



## Removal of nickel ions from synthetic wastewater by bulk liquid membrane

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**Abstract**— Heavy metals extraction and separation from industrial wastewater has become a major concern for both environmental and economic reasons. This paper describes a comparative kinetic study of the removal and recovery of nickel ions from aqueous solutions by bulk liquid membrane (BLM) using coupled facilitated transport mechanisms and two carriers of different chemical nature: tributyl phosphate (TBP) and di-2-ethylhexyl phosphoric acid (D2EHPA). Xylene oil was used as the liquid membrane phase. In addition, environmentally friendly materials such as vegetable oils (soybean oil) used as a suitable replacement for the conventional organic solvents in this work. A comprehensive kinetic study was carried out and effect of various parameters such as, pH of feed and stripping phase, initial concentration of metal ions, concentration of extractant in the membrane phase and stirring speed were studied. The chelating characteristics of EDTA was used as stripping agent as well as precipitating agent to enhance the transport efficiency of the nickel ions. The extraction and recovery efficiency were found as 80.89% and 87.80% respectively for nickel ions. At the optimum process conditions for transport of Ni(II) were found as follows: pH in the feed phase (4), pH in the stripping phase (8), initial concentration of nickel ions (120 ppm), carrier concentration (12%) (v/v) TBP and stirring speed (125±10 rpm), respectively.

**Keywords**— bulk liquid membrane; xylene oil; soybean; extraction; kinetic.

### 1. Introduction

The discharge of heavy metals into the environment is a serious problem facing numerous industries. Because metal pollutants are not biodegradable and toxic, they tend to accumulate in living organisms causing various disorders and diseases [6]. Therefore, their concentrations must be reduced to acceptable level before discharging them into the environment.

The rapid development of industries is responsible for the release of heavy metals into the environment such as fertilizer industries, petrochemical refinery, pesticides, electroplating, mining operations, paper industries, tanneries, batteries, metal plating, hydrometallurgy, etc. [7]. The heavy metals of most immediate concern are zinc, copper, iron, mercury, lead, iron, chromium, cadmium, nickel, etc., according to World Health Organization WHO [22]. Acute nickel poisoning causes cancer, nervous system

damage, severe gastroenteritis characterized by abdominal pain, anorexia, dehydration and in extreme cases, death [10]. Heavy metal removal from inorganic synthetic wastewater can be achieved by conventional treatment processes such as ion exchange, chemical precipitation [8], adsorption [21], and electrochemical removal [3], biosorption [18], etc. In recent years, a lot of study has been done on liquid membrane separation. Liquid membranes have been successfully used to treat heavy metal ions from synthetic wastewater like nickel [23]. Liquid membrane has the advantages of high selectivity, energy-saving, high efficiency and time-saving [24]. It consists of liquid phase that serves as a membrane barrier between two phases of aqueous solution. The driving force used in liquid membrane process is concentration gradients [17]. These membranes include supported liquid membrane (SLM), emulsion liquid membrane (ELM), bulk liquid membrane

(BLM) [12]. The bulk liquid membrane (BLM) represent one of the liquid membrane technique in which a mobile carrier governs the selectivity and efficiency of the liquid membrane transport. The technique is inexpensive and easy to use to improve the efficiency of the separation proces.

The BLM consists of feed, membrane and stripping phases [15]. The feed phase containing the metal ion to be transported, the membrane phase contains the carrier

which is responsible for the transport of metal ions, having it positioned between feed and stripping phases and the stripping phase in which metal ions will be released [1]. In this work, simultaneous extraction and recovery of Ni (II) from synthetic wastewater by bulk liquid membrane was conducted with selection a suitable liquid membrane (xylene, and soybean oil), and a suitable mobile carrier (TBP, and D2EHPA). Studying the detailed kinetic of the three phase transport process in the BLM, and Optimizing the operating parameter, such as the pH in feed and stripping phase, heavy metals initial concentration, carrier concentration in the membrane, the rate of stirring, stripping agent, for maximum extraction and stripping efficiency were investigated.

## 2. Experimentals

### 2.1 Chemicals

All materials used in this work were purchased from local market: Xylene (CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> of 98% purity and soybean oil (vegetable oil) 95% purity, were used as diluent. Tri-n-butyl phosphate C<sub>12</sub>H<sub>27</sub>O<sub>4</sub>P of 99 % purity (GMBH Chemicals FERAK company, BERLIN) and di(2-ethylhexyl) phosphoric acid C<sub>16</sub>H<sub>35</sub>PO<sub>4</sub> of 98% purity (MERAK company, GERMANY) were used to facilitate metals ions transport. The following inorganic heavy metal nickel nitrate (98%) (CDH Chemicals Ltd company, INDIA) were fed into the feed phase chamber of BLM at different initial concentrations. Ethylenediaminetetraacetic acid (EDTA) of (99%) purity was selected as stripping agent to the receiving phase.

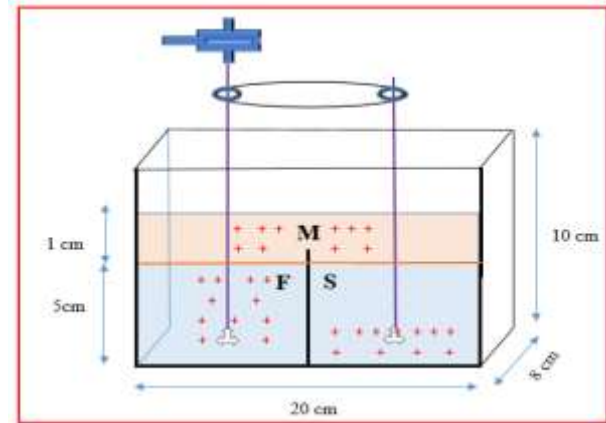
### 2.2 Analytical instruments

Concentrations of nickel ions in the feed, stripping solution were obtained using atomic absorption spectrometer (AAS) (Australian) using flame mode. PH meter (WTW, Germany) was used to measure pH in feed and stripping phase.

