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Nickel Ion Coupled Counter Complexation and Decomplexation through Modified Supported Liquid Membrane System

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Abstract

A modified supported liquid membrane reactor was designed and used for nickel removal from aqueous solutions using impregnated polyacrylonitrile hydrophobic fluoropore membrane by di-2-ethylhexyl phosphoric acid (D2EHPA) as carrier in kerosene. Screening experiment using factorial design was carried out to find the effect of selected variables (factors) on nickel removal efficiency, followed by face centered composite design (FCCD) to obtain the optimum operating conditions, using response surface methodology (RSM). The factors considered in the designs were feed phase pH, carrier concentration, shaking time, stirring time, stripping agent concentration, stirring speed, inert salt concentration and phase modifier concentration. It was found that feed phase pH, carrier concentration, interaction between feed phase pH and carrier concentration, stripping agent concentration and stirring time have significant effect on nickel removal. Optimum conditions were feed phase pH 4.8, [D2EHPA]: 0.156 M, stirring time: 450 minutes and stripping phase agent at 1.5 M of H_2SO_4 which resulted in 95.38% of nickel removal. Stoichiometric coefficients of complexation and decomplexation reactions were obtained by Job's continuous variation method, loading capacity and loading test and the results confirmed that one nickel ion is extracted to the organic phase by two dimeric D2EHPA molecules. Mass transfer coefficient (k) for optimum condition was 2.3×10^{-6} m/s.

Keywords:

Supported liquid membrane, Nickel, Di-2-ethylhexyl phosphoric acid, complexation

1. Introduction

Industrial wastewaters are serious pollution source of environment and contain various heavy metals which are toxic and need to be removed properly. Nickel is a toxic and hazardous heavy metal and is released into aquatic phase of environment from various sources such as battery manufacturers, metal plating, car manufacturers, coins, etc. [1]. Exposure to nickel has direct and serious consequences of toxicity on human body and health such as cancer in respiratory system, headache, nausea, skin allergies, lung fibrosis, etc. [2-7].

Conventional methods of nickel and other heavy metals removal from industrial wastewater, such as electro-flocculation and coagulation, ion exchange, adsorption, etc., have been studied widely and amongst them, using membranes for industrial processes techniques is considered a promising method with high efficiency and applicability in industrial scale by lower costs and better results [8-13].

High selectivity, design simplicity, ease of scale up, low space requirement and relatively low energy consumption, can be considered as advantages of membrane technique compare to other methods [14]. Liquid membrane, including supported liquid membrane (SLM), bulk liquid membrane (BLM) and emulsion liquid membrane (ELM), has advantages such as low operation costs, high efficiency and potential usage of environmentally friendly materials.

Liquid membrane (LM) is an insoluble (immiscible) liquid with aqueous feed and stripping phases. Once a specific solute in a mixture moves through the liquid membrane from feed phase towards the stripping phase, extraction can be achieved. LM can be applied for different purposes such as selective removal and recovery of heavy metals, gas separation, ion exchange, dyes and pigments removal, metallurgical purifications, etc. [15-19].

The term liquid-liquid extraction (LLE) refers to the distribution of a solute between two immiscible liquid phases, which are in contact with each other [20].

Solute transport in LM techniques can be divided into four major transport mechanisms:

a) *Simple transport* in which solute moves through LM based on the solute solubility [21,22].

b) *Facilitated transport* of solute through liquid membrane in which a carrier mediated LM accelerates the solute diffusion through the membrane [23].

c) *Coupled counter transport* (co-transport) which can be considered as a specific type of *facilitated transport* in which feed and stripping phases acidity play the major role in solute-carrier complexation, decomplexation and couple transport of protons [24].

d) *Active transport* which is based on oxidation-reduction and biochemical conversions in feed-membrane and membrane-strip phase interfaces [25].

In supported liquid membranes (SLM) a thin micropourous filter is installed as a support between feed and stripping phases. The support is impregnated by an organic carrier to facilitate the extraction process. SLM has been used in various studies for different applications, such as heavy metals removal, radioactive wastes treatment, dye contaminated water sources treatment, etc. [26]. SLM system in comparison with other LM Processes has advantages such as small operation area and low operation time of analysis but module designs difficulties can be considered as an important disadvantage [27].

Since the inception of liquid membrane application by Li in 1968 [28] hitherto, many researchers have attempted to enhance and improve the LM technique efficiency and for this purpose different LM modules and modifications have been tried. In the case of facilitated metal extraction by LM, D2EHPA has been the most favorite carrier (extractant) due its chemical stability, low aqueous solubility and high loading characteristics, which make D2EHPA one of the most versatile extractants [29].

Numerous researchers have investigated liquid membrane based metal extraction process using D2EHPA as carrier. Ren et al. [30] used a hollow fiber renewal liquid membrane (HFRLM) and reported that the overall mass transfer coefficient increased with D2EHPA concentration in the organic phase and decreased with initial metal concentration in the feed phase [30]. In another study, Babakhani et al. [31] studied the nickel and cadmium extraction efficiency with D2EHPA on SLM and concluded that in the presence of the sole D2EHPA, the percentage of extraction for both cadmium and nickel increased with equilibrium pH.

Most studies and investigations have a point in common. The most widely used reaction for metal-carrier complexation in the case of using D2EHPA as carrier, is

$$M^{2+}_{aq} + n\ (HR)_{2,org} \rightarrow MR_2(HR)_{n,org} + n\ H^{+}_{aq} \qquad (1)$$

where M^{2+} represents metal ion, HR represents carrier dimers, and n is the number of dimers of carrier engaged in the reaction [32].

In order to determine the n value in Eq. 1., most researchers have used log D vs pH plot. In this method, the carrier concentration is fixed at a certain value and the effect of pH on distribution ratio is plotted. The slope of this plot represents an estimation of the n value in Eq. 1. However, it should be noted that since metal extraction process by D2EHPA is highly pH dependant, the D2EHPA concentration affects the pH as well as distribution coefficient. Thus the relation between distribution coefficient, pH and carrier concentration can be expressed by

$$\log D = \log K_c + [(a + b)/2] \log [(HR)_2] + a\ pH \qquad (2)$$

where D is distribution coefficient, K_c is equilibrium constant, a is the valence of metal species and b is the number of D2EHPA molecules engaged in the complexation [32]. Eq. 2. shows that D is a function of both pH and carrier concentration simultaneously, meaning that using different [D2EHPA] results in different distribution coefficients, and as a consequence different n values. Daiminger et al. [33] reported n values of 1.5 and 2.5 for zinc and nickel extraction, respectively, using a D2EHPA facilitated hollow fiber module, while Komasawa et al. [34] found that n value for similar system (nickel extraction by D2EHPA) varies from 2 to 3, depending on the diluent characteristics. In another research, it was reported that stoichiometric coefficients (n value) of cobalt and nickel, were equal to 4 when D2EHPA was used as carrier in kerosene [35].

