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Kinetics of transport of sodium chloride using supported liquid pertraction

Ahmed A. El-Shafei[a,*], Abeer A. Moneer[b], Mahmoud M. Elewa[c], Mona M. Naim[d]

[a]*Faculty of Agriculture, Associate Professor of Agricultural and Bio-Systems Engineering, Alexandria University, Alexandria, Egypt, Tel. +20 1006159433; Fax: +20 35922780; email: ahmed.elshafi@alexu.edu.eg*
[b]*Marine Pollution Department, Marine Environmental Division, National Institute of Oceanography and Fisheries, Alexandria, Egypt, email: yrwah@yahoo.com*
[c]*Head of Research and Development Department, Arab Academy for Science, Technology and Maritime Transport, Alexandria, Egypt, email: mahmoud.elewa@gmail.com*
[d]*Faculty of Engineering, Professor of Chemical Engineering, Alexandria University, Alexandria, Egypt, email: monanaim66@gmail.com*

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ABSTRACT

In the present work, the removal of NaCl using the present type of supported liquid membrane technique has been investigated. A simple apparatus devised and constructed was used to conduct the experiments. Various factors that would affect the progress of transport were studied and these were initial concentration (C_i) of simulated seawater in donor phase (DP), presence of mobile carrier (MC) in the liquid membrane (LM), concentration of MC in LM, presence of sequestering agent (SA) in the receptor phase (RP), and speed of stirring. The volume ratio of DP to RP was kept constant at 2:1. Type (1,2 dichloroethane (DCE)) and thickness (2 mm) of LM were kept constant. Cellophane constituted the support for the LM. The most important findings emphasized the importance of the presence of a MC in the LM to enhance mass transfer through the LM and that an optimum concentration of MC existed. Also the importance of stirring in promoting mass transfer by minimizing the boundary layer intact to the cellophane support was elucidated. The best conditions arrived at were MC = 0.0538 mol/l (mol of dibenzo-18-crown-6/l of LM), SA = 0.0617 mol/l (mol of soluble starch/l of RP), slow stirring (100 rpm) of DP, and using DCE as LM. The mass transfer of NaCl was analyzed based on kinetic laws of two consecutive irreversible first-order reactions, and kinetic parameters (k_{1d}, k_{2m}, k_{2r}, R_m^{max}, t_{max}, J_d^{max}, J_r^{max}) for the transport of NaCl were investigated. The values obtained demonstrate that the process is diffusion-controlled. Results indicate that the membrane entrance and exit rate constants (k_1, k_2) increase directly with C_i and inversely with quantity of SA.

Keywords: Kinetics; Mobile carrier; Sequestrant; Sodium chloride; Supported liquid membrane

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*Corresponding author.

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1. Introduction

Liquid membranes (LMs) have gained wide interest since their discovery by Li [1], they offer great potential and merits compared to solid membranes, such as higher permeability, simplicity in operation, higher selectivity, low energy consumption, and absence of pores to be blocked or fouled as in solid membranes [2]. LMs are cost-effective since they consume little energy while permitting high rates of mass transfer than solid membranes. They can be divided into emulsion, supported, bulk, hollow fiber contained, electrostatic pseudo, spirally wound, and flowing LMs and a few more [2].

The LM itself separates two miscible phases from each other and is insoluble in these phases. The two miscible liquid phases, which may be referred to as donor phase (DP) and receptor phase (RP), are spatially separated by a third liquid (LM), immiscible and practically insoluble in the former two liquids. Due to the favorable thermodynamic conditions, created at the interface between DP and RP, some components are extracted from DP and transported into the LM [3]. Simultaneously, at the second interface (LM/RP), conditions are created, which favor the reverse transport, i.e. the extraction of the above-mentioned components from the LM and their accumulation in RP [4].

The term supported liquid membrane (SLM) usually defines solid (polymer or ceramic) porous membranes, the open pores of which are soaked with the LM. In broader sense, this term refers also to much thicker membranes, supported on both sides by porous solid barriers. These homogeneous liquid films, supported on both sides, may be termed as a SLM. The method of impregnated LM has become more and more popular. By impregnating fine-pore polymer films with a suitable LM, relatively stable heterogeneous solid–liquid membranes are obtained. These membranes are shaped as thin flat barriers or as hollow fibers [5]. Usually, they are manufactured from oleophilic polymers, wettable by the LM. The two interfaces DP/LM and LM/RP have equal or close areas, which can be made very large employing modules of spirally wound flat membranes or bundles of hollow fibers. The studies of pertraction processes using SLMs are most often performed with simple cells of a vertical or horizontal type depending on the position of the impregnated support [2]. Pirom et al. [6] studied the separation of amoxicillin via hollow fiber supported liquid membrane (HFSLM) under various operating conditions to find the optimal parameters. They found that percentages of extraction and recovery of amoxicillin from the feed phase reached 85.21 and 80.34%, respectively. The same authors [7] investigated the influence of temperature on the separation of amoxicillin via HFSLM containing the carrier Aliquat 336. Mass-transfer parameters including distribution ratio and flux as well as thermodynamic properties were also determined at different temperatures. The positive value of the enthalpy change indicated that the extraction process is endothermic reaction. Further, the positive value of the entropy change and the negative value of the Gibbs free energy indicated that the extraction process is forward reaction. It was found that by increasing the temperature of the system from 278.15 to 318.15 K, extraction of amoxicillin increased from 81.81 to 89.65% and the stripping of amoxicillin increased from 76.63 to 84.70%, respectively.

The main advantage of SLMs is the insignificant amount of LM required for impregnation of the support matrix. For example, 10 cm^3 of LM are sufficient to impregnate 1 m^2 of a membrane of 20 μm thickness and 50% porosity. Regardless of the fact that extremely thin pores of the LM are used, this method cannot provide diffusion fluxes acceptable for practical use intensities. This drawback is compensated for by the large specific area up to 2,000–5,000 m^2/m^3 using spirally wound modules or hollow fiber modules, containing thousands of tiny capillaries [2]. Urtiaga and Irabien [5] studied the internal mass transfer in HFSLMs. This work describes a hollow fiber SLM module analyzing the influence of the internal mass transfer on the design of such systems. The simultaneous separation concentration of phenol from aqueous solutions with HFSLMs was performed. The influence of the flow rate of the inner aqueous phase on the phenol separation rate was studied. Kazemi et al. [8] also studied the stability and extraction of phenolic wastewater treatment by SLM using tributyl phosphate and sesame oil as LM. Another system for the removal of phenol using SLM was tried by Yang et al. [9]. They investigated phenol transport from the aqueous solution through an SLM impregnated with bis(2-ethylhexyl) sulfoxide in kerosene. The authors used NaOH as the stripping solution.

