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An environmentally friendly method for removal of salts from produced water brine

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ABSTRACT

Produced water is a complex mixture of organic and inorganic compounds and it is mainly salty water. It represents the largest volume of by-products generated during oil and gas recovery operations. As a result, water to oil ratio is around 3:1 that is water cut is 70%. Increasing volume of wastewater over the world has become a big issue of concern, and treatment of this wastewater can generate additional sources of potable water. Therefore, research efforts are devoted to developing a cost-effective technique to reduce high salinity of produced water to a lower value. A new approach is investigated, to remove/reduce salts from moderate to high concentration brine. This method is based on liquid-liquid extraction, and uses an organic phase containing ethanol, cyclohexane and sunflower oil. Experiments were successful to reduce the salinity of brine to approximately 27%–64%, in a single stage, with different concentrations of brine from 40,000 ppm up to 140,000 ppm. This method, is considered to be simple, efficient, environmentally-friendly and uses a sustainable system.

Keywords: Produced water; Brine; Salts; Liquid-liquid extraction; Removal

1. Introduction

Oil and gas are the most important world energy resources, and their continuous supply is crucial for sustainable development of advanced society. A large volume of wastewater is produced every day around the globe [1]. It has become a global environmental issue due to its huge volume and toxicity that poses detrimental effects on receiving environment [2]. Desalination is known as a popular and well-argued alternative [3]. Many of technology development efforts for water desalination so far have focused on the treatment of seawater or brackish ground water, while brine water with salinity equals or higher than 50,000 ppm has received little attention [3–5]. There is an increasing need for the desalination of high concentration brine efficiently and economically, either for the treatment of produced water or minimizing the environmental impact of brine from existing desalination plants. Produced water is subsurface formation water coproduced in the oil and gas production [6] and has been described as the largest offshore discharge associated with fossil fuel extraction [7]. It represents around 70% of total wastewater produced during oil production. In many instances, this waste stream is seven to eight times greater by volume than oil produced at any given oilfield. About 65% of this water is reinjected to the well for pressure maintenance, 30% of the total is injected to deep well for final disposal in the case of proper aquifer conditions and the rest of the water is discharged to surface water. These waters are characterized by a high content of salt ranging from 50,000 ppm up to 300,000 ppm [8–10] and contains suspended solids, potentially toxic elements, soluble and insoluble organic matter, suspended oil, and

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chemicals (Table 1). All these elements make the produced water a highly polluting source and difficult to discard, worsened by the significant volume involved [1,10,12–15].

Several methods are available for water desalination in recent years. The most common, modern methods of desalination are thermal (distillation or evaporation) and membrane processes. Reverse osmosis (RO), is the most widely used membrane process for desalination currently. While it is less effective and not practical for brine desalination because it requires considerable pretreatment for maintenance and preventing membrane fouling especially at high concentration of salt [3,10].

The suitability of using algae ponds for brine water disposed from desalination as a new conceptual technique under the natural circumstances was reported [11,12]. The basins had several concentrations of saline water from 40,000 ppm up to 80,000 ppm with several runs to get the total dissolved solid (TDS) removal efficiency. The experimental work showed that the removal efficiency for TDS salinity between 13% (for 1 d) and 63% (for 6 d). These variations were due to inlet TDS concentration, retention time in the basin and the climatic conditions (temperature and sunlight period).

Some researchers [13] studied the fraction extraction of sodium chloride from brine containing sodium sulfate by liquid–liquid extraction using thermo-responsive polymers as a novel concept. Four different polymers (Dehypon_ LS 54, PPG 425, Pluronic_ L31 and Triton_ X – 15) were tested. The polymer PPG 425 obtained high percentage of extracted sodium chloride about 31% with distribution coefficients 0.44 from concentration of sodium chloride 10,000 ppm and about 10% with 100,000 ppm concentration of brine.

The purifications of high salinity brine using multistage ion concentration polarization (ICP) desalination was reported [9] and it was demonstrated ICP desalination for treating ultra-high salinity water treatment 60,000–100,000 ppm of sodium chloride with percentage removal 50%. Its simultaneous removal of suspended solids (crude oil emulsions and bacteria) and salts, make their process less susceptible from scaling/membrane fouling.