It is therefore necessary to use other approaches to confirm the n value. In the present study, apart from the detection of the pH and carrier concentration on distribution ratio, loading test and Job's continuous variation method were applied in order to determine and confirm the n values of complexation and decomplexation reactions between nickel and D2EHPA. In loading test, D2EHPA to nickel molar ratio in organic phase versus nickel initial concentration at a fixed pH is plotted. The constant value from the curve shows the number of carrier molecules attached to the metal ion forming a metal-carrier complex. Job's continuous variation method (also called the Method of Continuous Variation) is an effective approach to the determination of chemical reaction stoichiometry [36]. In this method a total concentration of nickel and D2EHPA is maintained at a specific value and nickel removal is plotted versus [D2EHPA] to total concentration of nickel and D2EHPA. The corresponding highest nickel extraction with molar ratio of [D2EHPA] to total concentration of nickel and D2EHPA is an estimation of nickel to D2EHPA complex ratio. The large D2EHPA molecules positioning in the coordination sphere tend to be replaced by another smaller molecules having the properties of a Lewis base and TBP is considered as a suitable modifier for this purpose [37].

Tributhylphosphate (TBP) which is a type of organophosphorous compound with formula $(C_4H_9O)_3PO$ is useful to prevent the formation of tetrahedral or octahedral coordination geometry of the metal-organic complex. Kerosene has no reaction with water and most common metal ions, and is considered as a stable diluent [38].

Mass transfer coefficient (k) can be calculated using Danesi equation [39]:

$$\ln [Ni^{2+}]_t/[Ni^{2+}]_{ini} = -(kA/v)\, t \qquad (3)$$

where $[Ni^{2+}]_t$ and $[Ni^{2+}]_{ini}$ are nickel concentrations at time of sampling and initial concentration in feed phase, respectively; A is membrane area (m^2), t is time (s) and v is the feed phase solution volume (m^3).

In the present study nickel ion removal using supported liquid membrane is investigated. Metal-carrier complexation and decomplexation is discussed and different methods of stoichiometric coefficients verification (such as loading test and Job's continuous variation method) are applied. The linear, quadratic and interactive effects of pH and [D2EHPA] is monitored Factorial design, faced centered composite design and response surface methodology are used for screening and optimization of LLE and SLM processes, studying various factors such as feed phase pH, carrier concentration, shaking time, stirring time, stripping agent concentration, stirring speed, inert salt concentration and phase modifier concentration. A new modification of SLM is designed, made and used in which any possible leakage between aqueous phases is prevented.

2. Materials and methods

2.1. Materials

Chemicals used in this study consisted of nickel sulphate ($NiSO_4{\cdot}6H_2O$, Merk), Di-(2-ethylhexyl) phosphoric acid (D2EHPA, 97%, Sigma-Aldrich) as carrier; Tributhylphosphate (TBP, Sigma-Aldrich) as phase modifier, kerosene ($C_{12}H_{26}$, R&M) as diluent, Na_2SO_4 (Analyticals, ≥99% purity) as inert salt. Sodium acetate ($C_2H_3NaO_2$, R&M) and acetic acid (CH_3COOH, Systerm) were used in feed phase buffer solution preparation. Hydrophobic polytetrafluoroethylene (PTFE) membrane was used with 1.0 µm pore size, 85% porosity and 150 µm thickness, manufactured by Milipore. Hydrophobic PTFE membrane is bonded to a high density polyethylene support with broad chemical compatibility with acids, bases and organic solvents.

All the experiments were performed at room temperature (27°C). Aqueous phase pH was measured by using HACH pH meter. Concentrated H_2SO_4 and NaOH were used for pH adjustment. Absorbance measurements were carried out by SHIMADZU atomic absorption spectrophotometer (AAS) for feed and stripping phases nickel concentration detection.

2.2. Extraction and stripping by LLE

In LLE experiments, several factors were examined to determine the highest nickel ion extraction and stripping. For extraction, initially a volume (10-50 mL) of the prepared organic phase was mixed with the prepared aqueous phase (containing 100 mg/L of nickel prepared by adding specific amount of nickel sulfate to distilled water loaded by sodium sulfate) at a specific organic to aqueous phase of kerosene and D2EHPA (with and without TBP) ratio in a conical flask. The bottles were shaken by an orbital shaker at 150 rpm. Samples were taken every 3 minutes from the aqueous phase to determine the shortest shaking time that the system required reaching equilibrium. The aqueous phase pH was measured before and after each run with a pH meter. If the pH was different from the desired value, it was adjusted with 1M H_2SO_4 or 1M NaOH. After determination of the equilibrium time, the mixture was transferred to a separating funnel and allowed to settle for 10 minutes. The organic phase was then separated for stripping experiments. In stripping process, various stripping agent concentrations were prepared and mixed with the loaded organic phase with highest nickel extraction in the extraction process. Samples were taken by syringe from 2 cm below the surface of the aqueous phase for nickel concentration measurement using atomic adsorption spectrophotometer (AAS).

The removal efficiency (E%) of nickel was calculated according to:

$$E\% = ([Ni^{2+}]_{org,\,eq}/[Ni^{2+}]_{aq,\,ini}) \times 100 \qquad (4)$$

where $[Ni^{2+}]$ represents the concentration of nickel ion and the subscripts *org*, *eq*, *aq* and *ini* denote the organic, equilibrium, aqueous and initial states, respectively.

The distribution ratio (D) was calculated from

$$D = [Ni^{2+}]_{org,\,eq} / [Ni^{2+}]_{aq,\,eq} = ([Ni^{2+}]_{aq,\,ini} - [Ni^{2+}]_{aq,\,eq})/[Ni^{2+}]_{aq,\,eq} \qquad (5)$$

2.3. SLM reactor design

An SLM reactor was designed and modified for experimental studies. Fig. 1. shows the technical information of the modified SLM reactor. Fig. 1A. shows the side view of feed and stripping cells and membrane. Fig. 1B. shows the top view schematic of solute flow from aqueous feed phase through the membrane into the aqueous stripping phase.

