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# Automated prototype for desalination by emulsion liquid membrane technique

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## ABSTRACT

In the present work, a prototype was devised and constructed as a preliminary step for the development of industrial scale process in which desalination by an emulsion liquid membrane (ELM) technique takes place. The process is intended to be a breakthrough in the field of desalination, which should compete with the currently used reverse osmosis (RO) technique. A drawback of RO is the high cost of membrane and intensive pretreatment of seawater. The prototype consists of three stages: emulsion formation, desalination operation, and separation of the product into two phases (desalinated water and spent emulsion). The latter could be then adjusted and recycled for reuse in a second cycle. Several investigated factors which could affect the desalination process were: initial concentration (Ci), volume ratio of liquid membrane (LM) to receptor phase (RP), quantity of emulsifier, type of liquid membrane, type and quantity of sequestering agent (SA), time and power of ultrasonication (US), presence of mobile carrier (MC) and finally treatment ratio (ratio of volumes of donor phase (DP) to emulsion) (TR). The best conditions arrived at were: volume ratio of LM:RP = 4:1, necessary in forming a stable emulsion. The optimum quantity of MC was found to be 6.86 g Span 80 for 80 ml chlorobenzene and 20 ml 20% soluble starch, so that best transfer of the NaCl could take place from DP to RP. Soluble starch (2% b.w.) is a suitable sequestrant for NaCl, chlorobenzene was better than chloroform, the latter is better than Soltrol 220 as LM. It was also found that 5 min at 180 Watts of US to provide a stable emulsion. The quantity of emulsifier and Ci are of crucial importance that affects directly the desalination process.

*Keywords:* Emulsion; Liquid membrane; Prototype; Desalination; Emulsifier; Mobile carrier

## 1. Introduction

Liquid membranes (LMs), developed by Li [1], have gained great acceptance as a separation technique. They are generally divided into bulk-, supported- and emulsion-LMs. The latter type in particular overcomes the problems encountered in solid membranes, in that it offers much more rapid mass transfer and also vast interfacial area for transfer that varies between 3000 to 6000 $m^2/m^3$ of equipment volume compared to 10–20 $m^2/m^3$ and 100–200 $m^2/m^3$ in the case of bulk LM and supported LM, respectively. This large mass transfer area can be achieved in small sized equipment without the need for mechanical support. Thus, emulsion liquid membrane (ELM) is an attractive alternative for the separation of mixtures in an efficient manner and has made significant impact in the field of separation engineering. ELM in different formulations renders it an extremely versatile process useful for different applications. This includes waste water treatment [2,3], minerals recovery [4–7], hydrocarbon separation [8,9] and a number of biochemical and biomedical applications [10,11].

ELMs consist of an internal aqueous receptor phase (RP) stabilized by a surface active agent (emulsifier) and

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dispersed as very fine droplets inside an organic membrane phase (LM). The resulting water-in-oil (W/O) liquid emulsion, is then dispersed as emulsion globules in the external feed (donor) phase (DP). The solute in the DP transfers across the LM phase into the RP during the extraction process. As a result, the emulsion is dispersed in the DP, and the solute transfers due to the concentration gradient between DP and RP, in which the organic LM phase functions as a barrier. The DP is subsequently separated from the emulsion by settling, followed by demulsification. The latter is carried out to separate the phases that makeup the emulsion (RP and LM phases). Finally, the membrane phase can be reused and the receptor phase (enriched in the recovered solute) can be recycled or recovered for solute [12].

From different types of LMs available in the literature, ELMs have the advantage of high surface areas, fast extraction/stripping process, high efficiency and require low energy and small quantities of extractant. ELM has been recognized as an effective method for ion separation and concentration, when the component to be extracted is present in very low concentration. Choosing a suitable extractant or MC, between other operational conditions, is one of the key factors that control the ion extraction efficiency. In order to achieve the best extraction conditions at the minimum operational time, different extractants have been used, among them, tertiary amines [13], TOPO/Cyanex921 and cyanex923 [14,15], trioctylamine [16], tributyl phosphate [17], aliquat-336 [18–20] and D2EHPA [21]. The size of the internal phase droplets, and organic phase stability are important factors related with the ELM efficiency. To enhance the ELM stability, additives in the organic phase, such us surfactants and paraffin (higher interfacial surface tension and viscosity) have been used by several researchers [21–25].

Although this method is very effective and has been successfully applied for removal of several types of pollutants, but so far its commercial applications have been limited by the emulsion instability. The common emulsion instability includes membrane leakage, coalescence, and emulsion swelling. The lack of stability of the emulsion globules will decrease extraction efficiencies. On the other hand, a too stable emulsion causes new problems during its settling and demulsification in the third stage. In order to solve the stability problem of ELM, its formulation design which is foremost important, includes selection of carrier, strip agent, surfactant, diluents, and preparation method.

Continuous operation is more suitable for treatment of large volume of waste water. Removal by ELM has been studied in various types of extractors, including packed column [26,27], mechanically agitated columns [28–30] , and spray column [31–36]. Among these, spray column has the advantage of being simplest in design. Depending upon the density, the dispersed phase is sprayed through the continuous phase either at the top or bottom of the extractor. The interfacial tension of ELM system is low due to the presence of surfactants, and the number of theoretical stages required is few due to use of the facilitated transport mechanism. The volumetric mass transfer coefficient in spray contactor is, however, low. For example, the coefficient was reported to vary between 0.003–0.008 1/s (aqueous velocity = 0.003 m/s and organic phase velocity = 0.001–0.0033 m/s) for acid–water system. This necessitates large contactor height to meet the stringent environmental regulations in waste water treatment [37].

In the present work, an automated prototype was constructed for the desalination of saline water using ELM technique. Different variables were investigated for their effect on the degree of desalination which were: volumetric ratio of membrane phase to receptor phase (LM:RP), initial salt solution concentration (Ci), type and quantity of LM, type and quantity of SA, kind and concentration of SA in RP, quantity of emulsifier, time and power of ultrasonication (US), quantity of mobile carrier (MC) in LM, and finally treatment ratio (volumetric ratio of emulsion- to saline water- phase (DP)).

