Removal of nitrate from water by bulk liquid membrane

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ABSTRACT

A bulk liquid membrane (BLM) containing dimethyldioctadecylammonium chloride (DODMAC) as the carrier reagent was developed for the removal of nitrate from water. DODMAC was found to be an efficient carrier for the nitrate transport through a solvent membrane containing 10 vol% chloroform and 90 vol% n-hexane. The optimum conditions of operation were found as: concentrations of feed, carrier and strip reagents of 0.00145, 0.012 and 0.8 M, respectively, and stirring speed of agitation of 250 rpm. At optimum conditions the extraction reached 99% after 7 h of operation while the stripping was also 97%. The latter reveals the high efficiency of the stripping phase in releasing the carrier. The long-term performance of the developed system was also appropriate where after 60 h of operation the extraction of nitrate was more than 92%. Effects of other parameters including the feed/membrane and membrane/strip phase ratios (v/v), nitrate salt, and type of strip reagent on the mass transfer of membrane system were also studied. The small amounts of remained chloroform in water were removed using air stripping method. Comparison between this work and other BLM works confirms the priority of developed system in removing nitrate from contaminated water.

Keywords: Nitrate; Bulk liquid membrane; Water treatment; Carrier; Extraction

1. Introduction

It is said that "*nitrate is the first world-wide environmental pollutant that resulted from human technology*" [1]. Nitrate is considered to be nontoxic for adults because it is quickly excreted by kidneys; however, concentrations more than 0.0007 M can be fatal for infants of under 6 months of age. In infants, nitrate is reduced to NO_2^- which could lead to "blue baby syndrome" [2]. The US Environmental Protection Agency (EPA) and Health and Welfare Canada established a maximum allowed concentration of 0.0007 M of NO_3^- [3–4]. European community has also established a maximum acceptable concentration of 0.0008 M of nitrate [5]. Nitrate is highly soluble and stable in water. As such, it is difficult to remove it by conventional technologies such as lime softening or filtration [2]. Therefore, more efficient technologies such as ion exchange, electrodialysis, reverse osmosis, catalytic denitrification and biological treatment are needed.

Two major disadvantages have been encountered with the ion exchange method: The first one is high amounts of required salt to regenerate the resins, and the second would be substantial waste solution releasing from the brine regeneration process which can cause regulatory problems [6–7]. On the other hand, reverse osmosis and electrodialysis are expensive processes and thus not viable to treat large amounts of polluted water. In contrast, biological treatment is neither expensive nor generates a brine by-product [8]. However, it requires a further treatment in order to remove the extra organic carbon courses, nutrient salts and pathogens. A low reaction rate followed by extreme sensitivity to pH, temperature, and salinity changes are other shortcomings of this process [9–10]. Although catalytic denitrification shows efficient in nitrate removal, however, it is still at research levels and different operating parameters such as the long-term stability of catalysts requires further studies [11]. Adsorption process is another method to remove nitrate from water in which various substances including activated carbon, nano-alumina, iron-modified pumice and other materials have been used as

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adsorbents [12–16]. The latter method is economic only in the cases that the dosage of the used adsorbent is low and the process duration is short.

Liquid membrane technique is another method that looks reasonable for the nitrate removal from water. This method is of high interest because of its high selectivity, technical simplicity and low energy consumption [17]. By using this system, separation and removal of a large number of cations as well as a number of anions have been investigated. Some of the anions include chloride [18], nitrite [19], nitrate [20], bromide [21], chromate [22] and iodide [23].

Neplenbroek et al. and Chiarizia successfully removed nitrate using supported liquid membrane [24–26]. Kemperman et al. used hollow fiber supported liquid membrane for the removal of nitrate from water [27]. Using the emulsion liquid membrane, Mohan and Li lowered the concentration of nitrate in water, while their process lasts more than 100 min [28,21]. Demircioglu et al. and Irdemez et al. reached almost 90% and 86% of nitrate removal, respectively, via bulk liquid membrane (BLM) systems [6,20].

In this work, a BLM system containing dimethyldioctadecylammonium chloride (DODMAC) as the carrier reagent was developed for the removal of nitrate anion from water. Using Design-Expert® software, based on the central composite method, optimum operational conditions were determined, and the effect of operating parameters on the BLM performance was studied. Feed/membrane and membrane/strip phase volume ratios as well as long-term performance of the system as economic criteria were also evaluated. High rate of transport through the membrane, high efficiency, long-term performance of the membrane, lack of contamination with chemicals, and ease of operation are some of unique features of the developed system.

2. Materials and methods

2.1. Materials

Sodium nitrate, strontium nitrate and DODMAC were purchased from Sigma-Aldrich (USA). Lithium chloride was provided by Scharlau (Spain), and aluminum nitrate nonahydrate was bought from Fluka (packed in Switzerland). Sodium chloride and hydrochloric acid were supplied from Dr. Mojallali Chemical Complex Co. (Iran), and organic liquids including n-hexane and chloroform were purchased from Merck (Germany). All chemicals were of analytical grade (high purity) and used without any further purification. Aqueous stock solutions were prepared with distilled water.

2.2. Preparation of membrane and aqueous solutions

Membrane phase consists of DODMAC as carrier dissolved in a mixture of chloroform (10 vol%) and normal hexane (90 vol%). Chloroform was used as the main solvent and n-hexane as its diluent. The volume of the membrane phase was 100 mL. The feed solution was prepared by dissolving sodium nitrate in distilled water where a stock solution was also made for further uses. Each experiment was set up by 100 mL of feed solution and retained for all experiments. Strip solution was prepared by dissolving sodium chloride in distilled water where a stock solution was also prepared for further uses. To figure out the effect of strip reagent on

the extraction and stripping outcomes, lithium chloride and hydrochloric acid were alternatively used. Stripping phase volume was fixed at 100 mL for each experiment. In particular cases, where the effect of membrane/strip phase volume ratio on the extraction and stripping values was investigated, the latter was decreased to 14.5 mL.

2.3. Apparatus

The body of the membrane cell was made from Pyrex, which possesses high chemical resistance against all used chemicals. The shafts and blades were made up of Teflon because of its high chemical stability. The agitation of the feed and strip solutions was provided by means of two mechanical stirrers. The speed of stirrers was synchronized. The compartment entrances were sealed by caps in order to prevent the solutions to evaporate while they could be used for sampling purposes. The schematic representation of the BLM cell apparatus is shown in Fig. 1.