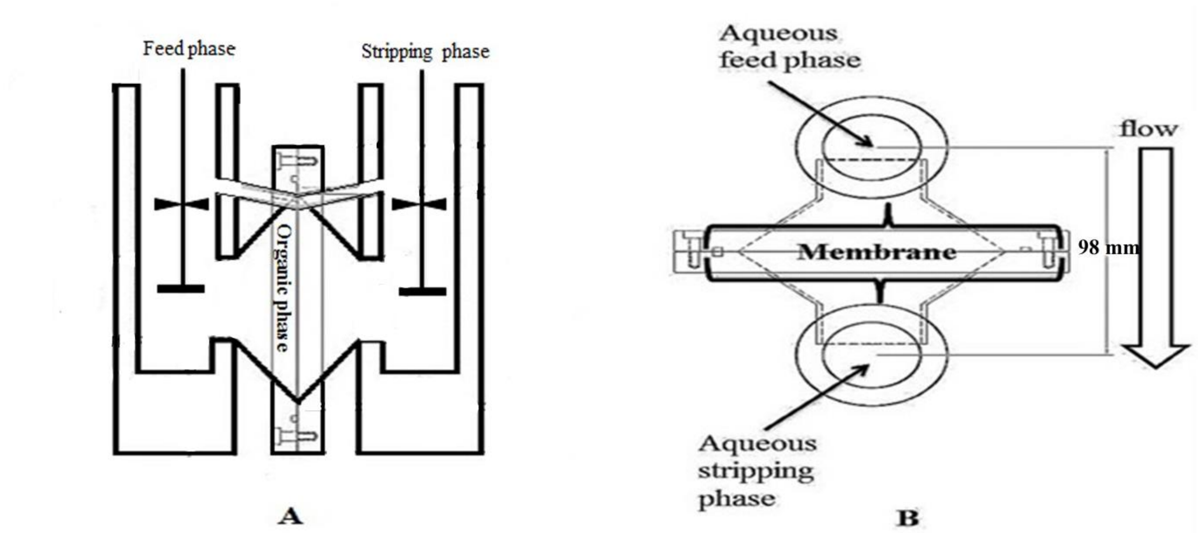

Fig. 1. The schematics of the A: SLM profile, B: SLM top view

In order to overcome the SLM reactor leak out between two aqueous phases, a modified design was approached by using a flange type membrane holder, sealed with an O-ring insertion. Each aqueous phase contains 150 mL of feed or stripping solution and a conical cut-off wall connects the two phases via a PTFE membrane (90 mm diameter). The conical-shape design allows large contact area between the feed phase and organic phase (membrane surface area). On the top of each phase a narrow bridge (with 10° slope up) was designed to prevent air blockage at the membrane section. Four blades stirrer bars (with vertical and axial vanes) were designed and modified for proper feed and stripping phases stirring.

2.4. SLM experiments

In SLM experiments, based on the initial results obtained in the LLE studies, feed phase solution was prepaid by dissolving specific amount of $NiSO_4$ and Na_2SO_4 in 0.1 M acetate buffer solution of the desired pH. Stripping phase for each run was prepared by adding certain amount of H_2SO_4 as stripping agent. Solid support was prepared by impregnation of PTFE membrane in kerosene loaded by various concentrations of D2EHPA and TBP for 24 hours prior to experiments.

Loading test was carried out in order to find the extraction stoichiometry with an organic phase containing D2EHPA (0.15 M) with varying Ni^{2+} concentrations in aqueous feed phase. Job's continuous variation method was applied to examine the Ni^{2+} extraction by various [D2EHPA] at the specific pH with total concentration of 0.1 M.

Table 1 gives the range of each factor in the stage of preliminary studies and the results were taken for the optimization process using RSM

Table 1
Selected factors used in LLE/SLM, and the related ranges.

Factor	Range
Feed phase pH (LLE, SLM)	1-6
Shaking time (LLE)	5-20 minutes
[D2EHPA] (LLE, SLM)	0.05-0.2 M
[TBP](LLE)	0.01-0.15 M
[Na_2SO_4] (LLE)	0.15-0.3 M
[H_2SO_4] (LLE)	0.5-2 M
Stirring speed (SLM)	300-500 rpm
Stirring time (SLM)	60 - 480 minutes

2.5. Design of experiments

Factorial design is a statistical method to find the relationship between studied parameters (factors), each at two levels (low and high) or more. Preliminary studies and related results provide necessary information about all the studied factors and enable the responses of a factor at different levels of another factor in the same experiment to be determined [40-41].

Response surface methodology (RSM) is a combination of mathematical and statistical methods which is considered as a useful tool for modelling and analysis of data. In RSM a response "*y*" (such as removal efficiency) is considered to be influenced by different independent variables "x_i" (such as pH, carrier concentration, etc.). The purpose of using RSM is to find the best levels of each independent variable that optimize the response [42].

The response is a function of the levels of independent variables:

$$y = f(x_1, x_2 \ldots x_k) \quad (6)$$

Experimental data was analyzed to fit the following second-order model

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i<j}\sum \beta_{ij} x_i x_j \quad (7)$$

where β_0, β_i, β_{ii} and β_{ij} are regression coefficients, and x_i and x_j are the coded variables[43].

In the present study, RSM was used to determine the optimum and experimental design matrix specified according to the face centered composite design (FCCD) method. FCCD design includes axial points placed on the face centers of a cube and each factor has three levels [44]. FCCD allows the desired response to be predicted by a second order equation which gives estimation of the main, quadratic and interactive effects of the factors on the factors under investigation [45].

The significance of each test and regression model has been analyzed using analysis of the variation (ANOVA). The regression model is said to be statistically significant when the P-value is lower than certain value, and that of the lack-of-fit is higher than the significance level employed in the analysis [46].

3. Results and discussion

3.1. Screening experiment

2^5 factorial design of experiments for LLE including: shaking time, [D2EHPA], [TBP], feed phase pH and [Na_2SO_4] coded as A_E, B_E, C_E, D_E and E_E, respectively, were carried out in order to screen the best studied range for nickel ions extraction. Fig. 2. shows the normal plot of the factors in their related ranges.