## 2. Materials and methods

### 2.1. Materials

Chlorobenzene (CB), chloroform (CF) and Soltrol 220 (product of Loba Chemie Pvt. Ltd, India) were used as membrane liquid (LM). Soluble starch (SS) and sucrose (Suc.S) (product of Fisher Chemical, Fisher Scientific, USA) were used as sequestering agent (SA). Dibenzo-18-crown-6 (product of Fluka, USA) was used as MC. Span 80 (Sorbitan mono-Oleate) (product of Fluka, USA) was used as emulsifier. Sodium chloride (product of El-Nasr Chemicals, Egypt) was used in preparing the saline solutions. Distilled water from our lab was used in preparing aqueous solutions.

### 2.2. Equipment

Ultrasonic Processor with specifications (750-Watt Ultrasonic Homogenizers with Temperature Controller, 230 VAC; Min sample size of 0.25 mL; Max sample size of 19000 mL; Frequency of 20 kHz). Conductivity meters (inoLab 7310 P advanced conductivity bench top meter with printer) with specifications (temperature range: 5°C–105°C; conductivity range: from 0 µS to 1000 mS; TDS range: 0–1999 mg/L; salinity range: 0.0–70 ppt; resolution: 3 significant digits). Windshield washer pump with specifications (flow rate 10 ml/s with fluid pressure 88 kPa; consumed voltage 24 V; no-load current 0.2–1 A; Max. continuous current ≤ 1.8 A; ingress protection IP44; insulation resistance ≥ 1 MΩ). Stir-Pak® high-speed, low-torque mixer system; with specifications (speed: 60–6,000 rpm, 230 VAC, Motor (hp): 0.1; Max torque (in-oz): 17; Propellers: Marine style).

### 2.3. Methods

A step by step approach was followed in which the variables were varied rationally, however, the steps followed in the present trials all fall within the following design and methodology. A schematic of the prototype is presented in Fig. 1.

#### 2.3.1. Prototype description

The automated prototype was constructed for conducting the semi-continuous pilot-plant investigation. The

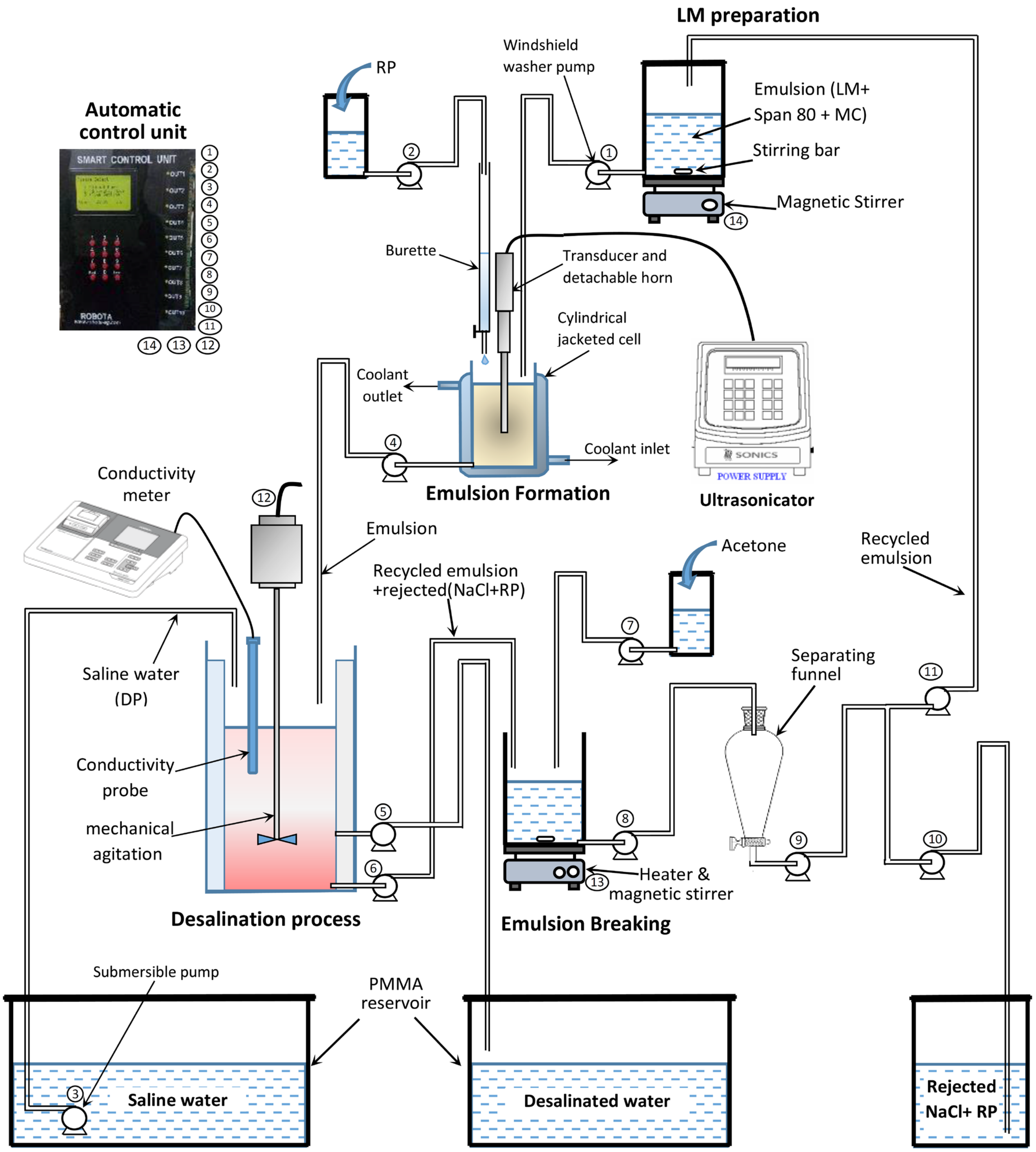

Fig. 1. Schematic diagram of the desalination emulsion liquid membrane prototype.

apparatus comprises an automatic control panel, a power supply, an ultrasonicator, a conductivity meter, a mixer, an electric heater, ten centrifugal pumps (windshield washer pumps), one submersible pump, seven pyrex beakers of different sizes, two large methyl-methacrylate (PMMA) reservoirs, and polyethylene tubing, all installed on a three-storey prototype frame.

