Study of progressive freeze concentration and eutectic freeze crystallization technique for salt recovery

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Abstract. In this industrial era, salt recovery from seawater has become an important issue from the environment perspective. Few freezing technologies have been proposed as capable way to separate the salt from the seawater because of the energy used in the previous technologies is higher. A study of Progressive Freeze Concentration (PFC) and Eutectic Freeze Concentration (EFC) method have been carrying out and further investigated on their performance in recovering the salt. For the PFC method, pure water crystallizes into crystal and the concentrate is left behind as in liquid form while for the EFC method, both ice crystals and salt crystallize at the same time when the initial concentration of water salt mixture is exactly the same as eutectic concentration. In EFC, salt sinks to the bottom while ice floats at the top of the crystallizer and both are separated by gravity separation. Effective partition constant and solute recovery are calculated to evaluate the efficiency of PFC and EFC. In this study, the PFC method has shown an effective partition constant of 0.28 and recovered solute of 0.88 g of sodium chloride per 1 g of initial sodium chloride while for EFC method, effective partition constant and solute recovery obtained are 0.59 and 0.66. Overall, both techniques are applicable for the seawater desalination process.

1. Introduction
Seawater is the water that comes from natural sources such as sea and ocean. Seawater is denser compared to the freshwater as it contains dissolved salt or sodium chloride. Salt can be separated from seawater through the desalination process [1]. Seawater desalination process have been limited to the desert climate throughout the world. Energy recovery equipment had been improved dramatically over the past years to accommodate the power needed by desalination process [2].

Currently, the evaporation process requires high cost due to the higher energy used in the process compare to the energy used in the freezing process. This is because of the heat of vaporization is six times higher compare to the heat of fusion [3]. Recently, fresh water is needed as the population increases and the lifestyle are changing [4]. Therefore, freezing technique are studied for the seawater desalination. In order to prove that the freezing process is applicable for seawater desalination, performance of freezing technique have been studied.

The installation for seawater desalination facilities is increasing during the past decade for water supply for some countries [5]. Current industry uses reverse osmosis [6,7,8], evaporation [1,9] and freeze concentration for the desalination process. PFC [10] and EFC [11,12] are the technology used for freeze crystallization technique in the desalination industry.

Progressive freeze concentration was introduced as it offers a simpler step for separation and lower maintenance cost are needed. This process forms a single block of ice crystal from layer by layer when the solution continuously introduces to the cool surface [13]. PFC process have been used well known for pharmaceutical, wastewater and fruit juices industry [14]. For PFC, the ice crystal purity is higher with the lower growth rate process. Theoretically, the formation of ice is started with ice nucleation when the solution starts to make contact with the cooled surface.
The nucleation process can be divided into few categories which are primary homogenous, primary heterogeneous and secondary nucleation [15]. During this process, fusion heat is directly transferred toward the cooled surface through the conduction process. Ice embryos start to appear around the solid surface. During this stage, a thin film of ices starts to form when the ice embryo spreads toward the wall of the crystallizer. The thin film of ices grows thicker and continuously until the visible ice layer is formed. After a certain time, the thickness of ice increases and it will promote higher resistance for heat transfer [16]. Nuclei that are formed at the high supersaturation resulting in produce smaller crystals.

Besides, the other method that can be used to desalinate the solution is by using EFC process. EFC is feasible to recover the ice and salt crystal by operating at the eutectic condition. When the process is operated at the eutectic temperature, the salt is not mixed because each salt has their own eutectic temperature [17]. This process produces two-layers of ice which are pure water and desired solution. Pure water will slowly and continuously be frozen while the desired solution will freeze at the eutectic temperature. This process does not need separation part as there is a difference of density between the ice and salt crystal [18].

For the crystallization process, heat transfer, reactor configuration, and cooling rate will play significant roles. All these factors are related to the kinetics of the system. This is proven when the solute concentration already exceeded the equilibrium concentration, the solution will start to crystallize. When the solution is more concentrated than equilibrium concentration, which called as supersaturated. Existing supersaturation will drive for nucleation and growth of crystal while crystallization will be driven by the supersaturation [19].

Theoretically, both methods which are PFC and EFC are applicable to separate the salt from the initial solution. Hence, both methods have been studied in order to figure out the capability to desalinate the seawater.

2. Materials and Methods

2.1. Materials
All chemicals are analytical reagent grade. Sodium chloride (NaCl) solution of 23300 mg/L is prepared by dissolving NaCl (Merck) in distilled water. An aqueous ethylene glycol solution containing 50% ethylene glycol (Merck) is used as a coolant. All chemicals are purchased from Avantis Laboratory Supply.