### 2.3 Bulk liquid membrane setup

The bulk liquid membrane BLM consisted of a rectangular glass container which is presented in Figure 1. The size of the vessel was (8 cm width × 20 cm length × 10 cm height). A glass wall was instilled in the middle of vessel (5 cm-height of thickness 0.4 cm), in which, the aqueous feed and stripping phase was separated by the barrier. The aqueous feed phase contained metals ions and the pH was maintained by adding HCl drops wise to the feed phase at

ambient temperature of (25±1 °C) for 5 hr. While the stripping phase contains distilled water with constant pH was adjusted by HCl or NaOH solutions. Finally, the liquid membrane phase was containing on the carrier and contacts with the feed and stripping phase.



**Figure 1:** Schematic diagram of bulk liquid membrane setup.

## 3. Theoretical Work

### 3.1 Calculus methodology

The performance of the two phases equilibrium distribution were obtained in term of % extraction and % stripping, calculated by following Eq. 1 and Eq. 2.

$$E\% = \frac{C_o - C_F}{C_o} \times 100 \quad 1$$

$$S\% = \frac{C_S}{C_o - C_F} \times 100 \quad 2$$

The distribution coefficients were applied according to Eq. 3.

$$K_d = \frac{C_M}{C_F} \quad 3$$

Where:

$C_o$ : The initial Ni(II) concentrations in the feed phase (ppm).

$C_F$ : Ni(II) concentration at any time in feed phase (ppm).

$C_S$ : Ni(II) concentration at any time in stripping phase (ppm).

$C_M$ : Ni(II) concentrations in the membrane phase (ppm).

### 3.2 Kinetic procedure

A simple kinetic model of mass transfer in bulk liquid membrane can be advanced by considering two consecutive reaction (extraction–re-extraction of the

nickel ions) with three diffusion steps in the feed, membrane and stripping phases.

The following kinetic parameter were evaluated: The average apparent first order-rate constants of solute extraction and re-extraction reaction ( $k_1$  and  $k_2$ ), the maximum reduced concentration in the membrane phase ( $R_{max}$ ), the time at which the maximums fluxe are achieved ( $t_{max}$ ) [2]. The reduced dimensionless concentrations in feed phase  $R_F$ , membrane phase  $R_M$  and stripping phase  $R_S$  were used for experimental purposes.

$$R_F = \frac{C_F}{C_{F0}} \quad R_M = \frac{C_M}{C_{F0}} \quad R_S = \frac{C_S}{C_{F0}} \quad 4$$

Where:

$C_{F0}$  is the initial  $Ni^{+2}$  concentration in the feed phase while,  $C_F$ ,  $C_M$  and  $C_S$  represent the metals concentrations in feed, membrane and stripping phases respectively.

The material balance with respect to the reduce concentration can be describing as follow:

$$R_F + R_M + R_S = 1 \quad 5$$

From this expression the kinetic behavior of the consecutive, irreversible first order reactions can be described as;



The above kinetic scheme for consecutive, irreversible reaction system can be described by the following rate equation.

$$\frac{dR_F}{dt} = -K_1 R_F = J_F \quad 7$$

$$\frac{dR_M}{dt} = K_1 R_F - K_2 R_M = J_M \quad 8$$

$$\frac{dR_S}{dt} = K_2 R_M = J_S \quad 9$$

Where: J stands for flux. When  $k_1 \neq k_2$ , integrating Eqs. (7) – (9) give.

$$R_F = \exp(-K_1 t) \quad 10$$

$$R_M = \frac{K_1}{K_2 - K_1 [\exp(-K_1 t) - \exp(-K_2 t)]} \quad 11$$

$$R_S = \frac{K_1}{K_2 - K_1 [K_2 \exp(-K_1 t) - K_1 \exp(-K_2 t)]} \quad 12$$

While, the maximum values of  $R_M$  (when  $dR_M/dt = 0$ ) and the corresponding  $t_{max}$  can be written. as follows:

$$R_M^{Max} = \left(\frac{K_1}{K_2}\right)^{\frac{K_2}{K_2 - K_1}} \quad 13$$

$$t_{Max} = \frac{\ln \frac{K_2}{K_1}}{K_2 - K_1} \quad 14$$

Combining Eqs. (11 and 12) the following relationship can be obtained:

$$k_2 = \frac{\ln \left(\frac{1}{R_M^{Max}}\right)}{t_{Max}} \quad 15$$

The value of  $k_1$  was directly obtained from Eq. 7, this value is introducing as a constant value in Eqs. 8 and 9. An initial value of  $k_2$  were obtained from Eq. 15 and introduced in Eqs. 11 and 12 and iterated [19].

By considering the first order time differentiation Eqs. 7 – 9 at  $t = t_{Max}$  leads to the final form of the flux equations:

$$\left(\frac{dR_F}{dt}\right)_{max} = -K_1 \left(\frac{k_1}{k_2}\right)^{\frac{-K_1}{(K_1 - K_2)}} = J_F^{Max} \quad 16$$

$$\left(\frac{dR_M}{dt}\right)_{max} = K_2 \left(\frac{k_1}{k_2}\right)^{\frac{-K_2}{(K_1 - K_2)}} = J_S^{Max} \quad 17$$

$$\left(\frac{dR_M}{dt}\right)_{max} = 0 \quad 18$$

$$-\left(\frac{dR_F}{dt}\right)_{max} = \left(\frac{dR_S}{dt}\right)_{Max} \quad 19$$

#### 4. Result and discussion

BLM separation methods are primarily associated with the selection of suitable solvent for transport of the required solute. In this work two different solvents Xylene oil and environmentally friendly materials vegetable oils (soybean oil) used as organic solvents based on their solubility were chosen to find the best fit for the transport of nickels. Experiment performed to find suitable carriers among TBP (tributyl phosphate), and D2EPHA (bis-2-ethylhexyl phosphate). Selective carrier toward the solute plays an important role to improve the extraction and stripping efficiency of the system. To increase the extraction and recovery of heavy metals, the selection of carriers is important. The aqueous solute ions metal molecules will bind to the selective carriers and form complexes, thus increasing the solubility of metals in the organic solvent. Two types of carriers were investigated to extract nickels from aqueous solutions: TBP (tributyl phosphate), and D2EPHA (bis-2-ethylhexyl phosphate). Table 1. shows the distribution coefficient of metals. The results indicate that the highest distribution coefficient of metals was achieved when TBP was used as the carrier. On the other hand, the distribution coefficient using D2EPHA was lower due to weak molecular interactions.