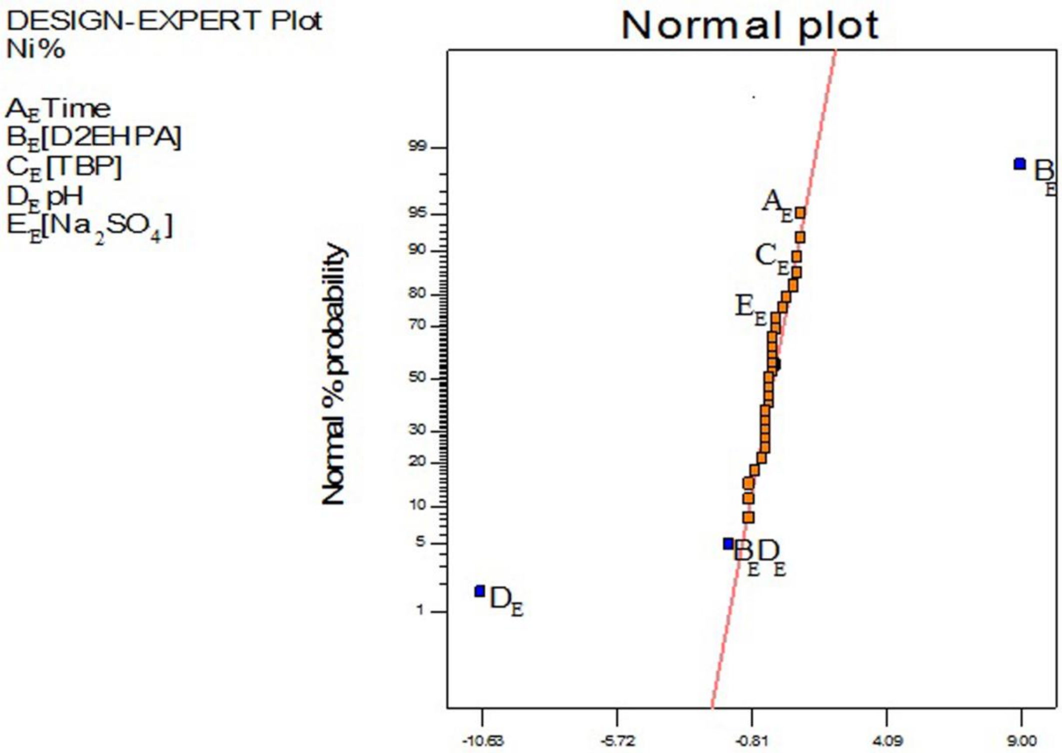

Fig. 2. Normal plot of the design for significant factors

It was found that amongst the studied factors, the carrier concentration [D2EHPA] (B_E) and feed phase pH (D_E) and the interaction between pH and [D2EHPA] (B_ED_E) are significant, while the other factors show no significant effect on nickel ion extraction in this stage. Table 2 shows the results of NOVA for screening experiment, after excluding the non-significant factors.

Table 2
ANOVA for selected factorial model, Analysis of variance of screening [Partial sum of squares**]**

Source	Sum of squares	DF	Mean square	F-value	P-value
Model	1572.25	3	524.08	237.64	< 0.0001
B_E	648.00	1	648.00	293.83	< 0.0001
D_E	903.12	1	903.21	409.51	< 0.0001
B_ED_E	21.13	1	21.13	9.58	0.0044
Residual	61.75	28	2.21		
Total	1643.00	31			
R-Squared	98.13				

The low P-values (< 0.05) obtained for the regression model and its variable terms (linear and interaction) indicate that the model was suitably fitted.

R^2 value of 98.31% indicates that 98.31% of the response variation can be explained by the combination of settings for the selected factors.

The regression equation for nickel removal is obtained:

$$Ni\ extraction\ (\%) = +50.50 + 4.50B_E - 5.31D_E - 0.81B_ED_E \qquad (8)$$

Factors with positive coefficient in high levels and those with negative coefficient at low levels will maximize the nickel extraction. The preliminary results show that in acidic condition of feed phase (pH 3-6) and when the carrier concentration was 0.2 M, the highest nickel removal (61%) occurred.

Screening experiment was followed by optimization of the significant factors ([D2EHPA] and pH) and based on ANOVA for the quadratic model (Table 3), the linear and quadratic effects of [D2EHPA] and pH are significant as well as the interaction between [D2EHPA] and pH (B_E, B^2_E, D_E, D^2_E and B_ED_E, respectively).

Table 3

ANOVA for selected factorial model analysis of variance for optimization of screening experiment

Source	Sum of squares	DF	Mean square	F-value	P-value
Model	5091.89	5	1018.38	141.39	< 0.0001
B_E	192.67	1	192.67	26.75	< 0.0013
D_E	620.17	1	620.17	86.11	< 0.0001
B^2_E	44.19	1	44.19	6.14	< 0.0424
D^2_E	3287.36	1	3287.36	456.43	< 0.0001
B_ED_E	42.25	1	42.25	5.87	0.0460
Residual	50.42	7	7.20		
Total	5142.31	12			
R-Squared	0.9902				

The final regression equation for nickel extraction is obtained:

$$Ni\ extraction\% = 92.00 + 5.67B_E + 10.17D_E - 4.00B_E^2 - 34.50D_E^2 + 3.25B_ED_E \qquad (9)$$

The significant interaction between the carrier concentration and pH observed in the results is in agreement with those of previous studies [32,47,48]. Total analytical concentration of the metal in organic and aqueous phases is a function of equilibrium pH and extractant concentration. When a metal ion (M^{2+}) is extracted to the organic phase the following reaction takes place:

$$M^{n+} + n(RH)_2 \rightarrow M(R\text{-}HR)_n + nH^+ \qquad (10)$$

where RH represents the carrier dimers, M^{2+} represents the metal ion and *n* is the number of dimers of carrier engaged in the reaction [49,50].

Slope analysis was carried out to determine the number of D2EHPA molecules involved in Ni-D2EHPA complex (*n* value in Eq. 10.).

Fig. 3. shows the relationship between logarithmic distribution ratio of [Ni^{2+}] in aqueous to organic phases (log D) versus pH.

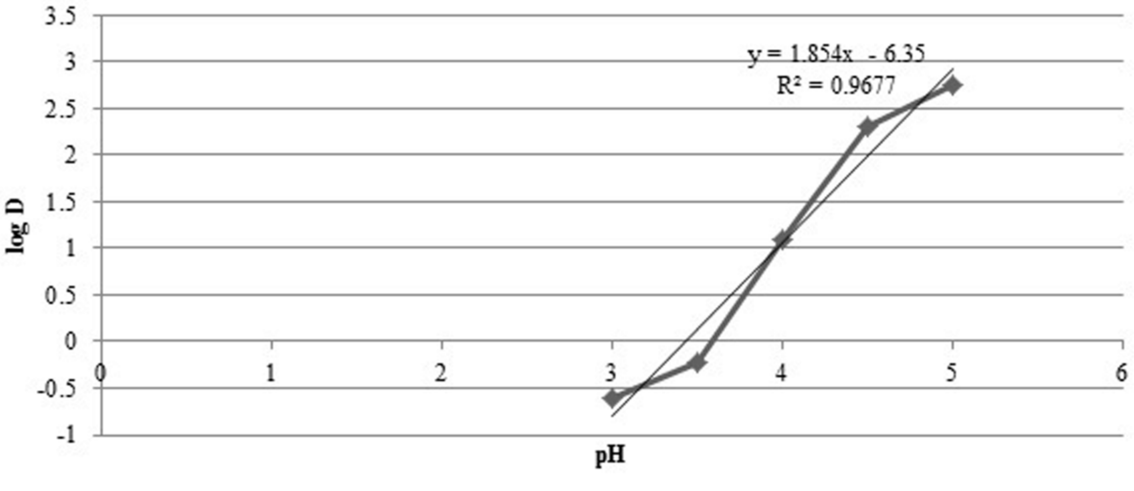

Fig. 3. log D versus pH with [D2EHPA]: 150 mM

A linear correlation with a slope of 1.85 was obtained (close to 2), suggesting that two hydrogen ions are released into the aqueous phase during the extraction. However, the significant interaction between pH and [D2EHPA] (p-values of 0.0044 and 0.0460 for the variable $B_E D_E$ in Table 2 and Table 3, respectively) led the study to the point that pH behaviour before and after extraction must be monitored and examined carefully. For this purpose, another set of LLE experiments were carried out by fixing the aqueous feed phase pH at a desired value. Aqueous solution then was mixed with the organic phase (kerosene loaded with D2EHPA). The mixture was shaken for 20 minutes and every one minute the aqueous phase pH was measured. These experiments were continued with various carrier concentrations ([D2EHPA]: 2-150 mM). It was observed that after each run of aqueous phase and organic phase mixture, the pH value dropped. The pH was set up again to the desired value using NaOH and LLE was continued until no change in pH value was observed. ΔpH was calculated based on:

$$\Delta pH = pH_{final,\ aq} - pH_{ini,\ aq} \qquad (11)$$

Based on the obtained results, ΔpH versus time was plotted and is presented as Fig. 4.