### *2.3.2. Emulsion preparation*

On the top storey the emulsion preparation takes place. The LM is mixed with emulsifier (Span 80) using magnetic stirrer. The LM phase is mixed with the starch solution (RP) using an ultrasonicator (US). The starch solution is added drop wise to LM phase in order to prepare the emulsion

[38]. The beakers are connected with windshield washer pumps by polyethylene tubing, and automatic means are used to control the flow of LM, RP, emulsion and saline water, etc. at specified preset times.

### *2.3.3. Desalination process*

The formed emulsion is pumped to the saline water (DP) container in the second storey, after the saline water has been pumped from the saline water reservoir in the third (bottom) storey by means of the submersible pump. The emulsion is pumped, all at once, to the dispersion container through the polyethylene tubing using a windshield washer pump, where it is dispersed in the saline water using the aforementioned mixer (adjusted to a specific speed for a specific time according to the automatic control). The dispersion was carried out in a 2-L glass beaker equipped with four baffles (the baffles' width equals 1/12 of the beaker diameter) to prevent vortex formation by providing proper mixing of the emulsion with the saline water. On completion of dispersion, the latter is left to separate into two phases, the upper being the desalinated water phase, while the lower one is the emulsion phase. The latter is composed of both the spent LM phase together with the starch solution plus captured salt, which will be withdrawn by a windshield washer pump to another container in which the emulsion is broken followed by recycling the LM phase to start another batch. The desalinated water phase is then withdrawn by pumping to the desalinated water reservoir. It is noteworthy that this water will be further treated by activated carbon to free it from any traces of organic matter.

### *2.3.4. Breaking the emulsion*

It should be made clear that the emulsion is broken by heating it to 50°C accompanied with moderate manual stirring, in the presence of a small amount of acetone, this process is of great importance to maintain recycling of the constituents of the emulsion for further using after adjustment of the quantities of these constituents in case of loss of any of them.

## 3. Results and discussions

### *3.1. Effect of volume ratio of LM:RP*

The effect of volume ratio of membrane to internal phase on the liquid emulsion membrane stability was studied by varying the ratio from 1:2 to 4:1. This factor is illustrated in Figs. 2 and 3 in which the ratio of LM:RP were studied at different initial concentrations under equal emulsion constituent ratios. Fig. 2 illustrates the effect of the ratio of LM: RP being 1:2, 2:1 and 4:1 (with adjusted emulsifier quantities) on the degree of desalination at $C_i$ = 17.5 g/L. It is observed from Fig. 2 that degree of desalination is in direct proportionality with this ratio, yielding about 15%, 23% and 30% desalination as the ratio increases from 1:2 through 2:1 to 4:1, respectively. This result could be attributed to the greater uniformity and sufficiency of the LM phase surrounding the internal RP droplets thus providing complete separation between DP and RP phases.

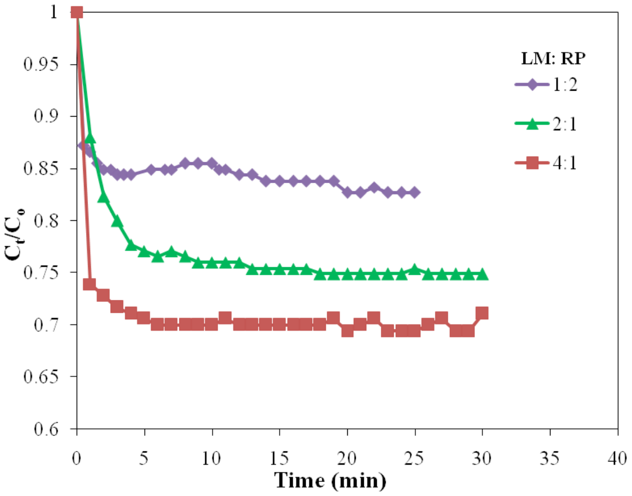

Fig. 2. Degree of desalination at different volume ratios of LM:RP; 1:2 (Emulsion = 3g Span 80 + 33 ml Soltrol 220 + 67 ml 2% SS), 2:1 (Emulsion = 6 g Span 80 + 67 ml Soltrol 220 + 33 ml 2% SS), and 4:1 (Emulsion = 7 g Span 80 + 80 ml Soltrol 220 + 20 ml 2% SS) at $C_i$ = 17.5 g NaCl/L, US = 5 min at 180 W, 200 rpm, TR = 1: 10.

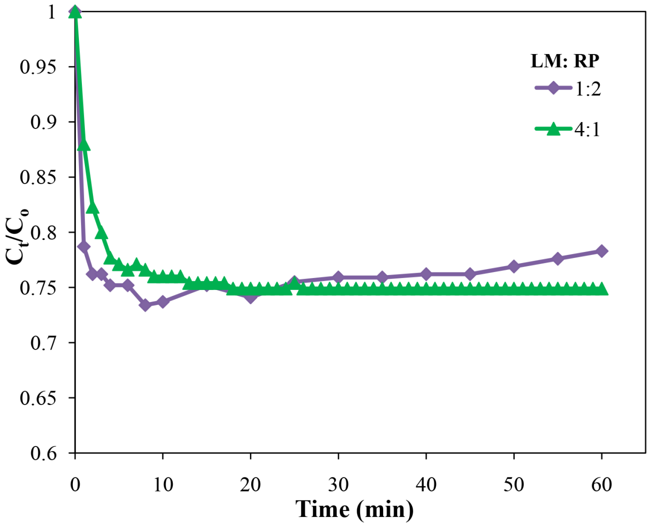

Fig. 3. Degree of desalination at different volume ratios of LM:RP; 1:2 (Emulsion = 3 g Span 80 + 33 ml Soltrol 220 + 67 ml 2% SS), and 4:1 (Emulsion = 7 g Span 80 + 80 ml Soltrol 220 + 20 ml 2% SS) at $C_i$ = 35 g NaCl/L, US = 5 min at 180 W, 200 rpm, TR = 1: 10.