As it can be seen, the membrane phase is placed on top of the aqueous phases because of its lower density. According to the BLM system, membrane phase has two different contact areas, one with the feed and another with the stripping phases while both aqueous phases are separated, entirely. The contact surface area between the membrane and each of the aqueous phases is 9.61 cm^2 (i.e., 3.5 cm in diameter). As shown in Fig. 1, the carrier forms complexes with nitrate ions at the membrane/feed interface, while the chloride ions in the carrier structure are released into the feed. Due to agitation in the membrane phase, the thickness of diffusion layer in the membrane phase decreases, and that would enhance the diffusion rate of the carrier-nitrate complex through the organic phase. At the membrane/stripping interface, the decomplexation reaction occurs, and the nitrate is released into the stripping phase. The carrier also takes another chloride anion and repeats the cycle.

2.4. Analysis

The concentration of nitrate ions was measured by ultraviolet-visible spectrophotometer (UV-1800, Shimadzu, Japan) at wave lengths of 220 and 275 nm provided by American Public Health Association (American Water Works Association). At wave length of 220 nm both nitrates and dissolved organic
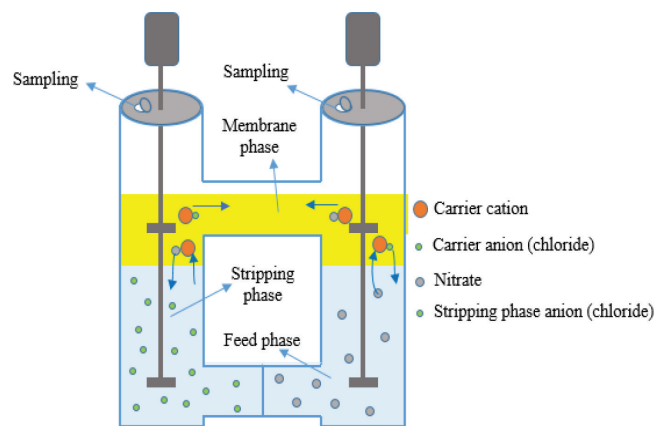

Fig. 1. Schematic presentation of bulk liquid membrane apparatus.

matters are absorbed, while at 275 nm only dissolved organic matters are absorbed. Therefore, the second measurement at 275 was also necessary. A correction factor should also be found to attain a correlation between the absorbance values obtained at these two wave lengths. The pure absorbance of nitrate ions is obtained by subtraction of the product of correction factor and absorbance value at 275 nm, from that obtained at 220 nm. In this work, the measured absorbance at 275 nm (for almost all samples) was close to zero, and thus the correction factor was empirically determined as unity. The concentration of chloroform in water was determined by gas chromatography equipped with an electron capture detector (GC-2010, Shimadzu, Japan) using the Chai et al. method [29]. Statistical design and data analysis were implemented using Design-Expert® software (v.7.0.0, Stat-Ease, Inc., Minneapolis, MN, USA) handling central composite design method.

3. Results and discussion

3.1. Optimization study

3.1.1. Experimental design method

BLM experiments were conducted after preparing all required solutions. Feed solution concentration (FC), carrier concentration (CC) in the membrane phase, strip concentration (SC) and stirring speed of agitation (SS) were chosen as four main factors to be investigated by Design-Expert® software applying central composite method, which is a category of Response Surface Method (RSM). The software offered 25-run experiments including 1 center point, full design. Each row of the designated table (Table 1) suggests a single test with given set of factors. The following polynomial model was employed for curve fitting.

$$Y = \beta_0 + \beta_1.FC + \beta_2.CC + \beta_3.SC + \beta_4.SS + \beta_{12}.FC.CC + \beta_{13}.FC.SC \\ + \beta_{14}.FC.SS + \beta_{23}.CC.SC + \beta_{24}.CC.SS + \beta_{34}.SC.SS + \beta_{11}.FC^2 \\ + \beta_{22}.CC^2 + \beta_{33}.SC^2 + \beta_{44}.SS^2$$

As it is shown in Table 1, each factor is provided in five levels: feed concentration (0.00145, 0.00242, 0.00484, 0.00726 and 0.00806 M); CC (0.001, 0.002, 0.0075, 0.013 and 0.014 M); concentration of sodium chloride in the strip solution (0.2, 0.3, 0.5, 0.7, 0.8 M) and SS (35, 50, 150, 250, 300 rpm). In order to minimize the effect of noise (uncontrollable factors), it was found appropriate to repeat every individual experiment. The mean recovery factors along with the predicted ones after 7 h of operation are given in Table 1. Since the experiments were conducted twice, the mean of recovery factor is presented

Table 1
Central composite design, 25-run experiment

Run	Feed concentration (FC, M)	Carrier concentration (CC, M)	Strip concentration (SC, M)	Stirring speed (SS, rpm)	Mean recovery factor (%)	Standard deviation (%)	Predicted recovery factor (%)	Error (%)
1	0.00242	0.013	0.7	50	80.2	1.1	80.5	0.4
2	0.00726	0.013	0.3	50	60.2	1.3	62.5	3.8
3	0.00726	0.002	0.3	50	24.2	1.6	23.0	5.0
4	0.00484	0.0075	0.5	35	50.3	1.7	53.3	5.9
5	0.00726	0.013	0.3	250	89.6	0.7	90.5	1.1
6	0.00242	0.002	0.3	250	83.8	1.3	80.6	3.8
7	0.00484	0.0075	0.8	150	79.3	0.5	79.1	0.2
8	0.00242	0.002	0.7	50	48.1	1.5	49.4	2.7
9	0.00242	0.013	0.7	250	97.2	0.4	99.0	1.8
10	0.00242	0.001	0.5	150	63.3	0.9	66.1	4.4
11	0.00242	0.002	0.7	250	84.2	1.8	83.4	1.0
12	0.00726	0.013	0.7	50	65.1	1.1	65.3	0.2
13	0.00242	0.002	0.3	50	47.2	0.7	46.6	1.3
14	0.00242	0.013	0.3	250	96.2	0.3	96.2	0.0
15	0.00484	0.014	0.5	150	89.5	0.7	88.8	0.8
16	0.00484	0.0075	0.5	300	89.7	1.6	88.9	0.9
17	0.00726	0.002	0.7	50	28.1	2.2	25.8	8.1
18	0.00726	0.013	0.7	250	94.4	1.7	93.3	1.2
19	0.00806	0.0075	0.7	250	94.0	1.6	92.4	1.7
20	0.00484	0.0075	0.2	150	75.1	1.3	74.9	0.3
21	0.00726	0.002	0.7	250	69.9	2.0	69.4	0.7
22	0.00242	0.013	0.3	50	81.3	1.1	77.8	5.0
23	0.00145	0.0075	0.7	250	98.8	0.2	100.1	1.3
24	0.00484	0.0075	0.5	150	78.3	0.7	77.0	1.7
25	0.00726	0.002	0.3	250	62.8	2.7	66.6	6.0