A recent study was done for removal high salinity from produced water [20] using natural gas hydrate to remove high salinity from produced water 76,244 mg/L, 135,700 mg/L. The results showed that the percentage removal of salts from produced water about 80% with 3-stages hydrate process.

The approach we propose is based on liquid–liquid removal process to reduce the concentration of salt to medium values from high concentration produced water at the natural conditions. The approach presented here is an initial attempt to develop and demonstrate a small-scale method that seems to work with environmentally friendly system. In this method an organic phase is contacted with the produced water containing high concentrated salt. The organic phase is a mixed solvent system (ethanol, cyclohexane and sunflower oil termed as organic phase) and is expected to remove salts sufficiently so that the resulting salt solution can be treated with a conventional membrane process, such as reverse osmosis (already used as an industrial process to produce water from seawater). The other liquid–liquid methods mentioned in Table 2 work ineffectively and fails to reduce high concentrated feed within reasonable time.

The purpose of the study is to examine the effects of the following:

- An organic phase of ethanol, sunflower oil, and cyclohexane on the removal of sodium chloride from produced water.
- Source solutions containing salt concentration ranging from 40,000 ppm up to 140,000 ppm using the organic phase.

2. Materials and methods

2.1. Materials

Sodium chloride (99.5%–100% pure) was purchased from Riedel-de Haen (UK). Ethanol (99.7%–100% pure) and cyclohexane (99.5% pure) were purchased from Sigma-Aldrich (USA). Sunflower oil (Noor brand) was purchased from Emirates Refining Co., UAE.

Sunflower oil is very high in monounsaturated fatty acids. General composition of the sunflower oil includes the following: stearic acid (50%–55%), palmitic acid (4%–7%), oleic acid (27%–30%) and linoleic acid (0%–1%). Sunflower oil (Noor brand) used in this investigation has no trans-fatty acid and due to its higher stearic acid contents, it provides desirable physical and chemical properties for industrial applications (manufacturer's information).

The brine solution was used as obtained from a local desalination plant Abu Dhabi Oil Refining Company (Takreer, Abu Dhabi, UAE) with concentration of salinity 58,800. The composition of brine is shown in Table 1.

2.1.1. Preparation of high concentrations of brine

High concentrations of brine were prepared by adding sodium chloride to the brine obtained from the desalination plant, with stirring using a magnetic stirrer of model Stuart (Japan). The pH meter was of model HQ 11d HACH (UK) used for measuring pH. The conductivity meter was of model HQ 14d HACH (UK) used for measuring brine concentration. The high salinity above 100,000 ppm were measured by dilution brine two times with deionized water.

2.2. Experimental procedure

2.2.1. Extraction of salts from equilibrium measurements of solutes

All the desalination experiments were conducted at room temperature of 25°C.

A brine with volume 20 mL contacted with equal volume of any pure solvent (either ethanol or sunflower oil or cyclohexane) in 40 mL centrifuge tubes. In next set of experiments, an organic phase containing all three solvents: ethanol, sunflower oil and cyclohexane was contacted with brine. The mixtures of organic phase were mixed for 10 min using a magnetic stirrer before contacted with brine. Then solution in tubes was mixed for a few minutes to allow molecules to partition. After mixing solution were allowed to settle for a maximum of 2 h to separate the two phases and obtain a clear bottom aqueous phase. Fig. 1a in the Appendix shows the steps of the experiment. The bottom aqueous layer was removed using a Pasteur Pipette model (CAPP Bravo) and analyzed for its salt content. The initial and final pHs for the aqueous phase were also measured.

2.2.2. Re-Extraction of salts from the organic phase

After removal of salts, the organic phase was separated from the brine, and contacted with the deionized water with the same volume of an organic phase and mix it for few minutes. After mixing the solution were allowed to settle for half an hour to separate the two phases and obtain the clear bottom aqueous phase. Fig. 1b shows the steps of the experiments. The bottom aqueous layer was removed using a Pasteur pipette and analyzed for its salt content. The initial and final pHs of the aqueous phase were also measured.

2.3. Analytical techniques

2.3.1. Procedure for measuring conductivity of brine using conductivity method

The values of concentration for the initial brine solution and the aqueous phases remained after the extraction experiments, were measured by the conductivity meter. The concentration values in the aqueous phase (brine) were measured, and the values of organic phase concentration were calculated from differences of initial and final aqueous phase concentrations. The apparent distribution constant, DE, is defined, as the ratio of the concentration of salt in the organic phase over that in the aqueous phase at equilibrium and can be described by the following expression [16]:

$$\text{DE} = \frac{C_{B(\text{org})}}{C_{B(\text{aq})}} \tag{1}$$

where $C_{B(\text{org})}$ and $C_{B(\text{aq})}$ are the concentration of brine in the organic and aqueous phase at equilibrium, respectively.