Fig. 3 illustrates the effect of LM:RP ratio at a $C_i$ double the previous value, on the degree of desalination at the minimum and maximum ratios studied in the present work (namely 1:2 and 4:1). It is observed that in the two cases the average desalination is in the thereabouts of 25%, however, it is realized that while a 1:2 ratio gave a rapid desalination rate at the onset of the process, however, the process started to slow down and even decrease gradually, which is probably attributed to the insufficiency of LM to cover the internal phase causing emulsion instability. On the other hand, at 4:1 ratio the rate was slower on the onset of desalination but as the latter progressed, the more stable emulsion droplets allowed desalination to withstand emulsion breakage and proceed in a stable manner. This finding proves that using Soltrol 220 as LM gave optimum desalination at a ratio = 4:1 both at $C_i$ = 17.5 and 35 g/L (30 and 25% in respective order). It is noteworthy, that the previous experiments were conducted in absence of mobile carrier.

Generally, increasing LM:RP ratio increases the emulsion stability. Kumbasar [39] reported that increasing the stripping solution volume made the emulsion unstable and there was leakage of stripping solution into the feed solution, due to an increase of the emulsion viscosity and also an increase of the internal droplets diameter. Increase in droplet diameter decreases the interfacial contact area between the emulsion and the continuous phase and thereby decreases the percentage extraction [40]. Other author reported that the thickness of film in droplets thin off when the volume of the stripping phase increases [41]. For lower LM:RP, the volume of membrane solution is not enough for enclosing all the stripping solution [16]. Conversely, higher LM:RP leads to a thicker and more stable membrane phase, which impedes the diffusing process and increases the consumption of membrane phase [42]. Mortaheb, et al. [43] also revealed that the strength of emulsion wall and its resistance against breakage increases with increasing LM:RP. In the experiment of Wan and Zhang [44], LM:RP could affect the surfactant concentration at the interface of membrane/aqueous phases and in the bulk membrane phase, thus affecting emulsion swelling. They found that entrainment and osmotic swelling increase with increasing LM:RP [4].

### 3.2. Effect of initial concentration

It is well known that many elementary steps are involved during the solute transport in ELM such as: (i) diffusion of the ions through the stagnant layers of DP and RP solutions; (ii) complexation and de-complexation reactions at organic-aqueous interface; and (iii) diffusion of the carrier and ion-carrier in the organic membrane phase; among others [25]. Generally, the complexation and de-complexation reactions do not show chemical limitations, because reaction rates in the membrane are very large compared to diffusion rates. In the present case, the NaCl transport through the LM is mainly governed by the (i) and (iii) steps, where the NaCl transport through the stagnant layer and organic membrane phase is usually represented by Fick's law. Effect of initial concentration can be studied by inspecting Figs. 4 and 5. In the first figure in which Soltrol 220 was used as LM and in which the exact conditions are stated in the figure caption, it is clear that as $C_i$ increases from 10 to 35 g/L so does the degree of desalination, the percent extract varies only between 14 and 27, yet the best result was when $C_i$ was 35.0 g/L, which was expected due to the increase in driving force. However, the relation relating $C_i$ to % desalination was not linear, partially due to the absence of mobile carrier and also the ratio of LM:RP not being optimum (1:2) as proven earlier.

In Fig. 5, CB was used instead of Soltrol 220, and 0.5 g MC were added to the LM phase whereas in case of experiments of Fig. 4. no MC was added, and the ratio of LM:RP was 4:1 instead of 1:2.Thus, much better extractions were achieved (53%, 50% and 77% in case of 35, 17.5 and 10.6 g/L, respectively). The important explanation of the effect of the ratio of LM:RP that was discussed is best explained by comparing Fig. 4 with Fig. 5. The results in Fig. 5 prove that desalination was better in case of dilute NaCl solution, contrary to those obtained in Fig. 4. The reason can be attributed to the presence of MC, which naturally contributes to the diffusion of NaCl through the LM phase by complexation and transfer from the DP/LM interface to the LM/RP interface. Therefore, less NaCl molecules present in the dilute solution are carried over quicker and easier, since no crowding of the complex and MC molecules takes place due to the shuttling effect of both of the aforementioned chemical species in opposite directions. Another reason is that CB was used, which later was found to be a better LM. In addition, the larger ratio of LM:RP was proven to produce a more stable emulsion and a higher percent extraction. Finally, the presence of more Span 80 (6.86 g as compared to 3 g in case of Fig. 4) resulted in a more stable emulsion. Moreover, it has been mentioned by Uddin and

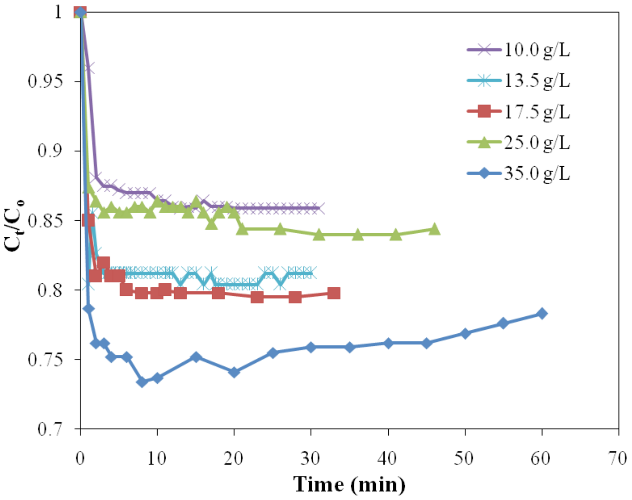

Fig. 4. Degree of desalination at different $C_i$s ($C_i$ = 10, 13.5, 17.5, 25 or 35g NaCl /L, Emulsion = 3 g Span 80 + 33 ml Soltrol 220 + 67 ml 2% SS, US = 5 min at 180 W, 200 rpm, TR = 1: 10, LM: RP = 1:2).