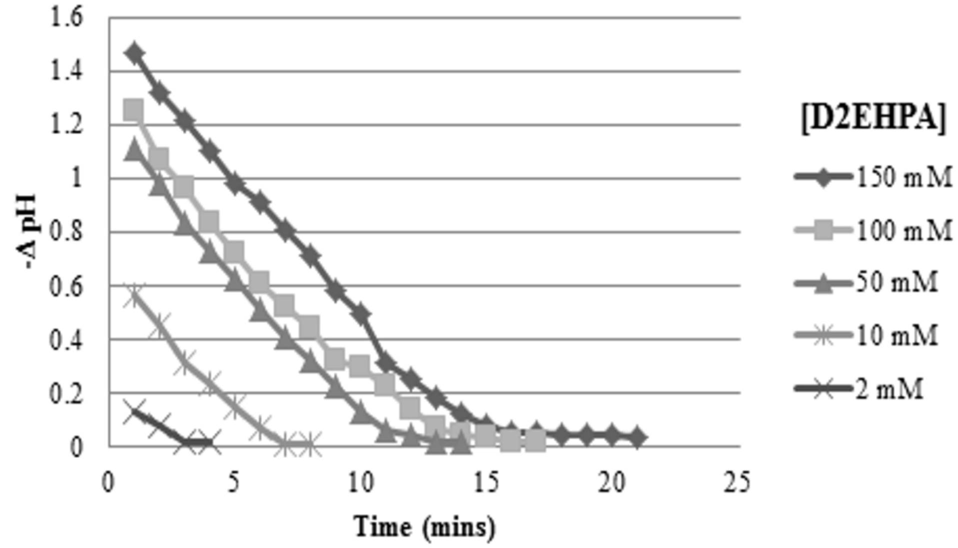

Fig. 4. pH variation after mixing the aqueous feed phase with organic phase loaded by 2, 10, 50, 100 and 150 mM of D2EHPA; initial aqueous phase pH of 4.5, initial nickel concentration of 100 mg/L.

Fig. 4. shows that pH value decreased after mixing the feed phase with the organic phase, until it reached to the equilibrium. The decrease in aqueous phase pH is due to the H^+ release into the aqueous phase as a result of Ni-D2EHPA complexation (Eq. 10.). This decrease in

pH is continued until the loading capacity of the organic phase reached maximum and there is no more complexation between nickel and D2EHPA occurred. As a consequence no more H^+ was released into the aqueous phase and hence no drop on pH value was observed, and ΔpH value remained unchanged. These results confirm that apart from log D versus pH plot as the most common method for complexation stoichiometric coefficients determination, other methods -rather independent of pH- must be carried out as well. For this purpose, log D Vs log [D2EHPA], loading test and Job's continuous method were carried out.

The effect of different [D2EHPA] on nickel extraction was examined and the results are shown in Fig. 5.

It shows that log D versus log $(RH)_2$ yields a linear correlation with slope of 2.06, suggesting that one Ni^{2+} is extracted as a complex with two dimers of D2EHPA molecules in organic phase since D2EHPA has shown to exist as dimers $(RH)_2$ in aliphatic diluents leading to formation of polymeric metal species [32].

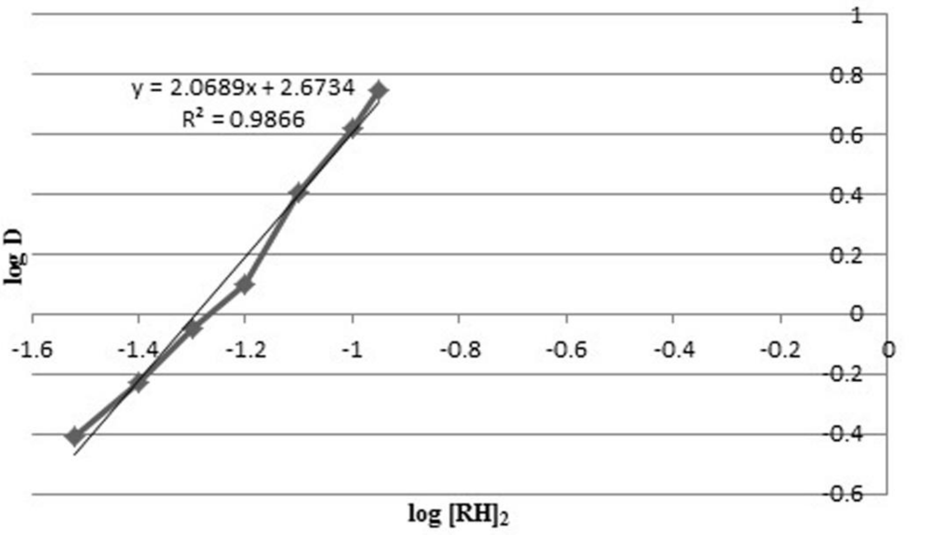

Fig. 5. log D versus log $[(RH)_2]$ with pH: 4.7

Nickel ions extraction stoichiometry was confirmed by running loading capacity test by contacting fresh aqueous phase (initial nickel concentration of 250 mg/L) with the organic phase (containing 150 mM D2EHPA) repeatedly. Fig. 6. shows the loading capacity of the organic phase.

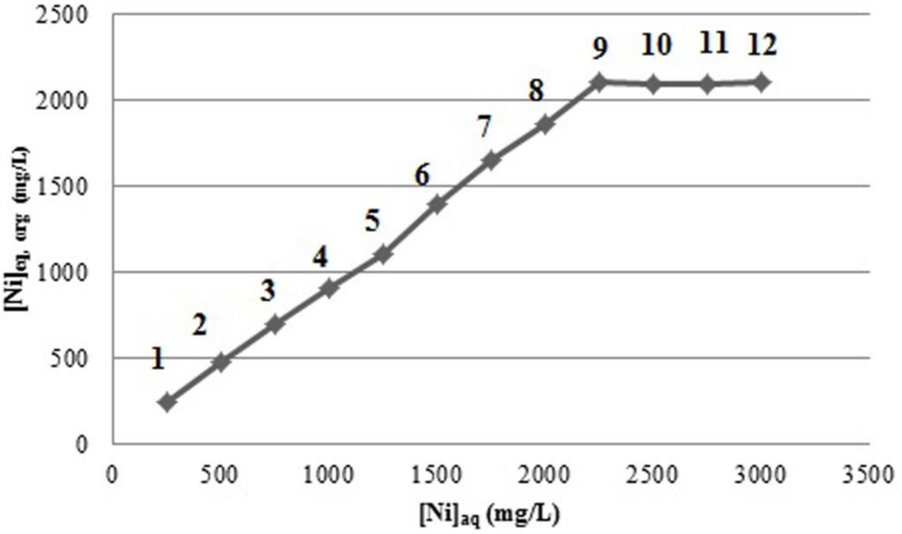

Fig. 6. Loading capacity of the organic phase

It reveals that the linear increase of nickel concentration in organic phase took 9 times contact with the fresh aqueous phase to reach to the equilibrium constant nickel ion extraction at 2250 mg/L (38.25 mM) of total nickel concentration.