2.3.2. Percentage of removal or extraction

The percentage removal or extraction is calculated, by using the initial and final concentrations of salt in the produced water after it has been contacted with the organic phase. The removal (or extraction) percentage is calculated, $E\%$, from the following expression (16):

$$E\% = \left(1 - \frac{C_f}{C_i}\right) \times 100 \tag{2}$$

where C_i and C_f are the initial and final concentrations of sodium chloride of the source solution respectively.

2.3.3. Re-extraction or percentage recovery of salts from the organic phase

The percentage recovery of salts from the organic phase related to the initial and final concentration of deionized water (DI) to initial and final concentration of brine. The percentage recovery is calculated, $R\%$, from the following expression (16):

$$R\,\% = \frac{\left(C_i - C_f\right)_{\text{DI}}}{\left(C_i - C_f\right)_{\text{brine}}} \times 100 \tag{3}$$

Table 1
Composition of brine at pH 7.86 and temperature of 20°C

pH	TDS (ppm)	Salinity (ppm)	COD (ppm)	Na^{+1} (ppm)	Mg^{+2} (ppm)	K^{+1} (ppm)	Ca^{+1} (ppm)
7.86	73,800	58,800	1,560	23,712	2,794	762	1,375

Table 2
Comparison with the literature studies for removal sodium chloride from high concentration brine

Methodology	Feed concentration (ppm)	Organic phase	% Extraction, time, stages	% Recovery of salts	References
Desalination	40,000–80,000	Algae ponds	TDS salinity 13% (1 d) and 63% (6 d)	–	[18,19]
Desalination	60,000–100,000	Ion concentration polarization	50% Multistage about 48 h	–	[9]
Desalination	76,244 and 135,700	Natural gas hydrate	About 80% 3 stages hydrate process about 32 h	–	[20]
Liquid–liquid extraction	10,000–100,000	Four different polymers: Dehypon_ LS 54 PPG 425 Pluronic_ L31 Triton_X–15	31% with 10,000 ppm and 10% with 100,000 ppm about 14 h	–	[17]
Liquid–liquid extraction	40,000–140,000	40% Ethanol, 10% Cyclohexanean, 50% Sunflower oil	64% with 40,000 ppm and 27% with 140,000 ppm single stage, 4 h	About 25% single stage	This work