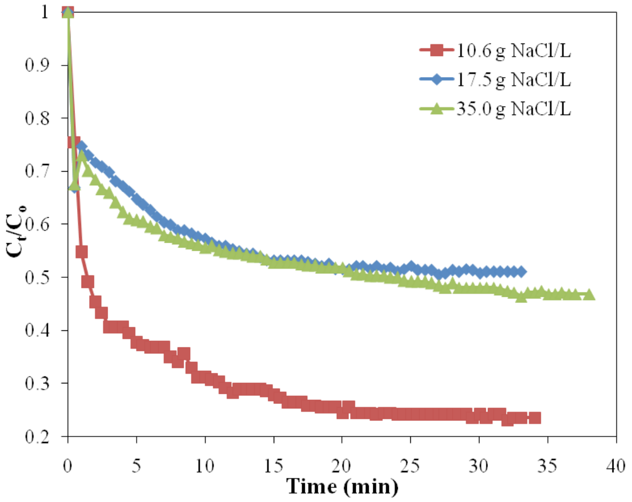

Fig. 5. Effect of initial concentration ($C_i$ = 10.6, 17.5 or 35 g NaCl /L, Emulsion = 6.86 g Span 80 + 80 ml CB+ 0.5 g MC+ 20 ml 2% SS, US= 5 min at 180 W, 200 rpm, TR= 1:10, LM: RP = 4:1).

Kathiresan [45] that some surfactants that are bi-functional act both as emulsifier and carrier, which was noticed in this work, in that Span 80 contributed in carrying NaCl through the LM from DP to RP.

### 3.3. Effect of quantity of emulsifier

Wan and Zhang [44] revealed that the selection of a surfactant is the key measure to reduce emulsion swelling and membrane breakage. Therefore, the choice and development of a suitable surfactant [46] and establishment of surfactant concentration correctly will determine the success of ELM process. The swelling rate increases with the increase in the surfactant concentration up to a certain value and then falls off with further increase in the surfactant concentration [44,47]. The quantity of Span 80 was increased from 1 to 4 g as shown in Fig. 6. In case of 1 g Span 80, the NaCl extraction efficiency was the lowest. This is due to the formation of larger emulsion droplets that provided lower mass transfer area. The effect of quantity of emulsifier is presented and it is shown that more emulsifier results in better extraction (desalination) up to 3 g Span 80, after which desalination decreases when 4 g Span 80 are added. Accordingly, this result follows the findings mentioned earlier [44,47], which may be also partly attributed to the increase in viscosity of the LM phase which is responsible for hindering mass transfer from DP to RP via LM. To this end, it may be noticed that as the mass of Span 80 increases from 1 to 4 g, the desalination increased in the following sequence: 13%, 16%, 20% and 18%, respectively, which has already been explained above.

### 3.4. Effect of type of membrane liquid (LM)

In case of diluent, according to Perera and Stevens [48] there are some requirements on the selection of the diluent i.e. low solubility in the internal and external aqueous phases, compatibility with the extractant and emulsifier and inability to form new phases, moderate viscosity (not too low as to compromise membrane stability), having a density that is sufficiently different to the aqueous phase, low toxicity, and high flash point. Aliphatics are generally preferred to aromatics as diluent because of its low solubility in water and produce better emulsion stability. Besides, the high density diluent is more favorable for O/W emulsion. In contrast, low density diluents are preferred for W/O emulsions. In addition, the viscosity of diluent is also an important parameter in the choice of diluent [41]. According to Ahmad, et al. [4] the most widely used LM for a W/O/W system is kerosene. It is believed that the properties of the emulsifier, carrier, RP, and membrane phase, as well as the stirring speed and contact time in the permeation process have significant effect on emulsion swelling and membrane leakage [4]. Under the conditions shown in the caption of Fig. 7, it is clear that Soltrol 220 which is a mixture of the aliphatic hydrocarbons (C13–C17) is preferred to CF, however, the difference on % desalination is only slight (17% for CF and 19% for Soltrol 220).On the other hand, Fig. 8 proves

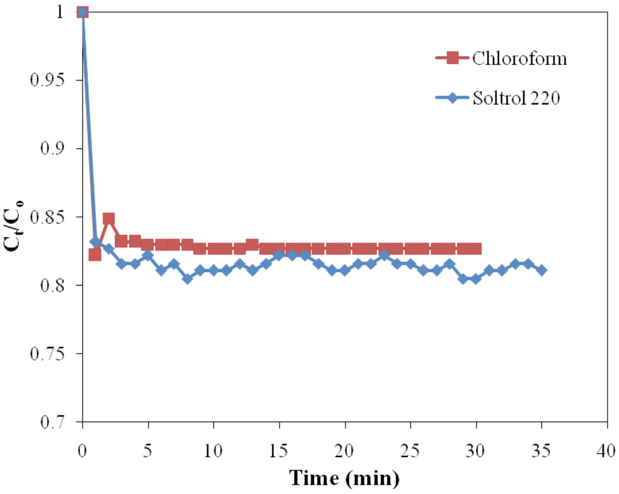

Fig. 7. Effect of type of LM ($C_i$ = 17.5 g NaCl /L, Emulsion = 3 g Span 80 + 33 ml (Soltrol 220 or CF)+ 67 ml 2 % SS, US = 5 min at 180 W, 200 rpm, TR = 1: 10, LM: RP = 1:2).

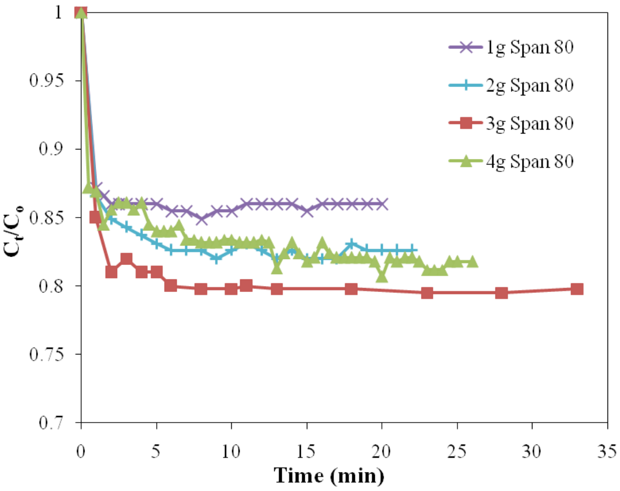

Fig. 6. Effect of quantity of Span 80 ($C_i$ = 17.5 g NaCl /L, Emulsion = 1, 2, 3 or 4 g Span 80 + 33 ml Soltrol 220+ 67 ml 2 % SS, US = 5 min at 180 W, 200 rpm, TR = 1: 10, LM: RP = 1:2).