Loading test and Job's continuous variation method can be applied to find out the stoichiometric complexation coefficients [51]. Determination of molar ratio of initial [D2EHPA] to loaded [Ni^{2+}] is shown in Fig. 7.

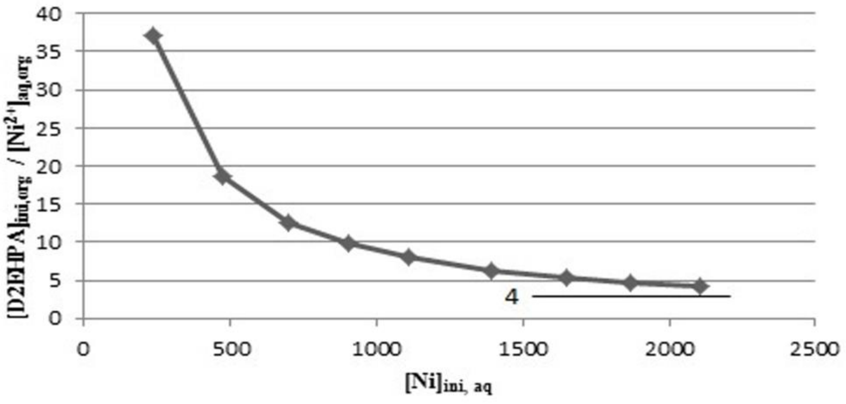

Fig. 7. Loading test for binding-stoichiometry estimation of D2EHPA with Ni^{2+}, pH: 4.7

The molar ratio of [D2EHPA] to the nickel equilibrium concentration decreased with increase in initial solute [Ni^{2+}] (mM) to approach a constant value of 4, which confirms that four molecules of D2EHPA (two dimers) are able to complex with one bivalent nickel ion.

Job's continuous variation method was performed to find the ratio of [Ni^{2+}] to [D2EHPA]. The results are presented in Fig. 8. The total D2EHPA and Ni^{2+} concentration of 10 mM was maintained and the extraction equilibrium was measured at various molar ratios of [D2EHPA] to the total concentration.

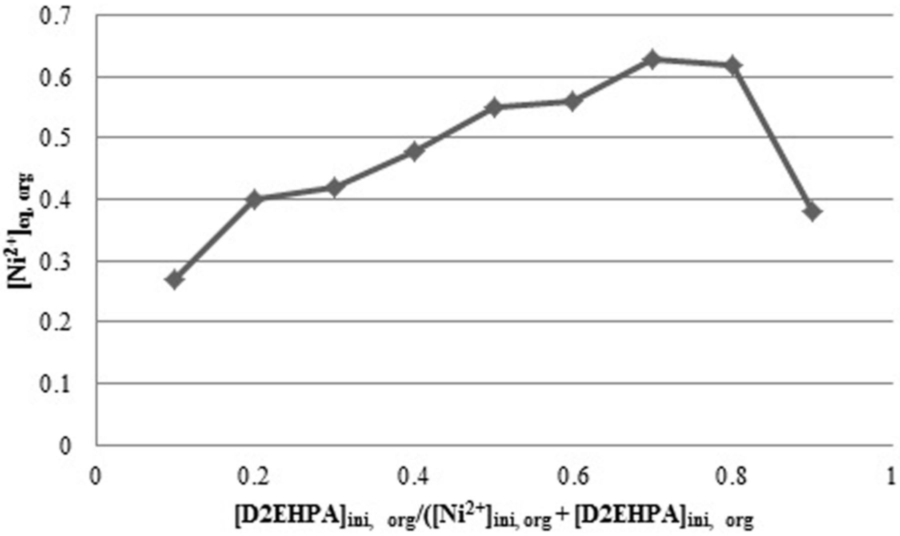

Fig. 8. Job's continuous variation method, pH: 4.7

Maximum Ni^{2+} extraction occurred when the molar ratio of initial [D2EHPA] in organic phase to total initial concentration of nickel and D2EHPA in aqueous and organic phase was 0.8. Therefore the ratio [Ni^{2+}]/ [D2EHPA] in the metal complex was confirmed at 1:4.

Based on slope analysis and stoichiometric experiments, complexation and decomplexation reactions at the feed phase-liquid membrane interface presented by Eq. 10, can be presented by

$$Ni^{2+} + 2(RH)_2 \rightarrow NiR_2(RH)_2 + 2H^+ \quad (12)$$

$$NiR_2(RH)_2 + 2H^+ \rightarrow Ni^{2+} + 2(RH)_2 \quad (13)$$

By applying the distribution coefficient (Eq. 5) as total analytical concentration of nickel ion in organic to aqueous phase, and considering that the aqueous complexations of Ni^{2+} and SO_4^{2-} are not taken into account and only a single species of the type $NiR_2(RH)_2$ is formed in the organic phase, then

$$D = [NiR_2(HR)_2] / [Ni^{2+}]_{ini} \qquad (14)$$

The equilibrium constants K_c for reaction (12) is

$$K_c = [NiR_2(HR)_2][H^+]^2 / [Ni^{2+}][(HR)_2]^2 \qquad (15)$$

Substituting $[NiR_2(HR)_2]$ from Eq. 14 into Eq. 15:

$$D = K_c\,[(HR)_2]^2 / [H^+]^2 \qquad (16)$$

Taking log gives:

$$\log D = \log K_c + 2\log[(HR)_2] + 2\,pH \qquad (17)$$

Eq. 17. justifies how distribution coefficient depends on pH and consequently the observed significant interaction of pH and [D2EHPA] is due to this dependency.

According to the similar previous researches, it had been found that extraction process was pH sensitive [38,48]. However, if the level of [D2EHPA] was higher than certain value of interaction, the increase in the concentration of D2EHPA resulted in higher metal extraction, independent of the pH level investigated. The high level of [D2EHPA] had shown highest metal ion removal percentage due to the higher amount of free D2EHPA [52].

Screening experiment was followed by determining the optimum concentration of the stripping agent. Various H_2SO_4 concentrations were examined in order to find the highest nickel stripping efficiency. At this stage, non-significant factors used in extraction were kept fixed but [D2EHPA] and $[H_2SO_4]$ was varied to find the optimum condition. Table 4 shows the ANOVA for nickel stripping as the response of quadratic model, including [D2EHPA] and $[H_2SO_4]$ as the stripping agent, designated as A_s, B_s, respectively.