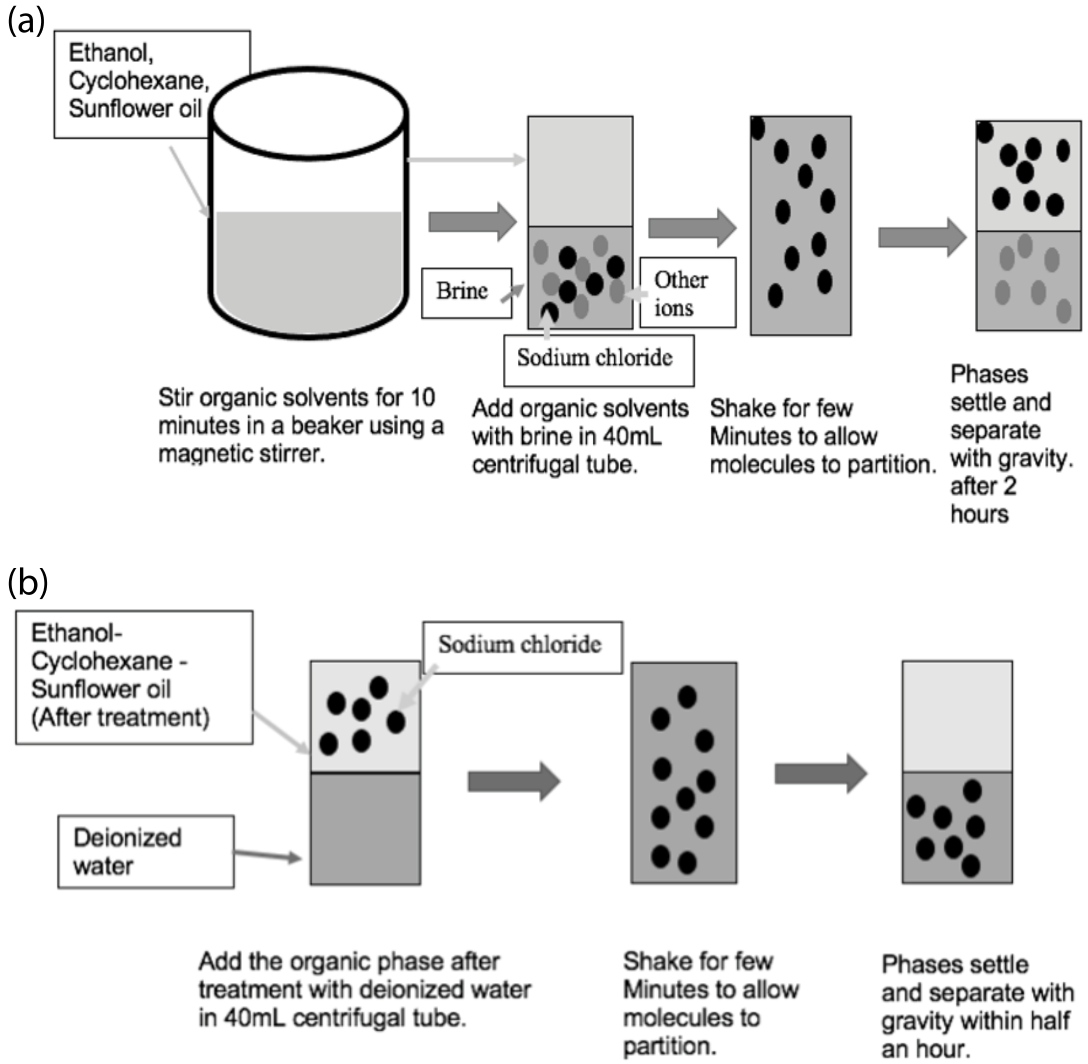

Fig. 1. (a) Schematic for the extraction of sodium chloride into the solvent phase and (b) schematic for the re-extraction of sodium chloride from the loaded solvent phase into deionized water.

where the subscripts DI and brine are for distilled water and brine solution, respectively.

3. Results and discussion

3.1. Extraction

All the experiments were duplicated, and errors are shown in figures. Mass balances were calculated using the overall values and the measured salt concentration in the aqueous phase at the end of each experiment. The differences were small, within 5%–7%.

The results for removal (or extraction) experiments are presented as the percentage extracted or removed, *E*%, as function of:

- The organic phase composition for a fixed concentration of brine sample;
- The aqueous feed salt concentration for a fixed organic phase composition;

3.1.1. Effect of pure ethanol, sunflower oil and cyclohexane on extraction

This effect of solvents on the percentage removal sodium chloride is shown in Fig. 2. It's clear that within the volume range 2–8 mL the percentage of extraction increased greatly (from 38% to 59%), after that increased ethanol volume did not seem to have much effect. The system might have reached its maximum solubility.

3.1.2. Effect of the ratio of sunflower oil/cyclohexane and cyclohexane/sunflower oil

As shown in Fig. 2, the effect of sunflower oil and cyclohexane as individual solvents is small on the percentage of extraction of sodium chloride compared to the result obtained with pure ethanol. When mixed with ethanol the combined solvent showed good removal percentage. The addition of sunflower oil to ethanol makes the overall phase more hydrophobic and will provide advantages

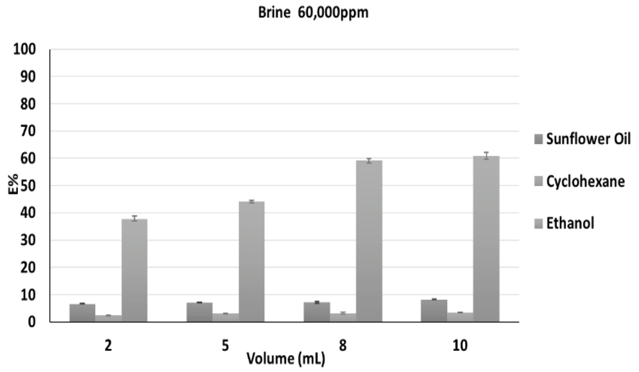

Fig. 2. Effect of pure ethanol, sunflower oil and cyclohexane in the organic phase on the percentage extraction (*E*%) of sodium chloride.