SLMs were investigated in the removal of heavy metals from different wastewater streams by numerous authors. Garmsiri and Mortaheb [10] studied enhancing performance of hybrid LM process supported by porous anion exchange membranes for the removal of cadmium from wastewater. They discovered that the proposed anionic supporting membranes can yield much higher fluxes for the removal of cadmium in high concentrations, compared to the same hybrid LM system with non-ionic polyvinylidene fluoride supporting membranes, while only insignificant loss in the removal efficiency is observed.

Moreover, Rodríguez de San Miguel et al. [11] discussed chromium(VI) transport through a SLM system containing the commercial ionic liquid CYPHOS IL101 as carrier. A reducing stripping phase was used as a mean to increase recovery and to simultaneously transform Cr(VI) into a less toxic residue for disposal or reuse. Also Suren et al. [12] conducted uphill transport and mathematical model of Pb(II) from dilute synthetic lead-containing solutions across hollow fiber SLM.

Chrisstoffels et al. [13] reviewed on mechanistic aspects of carrier-assisted transport through SLMs. They developed the carriers for the selective transport of neutral molecules, anions, cations, or zwitterions species. They described the transport by subsequent partitioning, complexation, and diffusion. Studies are mainly focused on the mechanism of diffusion-limited transport, in which diffusion of the complex through the membrane phase is the rate-determining step of the transport. Kinetics in membrane transport have been explained with the carriers for which the rate of decomplexation determines the rate of transport. Koenig et al. [14] investigated membrane carrier selectivities identified by competition transport experiments. The ion transport selectivity toward a given set of metal cation can be determined for a membrane carrier in bulk liquid membranes (BLMs) and SLMs. A single competition transport experiment with ten metal nitrates and subsequent simultaneous metal ion analysis of the RP by inductively coupled plasma optical emission spectroscopy yield the transport selectivity pattern of a carrier for a given set of metal cations.

Naim and Monir [15] conducted desalination of saline water by SLM. The variables that would affect the degree of desalination such as type of LM, thickness of LM, presence of MC in the LM, concentration of MC in LM, presence of polyelectrolyte in the RP and presence or absence of magnetic stirring, the volume ratio of DP to RP, and cellophane constituting the support for the LM were investigated.

Kocherginsky [16] proved that one of the major obstacles to the practical application of SLMs is their very short lifetime. The latter is determined at least in part, by leaching of the partially hydrophobic carrier from the membrane. If MC is also with hydrophobic nature, the transport rate is low due to the phase separation of the carrier, and hydrophilic species to be transferred. The authors suggested using the more complex system for facilitated transport, which has the extremely hydrophobic carrier, and at least one mildly hydrophilic mediator (interface catalyst). In the case of trans-membrane electron transfer, this system is similar to the chain of electron transport in bio-membranes. A theoretical steady-state description of the process with one mediator and one carrier was presented. The model assumes the simultaneous and parallel diffusion and reaction, both in aqueous solutions and LM. It was demonstrated that small concentrations of effective mediator can dramatically change the kinetics of trans-membrane processes.

The kinetic parameters of the different variables, which affect the transport of the specified specie from the DP to the RP across the organic LM, were studied by numerous workers [17–24]. Nosrati et al. [25] investigated the kinetics of vanadium(IV) transport through ionic SLM. Singh et al. [26] studied kinetics of permeation of uranium(VI) from phosphoric acid medium through SLM comprising a binary mixture of PC88A and Cyanex 923 in n-dodecane as carrier. On the other hand, kinetics of carrier-mediated alkali cation transport through SLM and effect of membrane solvent, co-transported anion, and support, were studied by Visser et al. [27].

The aim of the present work was to investigate the possibility of desalination of saline water by the application of LMs instead of solid membranes. An experimental laboratory-scale set-up, which includes the module, was constructed. Experiments are then conducted to investigate the different variables on the extent of desalination. The numerous factors that are to be tested for their effect on the extent of desalination include the following: initial salt solution concentration, presence of MC in the LM, quantity of MC, presence of SA and its quantity in the RP, and effect of stirring speed. Moreover, a kinetic study of the results is to be implemented.

2. Materials and methods

Sodium chloride (NaCl) (Fluka Chemica, Switzerland) was used for the preparation of simulated salt solutions, and dibenzo-18-crown-6 (CE_{org}) (Mw = 360.4 g/mol, Fluka Chemica, Switzerland) was used as the mobile carrier (MC). Soluble starch (a polysaccharide) (S.S) (Mw = 126.16 g/mol, Fisher Chemical (was used as the sequestering agent (SA) in the RP. Dichloroethane (DCE) (BDH Chemicals Ltd, England) was chosen as the LM.

2.1. Set-up

Fig. 1 presents a schematic diagram of the devised cell. It is composed of a cylindrical 600-ml beaker, in which a glass cylinder having a diameter of 6.5 cm and opened from both ends is suspended, using a plexi-glass sheet to grip onto it firmly and keep it in place. The lower end of the inner cylinder is veiled

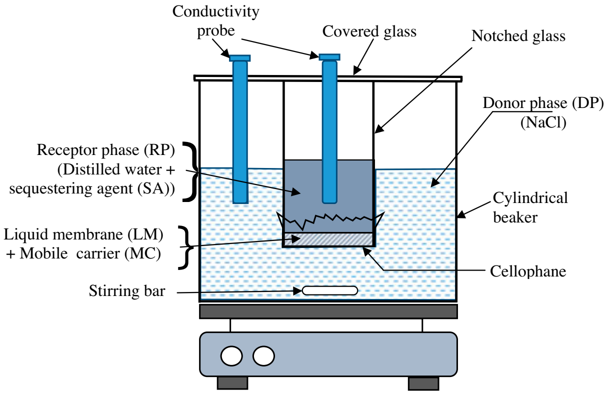

Fig. 1. Apparatus used in SLM experiments.

with a cellophane membrane, which is stretched and held firmly in position using rubber bands. The DP is added to the beaker and the RP is added to the inner notched cylinder above the LM placed onto the cellophane. The cell is covered with a watch glass to prevent evaporation. Agitation of the lower phase inside the beaker is induced by magnetic stirring.