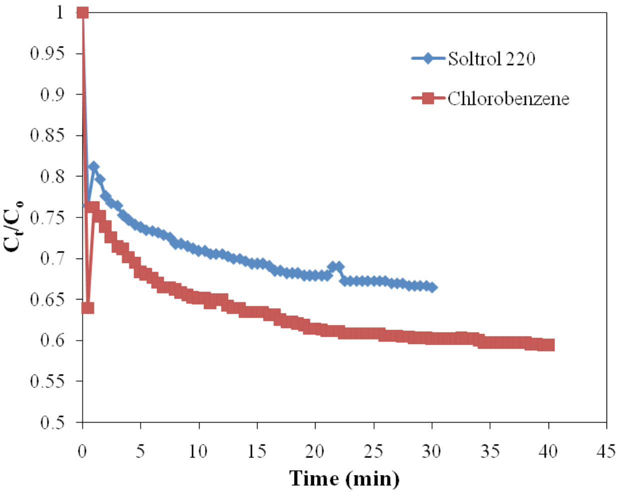

Fig. 8 Effect of type of LM ($C_i$ = 35 g NaCl /L, Emulsion = 6.86 g Span 80 + 80 ml (Soltrol 220 or CB) + 20 ml 2% SS, US= 5 min at 180 W, 200 rpm, TR = 1:10, LM: RP = 4:1).

that under the conditions stated in the figure caption, CB gave a slightly improved result compared to Soltrol 220 (41% for CB compared to only 33% for Soltrol 220).

By inspecting Table 1 which indicates the physical properties of different LMs used in the present work, and from the experimental results, it was observed that the extraction of NaCl showed the following tendency: CB > Soltrol 220 > CF. This behavior is due to the viscosity of CB (0.80 cP) is much lower than that of Soltrol 220 (1.55 cP) which led to higher rate of mass transfer, and which limited the choice between CB and Soltrol 220. The density of the diluents is another parameter that decides the thickness and permeability of the membrane for the solute. The extraction results may be also due to the values of diluents density (0.794 g/cm³ for Soltrol 220 and 1.11 g/cm³ for CB); as mentioned before, the higher density is the more preferable, which make the choice go to CB. Another factor which is of great importance is the flash point, the higher the flash point is the preferred diluent, despite that Soltrol 220 has much higher value of flash point than CB, but still the CB viscosity being less and higher density are dominant. Accordingly, CB is recommended to use as a LM. It is worth mentioning that in spite that CB is more toxic than Soltrol 220, yet, the final traces which are expected to exist in the desalinated water could be removed by adsorption and/or pervaporation, which are carried out in our lab for separation of organics from water.

### 3.5. Effect of type and quantity of sequestering agent (SA)

A sequestering agent (SA) is a substance that removes ions from a solution system by surrounding them, and which does not chemically react with the ion that is removed. The ions can no longer react since the resultant molecule holds them securely. A chemical SA surrounds another molecule or atom and holds it "in seclusion". In this process, the chemical SA hides the molecule or atom and prevents it from entering into chemical reactions.

Initially, sucrose (Suc.S) was attempted as SA. Fig. 9 shows the result of using 2% Suc.S, 10% Suc.S, 40% Suc.S, 2% SS and 2.5% SS solution, from which it is clear that no difference was noticed between the two cases of 10% Suc.S and 40% Suc.S, and percent desalination was less than 20. Accordingly, another sequestrant was examined, namely: soluble starch (SS). Fig. 9 also illustrates a comparison between 2% Suc.S, 2% SS and 2.5% SS solutions. The figure proves that SS solution, added in the quantity mentioned in the figure caption, is much preferred to 2% sucrose solution. Using 2% Suc.S resulted in only 13% desalination while using 2% SS increased the % desalination to 20, which directs us to using SS in the forthcoming work as the preferred SA in order to obtain the remaining optimum conditions. Two reasons are expected for this result: firstly, that starch is a polysaccharide of a high molecular weight. Therefore, it is retained in the RP contrary to sucrose, which is liable to partially diffuse back to the DP for its small molecular size compared to SS. In addition, starch sequesters the NaCl molecule through coordinating with the hydroxyl groups of the starch in the an hydro-glucose units in the RP forming –ONa$^+$ which for electro-neutrality reasons attract the negative chloride ion, thereby retaining the NaCl molecules in the RP and preventing them from back- diffusion to the LM phase. This does not take place in case of sucrose since the latter does not contain enough hydroxyl groups to sequester the salt, being formed of glucose and fructose ring units condensed with each other. In addition, fructose contains a keto group, which decreases the number of available hydroxyl groups able to coordinate with the NaCl molecule.

**AQ1**

### 3.6. Effect of time and power of ultrasonication (US)

This factor is illustrated in Fig. 10 from which it is clear that the effect of time and power of US is insignificant and that the difference in the degree of desalination is immeasurable since the four curves almost coincide, and the three times tried gave almost the same % desalination (18%). Accordingly, the remaining experiments were carried out

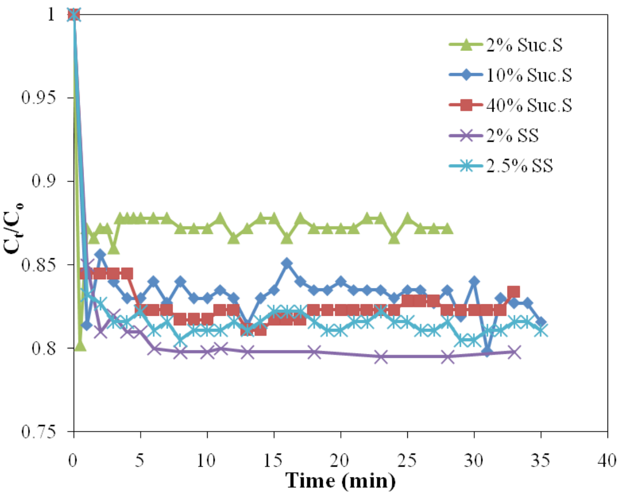

Fig. 9. Effect of quantity of Sucrose; $C_i$ = 17.5 g NaCl /L, Emulsion = 3g Span 80 + 35 ml Soltrol 220 + 67 ml 2% Suc.S, 10% Suc.S, 40% Suc.S, 2% SS or 2.5% SS, US = 5 min at 180 W, 200 rpm, TR = 1:10, LM: RP= 1:2.