**Table 1:** Distribution coefficient of Ni<sup>2+</sup> at different concentration of TBP and D2EHPA as carrier.

Metals	Kd. TBP	Kd. D2EHPA
Ni (II)	0.252	0.228

**4.1 Effect of pH in the feed phase**

To study the effect of feed pH on the extraction efficiency for nickel ions. The study was carried out at different pH ranging from 2 to 6 where, pH was maintained by adding HCl drop wise to the feed phase at ambient temperature of (25±1 °C) for 5 hr. The extraction of nickel ions increases with increases in pH up to 4 and decreases thereafter. as shown in Fig. (2). Where at the pH 4, the extraction efficiency (E %) are 80.89 %.

In the mildly acidic condition (pH=4) metal ions is ionized and cation Ni<sup>2+</sup> are available in the feed phase for subsequent complexations at aqueous feed membrane interface. The formation of metals carrier complex was high beyond pH (4) and then began to decreased thereafter at higher pH value, probably due to the incomplete protonation of TBP in the source/membrane interface. Therefore, at higher pH values there was a decrease in the transport rate of Ni(II) this decline can be due to a decrease in the hydrogen ion concentration with increasing pH which can cause a decline in the formation of the carrier and the metals ions complex, due to the resulting in the increase in the solubility of tri-n-butyl phosphate in the aqueous feed phase leading, to the membrane bleading [19].

Table 2: shows the distribution coefficient of Ni<sup>2+</sup> at different feed pH. As can be seen from this table, this coefficients values of the Ni(II) are extremely high under the condition of pH (2-4). Where the value of distribution

**Table 2:** Distribution coefficient of Ni<sup>2+</sup> at different, feed pH

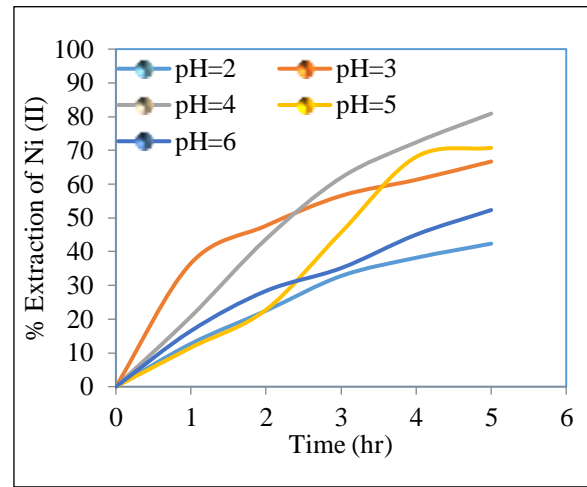
Feed pH	2	3	4	5	6
K <sub>d</sub>	0.176	0.228	0.252	0.238	0.197

**Table 3:** The kinetic parameter for the transport, of Ni<sup>2+</sup> at different, feed phase pH.

PH	K <sub>1</sub> (hr <sup>-1</sup> )	K <sub>2</sub> (hr <sup>-1</sup> )	R <sub>M</sub> <sup>max</sup>	t <sub>max</sub> (hr)	J <sub>F</sub> <sup>max</sup> (hr <sup>-1</sup> )	J <sub>S</sub> <sup>max</sup> (hr <sup>-1</sup> )
2	0.087	0.711	0.091	3.364	-0.065	0.065
3	0.162	0.812	0.133	2.479	-0.108	0.108
4	0.224	0.930	0.153	2.015	-0.142	0.142
5	0.178	0.831	0.142	2.358	-0.117	0.117
6	0.114	0.702	0.114	3.087	-0.080	0.080

coefficient increase from (0.176 - 0.252), then these values drops sharply for pH greater than 4. The characteristic of metal ions in different pH medium may cause this behavior.

The values of kinetic parameters for nickel ions as shown in Table 3: When increase the pH. value of the feed phase from (2-4), it was observed the maximums transport of Ni(II) was increased, where, k<sub>1</sub> and k<sub>2</sub> becomes (0.224 and 0.930 hr<sup>-1</sup>) and it can be seen that both flux J<sub>F</sub><sup>max</sup> and J<sub>S</sub><sup>max</sup> increased from (0,065 - 0.117 hr<sup>-1</sup>) and decrease when increase in pH above 4. Whereas the maximums time (t<sub>max</sub>) to reach transport decreases from (3.364 - 2.015 hr).



**Figure 2:** pH effect on the extraction efficiency of nickel (II) [Co= 120 mg/l; TBP=12%(v/v); pH stripping=8].

### 4.2 Effect of pH of strip phase

The effect of pH of stripping phase on the receiving of nickel ions at aqueous stripping phase through a bulk liquid membrane BLM, was measured within the range from 4 to 12. Where, pH was maintained by adding NaOH and HCl drop wise to the strip phase for adjusting the required pH, at ambient temperature of (25±1 °C) and stirring speed at 125±10 rpm for 5 hr.

As shown in Fig (3). it attains a maximum stripping 87.80%, when the pH of stripping phase increased up to 8, due to from the increase of proton in the receiving phase for metal ions and recovery declines at higher pH region. The significant decrease in the stripping efficiency observed at lower and higher pH value could be related to the decreased dcomplexing. ability of carrier in the membrane/ stripping interface. On the other hand, the decrease of %S at pH=8 caused by the saturation of driving. force for diffusion through xylene oil based bulk liquid membrane (BLM). Thus, a pH gradient between the source and the receiving phases is the driving force for the transport of nickel ions through the liquid membrane. Therefore, it is needed that pH of the stripping phase is higher than pH of the feed phase for the effective transport efficiency [14]. The values of distribution coefficients for Ni+2 is listed in Table 4. as a function of pH stripping phase, which indicated that metal ions distrebuted at maximum rate in the pH of 8, respectively. With increases the pH in the stripping phase from (4 - 8) the stripping distribution coefficient of Ni(II) increases from (0.186 to 0.252), respectively. Increasing the pH in the stripping phase greater than (8) decrease the distribution of heavy metal ions between the receiving phase and memebrane phase.