2.2. Procedure

A known volume of saline water (DP) is added to the beaker. The cylinder with the stretched cellophane in place is then placed inside the beaker such that it is suspended in its center. A known volume of the organic LM is added to the cylinder, followed by a known volume of the RP which contains a complexation agent, after which the cylinder is covered with the watch glass. The levels of both DP and RP are marked on the glass. Magnetic stirring is then started in the DP. Conductivity meter was used to follow the salinity of DP and RP at time intervals.

2.3. Transport equations

The SLM system under study consists of two aqueous phases and an organic LM phase, which contains the carrier. The organic membrane serves as a uniform barrier between the two aqueous phases. This technique contains two processes in a single stage: (i) extraction of sodium ion from the aqueous DP to the organic LM phase and (ii) re-extraction of the sodium ions from the LM to the aqueous RP [28].

In the present case, the mechanism of LM permeation is typically facilitated uphill transport in which a dibenzo-18-crown-6 (CE_{org}) in the LM phase complexes with the Na^+ of the carrier diffuses from the DP/LM interface to the LM/RP interface due to the concentration gradient, then decomplexes giving up the Na^+ to the RP. The free CE_{org} diffuses back from the LM/RP interface to the LM/DP interface as a result of its concentration gradient, and the cycle of forward and backward diffusion within the LM is repeated. In this way, the Na^+ is transported across the LM to the RP and the water becomes desalinated. The Cl^- anion is attracted to the positive Na^+ cation due to electro-neutrality reasons and is thereby transported along with it across the LM phase to the RP. It is noteworthy that the role of the semipermeable cellophane is to hold the LM layer while concomitantly preventing it from diffusion to the DP due to its hydrophilicity. Fig. 2 depicts the mechanism by which the Na^+ forms a complex with the CE_{org} showing the attracted Cl^- anion to the Na^+ cation.

In the DP/LM interface, sodium ions react with the dibenzo-18-crown-6 (CE_{org}) as follows [13,20,29,30]:

$$CE_{org} + Na^+Cl^- \xrightarrow{k_{1d}} (CE - NaCl)_{org} \quad \text{(complexation)} \tag{1}$$

The reaction on the LM/RP interface will be:

$$(CE - NaCl)_{org} \xrightarrow{k_{2m}} CE_{org} + Na^+Cl^- \quad \text{(decomplexation)} \tag{2}$$

Soluble starch (S.S) is a relatively inexpensive and biodegradable biopolymer, which is expected to cause minimum pollution to the environment, and was chosen in our work as a SA for sodium ion while the latter carried over chloride ions with it. It is known that starch consists of amylose (a straight chain polymer) and amylopectin (branched chain polymer) [31]. The presence of hydroxyl groups in the starch molecules is known to form a relatively stable complex with cations such as sodium ion through a coordinate bond in which the slight electronegativity of the oxygen

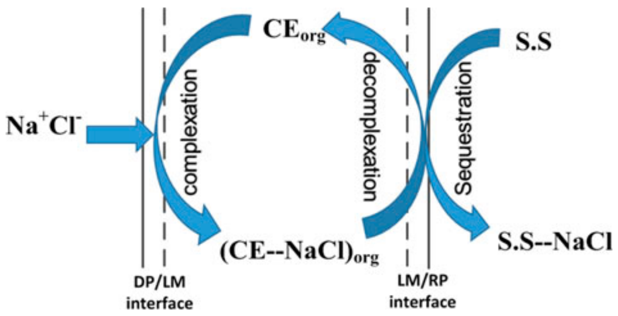

Fig. 2. Schematic of NaCl transport through the SLM.

atom renders it attracted to the positive sodium cation. Concomitantly, the negative chloride ion is attracted to the electropositive hydrogen atom of the hydroxyl group. In this way, Na^+ ion is attracted to both O atom of the hydroxyl group fixed on the starch chain, plus a Cl^- ion, while Cl^- ion is attracted to both H^+ of the hydroxyl groups and Na^+ ions, thus forming a coordinate bond [17,32,33]. This reaction could be expressed as the following:

$$\mathrm{S.S} + \mathrm{Na^+Cl^-} \xrightarrow{k_{2r}} \mathrm{S.S-NaCl} \quad \text{(sequestration)} \tag{3}$$

Kinetic behavior can be successfully described by general scheme involving two consecutive irreversible first-order steps and the first-order reactions occurred in the carrier-mediated LM systems, and can be analyzed by non-steady state kinetics approximation as [18,19]:

$$\mathrm{DP} \xrightarrow{k_1} \mathrm{LM} \xrightarrow{k_2} \mathrm{RP} \tag{4}$$

where k_1 and k_2 refer to the apparent membrane entrance and exit rate constants, respectively.

The NaCl concentrations in the DP, LM, and RP at time t are C_d, C_m, and C_r, respectively. Since the dimensionless concentration changes are very small, reduced concentrations (R) are used and defined as [20,22]:

$$R_d = \frac{C_d V_d}{C_{d_0} V_{d_0}}, \quad R_m = \frac{C_m V_m}{C_{d_0} V_{d_0}}, \quad R_r = \frac{C_m V_m}{C_{r_0} V_{r_0}} \tag{5}$$

where R_d, R_m, and R_r are reduced NaCl concentrations in DP, LM, and RP, respectively; V_d, V_m, and V_r are volumes of DP, LM, and RP, respectively; and C_{d0} and V_{d0} is the initial concentration of NaCl and the volume of DP at $t = 0$, respectively.