Table 4

ANOVA for response surface quadratic model for nickel ions stripping

Source	Sum of squares	DF	Mean square	F-value	P-value
Model	839.23	5	167.85	212.07	< 0.0001
A_s	0.17	1	0.17	0.21	< 0.6602
B_s	541.50	1	541.50	684.18	< 0.0001
A^2_s	3.06	1	3.06	3.86	< 0.0902
B^2_s	273.34	1	273.34	345.46	< 0.0001
$(AB)_s$	0.000	1	0.000	0.000	< 1.0000
Residual	5.54	7	0.79		
Total	844.77	12			
R-Squared	0.9934				

The results showed that different [D2EHPA] in feed phase has not any significant effect on stripping efficiency. In other words the linear and quadratic significant effect of [H_2SO_4] is totally independent of the feed phase parameters. Fig. 9. shows the effect of different concentrations of stripping agent on nickel ion stripping from loaded organic phase.

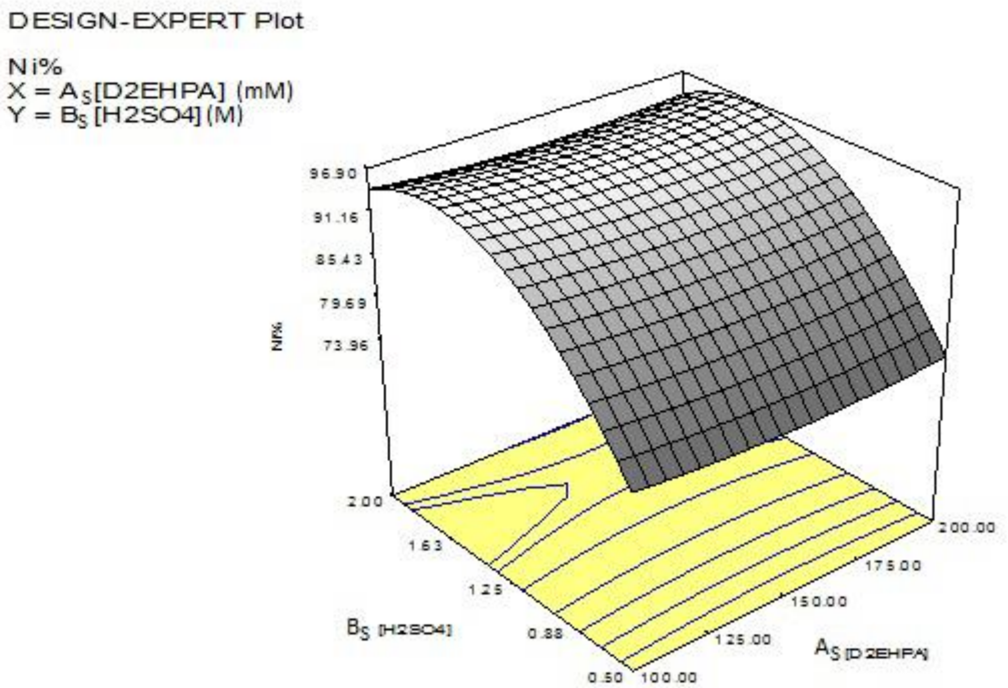

Fig. 9. Three-dimensional response surface for nickel stripping as a function of [D2EHPA] and [H_2SO_4]

Fig. 9. reveals that 96.90% of the nickel ions are extracted when the sulphuric acid concentration is around 1.6 M and the extraction trend becomes constant at higher concentration. It also shows that regardless of the carrier concentration used in extraction (in the range of 0.1-0.2 M), the stripping efficiency increases with sulphuric acid concentration. The lower nickel ion stripping in low concentration of sulphuric acid is due to lower concentration of H^+ which is a crucial parameter in complexation-decomplexation chain reaction (Eq. 10) [53]. On the other hand, a comparison between feed phase pH and concentration of sulphuric acid in stripping phase which led to the highest nickel removal (96.90%) suggests that pH gradient between the feed phase and the stripping phase was the main driving force of the mass transfer in this system. The effect of feed phase and stripping phase pH on metal ions transport in SLM system has been reported by many researches and is reported that in SLM, extraction efficiency is strongly influenced by acceptor and donor phases pH [54-57].

The regression equation for nickel stripping is:

$$Ni\ stripping\% = 93.41 - 0.17A_s + 9.50B_s + 1.05A_s^2 - 9.95B_s^2 \qquad (18)$$

3.2. SLM process optimization

Based on the preliminary results, the related range for each factor was chosen for optimization of nickel ion extraction and stripping by SLM, using face center composite design (FCCD) and response surface methodology (RSM). The affecting parameters for extraction and stripping of nickel ions were fixed at the related optimum condition achieved in screening phase and two more factors, namely stirring time (A) and stirring speed (B) were introduced for SLM process optimization.

Response surface plots and contour plots were generated from the model equations obtained in the regression analysis.

The results of analysis of variance (ANOVA) for the quadratic models summarize the analysis of each response and show the significant model terms. Table 5 shows the ANOVA for nickel removal as the response of quadratic model, including operation time (*A*) and stirring speed (*B*), while feed phase pH was fixed at 4.7, [D2EHPA] at 0.15 M, [TBP] at 0.65 M, [Na_2SO_4] at 220 mM and [H_2SO_4] was fixed at 1.5 M.

Table 5
ANOVA for response surface quadratic model of optimization

Source	Sum of squares	DF	Mean square	F-value	P-value
Model	509.52	5	101.90	7.55	< 0.0067
A	352.67	1	352.67	26.13	< 0.0009
B	37.50	1	37.50	2.78	< 0.1341
A^2	61.19	1	61.19	4.53	< 0.0659
B^2	13.06	1	13.06	0.97	< 0.3541
AB	1.00	1	1.00	0.074	< 0.7924
Residual	107.98	8	13.50		
Total	617.50	13			
R-Squared	0.8251				

According to Table 5, stirring time (*A*) shows significant effect on nickel removal independently, with P-value of 0.0009; the interaction between stirring time and stirring speed (*AB*) and also the linear and quadratic effect of stirring speed (*B* and B^2) in selected range (300-500 rpm) were insignificant with p-values of 0.1341, 0.3541 and 0.7924, respectively.

The optimum regression equation for nickel removal by SLM is:

$$Ni\ removal\ (\%) = 90.41 + 7.67A - 2.50B - 4.65A^2 - 2.15B^2 + 0.50AB \quad (19)$$

The factors with positive coefficients indicate a positive effect on the nickel ion removal and those with negative coefficients give negative effect. The highest nickel removal of 95% was obtained at stirring time of 450 minutes.

Fig. 10. shows the three dimensional response surface that represents the empirical functional relationship between nickel removal and two varying factors (stirring time and stirring speed), while the five other factors (feed phase pH, [D2EHPA], [TBP], [H_2SO_4] and

[Na_2SO_4] are held constant at their optimal values determined in liquid-liquid extraction and stripping processes.