in Table 1. The standard deviation was also calculated and reported to represent the difference between answers and the mean recovery factors. Fig. 2(a) represents the normal plot of residuals (errors) where the normality of errors is acceptable. It is notable that the normal and studentized residuals have been calculated by Eqs. (1) and (2), respectively:

$$r_i = y_i - \hat{y}_i \tag{1}$$

$$\text{Studentized residual} = \frac{r_i}{\sigma_i} \tag{2}$$

where r_i is residual of i; y is the response value (extraction); $\hat{y}$ is the fitted response value and σ_i is standard deviation of residuals. In this work, statistical parameters including sum of squares, degree of freedom of parameters, mean of squares, F value, p-value, SNR (signal to noise ratio) and different R-squared values related to the model were reported. Holding significant influence of the factors, p-value ≤0.05 is required. It is noteworthy that no matter the higher values of response are favorable or the lower ones, the SNR value should be as high as possible because its higher values confirm the model precision. Eq. (3) represents the formula through which SNR has been calculated:

$$\text{SNR} = -10\log(\frac{1}{n}\sum\frac{1}{y_i^2}) \tag{3}$$

where n is the number of experiments, and y_i is the response. Model prediction by the software is conducted through Eq. (4). Fig. 2(b) shows the predicted vs. the observed recovery factors. Eqs. (5) and (6) represent the calculation procedure for the recovery factors and stripping efficiencies. Eq. (7) calculates the error caused by the difference between the observed and predicted recovery factors.

Extraction (%)

$$=35.14-0.092FC+4.39\times10^3CC+6.97SC+0.29SS$$
$$+2.6FC.CC+1.6\times10^{-4}FC.SS-7.2CC.SS-1\times10^5CC^2$$
$$-4.4\times10^{-4}SS^2$$

(4)

In Eq. (4), sodium nitrate and sodium chloride are considered as the dissolved salts in the feed and stripping phases, respectively. In addition, feed/membrane and membrane/strip phase volume ratios are assumed equal to 1:

$$\text{Recovery factor} (\%) = (1 - \frac{C_F}{C_{F,0}}) \times 100 \tag{5}$$

$$\text{Stripping efficiency} (\%) = \frac{V_s C_s}{V_F (C_{F,0} - C_F)} \times 100 \tag{6}$$

where $C_{F,0}$ is the initial nitrate concentration in the feed phase while C_F, C_S and V_F, V_S are concentrations and volumes of the feed and stripping phases, at time t, respectively.

$$\text{Error} (\%) = \frac{|\text{Observed recovery factor} - \text{Predicted recovery factor}|}{\text{Observed recovery factor}} \times 100 \tag{7}$$
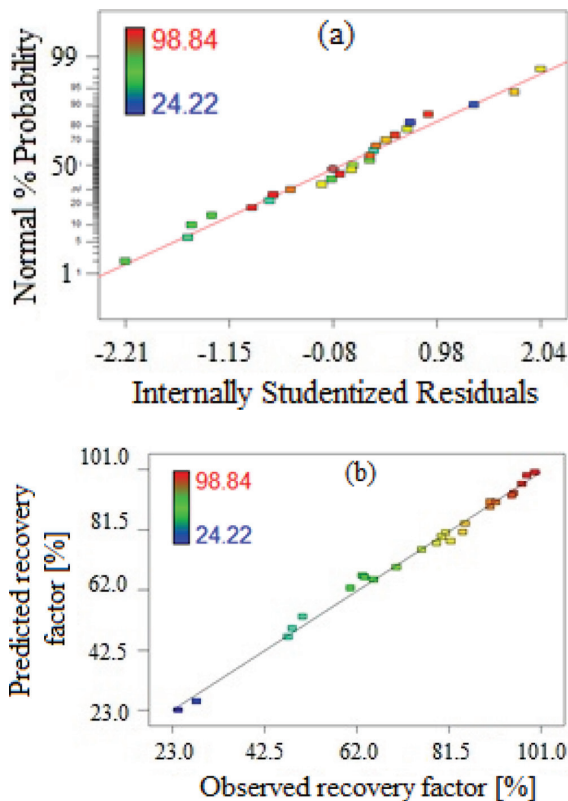
3.1.2. Analysis of variance

Table 2 provides the analysis of variance (ANOVA) data for quadratic model suggested by the software. The model F-value of 217.66 followed by p-value less than 0.0001 indicates the reliability of the model. If a parameter in ANOVA was significant, it would highly affect the response. As can be seen in Table 2, not only the main parameters but also some of the interactions and squares are also significant. It could be also deduced that the CC and SC have the highest and the lowest effects on the extraction, respectively.

Table 3 represents R-squared and SNR values for the model. The higher and closer together R-squared values, lead to the higher precision of the model. As it is provided in Table 3, the model R-squared is 0.9924; the adjusted R-squared reaches 0.9878; and the predicted R-squared value is 0.9778. The SNR value of the model is equal to 52.575, which seems quite acceptable.

After conducting all the designed experiments and gaining the important ANOVA data, optimal values for the factors resulting in the maximum recovery factors should be determined. The optimization was implemented using the desirability function. In the present study, to reach the maximum desirability, all the four main factors were set in the range, while the maximum level of recovery factor was selected. The ranges were FC: 0.00145–0.00806 M, CC: 0.001–0.014 M, SC: 0.2–0.8 M and SS: 35–300 rpm. According to the numerical optimization of Design-Expert® software,

Fig. 2. (a) Normal plot of residuals and (b) predicted vs. observed recovery factors (%).