The variation of NaCl concentration with t was measured directly in DP and RP, while the corresponding change in the LM was established from the material balance ($R_d + R_m + R_r = 1$). Using reduced concentrations, the following rate equations may be written for the above proposed kinetic scheme using first-order time differentiation, which leads to the final forms of flux equations [18,20,23,24,28]:

$$\frac{dR_d}{dt} = -k_1 R_d \equiv J_{d/m} \tag{6}$$

$$\frac{dR_m}{dt} = k_1 R_d - k_2 R_m \tag{7}$$

$$\frac{dR_r}{dt} = k_2 R_m \equiv J_{m/r} \tag{8}$$

Integration of the first-order differential equations Eqs. (6)–(8) leads to relationships giving the time evolution of NaCl concentration in the three phases and non-steady state kinetic regime may be described by the following rate equations [18,20,23,24]:

$$R_d = \exp(-k_1 t) \tag{9}$$

$$R_m = \frac{k_1}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \tag{10}$$

$$R_r = 1 - \frac{1}{k_2 - k_1}[k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] \tag{11}$$

Substituting Eqs. (9)–(11) in the first-order time differentiation of Eqs. (6)–(8) leads to the final forms of flux equations as [21,23]:

$$\frac{dR_d}{dt} = -k_1 \exp(-k_1 t) \equiv J_{d/m} \tag{12}$$

$$\frac{dR_m}{dt} = \frac{k_1}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \tag{13}$$

$$\frac{dR_r}{dt} = \frac{k_1 k_2}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \equiv J_{m/r} \tag{14}$$

R_m has a maximum, the time at which it occurs being obtained from $dR_m/dt = 0$ [23]:

$$t_{max} = \left(\frac{1}{k_1 - k_2}\right) \ln\left(\frac{k_1}{k_2}\right) \tag{15}$$

The maximum value of R_m (when $dR_m/dt = 0$) is calculated from [20,21]:

$$R_m^{max} = \left(\frac{k_1}{k_2}\right)^{-k_2/(k_1 - k_2)} \tag{16}$$

The complexity of these equations prevents simple comparison of kinetics observed for different membrane materials. Therefore, it is useful to examine and compare maximum release rates, which can be attained in a given experimental condition. Substituting t in Eqs. (12)–(14) by its maximum value obtained in Eq. (15), one can obtain [22]:

$$\left.\frac{\mathrm{d}R_{\mathrm{d}}}{\mathrm{d}t}\right|_{\max} = -k_1\left(\frac{k_1}{k_2}\right)^{-k_1/(k_1-k_2)} = J_{\mathrm{d}}^{\max} \tag{17}$$

$$\left.\frac{\mathrm{d}R_{\mathrm{m}}}{\mathrm{d}t}\right|_{\max} = 0 \tag{18}$$

$$\left.\frac{\mathrm{d}R_{\mathrm{r}}}{\mathrm{d}t}\right|_{\max} = k_2\left(\frac{k_1}{k_2}\right)^{-k_2/(k_1-k_2)} \equiv J_{\mathrm{r}}^{\max} \tag{19}$$

We see that, $t = t_{\max}$, the system is in steady state since the concentration of NaCl in the membrane (R_{m}) does not vary with t, Eq. (18). Because the penetration (J_{d}) and exit (J_{r}) fluxes are equal but of opposite sign [18,22]:

$$-J_{\mathrm{d}}^{\max} = +J_{\mathrm{r}}^{\max} \tag{20}$$

From the kinetic model given above, the actual numerical analysis was carried out by non-linear curve fitting using a JavaScript iteration program [34]. The first rate constant, k_1, was obtained from Eq. (9) using the DP data and referred as ($k_{1\mathrm{d}}$), while the membrane exit rate constant, k_2, may be obtained either directly from the RP kinetic data ($k_{2\mathrm{r}}$) using Eq. (11) or indirectly from the membrane phase data calculated on the basis of Eq. (10) ($k_{2\mathrm{m}}$). In both cases, the $k_{1\mathrm{d}}$ value obtained from Eq. (9) was used in the calculations. The values of $t_{\max}$, $R_{\mathrm{m}}^{\max}$, $J_{\mathrm{d}}^{\max}$, and $J_{\mathrm{r}}^{\max}$ were calculated by means of substituting the values of the kinetic rate constants in related Eqs. (15)–(19), respectively. In addition, NaCl concentrations in each phase were determined using the kinetic model Eqs. ((9)–(11)).

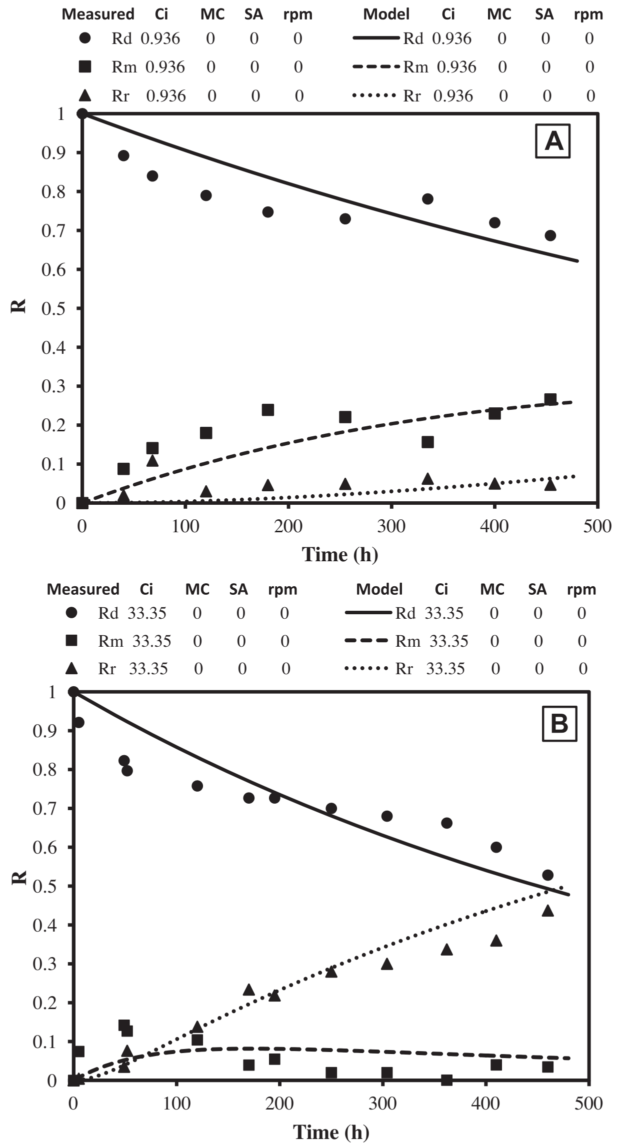

Fig. 3. Time variation of reduced concentrations of NaCl in DP, LM, and RP (R_{d}, R_{m}, and R_{r}) at MC = 0 for initial donor concentration (A) 0.936 g/l and (B) 33.35 g/l.