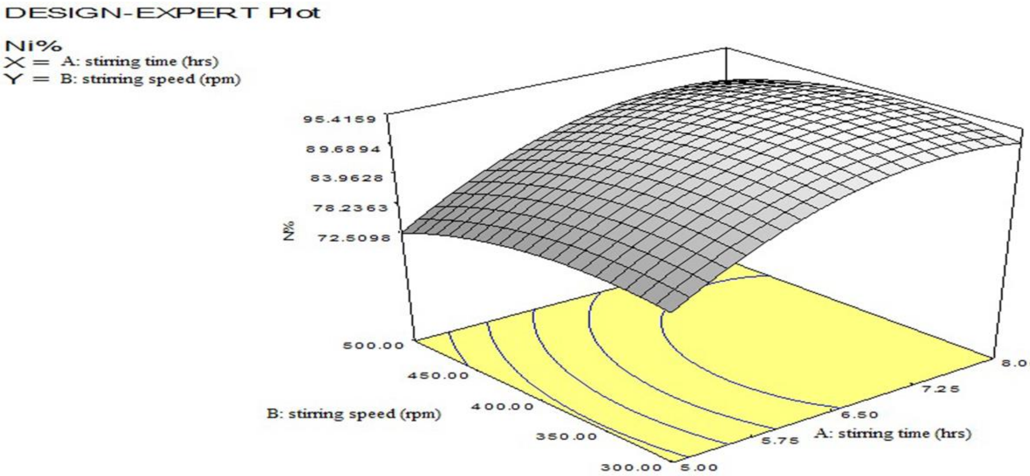

Fig. 10. Three-dimensional optimized response surface for nickel removal as a function of stirring time and stirring speed

Fig. 11. shows the nickel transport kinetics.

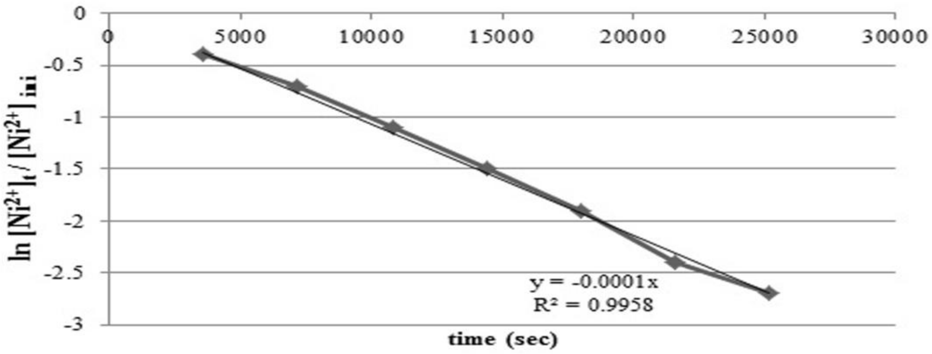

Fig. 11. Kinetics plot for nickel ions transport

The ln $[Ni^{2+}]_t/[Ni^{2+}]_{ini}$ versus time profile of nickel extraction was studied for up to 7 hours of the operation. It can be observed that nickel concentration in the aqueous feed phase decreased with time by a first order kinetics that can be represented by

ln $[Ni^{2+}]_t/[Ni^{2+}]_{ini} = -1\times10^{-4}$ t with $R^2 = 0.9654$ and mass transfer coefficient equal to 2.4×10^{-6} (m/s) was obtained.

Conclusion

The effects of feed phase pH, shaking time, carrier concentration, stirring time, stirring speed, inert salt, phase modifier concentration and stripping agent concentration on nickel removal by supported liquid membrane using D2EHPA as carrier and kerosene as diluent were optimized. Face Centered Composite Design (FCCD) were applied for generating model equations by regression analysis using MINITAB software. The LLE screening experiment revealed that nickel ions extraction was influenced by two factors (pH and [D2EHPA]) while the effect of other studied factors such as [TBP], [Na_2SO_4] and shaking time were not significant in the studied range. The result of LLE screening phase revealed that in optimum condition, where [D2EHPA]: 0.156 M and pH of 4.8, 93.4% of nickel ion extraction could be achieved. The experiments in order to find the optimum stripping agent dosage led to 95.6% of nickel ions stripping when [H_2SO_4] were at 1.54 M. The optimum conditions of both extraction and stripping screening experiment was used in SLM system and two extra factors (stirring time and stirring speed) were added for optimization process and the results revealed that 95.4% of nickel ions were removed by 7.5 hour of operation time, where feed phase pH was adjusted at 4.8, [D2EHPA] of 0.156 M, [TBP] of 60 mM, [Na_2SO_4] of 220 mM, [H_2SO_4] of 1.56 M and stirring speed of 378 rpm. The ratio of [Ni^{2+}]/[D2EHPA] in the metal complex was estimated to be 1:4, suggesting that one Ni^{2+} is extracted as a complex with two dimers of D2EHPA molecules in organic phase, confirmed by Job's continuous method and loading test. Nickel concentration in the aqueous feed phase decreased with time by a first order kinetics and mass transfer coefficient equal to 2.4×10^{-6} (m/s) was obtained.

Nomenclature

SLM	Supported liquid membrane
BLM	Bulk liquid membrane
ELM	Emulsion liquid membrane
LM	Liquid membrane
LLE	Liquid-liquid extraction
D2EHPA	Di-2-ethylhexyl phosphoric (M, mM)
M	Molar
TBP	Tributhylphosphate (M, mM)
$[Ni^{2+}]_t$	Nickel concentrations at time of sampling (M, mg/L)
$[Ni^{2+}]_{ini}$	Nickel initial concentration (M, mg/L)
k	Mass transfer coefficient (m/s)
m/s	Meter per second
A	Membrane area (m^2)
v	Feed phase volume (m^3)
t	Time (second, minute)
$NiSO_4$	Nickel sulphate
$C_{12}H_{26}$	Kerosene
Na_2SO_4	Sodium sulphate
$C_2H_3NaO_2$	Sodium acetate
CH_3COOH	Acetic acid
PTFE	Polytetrafluoroethylene
µm	Micro meter
H_2SO_4	Sulfuric acid
NaOH	Sodium hydroxide
AAS	Atomic adsorption spectrophotometer
mL	mili liter
mg/L	mili gram per liter
rpm	Round per minute
D	Distribution ratio
$[Ni^{2+}]_{org,\,eq}$	Nickel concentrations in organic phase equilibrium (M, mg/L)
$[Ni^{2+}]_{aq,\,ini}$	Initial nickel concentrations in aqueous phase (M, mg/L)
$[Ni^{2+}]_{aq,\,eq}$	Nickel concentrations in aqueous phase equilibrium (M, mg/L)
RSM	Response surface methodology
FCCD	Face centered composite design
ANOVA	Analysis of the variation
R^2	R squared
M^{2+}	Metal ion
RH	Carrier dimer
n	Number of molecules of carrier in metal-carrier complx
mM	mili molar
SO_4^{2-}	Sulphate ion
$NiR_2(RH)_2$	Nickel- carrier complex
K_c	Equilibrium constants
H^+	Hydrogen ion

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