Table 2
Parameters of statistical analysis for quadratic model

Factor	Sum of squares	Degree of freedom	Mean of squares	F-value	p-value
Model	10,526.63	9	1,169.63	217.66	<0.0001
FC	755.77	1	755.77	140.64	<0.0001
CC	2,264.78	1	2,264.78	421.46	<0.0001
SC	42.62	1	42.62	7.93	0.0130
SS	1,128.64	1	1,128.64	210.03	<0.0001
FC.CC	86.35	1	86.35	16.07	0.0011
FC.SS	106.71	1	106.71	19.86	0.0005
CC.SS	263.05	1	263.05	48.95	<0.0001
CC^2	46.46	1	46.46	8.65	0.0101
SS^2	116.99	1	116.99	21.77	0.0003
Residual	80.60	15	5.37	–	–

Table 3
R-squared and SNR values

ANOVA parameter	Value
R-squared	0.9924
Adjusted R-squared	0.9878
Predicted R-squared	0.9778
SNR	52.5750

desirability is an objective function that can be normally in the range of zero to one. The desirability value of 1 indicates that the case is ideal; however, the desirability value of zero signifies that the responses fall outside the desirable limits. Table 4 represents the optimal values, which resulted in maximum recovery factor with the desirability of 0.999. According to data of Table 5, for the optimized values of the parameters, recovery factor of 100.6% was predicted. At the optimum conditions suggested by the software, an experimental test was conducted. The observed recovery factor was 99.0, and thus the error was 1.6%.

The optimization was performed for the four main parameters while other factors were constant, that is, type of nitrate salt (sodium nitrate), strip reagent (NaCl), feed/membrane phase ratio (1) and membrane/strip phase ratio (1). After determining the optimum conditions, in addition to four main factors, the effect of other mentioned factors on the recovery factor was also investigated. Optimum conditions have been also determined by some of researchers using different experimental design software [30–32].

Table 5
Phase ratio and long-term performance of liquid membrane

Research	Phase ratio (v/v)	Recovery factor (%)		
Demircioglu et al. [20]	$V_f/V_m = 0.35$ $V_m/V_s = 2.85$	Recovery factor at times ≥6.25 h not reported		
Irdemez et al. [6]	$V_f/V_m = 0.5$ $V_m/V_s = 2$	Recovery factor at times ≥7 h not reported		
Present work	$V_f/V_m = 1$ $V_m/V_s = 1$	@35 h 96.24	@63 h 91.81	@91 h 48.23
	$V_f/V_m = 4$ $V_m/V_s = 1$	@35 h 92.04	@63 h 71.81	@91 h –

3.2. Effect of operating parameters on recovery factor

3.2.1. Effect of feed concentration

As shown in Fig. 3(a) increasing the feed concentration results in a decrease in the extraction. Increase in the feed concentration from 0.00145 to 0.00242 M leads to slight decrease in extraction. However, further increase in the feed concentration (up to 0.00806 M) would cause an intensified decrease in recovery factor. The decrement in nitrate extraction, especially for feed concentrations ≥0.00242 M, is due to the lack of enough carrier at the membrane/feed interface to form the desired complexes required for the extraction. In addition, the decrease in recovery factor can be attributed to increment of ionic strength of the feed. As ionic strength decreases, it lowers the activity of nitrate ions, which limits the complex formation at the membrane/feed interface [33].

Fig. 3(b) shows the time dependency of recovery factor for the feed concentration of 0.00145 M. Accordingly, until 3 h, the nitrate extraction increases with a relatively steep slope, in which 89% of nitrate is extracted. After this period, recovery factor enhances slightly to reach the value of 99% at 7 h. Although the nitrate removal value is considerable at 4–6 h, but process time of 7 h was also selected to be used for other experiments due to its highest recovery factor. Selection of this run time also helps to better comparison between this study and other BLM studies (i.e., Demircioglu et al. [20] and Irdemez et al. [6]).

3.2.2. Effect of carrier concentration

Fig. 3(c) demonstrates the effect of CC on the recovery factor. Increase in the CC from 0.001 to 0.014 M result in enhancing the extraction. Increase in the carrier ions present at the membrane/feed interface would enhance the capacity of carrier-nitrate complex formation and consequently the extraction of nitrate ions. As the CC reaches its terminal value, further increase would not enhance the extraction. As such, the CC of 0.012 M was chosen as an optimum value.

Table 4
Results of the statistical model at the optimum conditions (after 7 h operation)