3. Results and discussions

3.1. Effect of initial concentration (C_i)

The results illustrating this variable are presented in Fig. 3(A) and (B), in which reduced concentrations (R_{d}, R_{m}, and R_{r}) plotted vs. time of operation. Fig. 3, in which the volume ratio of DP: RP = 2:1, with no stirring, no MC, and no SA added, indicates that when C_{i} of DP was in the range of simulated seawater (33.35 g/l), the rate of decrease in R_{d} was moderate and the percent extraction of NaCl from DP was about 50%, and it is obvious that the driving force was the concentration gradient, even though no MC and no stirring were used. This result proves that in the present technique, the LM supported on cellophane sheet allowed NaCl to diffuse through it from DP to RP, since the LM is very thin. Accordingly, the resistance to diffusion in the LM is very low. On the other hand, when C_{i} was very dilute (0.936 g/l), the concentration driving force was very small between the DP and RP, and therefore, the rate was appreciable during the beginning of the experiment in the two phases, after which R_{d} did not undergo any change and the % extraction was only 38%. A final note is that over 500 h were necessary for the DP and RP plots to cross each other, i.e. for desalination to take place in case of high concentration of NaCl. This result proves that the present SLM technique might be promising in case a suitable MC and SA are present in both LM and RP, respectively, especially in the presence of specific stirring speed of the DP.

This result found disagreement with that obtained by Naim and Monir [15] who conducted desalination of saline water by the SLM technique, in which preliminary work with chloroform (CF) as LM and no additives, in either LM or RP that did not result in any desalination, and in which 13 ml of DCE was used as LM phase, containing 3 g of CE, and 100 ml of RP with a volume ratio of DP: RP, kept constant at 4:1, was used. It was found that the mass transfer is very slow and mass of NaCl transported was negligible, and very poor desalination took place. The large volume ratio of DP: RP must have been one main reason for this result. However, it should be observed that the volume of DCE used in the present work was only 2 ml, accordingly, in the following experiments, 0.0538 mol of MC/l of LM were added. It is observed that under simulated seawater concentration conditions, the rate of change of R_d with time was higher in the presence of MC than in its absence (Fig. 4(A) and (B)). The rate of change after about 60 h was triple than that in the absence of MC in both DP and RP phases, which shows the importance of the MC in transporting the NaCl through the LM phase. From Fig. 4(B) also, brackish water concentration (15.5 g/l) resulted in slower transfer of NaCl in the DP but appreciable increase in the RP. This was expected since neither stirring was applied in the DP nor RP phases in the present cases, which took 60 h of operation required which is almost triple the time in the absence of MC. It was also noted that R_d and R_r plots crossed each other almost at the same time, which clarifies the importance of presence of MC which is much more important than the C_i.

By inspecting Table 1, it is obvious that the membrane entrance (k_{1d}) rate constant was much higher in case of high C_i. The same observation was also concluded for both (k_{2m}) and (k_{2r}) rate constants which were much higher; additionally, using high C_i led to a great decrease in t_{max} and great increase in J^{max} which clarifies the importance of the concentration driving force in the transfer of the NaCl molecules from DP to RP. This conclusion can be observed from Table 2 in which the C_i was 32.12 and 15.5 g NaCl/l which is not the same great difference as in the previous case. Here, we can find that the constants are close to each other, also t_{max} and J^{max}, but they are very far from that of the previous case in which no MC was used, which signifies that using MC in the LM is a crucial factor. Furthermore, by inspecting the values of R_m^{max} in the two cases (0.936 and 33.35 g/l as C_i), it can be concluded that with low C_i, there is no driving force to enhance transfer of NaCl, and consequently, t_{max} was 5 times that of the high C_i and also J^{max} in case of high C_i is threefold that of the low C_i. The values of k_{1d}/k_{2m} ratio express the transport efficiency [20].

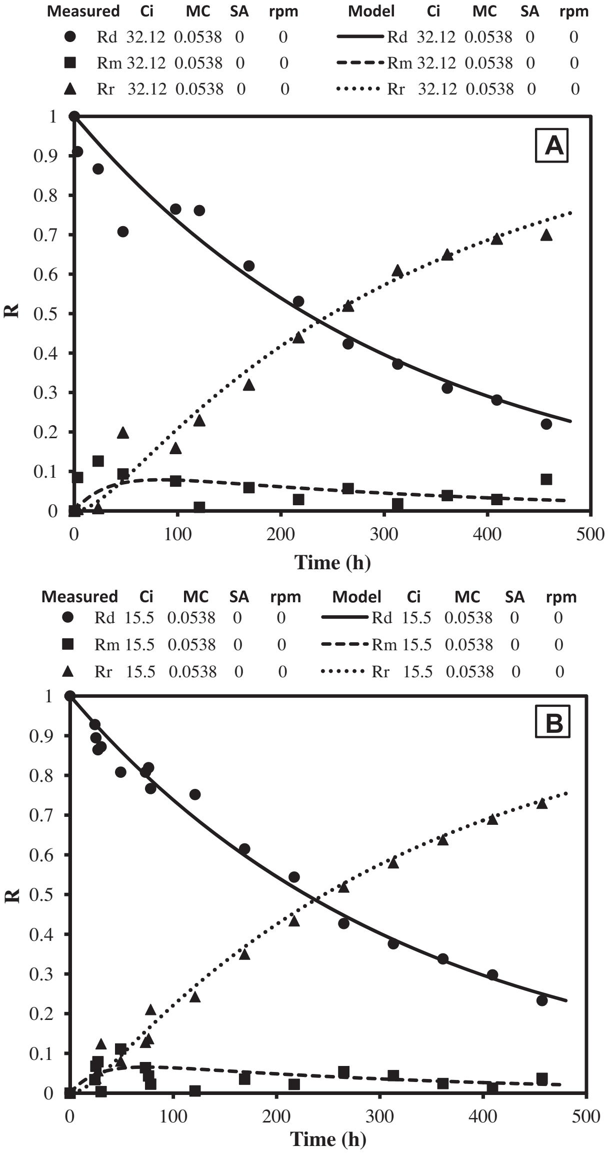

Fig. 4. Time variation of reduced concentrations of NaCl in DP, LM, and RP (R_d, R_m, and R_r) at MC = 0.0538 mol/l of LM for initial donor concentration (A) 32.12 g/l and (B) 15.5 g/l.