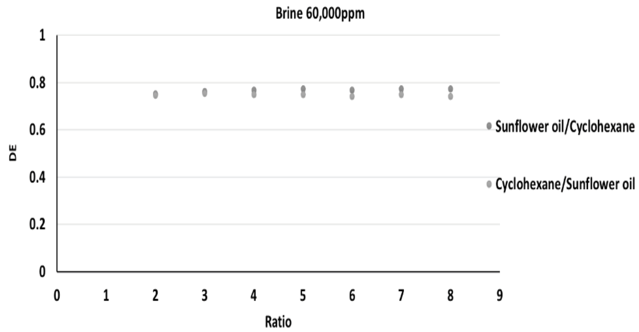

Fig. 3. Effect of different ratio of sunflower oil/cyclohexane and cyclohexane/sunflower oil with 2 mL of ethanol on the distribution coefficient (DE).

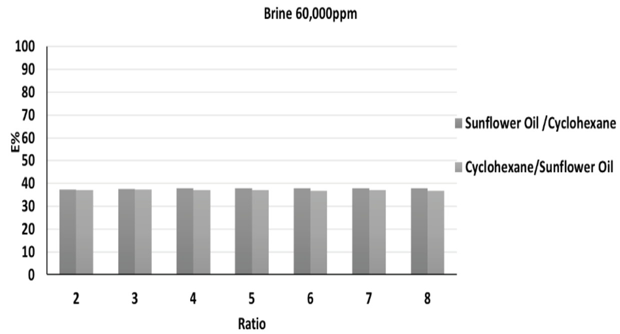

Fig. 4. Effect of different ratio of sunflower oil/cyclohexane and cyclohexane/sunflower oil with 2 mL of ethanol on the percentage extraction (*E*%).

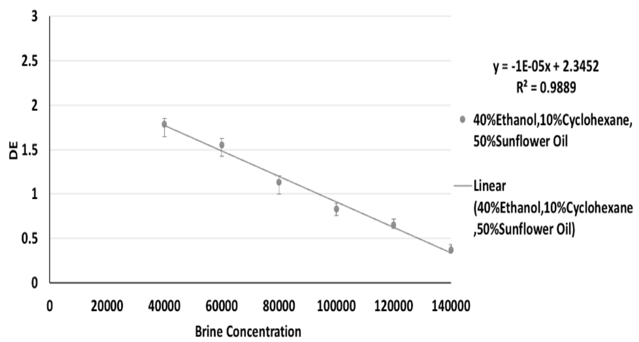

Fig. 5. Effect of 8 mL of ethanol (40% of the total volume) on different concentrations of brine on distribution coefficient (DE).

in a commercial membrane contactor. Ethanol facilitates the removal of salt without dissolving in sunflower oil. In a hydrophobic membrane module, the aqueous phase and the organic phase are expected to be separated from the start and the salt will be removed in the oil phase. This will allow re-extraction of salt from the organic in a separate step and allow recycle of the organic phase to the main extraction step. Addition of cyclohexane makes the solvent phase clearer compared to solvent phase of ethanol and sunflower oil. A change in the ratio of cyclohexane/sunflower to ethanol (with ethanol kept at 2 mL) did not affect the values of DE (shown in Fig. 3) and percentage removal of salts significantly (Fig. 4) for the feed with salt concentration of 40,000 ppm. The removal of salt can be improved by adding more ethanol in the combined organic phase (Fig. 2).

3.2. Effect of different concentrations of brine on extraction (%E) of sodium chloride

Based on results shown in Fig. 2 with 40% (8 mL) of ethanol and brine 60,000 ppm the percentage of extraction was high around 60%. This removal of salt reduces the treated produced water concentration of 25,000 ppm and that can be further reduced by processing with RO. The percentage extraction decreased if produced water with higher concentration is treated. The values of the distribution coefficient (DE) for higher brine concentrations are lower, as shown in Fig. 5 for the range 40,000–140,000 ppm. As a result, the percentage extraction is much lower (27%), at very high concentration of 140,000 ppm and it is moderate (42%), at concentration of 80,000 ppm, as shown in Fig. 6. These values can be improved by using multiple stages as discussed in the literature [9].