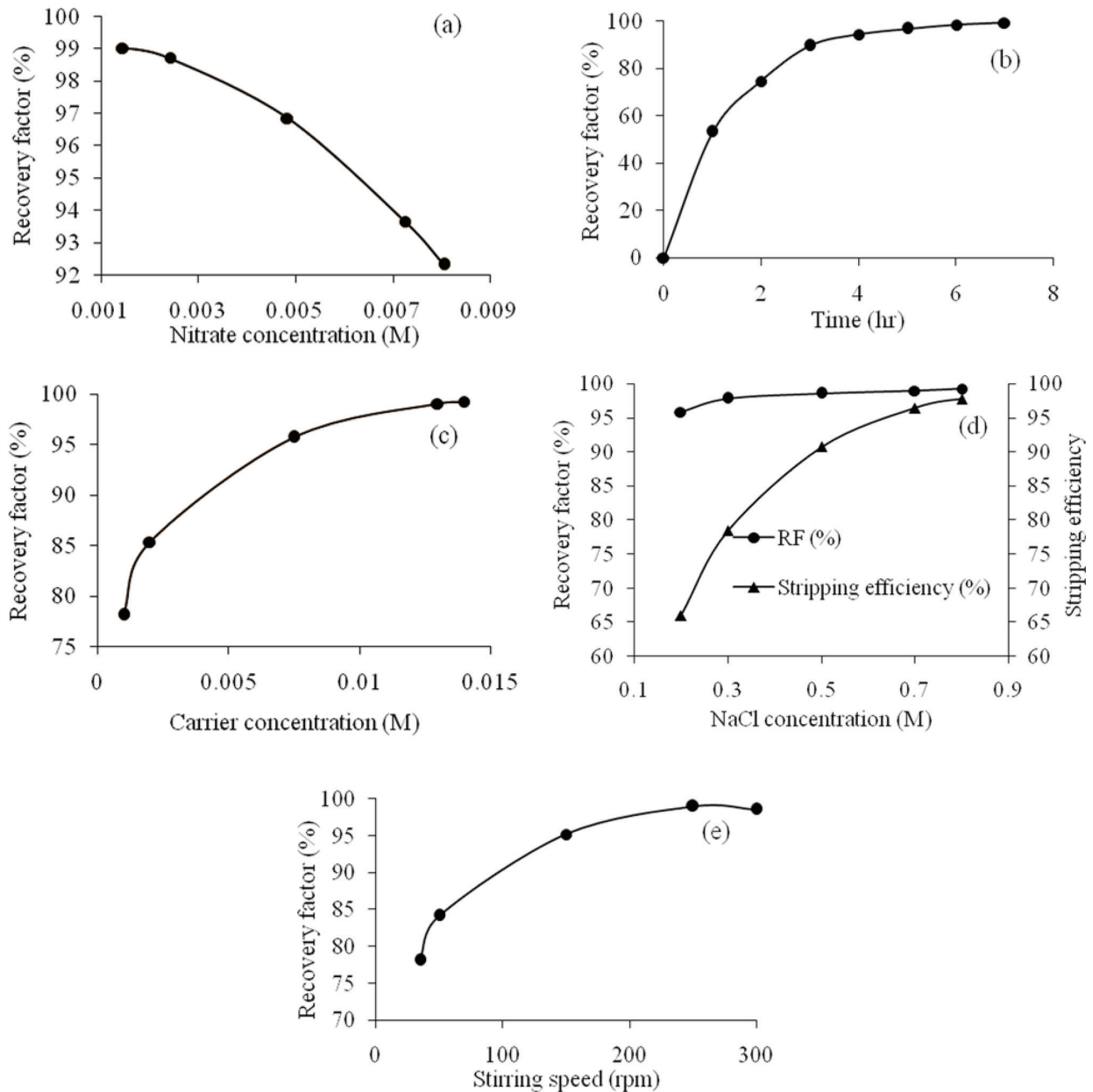| Operating parameters						
Feed concentration (M)	Carrier concentration (M)	Strip concentration (M)	Stirring speed of agitation (rpm)	Observed recovery factor (%)	Predicted recovery factor (%)	Error (%)
0.00145	0.012	0.8	≈250	99.0	100.6	1.6

Fig. 3. Effect of (a) feed concentration, (b) contact time, (c) carrier, (d) strip concentrations and (e) stirring speed of agitation on recovery factor.

Note: C_{feed} = 0.00145 M; $C_{carrier}$ = 0.012 M; C_{strip} = 0.8 M; Stirring speed = 250 rpm; feed phase salt: NaNO$_3$; membrane phase: 10% chloroform + 90% n-hexane (v/v); strip reagent: NaCl; feed/membrane phase ratio: 1 (v/v); membrane/strip phase ratio: 1 (v/v).

3D response surface plot of Fig. 4(a) represents the combined effect of carrier and feed concentrations on the recovery factor. The graph which is plotted based on predictive quadratic model (Eq. (4)) is in excellent agreement with experimental data provided in Figs. 3(a) and 3(c).

3.2.3. Effect of strip concentration

Fig. 3(d) reveals that increasing NaCl concentration as strip reagent in the stripping phase would not considerably enhance the extraction. Where the concentration of strip reagent was 0.2 M, the extraction is high. This is due to the fact that high capacity and chemical tendency of the carrier leads to the formation of nitrate complexes at the membrane/ feed interface.

In order to use the membrane phase for several times, it was necessary to recover it at every 7 h of operation. It means that nitrate ions that present in the carrier structure instead of chloride ions should be released to the stripping phase and substituted by chloride ions. The presence of nitrates in the membrane phase causes a main problem: It lessens the number of chloride-carrier complexes present at the
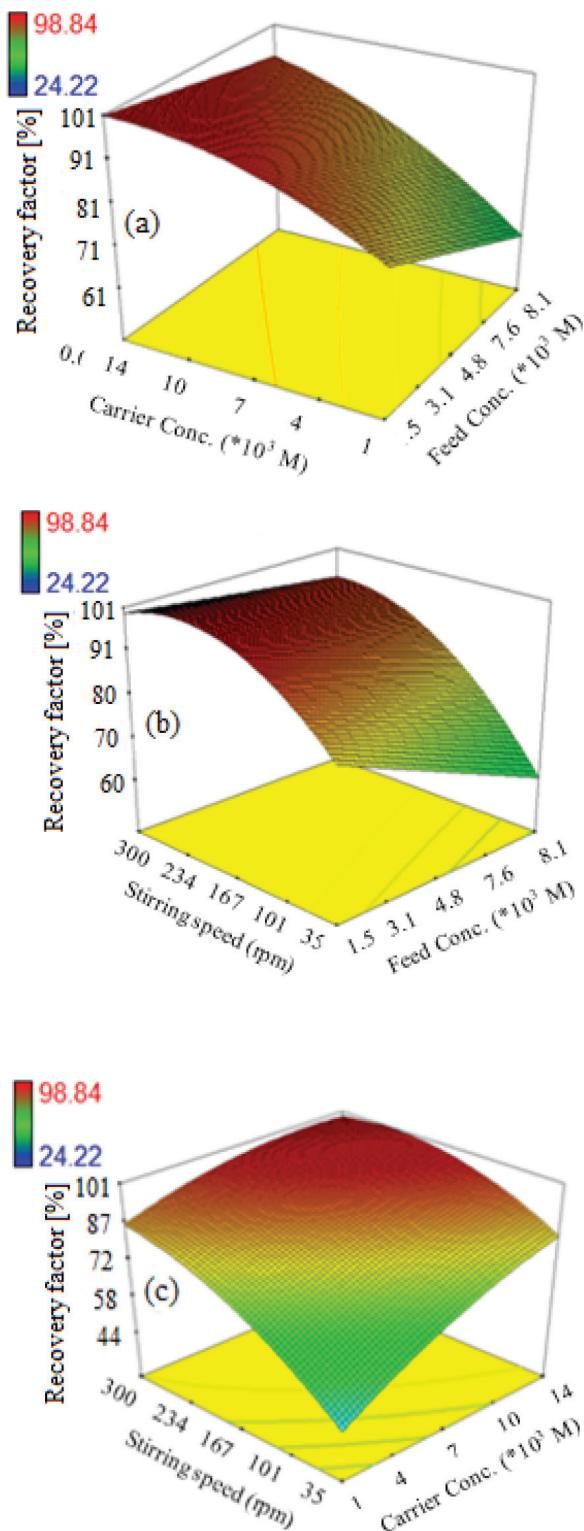
Fig. 4. Response surface plots for the combined effect of (a) feed concentration and carrier concentration, (b) feed concentration and stirring speed and (c) carrier concentration and stirring speed on recovery factor.
Note: C_{feed} = 0.00145 M; $C_{carrier}$ = 0.012 M; C_{strip} = 0.8 M; Stirring speed: 250 rpm; feed phase salt: NaNO$_3$; membrane phase 10% chloroform + 90% n-hexane (v/v); strip agent: NaCl; feed/membrane phase ratio: 1 (v/v); membrane/strip phase ratio: 1 (v/v).