3.2. Effect of C_i in presence of MC

The MC selected in the present work was not chosen haphazardly. A macrocyclic ligand (crown ether) was specifically chosen to do the job. Peterson and Lamb [35] managed to prepare numerous crown ethers that contain cavities of different sizes formed of

Table 1
Kinetic parameters at different initial concentrations (MC = 0, SA = 0, and no stirring)

C_i (g/l)	$k_{1d} \times 10^{-3}$ (h^{-1})	$k_{2m} \times 10^{-3}$ (h^{-1})	$k_{2r} \times 10^{-3}$ (h^{-1})	R_m^{max}	t_{max} (h)	k_{1d}/k_{2m}	$J^{max} \times 10^3$ (h^{-1})
0.936	0.991 ± 0.29	1.542 ± 0.98	0.798 ± 0.69	0.290	802.4	0.643	0.395
33.35	1.538 ± 0.28	14.421 ± 3.92	36.396 ± 18.50	0.082	173.7	0.107	1.284

Table 2
Kinetic parameters at different initial concentrations in the presence of MC (MC = 0.0538 mol/l of LM, no SA, and no stirring)

Initial conc. (g/l)	$k_{1d} \times 10^{-3}$ (h^{-1})	$k_{2m} \times 10^{-3}$ (h^{-1})	$k_{2r} \times 10^{-3}$ (h^{-1})	R_m^{max}	t_{max} (h)	k_{1d}/k_{2m}	$J^{max} \times 10^3$ (h^{-1})
32.12	3.089 ± 0.76	30.287 ± 9.26	41.659 ± 22.18	0.079	83.9	0.102	2.453
15.5	3.036 ± 0.26	37.138 ± 7.34	57.958 ± 15.06	0.065	73.4	0.082	2.517

ether groups linked to each other, within which positive cations may be held by attraction of the negative ether groups in the cyclic polyether structure. If the atomic volume of the cation is larger than the cavity size of the polyether ring, the former cannot be contained within the polyether cavity, accordingly the crown ether is unable to complex with the cation and the latter will not be transported across the LM phase. On the other hand, if the cation volume is smaller than the cavity size, the attraction between the positive cation and the negative ether moieties will be weak, such that the required complex between them will not be possible due to the larger distance between both cation and negative ether moieties, resulting in a weak electrostatic bond, causing a poor complex unable to transfer the cations to the RP. To this end, dibenzo-18-crown-6 was specifically chosen for the extraction of the NaCl molecules from the DP, in which the Na ion will exactly fit inside the polyether cavity and can be decomplexed at the same time. In other words, complexation and decomplexation can be easily effected when conditions are favorable [17].

Fig. 4 presents the effect of presence of MC in the LM. The figure shows that the presence of MC accelerates diffusion of NaCl via the LM and that the time required for reaching the highest reduced concentration of NaCl in the LM was 73.4 and 83.9 h at initial NaCl concentrations 15.5 and 32.12 g/l, respectively (Table 2). On the other hand, the absence of MC led to the to and fro diffusion of NaCl in the DP since no complexation in the LM will occur, and thus, mass transfer from DP to LM will not take place.

3.3. *Effect of quantity of MC*

Many authors investigated the presence of MC in the LM phase [15,36–43] and they found that the presence of MC in the LM is of utmost importance in order to enhance the rate of mass transfer. Fig. 5(A) and (B) clarifies the effect of quantity of the selected MC in which the latter is 0.0538 and 0.0269 mol/l of LM, respectively. It is noteworthy that in the second experiment, the quantity of MC is half that of the first, the other variables remaining constant ($C_i \cong 31$ g/l, SA = 0.0617 mol/L of RP, 100 rpm). It is observed that the initial rate of mass transfer was higher when MC was halved. However, the rate in the case of the higher quantity of MC increases after the point of intersection. An explanation to this observation is as follows: initially due to the presence of large quantity of NaCl molecules, the higher MC dose results in crowding of the LM phase due to the to and fro motion from DP to RP of the complex, and free MC in the reverse direction, respectively, causing uneasy diffusion and a sort of traffic jam within the LM phase [44–48]. On the other hand, when half the dose of the amount of MC is present, this phenomenon was not observed since much less traffic jam due to shuttling of the MC within the LM takes place. However, as plenty of the NaCl has been transferred, the LM phase was depleted in NaCl resulting in free diffusion due to decrease in crowding in the LM, and in this case, the greater amount of MC assisted in the rapid transfer within the LM.

As shown in Table 3, it was demonstrated that the rate constants were not that much different in both cases when using 0.0269 and 0.0538 mol of MC/l of LM. However, t_{max} was higher in case of the smaller

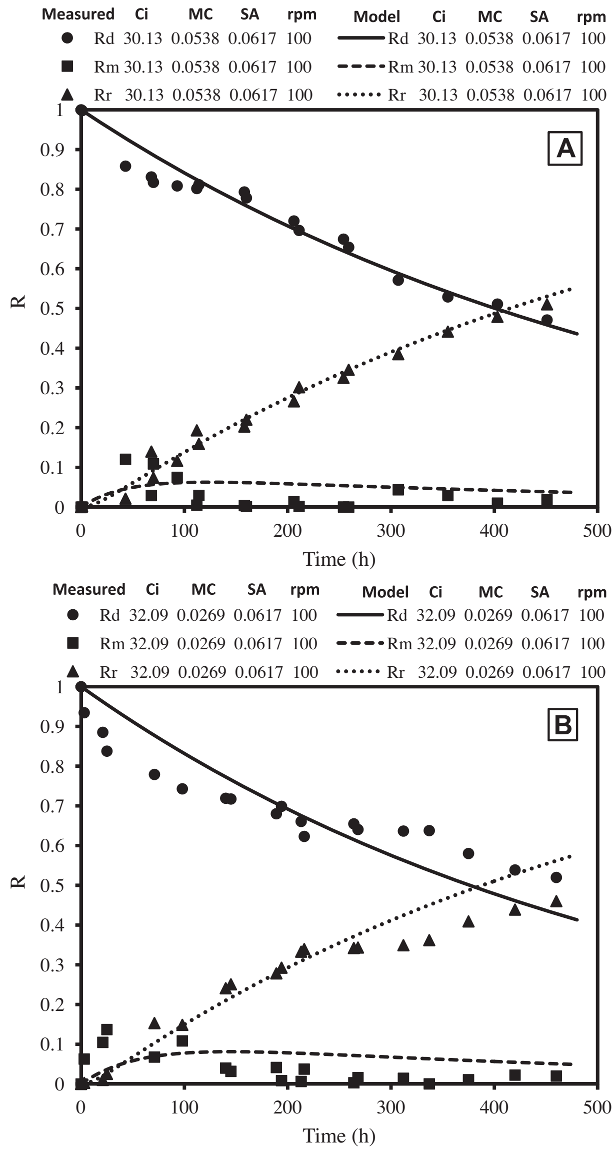

Fig. 5. Time variation of reduced concentrations of NaCl in DP, LM, and RP (R_d, R_m, and R_r) at $C_i \cong 31$ g/l for quantity of MC (A) 0.0538 mol/l of LM and (B) 0.0269 mol/l of LM.