From Table 5. shows the corresponding kinetic parameters k1, k2, tmax, JFmax and JSmax for the transports of Ni+. The maximums transport of metal ions was increased, where, k1 becomes (0.224 hr-1) and k2 (0.930 hr-1), respectively, and decrease (k1, k2) and flux when increase in strip pH above 8. Moreover, the maximum time (tmax) to reach transport decreases from (3.334 - 2.015 hr) and it can be seen that both flux (JFmax and JSmax) increased from (0.076 - 0.142 hr-1).

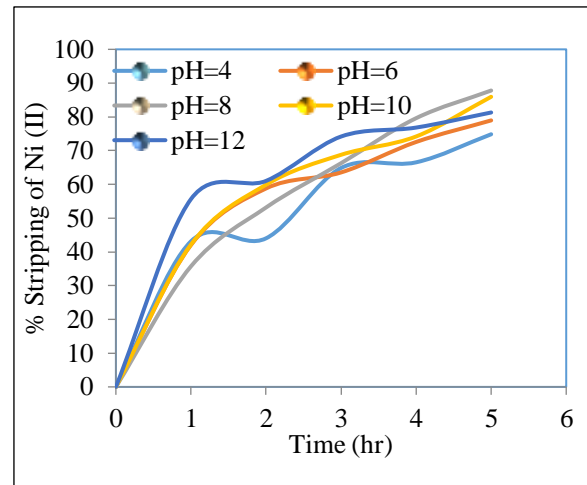


Figure 3: pH effect on the stripping efficiency of nickel (II) [Co= 120 mg/l; TBP=12%(v/v); pH feed=4].

Table 4: Distribution coefficient of Ni+2 at different strip pH.

Stripping pH	4	6	8	10	12
Kd	0.186	0.198	0.252	0.241	0.205

Table 5: The kinetic parameter for the transport of Ni+2 at different stripping phase pH

pH	K <sub>1</sub> (hr <sup>-1</sup> )	K <sub>2</sub> (hr <sup>-1</sup> )	R <sub>M</sub> <sup>max</sup>	t <sub>max</sub> (hr)	J <sub>F</sub> <sup>max</sup> (hr <sup>-1</sup> )	J <sub>S</sub> <sup>max</sup> (hr <sup>-1</sup> )
4	0.110	0.634	0.120	3.334	-0.076	0.076
6	0.132	0.682	0.131	2.978	-0.089	0.089
8	0.224	0.930	0.153	2.015	-0.142	0.142
10	0.201	0.805	0.157	2.299	-0.126	0.126
12	0.148	0.731	0.135	2.739	-0.098	0.098

### 4.3 Effect of extraction concentration

The variation of initial concentration on the transport of nickel (II) was investigated by varying the metal ions concentration in the range of 40 to 150 ppm. Fig. 4. shows the effect of initial feed concentration on extraction and stripping results. The maximum transport rate occurred at initial concentration of 120 ppm, in which the extraction and stripping efficiency were 80.89% and 87.80%, respectively.

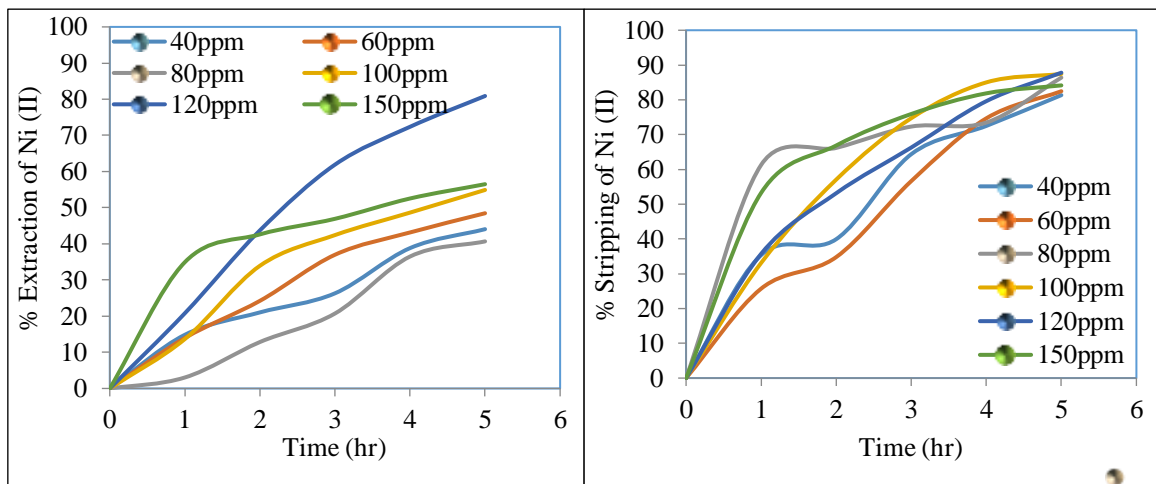
Which, clearly indicates. that with increasing initial feed concentration of metal ions in the aqueous feed phase to optimum concentration, the mass transfer rate of metal ions is increased. The above fact could be attributed to the following reason. According with the Feck’s law, an increases in the initial feed concentration will raise the metals ions driving force in both, stagnant aqueous. layer and organic phase, which in turn produce an increase in the overall metals ions flux rate through the bulk liquid membrane. However, the percentage transport of metal ions decreases with increasing initial concentration in the aqueous feed phase. This decrease may be due to the driving force for the metal ions transport between the aqueous and orgenic phases remains low, perhaps could be attributed to the fact. that membrane phase quickly got saturated with the metal ions affecting mass transfer in the feed membrane interphase. On the other hand, it may be due to the competitions between metal ions at very high concentrations, therefore, the organic extractant cannot able to transport the metal ions from the aqueous feed phase (donor phase) to stripping phase (acceptor phases). Hence, 120 ppm for Ni(II) concentration was chosen for throughout the experiments.

From the amount of the contaminant extraction on the membrane phase to the concentration of contaminant remaining in the feed phase as shown in Table 6. The extraction distribution coefficient of Ni+2 increases from (0.147 to 0.252), respectively, with increasing the metal ions concentration from (40 to120 ppm), respectively and found that with increases the initial concentration in feed phase above of optimum concentration, decreases the distribution of metal ion between feed and membrane phases.