membrane/feed interface. Therefore, the NaCl concentration equal to 0.8 M was chosen as the optimum concentration for stripping reagent.

3.2.4. Effect of stirring speed

Increasing the SS in the feed and stripping phases leads to better movement of nitrate and chloride ions from the bulk to the membrane/feed and membrane/strip interfaces, respectively. Vigorous agitation has two positive effects: (i) It would facilitate the movement of carrier ions from the bulk membrane to the membrane/feed interface and (ii) it would facilitate the faster movement of complexes from the mentioned interface to the membrane/strip interface for complex dissociation reaction and carrier recovery. Fig. 3(e) represents the effect of SS on the recovery factor. While SS up to 250 rpm increases the extraction, further increase in the speed of agitation would not enhance the extraction process.

Figs. 4(b) and 4(c) show 3D RSM plots represent the combined effect of SS-feed concentration and SS-CC on the nitrate extraction, respectively. Similar to Fig. 4(a), the mentioned graphs were plotted based on predictive quadratic model (Eq. (4)) which confirms the observed trends in Figs. 3(a), 3(c) and 3(e).

3.2.5. Effect of feed/membrane phase ratio

Since the number of carrier ions present in the membrane phase is proportionally decreased with its volume, carrier ions can form fewer complexes with nitrate ions, and consequently, the extraction would decrease. Fig. 5(a) shows the effect of feed/membrane phase ratio (v/v) on the recovery factor. This parameter was studied to figure out how BLM performs with a more economic phase ratio. The results show that the performance is acceptable even where the membrane phase volume is considerably less than that of the feed (e.g., feed/membrane phase ratio of 4).

3.2.6. Effect of membrane/strip phase ratio

Reduction of stripping phase volume (chloride ions) may lead a decrease in the rate of decomplexation of carrier-nitrate complexes, and thus reducing the stripping efficiency and recovery factor values. The maximum stripping value of 96.95% was obtained for the membrane/strip phase ratio of 1. However, according to Fig. 5(b) stripping is acceptable even at membrane/strip phase ratio of 4 where the membrane phase volume is 100 mL.

3.2.7. Effect of feed phase salt

Since the nitrate is available in different salts, in addition to sodium nitrate, two different nitrate salts, namely strontium nitrate and aluminum nitrate nonahydrate, were tried in the feed phase. The present BLM system gives almost the same extraction for all nitrate salts. This observation shows that the substitution reaction which takes place at the membrane/feed interface is not affected by the cation in the used salt and the carrier-nitrate complex is easily formed for all cases (Fig. 5(c)).
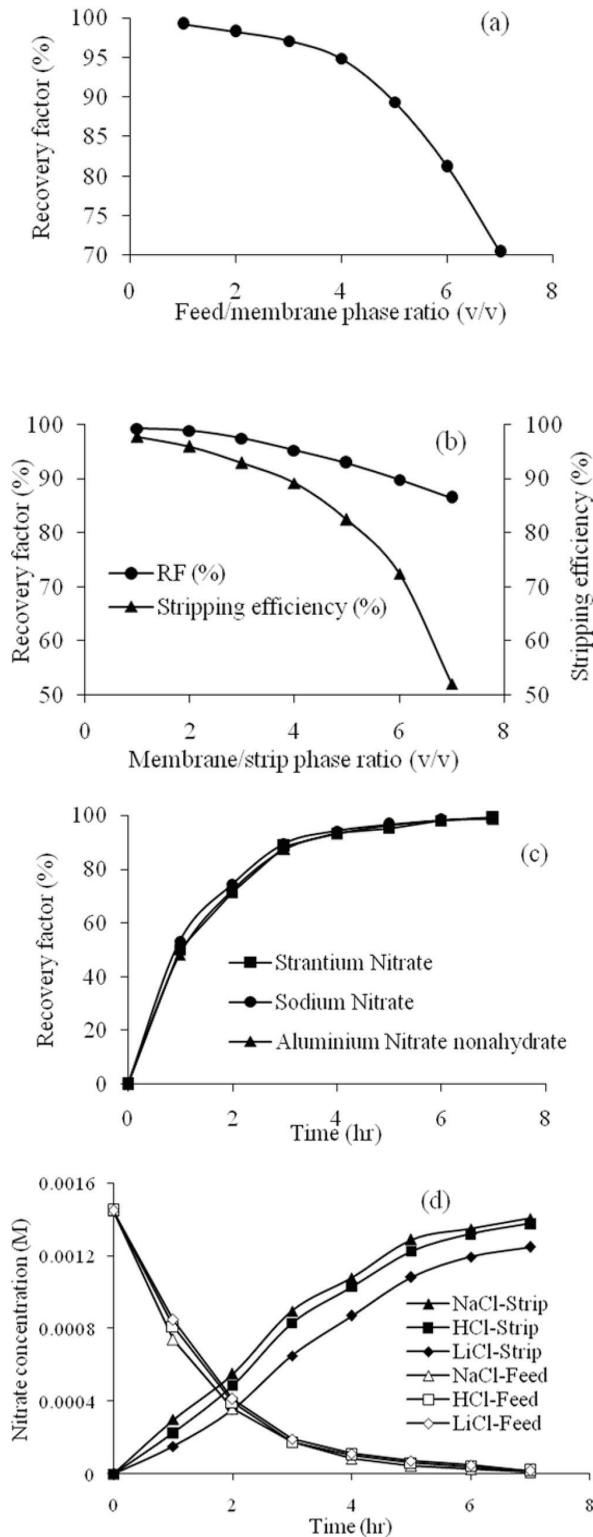
3.2.8. Effect of stripping reagent

In addition to NaCl, two other chemicals that supply the chloride ion, that is, HCl and LiCl, were also examined in the stripping phase. As Fig. 5(d) illustrates, NaCl and HCl give higher stripping values than LiCl. However, the recovery factor values for all strip reagents are almost the same. Since the membrane phase is supposed to be used for several consecutive times, it should be recovered at any 7-h operation. As such, NaCl was selected as the strip reagent because of its high performance.