Table 1
Physical properties of used membrane liquids (LM)

| Physical property | Chloroform (CF) | Colorobenzene (CB) | Soltrol 220 |
|---|---|---|---|
| Viscosity | 0.57 cP at 20°C | 0.80 cP at 20°C | 1.55cP at 100°F (38°C) |
| Solubility in water | 0.815% at 20°C | 0.05% at 20°C | Negligible |
| Flash point | None | 82°F (28°C) | 213.1 °F (100.6 °C) |
| Density | 1.489 g/cm³ | 1.11 g/cm³ | 0.794 g/cm³ |

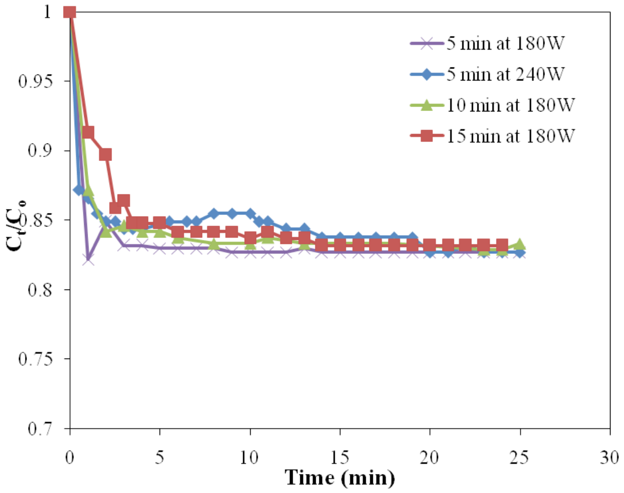

Fig. 10. Effect of time of ultrasonication (US) ($C_i$ = 17.5 g NaCl/L, Emulsion = 3 g Span 80 + 33 ml Soltrol 220 + 67 ml 2% SS, US = 5, 10 or 15 min at 180 W and 5 min at 240 W, 200 rpm, TR = 1: 10, LM: RP = 1:2).

for 5 min at 180 W only in order to minimize electrical energy expenses. With an increase in sonication time and power, the temperature of the emulsion is increased; therefore, the interfacial tension and viscosity are expected to decrease considerably. However, increasing the sonication time above a certain limit has an adverse effect on emulsification as it leads to ‘‘over-processing’’ which results in re-coalescence of emulsion droplets, consequently, the sonication time did not increase beyond 15 min in the present work to avoid these drawbacks [49].

According to Ahmad, et al. [4], in emulsion preparation, energy must be supplied to produce such meta-stable mixtures. Energy may be provided through various means. The most widely applied method to produce emulsions is mechanical agitation including stirrer, mixer, homogenizer, etc. Another method is ultrasound generation which is an alternative method to dissipate mechanical energy, required for droplet disruption, in a liquid. Ultrasound processing is a very efficient emulsification technique compared with mechanical agitation [50]. With ultrasound, the drop size (D = 32 down to 0.3 μm) is much smaller than that produced by mechanical agitation under the same conditions, which makes emulsions more stable. A rather stable emulsion can therefore be formed in a relatively shorter processing time. Although ultrasound has been proven to be of potential for emulsification, only few studies focused on using this technique for preparing the W/O emulsions [41,51]. For ELM separation process, ultrasound emulsification must be managed very well; otherwise it may produce too stable emulsions in relatively short times, causing another problem in the following demulsification process.

To this end, this was another reason why a 5 min US was preferred in the present work to 10 or 15 min. The ultrasound emulsification studies in production of W/O emulsions resulted in globules diameter ranging from 0.01 to 0.1 mm [51]. The literature indicated that ultrasound power, irradiation time, and probe position are the important parameters on the emulsion stability. Study showed that under certain experimental conditions, percentage emulsion breakage decreases with the increase of the ultrasound power until a certain ultrasonic power. Chiha et al. [41] prepared the emulsion at various power (5–35 W) and times (1–10 min) for 20 ml emulsion volume. They found that the lower emulsion breakage was obtained at an ultrasonic power of 20 W, an emulsification time of 3 min and a distance of 20 mm of the probe from the bottom of emulsification cell which gave fine droplets of the internal aqueous phase. Therefore, sufficient power and time are needed to make a stable emulsion. If the power is too low, the sound field is insufficient to give necessary energy for a good dispersion of aqueous droplets in the membrane phase [41]. On the other hand, if the power is too high, the phenomenon of coalescence is more significant due to the enhanced collision frequency of small droplets with an increase in the number of droplets and increase in the acoustic streaming velocity [41]. Accordingly, in present work, a power of 180 W was used, and was found to give a sufficiently stable emulsion. Therefore, 5 min at power 180 W was chosen.

### *3.7. Effect of presence of mobile carrier*

Fig. 11 indicates the effect of addition of MC to the LM phase. It is clear that the presence of 0.5 g MC improves the degree of desalination from 40% to about 53% under the conditions specified in the figure caption for $C_i$ = 35 g/L. A mobile carrier acts as a ‘shuttle’ to carry the chemical species through the LM [52]. However, its presence in membrane phase can decrease the emulsion stability. This is caused by the competitive adsorption with the surfactant as they have opposite behavior. Interfacial tensions increase with an increase in carrier concentration in the membrane phase leading to formation of larger sized emulsion globules in the dispersed emulsion conversely, interfacial tensions decrease by increasing the surfactant concentration up to a specific value.