**Table 6:** Distribution coefficient of Ni<sup>+2</sup> at different initial concentration.

In Conc	40	60	80	100	120	150
Kd	0.147	0.164	0.210	0.243	0.252	0.193

It is clears from Table 7. The result that both kinetic constant k1, k2 and flux value are dependent on the initial concentration of nickel ions and increase gradually with increase in initial concentration until 120 ppm, respectively. Where k1, k2 and flux values become (0.930 hr-1) and (0.142 hr-1), respectively. After that these values decrease when increase in metal ions concentration above optimum concentration. On the other hand, the maximum time (tmax) to reach transport decreases from (3.415 to 2.015 hr), respectively.



**Figure 4:** concentration effect on extraction and stripping efficiency of nickel (II)

[pH feed=4; pH stripping=8; TBP=12%(v/v)]

**Table 7:** The kinetic parameter for the transport of Ni<sup>+2</sup> at different stripping phase pH.

Conc ppm	K <sub>1</sub> (hr <sup>-1</sup> )	K <sub>2</sub> (hr <sup>-1</sup> )	R <sub>M</sub> <sup>max</sup>	t <sub>max</sub> (hr)	J <sub>F</sub> <sup>max</sup> (hr <sup>-1</sup> )	J <sub>S</sub> <sup>max</sup> (hr <sup>-1</sup> )
40	0.116	0.593	0.131	3.415	-0.078	0.078
60	0.132	0.672	0.132	3.006	-0.089	0.089
80	0.186	0.781	0.152	2.405	-0.119	0.119
100	0.215	0.88	0.154	2.115	-0.136	0.136
120	0.224	0.930	0.153	2.015	-0.142	0.142
150	0.167	0.717	0.149	2.649	-0.107	0.107

**4.4 Effect of carrier concentration**

The carrier concentrations in the organic membrane phase play an important role for transport metal ions in the liquid membrane process. The main function of carrier is to transfer selectively the targeted metal ions through the liquid membrane LM. It is a general trend that effectiveness of membrane transport increases as carrier concentrations increases and gets saturated at some point and after that carrier concentration delays diffusion rate as viscosity of membrane increases [4]. To examine the effect of carrier concentration (TBP) on nickel ions transport kinetic recovery in the acceptor phase, experiment was carried out with different carrier concentration ranging from 3 to 15% (v/v) dissolved in xylene oil at ambient temperatures of (25±1 °C) and mixing speed at (125±10 rpm) for 5 hr. As shown in Fig. 5. it was observed that the effectiveness increased with an increase in carrier concentration (TBP) up to 12% (v/v). Where, in presence of a carrier as (TBP) dissolved in

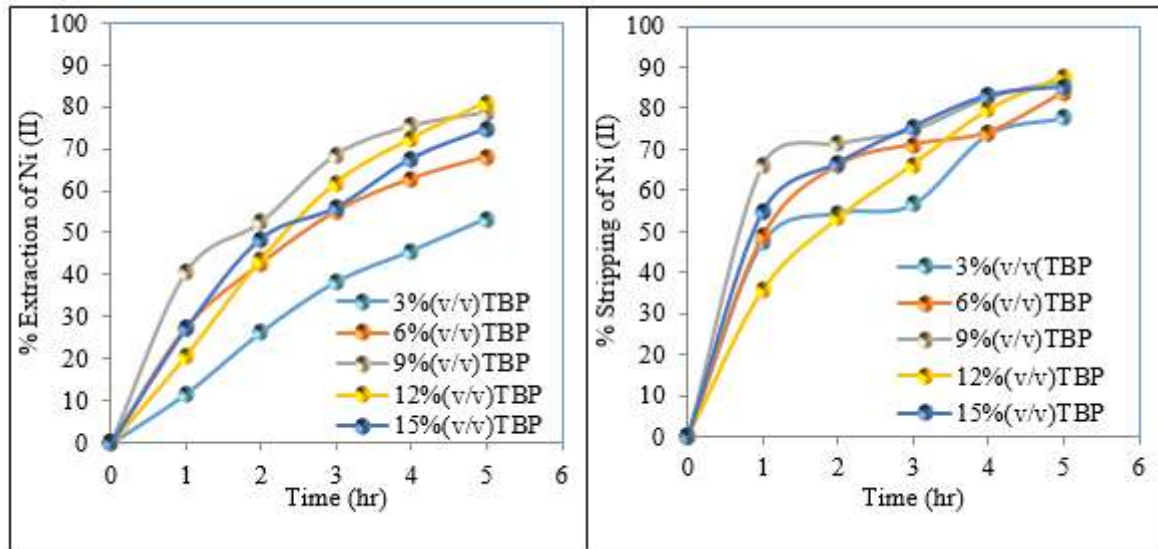
xylene oil in the membrane phase, a metal carrier complex (Ni-TBP complex in this case) is formed at the feed-membrane interface which results in the increases of mass transfer rate through the interface and hence higher

separation is achieved. The maximum extraction and stripping efficiency were become 80.89% and 87.80%, respectively. This can be attributed to that the interface between the feed and the membrane phase is not saturated by the carrier in lower concentration, while this interface is saturated in higher concentration. On other hand, the diffusion rate of metal ions complex through the membrane phase become lower and the recovery decrease at optimum carrier due to the complex formed by the TBP effect in the organic membrane or due to increase in viscosity of membrane phase which decrease the transport. The optimum carrier concentration (TBP) in membrane phase was thus taken to be 12% (v/v) were achieved in 5 hr of operation [5-12]. The distribution coefficient of nickel ions under optimum conditions was estimated as shown in Table 8. The coefficient of Ni(II) increases from (0.176 to 0.252), respectively with increasing carrier concentration (TBP) from (3 to 12) % and decreases sharply with increasing carrier concentration (TBP), which may be due to competitive between metal ions with protons of TBP as carrier. The kinetic parameter for the transports of Ni(II) are presented in Table 9.

It can be noticed reveal that the flux values, k1 and k2, increased where become (0.224) and (0.930), respectively, as well as J<sub>F</sub>max and J<sub>S</sub>max increased with an increase TBP volume ratio to 12% (v/v). While t<sub>max</sub> decreases from (3.048 to 2.015), respectively with an increase of carrier concentration (TBP).