amount of MC, while J^{max} was not higher in case of using large amount of MC. Conclusively, and as mentioned before, it is preferable to use the small amount of MC to avoid the crowding of MC molecules at the membrane RP interface. It is worth noting that less quantity of MC leads to cost saving.

3.4. Effect of quantity of SA

Inspecting Fig. 6(A) and (B) proves that the presence of SA in the RP concomitantly with the MC causes the DP and RP relationships with time to be steadier than the previous cases aforementioned, due to the presence of the MC and SA combined. This is manifested by the higher values obtained for the correlation coefficient in the two cases studied. It is observed that the presence of 0.0617 mol of SA/l of RP improved the rate of transfer of NaCl as compared to the case in which 0.1233 mol of SA/l of RP was added and consequently improved the % extraction to be 64% when using 0.0617 mol of SA/l of RP instead of only 46% when using 0.1233 mol of SA/l of RP (Fig. 6(A) and (B)). This is surely attributed to the increased viscosity of the soluble starch, which caused the rate of diffusion through the stagnant RP to slowdown in the case of the higher dose of SA. However, in the case of 0.1233 mol of SA/l of RP, it is shown that the two DP and RP curves level off by time and it appears that they are not expected to intersect. Conclusively, from this figure, it is confirmed that SA = 0.0617 mol/l of RP is preferred to 0.1233 mol/l of RP. Accordingly, despite that no stirring is conducted in the DP, yet in the presence of the most suitable doses of SA plus MC, the time necessary for complete transfer of NaCl from DP to RP computed from this figure is dependable, and expected to be the most accurate.

These observations can be concluded also from Table 4 in which it is clear that the entrance rate constant (k_{1d}) describing the higher rate of transfer of NaCl in case of 0.0617 mol/l of RP than in the other case, also the flow rate is higher (J^{max}).

3.5. Effect of stirring speed of DP

Two different conditions are investigated in which either slow stirring (100 rpm) or moderate stirring (200 rpm) in the DP was applied. Fig. 7(A) indicates

Table 3
Kinetic parameters at different quantities of MC ($C_i \cong 31$ g/l, SA = 0.0617 mol/l of RP, and 100 rpm)

Quantity of MC (mol/l of LM)	$k_{1d} \times 10^{-3}$ (h^{-1})	$k_{2m} \times 10^{-3}$ (h^{-1})	$k_{2r} \times 10^{-3}$ (h^{-1})	R_m^{max}	t_{max} (h)	k_{1d}/k_{2m}	$J^{max} \times 10^3$ (h^{-1})
0.0269	1.842 ± 0.15	17.382 ± 2.63	84.259 ± 54.94	0.081	144.4	0.106	1.626
0.0538	1.729 ± 0.09	22.266 ± 3.72	72.193 ± 23.72	0.063	124.4	0.078	1.525

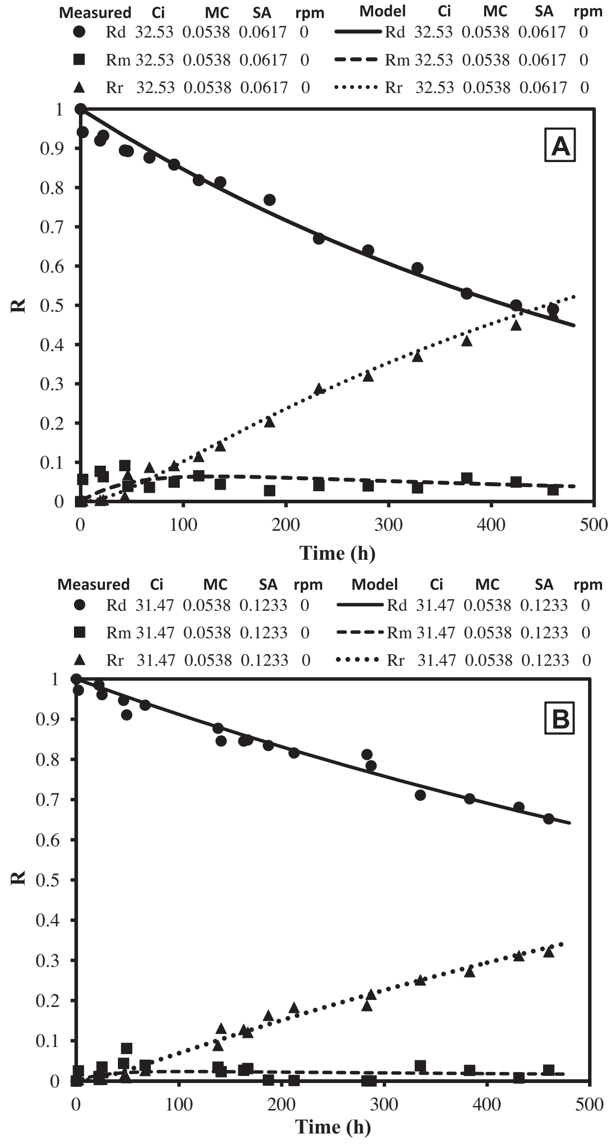

Fig. 6. Time variation of reduced concentrations of NaCl in DP, LM, and RP (R_d, R_m, and R_r) at $C_i \cong 32$ g/l for quantity of MC (A) 0.0617 mol/L of RP and (B) 0.1233 mol/L of RP.