3.3. Comparison of removal sodium chloride with some studies

Our results are compared with the literature studies as shown in Table 2. In a previous study [17], high brine concentration of up to 100,000 ppm was reported and they used technique similar to our technique which is (liquid–liquid extraction), but they obtained low percentage extraction range from 10% to 31% after 14 h. In other studies [18,19], it was shown that the percentage extraction of sodium chloride was about 63% after 6 d from high concentration brine in the range 40,000–80,000 ppm. The percentage extraction of sodium chloride reported was about 50% from brine concentration up to 100,000 using multi-stage in 48 h [9]. With higher number of stages (3 stages) and long operation time (48 h), better percentage extraction ca. at 80% was reported [20] for concentrations up to 135,000 ppm. The new method, developed in this report, show removal percentage of sodium chloride about 27% from a feed of 140,000 ppm and 64% from a feed of 40,000 ppm and in one stage within 4 h. Compared to the methods discussed

Table 3
Percentage recovery (%) of sodium chloride from the loaded organic phase

Salts concentration in brine (ppm)		pH				Salts concentration in DI water (ppm)		pH		
Initial	Final	Initial	Final	DE	E%	Initial	Final	Initial	Final	%Recovery
60,000.00	17,659.00	7.94	7.62	2.3	71	0	10,300.00	8.17	7.75	24
100,000.00	40,629.00	7.81	7.64	1.5	59		14,800.00		7.66	25
140,000.00	69,859.00	8.1	7.71	1.0	50		17,400.00		7.65	25

*Organic phase and deionized water were equal volume.
*The contact time for all equilibrium experiments were half an hour.

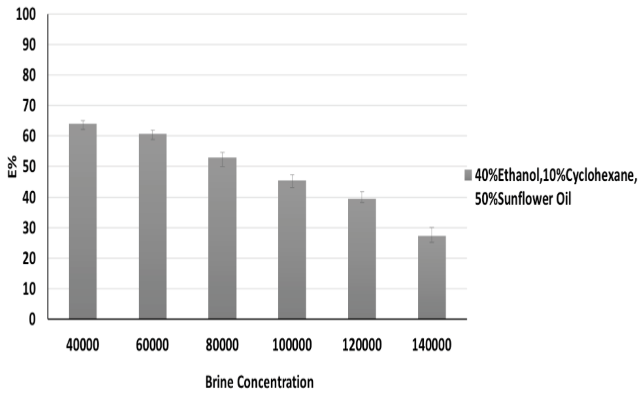

Fig. 6. Effect of 8 mL of ethanol (40% of the total volume) on different concentrations of brine on the percentage of extraction (%E)

above, this method investigated examined in this report is considered simple, moderately efficient and uses environmentally friendly system of ethanol, cyclohexane and sunflower oil. If the process is operated in multiple stages, the percentage extractions of sodium chloride can be increased even higher.

3.4. Percentage of recovery of salts from the organic phase

The percentage recovery of sodium chloride from the loaded organic phase was about 25% in a single stage using deionized water as shown in Table 3. This can be improved if the recovery process is optimized and more stages are used. Thus, this method has the potential to recycle/reuse of the organic phase, further minimizing the overall cost of the process.

4. Conclusions

The experimental results for removal of sodium chloride from brine using a solvent phase of ethanol, cyclohexane and sunflower oil, have been presented. The remarks are:

- The organic phase (40% ethanol, 10% cyclohexane, 50% sunflower oil) performed very good with percentages removal of app. 60% from brine concentration of 60,000 ppm.
- This reduces salt concentration of produced water from 60,000 ppm to a value of 24,000 ppm that can be treated by the conventional membrane process such as reverse osmosis (RO), to produce further water source.
- Using the organic phase, produced water with high concentration of salt up to 140,000 ppm can be treated. The percentage extraction decreased to lower value, approx. 27% for feed of 140,000 ppm brine concentration. This could be improved using multiple stages.
- Use of sunflower oil in such removal process is new, it is from sustainable source with benefits including less toxicity, less corrosiveness, low environmental, health and safety issue.
- The percentage recovery of sodium chloride from the loaded organic phase (with 40% ethanol, 10% cyclohexane, 50% sunflower oil) was about 25% using deionized water.

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