**Table 8:** Distribution coefficient of Ni<sup>+2</sup> at different carrier concentration.

Carrier Conc	3%	6%	9%	12%	15%
K <sub>d</sub>	0.176	0.213	0.241	0.252	0.249



**Figure 5:** TBP % (v/v) effect on extraction and stripping efficiency of nickel (II)

[ $C_o = 120 \text{ mg/l}$ ;  $\text{pH}=4$ ;  $\text{pH} = \text{stripping}=8$  ]

**Table 9:** The kinetic parameter for the transport of Ni<sup>2+</sup> at different carrier

Carrier %	$K_1(\text{hr}^{-1})$	$K_2(\text{hr}^{-1})$	$R_M^{\max}$	$t_{\max}(\text{hr})$	$J_F^{\max}(\text{hr}^{-1})$	$J_S^{\max}(\text{hr}^{-1})$
3%	0.117	0.707	0.116	3.048	-0.081	0.081
6%	0.167	0.785	0.140	2.502	-0.110	0.110
9%	0.194	0.812	0.152	2.314	-0.124	0.124
12%	0.224	0.930	0.153	2.015	-0.142	0.142
15%	0.213	0.845	0.158	2.181	-0.133	0.133

#### 4.5 Effect of Stirring rate on transport

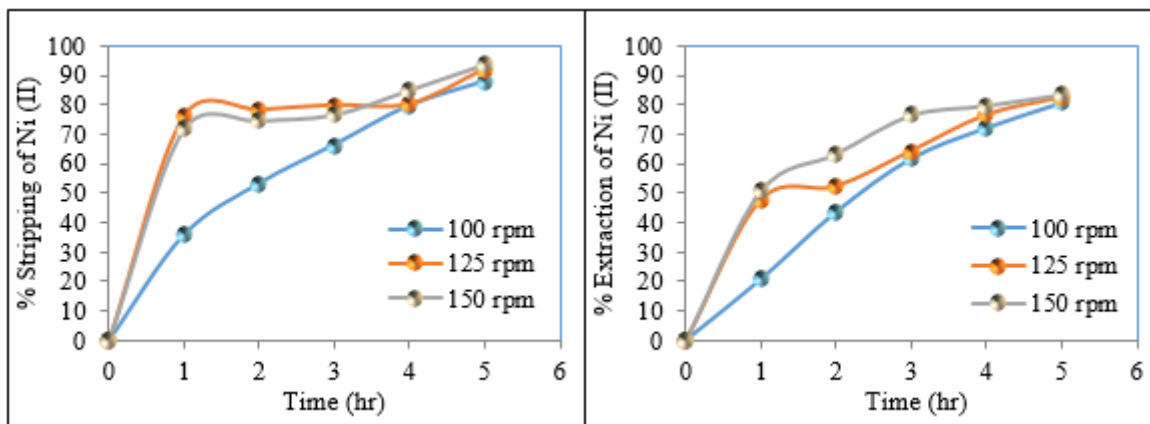
A gentle stirring was providing to the mixtur of feed and stripping phases to minimize the concentration

polarization, the thickness of boundary layer of metals and/or metals-extractant complex at the interface. However, at high stirring speed emulsion is formed between the membrane aqueous phases. Hence, the speed of stirring was optimizing for the efficeint extraction. Inorder to determine the optimam stirring speed, three stirring speed were used (100,125, and150 rpm), respectively allowing the liquid mambrane stability at  $(25 \pm 2 \text{ }^\circ\text{C})$ . At stirring rate 100 to 150 rpm, mixing of feed (donor) and stripping (acceptor) phase occurs. The experimental result was reported in Fig. 6. It was observed that extraction and stripping efficiency increased to a great

extent with increase in stirring speed, where, the maximum efficiency of extraction and stripping for Ni(II) was become (83.57% and 93.73%), respectively. It indicates that the transport efficiency of nickel ions increases on the

feed phase as well as increases on the receiving phase due to decrease of the thickness of the diffusion boundary layers at both interfaces of the membrane phase with time and reached a maximam at 5 hr [16]. The results indicate at Ni(II), that the kinetic parameter, i.e.,  $k_1$  and  $k_2$  as well as  $J_F^{\max}$  and  $J_S^{\max}$  increased from source to receiving phases with an increase in the stirring speed from (100 to 150), as shown in Table 10. While, the maximum time ( $t_{\max}$ ) to achieve steady state is decreased from (2.081 to 1.616 hr), respectively.





**Figure 6:** Efficiency of extraction and stripping at different speed of the feed and stripping phase, [C<sub>0</sub>=120ppm, carrier conc. 12 % ( v/v), pH feed=4 and stripping=8].

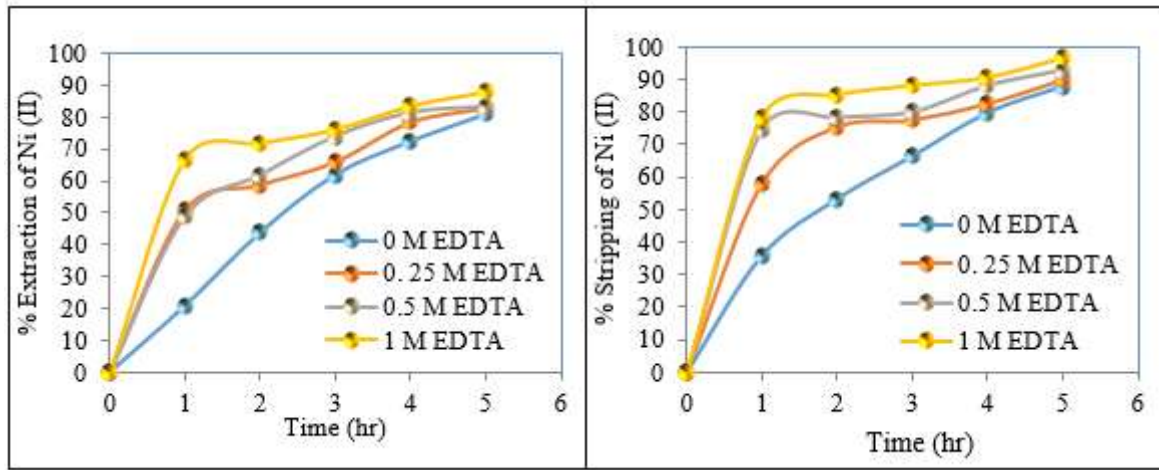
**Table 10:** The kinetic parameter for the transport of Ni<sup>2+</sup> at different stirring speed.