Gu et al. [53] revealed that the key criterion in selecting a carrier is that it and the complex formed must be soluble in the membrane phase, but not soluble in both the receptor and feed phase. Further, from an economic point of view, a lower concentration of carrier is always preferred since it is the most expensive agent among the other components of membrane. It is noteworthy, that the selected carrier (di-benzo-18-crown-6) was selected, in particular, since the size of its cavity allows the Na ion to fit in properly so that the attraction between the positive Na ions and the negative ether moieties in the ring of the polycyclic molecule is neither too strong nor too weak. In this way the complex can carry the Na ions from the DP/LM interface to the LM/RP interface, and there, de-complexation takes place, since thermodynamics favour de-complexation at this interface, and the Na ions become sequestered by the SA present in the RP. It remains to be mentioned that the presence of the two benzene rings on either side of the polycyclic ring assists in making the MC less soluble in water, and is thus retained in the LM phase during operation.

### *3.8. Effect of treatment ratio*

Influence of treatment ratio (emulsion: DP) (TR) on NaCl removal efficiency is shown in Fig. 12. It is evident that the

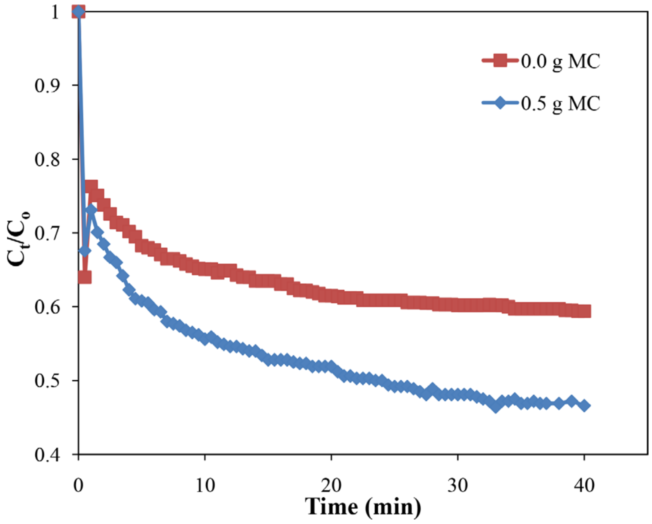

Fig. 11. Effect of presence of MC ($C_i$ = 35 g NaCl /L, Emulsion = 6.86 g Span 80 + 80 ml CB+ 0.0 or 0.5 g MC + 20 ml 2% SS, US =5 min at 180 W, 200 rpm, TR = 1:10, LM: RP = 4:1).

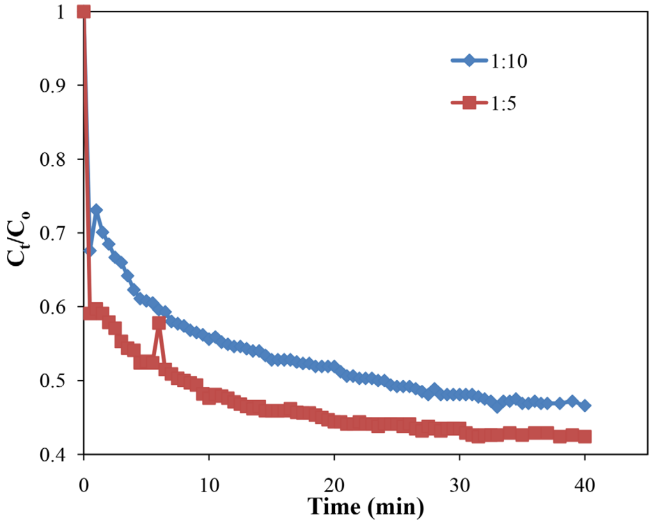

Fig. 12. Effect of treatment ratio ($C_i$ = 35 g NaCl /L, Emulsion = 6.86 or 13.72 g Span 80 + 80 or 160 ml CB + 0.5 or 1 g MC + 20 or 40 ml 2% SS, when TR = 1:10 or 1:5 respectively, US =5 min at 180 W, 200 rpm, LM: RP = 4:1).

smaller TR (1:10) the less is the degree of desalination, as expected, since in this case more NaCl is to be removed as compared to the larger TR (1:5). In addition, more MC, Span 80, and LM are present to preserve their ratios in the LM phase. However, it is practical to work with a smaller TR in order to desalinate more volume of saline water per unit time. In fact, application of large volume of emulsion is not economically feasible, since, as the volume of viscous emulsion decreases, the system will be dispersed properly and the emulsion globules size is much smaller. This is the main phenomenon that causes better desalination to be achieved, as the volume of the emulsion is decreased. The TR controls the interfacial mass transfer across the ELM process and a decrease in the ratio improves the dispersion of emulsion molecule in the DP leading to an increase in the mass transfer through the interface. Furthermore, higher TR can also have a tendency of increased swelling of the emulsion which is not acceptable [54]. Accordingly, in all the experiments a TR equal to 1:10 was applied.

## 4. Conclusions

From the present work the following conclusions were arrived at: It has been shown that desalination using ELM technique could be affected readily, under the particular conditions, which were determined in the present work. The percent desalination is affected by various parameters namely: initial salt solution concentration, volume ratio of LM/RP, quantity of MC, type and quantity of SA, type of LM, time and power of US, TR and quantity of emulsifier. The volume ratio of LM/RP is important in forming a stable emulsion and a ratio 4:1 yields higher % desalination than both 1:2 and 2:1.The optimum quantity of Span 80 as emulsifier was found to be 6.86 g for 80 ml of CB + 20 ml 2% of SS; and 3 g for 33 ml of Soltrol 220 + 67 ml 2% SS, so that best transfer of the NaCl could take place from DP to RP, 2% b.w. SS is a more suitable SA for NaCl than sucrose. CB was better as LM than CF, the latter is better than Soltrol 220. It was found that 5 min of US at 180 W is preferred to 10 min since the former was sufficient to give a stable emulsion. Ratio of emulsion volume to feed volume (TR) affected the percent desalination in direct proportionality. The quantity of emulsifier is of crucial importance, since it plays an important role in emulsion stabilization and actually also contributes in carrying the NaCl from DP to RP as well. The initial solution concentration affects directly the extraction of NaCl from DP to RP via the LM.

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