3.2.9. Effect of presence of sulfate (SO_4^{2-}) salt in feed phase

To see the effect of the other anions on the recovery factor and carrier performance, sulfate as a divalent anion was applied in feed phase, where sodium sulfate was the salt used. As it could be seen in Fig. 6(a), various concentrations of SO_4^{2-} was applied (i.e., from 0.02 to 0.4 M). DODMAC is a monovalent ammonium salt showing excellent chemical tendency to form complex with nitrate. However, in order to present this high tendency in a clearer way, two different parameters were evaluated in presence of sulfate: recovery factor and separation factor. As obvious in the Fig. 6(a), low concentrations of sulfate (0.02 and 0.05 M) resulted in a very slight decrement in the recovery factor value. Even applying

Fig. 5. Effect of (a) feed/membrane phase ratio, (b) membrane/strip phase ratio, (c) feed phase salt and (d) strip reagent, on recovery factor/stripping efficiency.
Note: C_{feed} = 0.00145 M; $C_{carrier}$ = 0.012 M; C_{strip} = 0.8 M; Stirring speed: 250 rpm; nitrate salt: NaNO$_3$; membrane phase: 10% chloroform + 90% n-hexane (v/v); strip reagent: NaCl; feed/membrane phase ratio: 1 (v/v); feed/strip phase ratio: 1 (v/v).
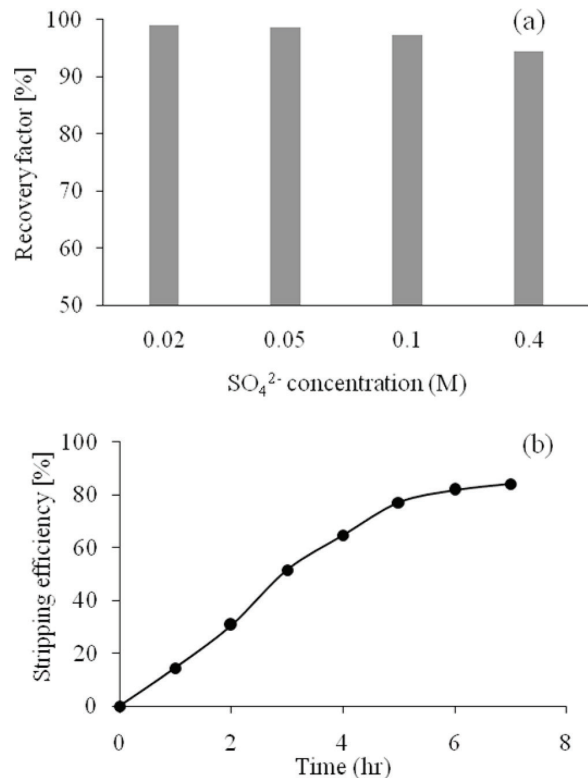
Fig. 6. Effect of (a) presence of sulfate in feed phase on recovery factor and (b) presence of nitrate in stripping phase on stripping efficiency.
Note: C_{feed} = 0.00145 M; $C_{carrier}$ = 0.012 M; C_{strip} = 0.8 M; Stirring speed: 250 rpm; nitrate salt: NaNO$_3$; membrane phase: 10% chloroform + 90% n-hexane (v/v); strip reagent: NaCl; feed/membrane phase ratio: 1 (v/v); feed/strip phase ratio: 1 (v/v).

the higher concentrations of this divalent anion could not lead to considerable decrease in the extraction. For sulfate concentrations of 0.1 and 0.4 M, values of the recovery factor are 97.24% and 94.36%, respectively. The reported reductions in the recovery factor (%) could be caused by two main reasons. First of all, some of the SO_4^{2-} ions present at the membrane/feed interface are engaged in complex formation with the carrier, in which reduces the DODMAC capacity to create complex with nitrate. In addition, presence of sulfate ions in feed phase (especially for higher concentrations) leads to more difficult movement of the nitrate ions from feed bulk to the membrane/feed interface.

However, competition between nitrate and sulfate in complex formation with DODMAC should be investigated to give the selectivity of the carrier. Eq. (8) calculates the separation factor (SF); where C_S and C_F are stripped and remained feed concentrations for each component, respectively. The separation factor was determined for a sulfate concentration of 0.00145 M, where the obtained value of 4,849.3 confirms the high selectivity of the carrier used in the present study.

$$SF(\%) = \frac{\left(\dfrac{C_S}{C_F}\right)_{nitrate}}{\left(\dfrac{C_S}{C_F}\right)_{sulphate}} = \frac{\dfrac{0.001435}{0.0000145}}{\dfrac{0.000029}{0.001421}} = 4,849.3 \qquad (8)$$

3.2.10. Effect of presence of nitrate salt in the stripping phase

To figure out whether the high concentration of nitrate in the stripping phase can ruin the decomplexation process, amount of $NaNO_3$ up to 800 mg/L was added to the stripping phase. In this case, the nitrate ions would replace the chloride ions at the membrane/stripping interface. Therefore, the nitrate ions at the membrane/stripping interface have a lower chance to be substituted by chloride ions. As a result, the membrane phase recovery is accomplished by a lower rate. Fig. 6(b) shows the stripping value after 7 h of 84.13%.

3.2.11. Long-term performance of liquid membrane

After several hours of operation, the nitrate ions might accumulate in the membrane phase. As the concentration of nitrate ions in the membrane phase increases, the same might happen at the membrane/feed interface, as well. That would lower the replacement of chloride ions with nitrates in the feed phase. However, as shown in Fig. 7, recovery factor value after long time uses of the membrane phase is acceptable at different phase ratios.