Speed rpm	K <sub>1</sub> (hr <sup>-1</sup> )	K <sub>2</sub> (hr <sup>-1</sup> )	R <sub>M</sub> <sup>max</sup>	t <sub>max</sub> (hr)	J <sub>F</sub> <sup>max</sup> (hr <sup>-1</sup> )	J <sub>S</sub> <sup>max</sup> (hr <sup>-1</sup> )
100	0.224	0.882	0.159	2.081	-0.140	0.140
125	0.232	1.090	0.140	1.802	-0.152	0.153
150	0.238	1.275	0.127	1.616	-0.162	0.162

#### 4.6 Effect of stripping agent concentration on transport

Selection of stripping agent is very important, for the efficient removal and recovery of metals. In this work, ethylenediaminetetraacetic acid EDTA is used as stripping agent (chelating agent.). It can form four or six bonds with a metal ion, and it forms chelates with both transition-metal ions and main-group ions. It re-extracts Ni(II) from the membrane strip interface and form metal ions EDTA complex (M+n + EDTA → Metal – EDTA Complex). Fig. 7. shows rate of transport for Ni(II) in different concentrations of EDTA from (0 to 1M) with keeping other parameters at constant level under the optimum experimental conditions. It was observed that the

transported amount of nickel ions increased with the increase in stripping agent concentration up to 1M EDTA. EDTA has a strong affinity for the formation of such complex, which is insoluble in aqueous medium, which the extraction and stripping efficiency reach 87.80% and 96.64%, respectively. The mass transfer of nickel ions has been analyzed on the basis of kinetic laws of two consecutive irreversible first order reaction. The stripping agent to enhance the stripping process were EDTA in the range of (0 - 1 M) [9]. As shown in Table 11. the transport rates such as k<sub>1</sub> and k<sub>2</sub> along with the flux value such as J<sub>F</sub><sup>max</sup> and J<sub>S</sub><sup>max</sup> increases with increase EDTA concentration in stripping phase from (0 to 1M), respectively and t<sub>max</sub> decrease from (2.068 - 1.228 hr) with increasing stripping agent.



**Figure 7:** Efficiency of extraction and stripping at different EDTA concentration of stripping phase, [C<sub>0</sub>=120ppm, carrier conc.=12 % ( v/v), pH feed=4 and stripping=8].

**Table 11:** The kinetic parameter for the transport of Ni<sup>+2</sup> at different EDTA concentrations.

EDTA Conc (M)	K <sub>1</sub> (hr <sup>-1</sup> )	K <sub>2</sub> (hr <sup>-1</sup> )	R <sub>M</sub> <sup>max</sup>	t <sub>max</sub> (hr)	J <sub>F</sub> <sup>max</sup> (hr <sup>-1</sup> )	J <sub>S</sub> <sup>max</sup> (hr <sup>-1</sup> )
0	0.224	0.891	0.158	2.068	-0.141	0.141
0.25	0.234	0.964	0.1544	1.936	-0.148	0.148
0.5	0.236	1.171	0.134	1.711	-0.157	0.157
1	0.263	1.850	0.102	1.228	-0.190	0.190

**4.7 Effect of Solvent organic**

Greener solvent such as environmentally benign vegetable oil based organic solvents to replace the conventional organic solvent in liquid membrane system are those of petroleum derivatives such as kerosene toluene, xylene and benzene organic solvents is indispensable. These solvent are usually nontoxic, inexpensive, inflammable, and biodegradable. Simultaneous extraction (removal) and stripping (recovery) for Ni(II) from aqueous solutions was conducted with tributylphosphate (TBP) and di-2-ethylhexylphosphoric acid (D2EHPA) (carrier) in a soybean oil (diluent). The extraction and stripping capacity of each carrier was measured as shown in Figure 8-9. Vegetable oils such as soybean oil showed the extraction and stripping efficiency 54.711% and 73.369% for TBP,

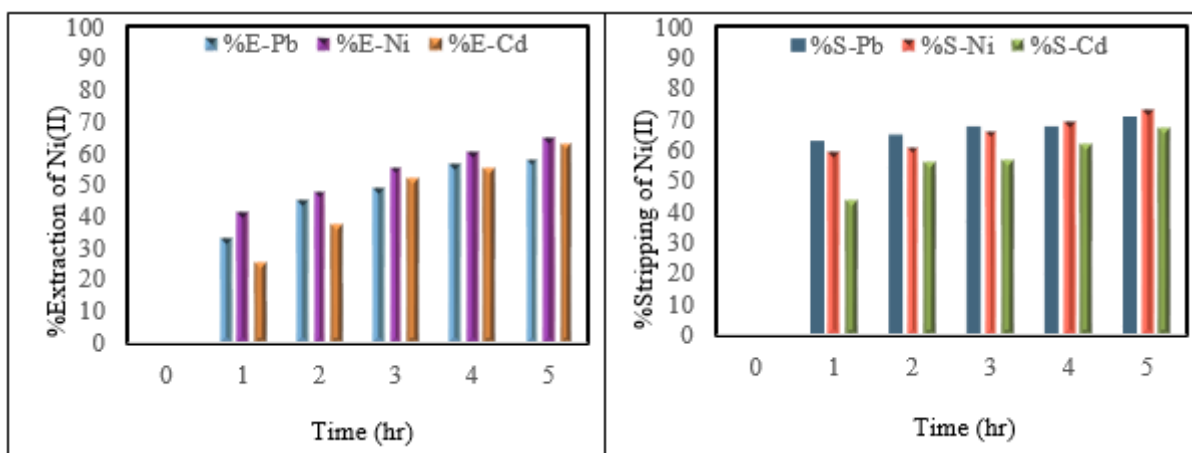
respectively. While, the extraction and stripping efficiency were become for D2EHPA in soybean oil 64.959% and 77.473%, respectively. High extraction capacity of soybean oil, in any extractant (TBP or D2EHPA), is not surprising. This increase may be due to decreased in the diffusion layer thickness of membrane interface, which leads to increased the formation of metal-carrier complex and the transport of metal ion from source to interface, which receiving phase [13]. There was variance clear in extraction and stripping efficiency of nickel ions by using tributylphosphate (TBP) and di-2-ethylhexylphosphoric acid (D2EHPA) as a carrier dissolved in xylene and soybean oil (diluent) as shown in Table 12.