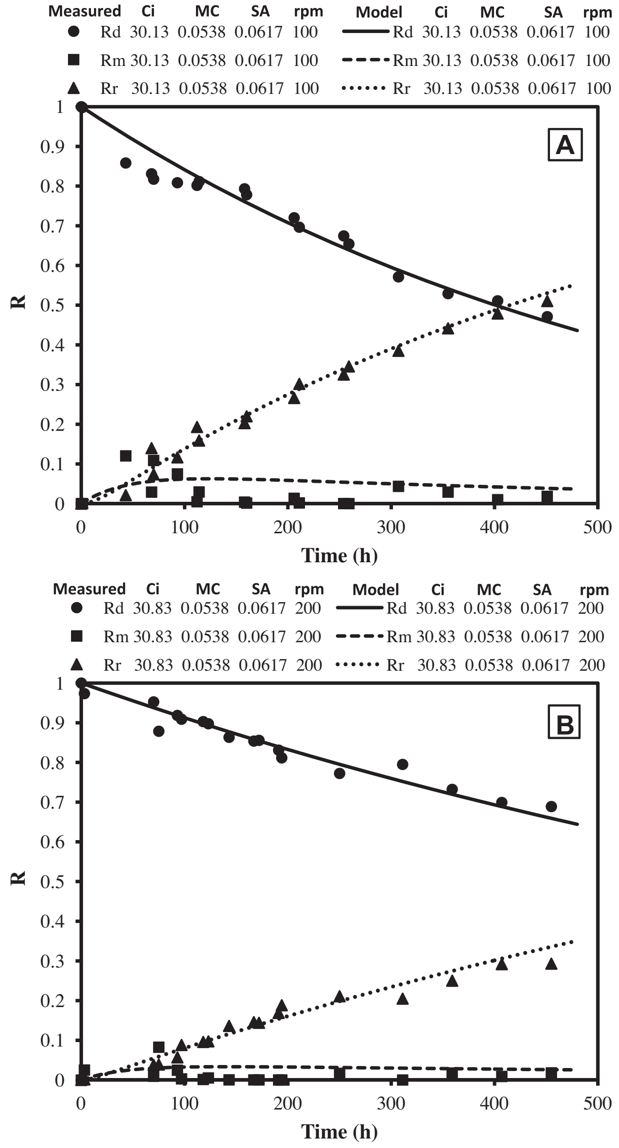

Fig. 7. Time variation of reduced concentrations of NaCl in DP, LM, and RP (R_d, R_m, and R_r) at $C_i \cong 30$ g/l for stirring in the donor phase (A) 100 rpm and (B) 200 rpm.

that slow stirring (in the presence of the indicated quantities of SA and MC arrived at) was better than at 200 rpm. This was expected since in case of moderate stirring, mass transfer from DP via the cellophane sheet, LM phase, to the RP depends on molecular diffusion, and convective mass transfer is almost absent.

Table 4
Kinetic parameters at different quantities of SA ($C_i \cong 32$ g/l, MC = 0.0538 mol/l of LM, and no stirring)

Quantity of SA (mol/l of RP)	$k_{1d} \times 10^{-3}$ (h^{-1})	$k_{2m} \times 10^{-3}$ (h^{-1})	$k_{2r} \times 10^{-3}$ (h^{-1})	R_m^{max}	t_{max} (h)	k_{1d}/k_{2m}	$J^{max} \times 10^3$ (h^{-1})
0.0617	1.669 ± 0.14	20.970 ± 4.20	26.865 ± 4.42	0.064	131.1	0.080	1.367
0.1233	0.924 ± 0.05	35.932 ± 4.59	44.161 ± 11.20	0.023	104.6	0.026	0.845

Table 5
Kinetic parameters at different speed of stirring ($C_i \cong 30$ g/l, MC = 0.1286 g, and SA = 0.5 g)

Stirring speed (rpm)	$k_{1d} \times 10^{-3}$ (h^{-1})	$k_{2m} \times 10^{-3}$ (h^{-1})	$k_{2r} \times 10^{-3}$ (h^{-1})	R_m^{max}	t_{max} (h)	k_{1d}/k_{2m}	$J^{max} \times 10^3$ (h^{-1})
100	1.729 ± 0.09	22.266 ± 3.72	72.193 ± 23.72	0.063	124.4	0.078	1.525
200	0.916 ± 0.05	24.037 ± 4.25	118.141 ± 87.41	0.033	141.3	0.038	0.865

Meanwhile, moderate stirring tends to slice the NaCl molecules away from the cellophane membrane, in such a way that it does not give enough time for NaCl molecules to diffuse through the cellophane to the LM then the RP, due to the formation of eddies below the cellophane surface. On the other hand, slow stirring obviates the drawbacks caused by moderate stirring. This result found disagreement with that obtained by Muthuraman et al. [39], who used tri-n-butyl phosphate (TBP) as carrier for the transport of chromium (VI) through a hexane BLM. The transport efficiency of chromium(VI) by TBP was found to be improved by increasing the speed of stirring till 300 rpm; however, this result agrees with those obtained by Naim and Monir [15], and Naim et al. [37].

Table 5 clarifies that applying slow stirring improves the flow of NaCl molecules (J^{max} = 1.525 and 0.865 at 100 and 200 rpm, respectively) and also reduces the t_{max} from 141.3 to 124.4 h at moderate and slow stirring rate, respectively.

4. Conclusions

From the present work, the following conclusions were drawn: desalination can be effected by LMs particularly SLMs, the presence of cellophane functioning as support for the LM presents an added resistance to diffusion. A suitable amount of MC is essential in effecting desalination, otherwise the rate is very low when MC = zero or is present in a larger than necessary dose. SA is favorable in capturing the NaCl in the RP, and its exact amount is crucial. Solubility of LM in water should be negligible. The volume ratio of DP to RP is not a crucial factor in controlling the degree of desalination arrived at. C_i is an important factor in the range of brackish water to seawater concentrations. Finally, applying slow stirring improves the flow of NaCl molecules and obviates the drawbacks caused by either absence of stirring or moderate stirring. The kinetics of NaCl transport across SLM is accomplished on the basis of a scheme implying two consecutive irreversible first-order reactions and the kinetic parameters k_{1d}, k_{2m}, k_{2r}, R_m^{max}, t_{max}, and J^{max} were also calculated. It was concluded that k_{1d}, k_{2m}, k_{2r} were of high vales in case of high C_i and when using 0.0617 mol of SA/l of RP, while maximum flux (J^{max}) was reached when C_i was in the range of brackish water, MC = 0.0538 mol/l of LM, no SA and no stirring. Also, t_{max} reached its minimum value under the same aforementioned conditions.

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