

Comesaña A, Rodriguez-Monsalve J, Francisco AC, Alguacil J, 2011. Non-dispersive solvent extraction with strip dispersion (NDSXSD) pertraction of Cd(II) in HCl medium using ionic liquid CYPHOS IL101. Chemical Engineering Journal, 175(15):228-232.

Djunaidi MC, Haris A 2003. Pemisahan logam berat menggunakan membran cair berpendukung dengan variabel konsentrasi ion logam dan ph fasa umpan. Jurnal Kimia Sains & Aplikasi, 6(2):1-4.

Donat R, Durmaz Ö, Cetişli H, 2015. Transportation and kinetic analysis of Mo(VI) ions through a MDLM system containing TNOA as carrier. Journal of Hazardous Materials, 294:17–26.

Donat R, Durmaz Ö, Cetisli H, 2017. The kinetic analysis of optimization and selective transportation of Cu(II) ions with TNOA as carrier by MDLM system. Chinese Journal of Chemical Engineering, 25(4):415-425.

Donat R, Eyice Mİ, 2018. Extraction of Cd^{2+} ions from MDLM System with TNOA carrier. Marmara Fen Bilimleri Dergisi, 4:467-477.

Donat R, Kunter A, Cetişli H, 2018. Mn^{2+} İyonlarının Kerozen İçinde Çözünmüş DİODFA ile geri kazanımı. 13. Ulusal Kimya Mühendisliği Kongresi, 03-06 EYLÜL 2018, Van.

Durmaz O, Donat R, Cetisli H, 2016. Transportation of Pb(II) ions with D2EHPA as Carrier by MDLM System. International Journal of Innovative Research in Science, Engineering and Technology, 5(12):47-56.

Erden KE, Donat R, Aytaş Ş, 2015. Simultaneous Extraction and Stripping of Uranium Ions via Multi-Dropped Liquid Membrane System. Russian Journal of Applied Chemistry, 88:1902–1912.

Erden KE, Donat R, 2018. Transportation and kinetic analysis of Zn(II) ions via MDLM system containing D2EHPA as carrier, Membrane Water Treatment, 19(1):23-31.

Eyice Mİ, 2013. Emülsiyon Sıvı Membran Tekniği ile Cu^{2+} ve Cd^{2+} İyonlarının Ekstraksiyonunun İncelenmesi, Pamukkale Üniversitesi Fen Bilimleri Enstitüsü, Yüksek Lisans Tezi (Basılmış).

Fu X, Yu L, Lin Y, Zhu H, Wang H, Zhou X, 2004. Structure Adjustment of Mesoporous ZrO_2 Prepared with the Middle Phase Formed in Extraction Systems. Solvent Extraction and Ion Exchange, 22(5):885–895.

Gheorge A, Stoica A, Floarea O, 2008. Emulsion liquid membranes stability. Universitatea Politechnica Bucuresti Scientific Bulletin, 70(3):23-30.

Gupta VK, Gupta M, Sharma S, 2001. Process development for the removal of lead and chromium from aqueous solutions using red mud-an aluminium industry waste. Water Research, 35:1125–1134.

Hamzah B, Jalaluddin N, Wahab AW, Upe A, 2011. Pengaruh ion kadmium(II) dan nikel(II) pada ekstraksi ion tembaga(II) dengan ekstraktan 4-benzoil -1-fenil-3-metil-2-pirazolin-5-on menggunakan emulsi membran cair. Natur Indonesia, 13(3):269-275.

Jayachandran J, Dhadke PM, 1997. Liquid-liquid extraction separation of iron (III) with 2-ethyl hexyl phosphonic acid mono 2-ethyl hexyl ester. Talanta, 44(7):1285–1290.

Kargari A, Kaghazchi T, Sohrabi M, Soleimani M, 2004. Batch extraction of gold(III) ions from aqueous solutions using emulsion liquid membrane via facilitated carrier transport. Membrane Science, 233(1-2):1-10.

Kobya M, Topçu N, Demircioğlu N, 1997. Kinetic analysis of coupled transport of thiocyanate ions through liquid membranes at different temperatures". Journal of Membrane Science, 130:7–15.

Kondo K, Matsumoto M, 1998. Separation and concentration of indium(III) by an emulsion liquid membrane containing diisostearylphosphoric acid as a mobile carrier. Separation and Purification Technology, 13(2):109-115.

Lazarova Z, Boyadzhiev L, 1993. Kinetic aspects of copper(II) transport across liquid membrane containing LIX-860 as a carrier. Journal of Membrane Science, 78:239–245.

Lupi C, Pilone D, 2000. Reductive stripping in vacuum of Fe(III) from D2EHPA. Hydrometallurgy, 57:201–207.

Nandre KP, Puyad AL, Bhosale SV, Bhosale SV, 2014. A novel donor-acceptor receptor for selective detection of Pb(2+) and Fe(3+) ions. Talanta, 130C:103–107.

Othman N, Mat H, Goto M, 2006. Separation of silver from photographic wastes by emulsion liquid membrane system. Membrane Science, 282(1-2):171-177.

Patel B, Kumar A, Menon SK, 2009. Liquid Membrane Transport Kinetics of Hg(II) by Dithio Derivatized Macrotricyclic Compound. Journal of Macromolecular Science R, Part A: Pure and Applied Chemistry, 46:1151–1155.

Pośpiech B, Walkowiak W, Woźniak MJ, 2005. Application of TBP in selective removal of iron(III) in solvent extraction and transport through polymer inclusion membranes processes. Physicochemical Problems of Mineral Processing, 39:89–98.

Praipruke S, Kriausakul K, Tantayanon S, 2012. Extraction of palladium from acidic chloride media into emulsion liquid membranes using LIX 984N-C. Nonferrous Metallurgy, 1:13-22.

Saji John K, Sajin J, Reddy MLP, Ramamohan, TR, Rao TP, 1999. Solvent extraction of titanium(IV) from acidic chloride solutions by Cyanex 923. Hydrometallurgy, 51:9–18.

Saji J, Reddy MLP, 2001. Liquid-liquid extraction separation of iron(III) from titania wastes using TBP-MIBK mixed solvent system. Hydrometallurgy, 61:81–87.

Tavşan E, 2012. Sıvı Membran Tekniği ile Toryumun Ekstraksiyonunun İncelenmesi, Pamukkale Üniversitesi Fen Bilimleri Enstitüsü, Yüksek Lisans Tezi (Basılmış).