3.3. Transport mechanism

Fig. 8 shows the molecular structure of the used carrier. The long carbonic chains make this molecule insoluble in water. Reactions R1 and R2 occur at the membrane/feed and membrane/strip interfaces, respectively. According to the standards of EPA for drinking water, the chloride concentration of 0.00706 M (i.e., 250 mg/L) in water is allowable and does not lead to health problems. Therefore, water solutions containing nitrate concentrations of about 0.00706 M could be treated using this system [34].
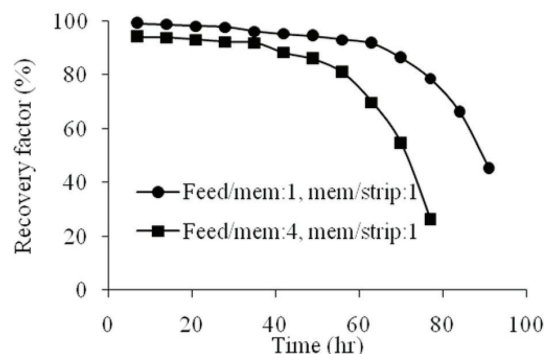
Fig. 7. Long-term performance of liquid membrane.
Note: C_{feed} = 0.00145 M; $C_{carrier}$ = 0.012 M; C_{strip} = 0.8 M; stirring speed: 250 rpm; membrane phase: 10% chloroform + 90% n-hexane (v/v); nitrate salt: $NaNO_3$; strip reagent: NaCl.

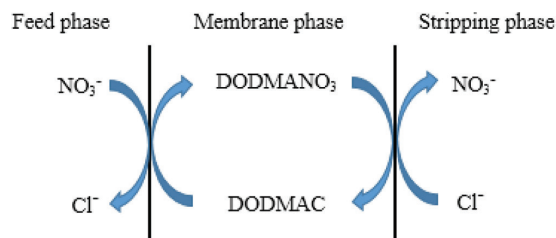Fig. 8. Molecular structure of dimethyldioctadecylammonium chloride.

Fig. 9. Mechanism of nitrate transport through the liquid membrane.

Fig. 9 shows the transport direction of nitrate through the liquid membrane as well as complex formation which occurs at the membrane/feed interface. The complex then moves through the membrane phase and reaches the membrane/strip interface, where decomplexation process occurs and the carrier is recovered.

$$NaNO_3 + DODMAC \rightarrow Nacl + DODMANO_3 \qquad (R1)$$

$$Nacl + DODMANO_3 \rightarrow NaNO_3 + DODMAC \qquad (R2)$$
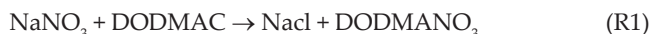
3.4. Comparison between this work and other BLM works

Table 5 shows comparison between the performance of this work at optimum conditions (feed concentration of 0.00145 M) and similar works reported in the literature. Higher performance of the system used in this work at both
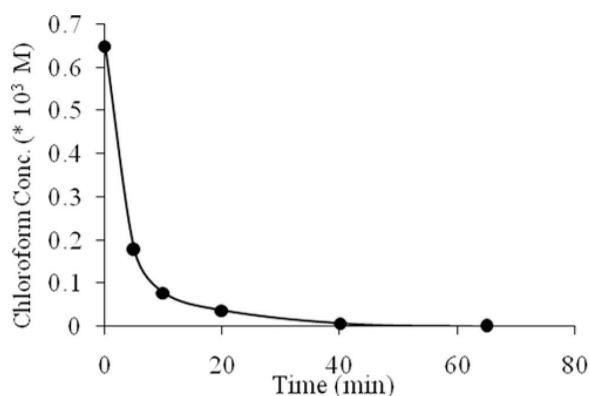
Fig. 10. Chloroform concentration in water vs. time via air injection.

extraction and long-term performance is mainly because of the carrier structure. The employed carrier is definitely strong and shows high tendency toward formation of nitrate complex. Meanwhile according to Neplenbroek et al., it has a significant effect on the long-term performance of liquid membrane [25]. In Table 5, the parameters V_F, V_m and V_S represent volumes of feed, membrane and stripping phases, respectively.

3.5. Chloroform removal from denitrificated water

Presence of chloroform can jeopardize human health. Therefore, EPA has established a threshold maximum contaminant level of 5.86×10^{-7} M (0.07 mg/L) in water [34]. In present study, after denitrification process, fresh air with a flow rate of 0.15 L/min was injected into the chloroform contaminated water, and chloroform concentration was determined by gas chromatography at different time intervals. Finally after 65 min, chloroform concentration decreased to less than 20 ppb (Fig. 10). Samadi et al. also used air stripping process to reduce the chloroform concentration from 100 ppb to less than 14 ppb [35].

In contrast, n-hexane is relatively insoluble in water, and also EPA has not established any maximum concentration level on this organic solvent in water. It has been used as solvent by different researchers to separate various contaminants from water by liquid membrane method [34,36–38]. However, Karimnezhad et al. employed modified Kevlar fabrics and separated trace amounts of this organic solvent from water where the extraction value was 94% [39].

4. Conclusions

A comprehensive study was performed on the transport of nitrate ions through a BLM using DODMAC as carrier reagent. The following results were obtained:

- The optimum experimental conditions which resulted in recovery factor and stripping efficiency values of 99% and 97%, respectively, were: C_{feed} = 0.00145 M (90 mg/L), $C_{carrier}$ = 0.012 M; C_{strip} = 0.8 M NaCl; SS: 250 rpm; feed phase salt: NaNO$_3$; membrane phase: 10% chloroform + 90% n-hexane (v/v); strip reagent: sodium chloride; feed/membrane phase ratio: 1 (v/v); and membrane/strip phase ratio: 1 (v/v).

- The system was also capable of removing ≥94% of nitrate, followed by stripping value of 89.14% even where the feed/membrane phase ratio increased to 4 and membrane/strip phase ratio (v/v) was 1.
- Long-term performance of the present BLM was highly reliable where for the feed/membrane phase ratio of 4, after 35 h, extraction value was ≥92%.
- Using air stripping method, excess amounts of chloroform were removed from denitrificated water which after 65 min of operation, chloroform concentration was less than 20 ppb.
- In comparison with other BLM works, presented BLM system has priority in extraction, stripping, long-term performance, and economic phase ratios.

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