**Table 12:** Type of diluent and carrier used in metal ions extraction using bulk liquid membrane processes

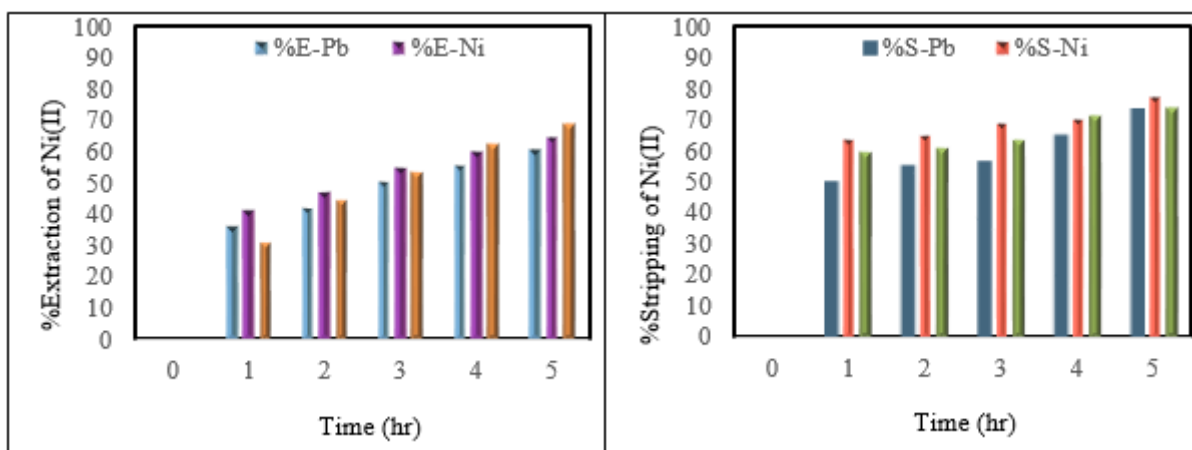
Metal ions	TBP				D2EHPA			
	Xylene		Soybean		Xylene		Soybean	
	%E	%S	%E	%S	%E	%S	%E	%S
Ni <sup>2+</sup>	80.89	87.8	54.711	73.369	62.595	85.896	64.959	77.473

From the results in above table, xylene oil showed highest extraction and stripping from soybean oil were

contained TBP and D<sub>2</sub>EHPA. Hence, xylene oil was chosen as the suitable solvent for further studied.



**Figure 8:** TBP % (v/v) with soybean oil effect on extraction and stripping efficiency of nickel (II).



**Figure 9:** D<sub>2</sub>EHPA % (v/v) with soybean oil effect on extraction and stripping efficiency of nickel (II).

## 5. Conclusions

The performance of bulk liquid membrane processes for extraction and recovery of nickel contaminate synthetic wastewater has been investigated. The toxic contaminate (nickel ions) were separated from aqueous, solution by using BLM. The major conclusions of this work are summarize below:

1- The bulk liquid membrane based techniques is applicable for simulteneous separation of nickel ions from wastewater.

2- The results indicate that TBP dissolved in xylene oil is the best extractant for heavy metals. While, D2EHPA the second best extractant viz. D2EHPA, was found to be an suiteble alternative.

3- The use of soybean oil has been an ideal green solvent in the liquid membrane processes to separate process of heavy metals.

4- The use of EDTA has been form a metal EDTA complex proved to be an excellint strip agent in receiving phase.

5- The results demonstrated that the optimam extraction and stripping of Ni (II) can be obtained at the following opareting condetions: pH of the feed phase = 4, pH of stripping phase = 8, initial metal concentration = 120 ppm, carrier concentration in the memibrane phase = 12% (v/v) TBP, stirring speed =125±10 rpm, and duration of extraction = 5 hr.

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## إزالة أيونات النيكل من مياه الصرف الصناعي بواسطة الغشاء السائل الحجمي

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**الخلاصة** – أصبح استخراج المعادن الثقيلة وفصلها عن مياه الصرف الصناعي مصدر قلق كبير لأسباب اقتصادية وبيئية. توضح هذه الورقة دراسة حركية مقارنة لأزالة واسترداد أيونات النيكل من المحاليل المائية بواسطة السائل الحجمي (BLM) باستخدام آليات النقل الميسر المقترنة وحاملتين ذات طبيعة كيميائية مختلفة (D2EHPA) and (TBP). تم استخدام زيت الزايلين كمرحلة غشاء سائل. بالإضافة الى ذلك، يتم استخدام مواد نباتية صديقة للبيئة (زيوت فول الصويا) كبديل مناسب للمذيبات العضوية التقليدية في هذا العمل. أجريت دراسة حركية شاملة وتمت دراسة تأثير العوامل المختلفة مثل درجة الحموضة في مرحلة التغذية والتجريد والتركيز الاولي لأيونات المعدنية وتركيز المستخلص في مرحلة الغشاء وسرعة التحريك. استخدمت خصائص EDTA كعامل تجريد وكذلك عامل ترسيب لتعزيز كفاءة نقل أيونات النيكل. تم العثور على كفاءة استخراج واستعادة 80.89% و 87.80% على التوالي لأيونات النيكل، في ظروف التشغيل المثلى لنقل Ni(II)، تم العثور على مايلي: الرقم الهيدروجيني في مرحلة التغذية (4)، الرقم الهيدروجيني في مرحلة التجريد (8)، التركيز الاولي لأيونات النيكل (120ppm)، وتركيز الناقل (12%) (ت/ت) TBP وسرعة التحريك (10±125) دورة في الدقيقة، على التوالي.

**الكلمات الرئيسية** – الغشاء السائل الحجمي. زيت الزايلين. فول الصويا. الأستخراج. حركي.