2.2. Methods

2.2.1. Progressive Freeze Concentration
Figure 1 shows the experimental setup for PFC. Chiller acts as a controller of the temperature for coolant. Retort stands and clamps are used to support the stainless-steel vessel and digital stirrer while refractometer is used to determine the refractive index or concentration of the solution.
Figure 1. Experimental set-up for PFC

The coolant temperature in the chiller is set to the desired temperature. Sodium chloride is mixed with the distilled water to produce sodium chloride solution. When the temperature of coolant reach at -12°C, the solution is added into the stainless-steel vessel and it is immersed in the chiller. The timer is set for 30 minutes and the digital stirrer is set at the 100 RPM.

After 30 minutes, the digital stirrer is stopped and it is removed from the stainless-steel vessel. Stainless-steel vessel is taken out from the chiller to ease the collection of the product sample. Pure ice crystal and concentrated solution are collected and separated into the different beakers. Volume of ice crystal and concentrated solution are measured by using a measuring cylinder and the concentration of the ice crystal and concentrated solution are tested by using a refractometer for analysis result. All the information is recorded and is used to calculate the effective partition constant and solute recovery. The experiment is repeated at the different stirring rate (200, 300, 400 and 500 RPM), cooling time (15, 20, 25, 35 minutes) and coolant temperature (-8, -10, -14 and -16 °C).

2.2.2. Eutectic Freeze Crystallization

Figure 2 shows the experimental setup for EFC. The coolant temperature in the chiller is set to the required temperature at -21°C. To produces sodium chloride solution, sodium chloride is mixed with the distilled water. When the temperature of coolant reached -21°C, the solution is added into the stainless-steel vessel and it is immersed in the chiller. The timer was set for 60 minutes as the two layers of ice start to form at that time and the digital stirrer is set at 300 RPM because that is the best operating condition of stirring rate for progressive freeze concentration.

After 60 minutes, two layers of ice are formed and digital stirrer is stopped and removed from the stainless-steel vessel. Stainless-steel vessel is removed from the chiller to ease the collection of the product sample. Pure ice crystal and the concentrated solution crystal are collected and separated into the different beakers. Volume of ice crystal and concentrated solution are measured by using a measuring cylinder and concentration of the ice crystal and concentrated solution are tested by using a refractometer for analysis result. All the information is recorded and is used to calculate the effective partition constant and solute recovery.

2.3. Response Variables

2.3.1. Effective Partition Constant
Effective partition constant (K) can be used to evaluate the effectiveness of separation or desalination process through the crystallization method [20,21]. The efficiency of the separation process increases when the value of K decreases. K for crystallization of ice and the liquid phase at the interface is defined as in equation (1) where $C_0$ is the initial concentration, $C_L$ is the concentration of the concentrated solution, $V_0$ initial volume and $V_L$ volume of concentrated solution [22].

$$K = 1 - \frac{\log \left( \frac{C_0}{C_L} \right)}{\log \left( \frac{V_L}{V_0} \right)}$$  \hspace{1cm} (1)

### 2.3.2. Solute Recovery

The effectiveness of the separation of salt from water using crystallization technique was determined through solute recovery [10]. Solute recovery is known as a ratio of the desired solution in concentrated solution to the initial solution as shown in equation (2). During the freezing process, the concentration of solute increases in the crystallizer. According to some process conditions, small amount of solutes is trapped into the ice crystal [23]. Where $C_L$ is the concentration of the desired solution and $C_0$ is the concentration of the initial solution, $M_L$ is the mass of the desired solution and $M_0$ is mass for the initial solution.

$$Y = \frac{C_L M_L}{C_0 M_0}$$  \hspace{1cm} (2)

### 3. Results and Discussion

#### 3.1. Progressive Freeze Concentration

##### 3.1.1. Calibration Curve

To produce the calibration curve, the sodium chloride solution is prepared at different concentration with the range 2, 4, 6, 8 and 10 (g/100ml). Figure 3, shows the plotted calibration curve which is tested using the refractometer.

![Graph of calibration curve for refractive index value vs concentration of sodium chloride solution.](image)

**Figure 3.** Graph of calibration curve for refractive index value vs concentration of sodium chloride solution.
3.1.2. Effect of Stirring Rate
The stirring rate was manipulated at the range of 100 to 500 RPM. For this part, the effect of stirring rate is evaluated by using effective partition constant, \( K \) and solute recovery, \( Y \). Graph of \( K \) and \( Y \) had been plotted against the stirring rate which represented the speed of the stirrer. Figure 4 shows that the effective partition constant is decreasing while solute recovery is increasing.

![Figure 4. Graph of effective partition constant (K) and Solute Recovery (Y) vs Stirring Rate (RPM)](image)

If the stirring rate is too high, there might be some potential that the ice layer surrounding of the stainless steel wall may be destroyed. When the ice layer breaks down, the concentration of the concentrated solution decreases because the ice diluted the concentrated solution. When the stirring rate is higher, the solute distributes well in the solution [21]. Therefore, number of solutes trapped in the ice layer decreases.

Hence, when the value of \( K \) is lower, and \( Y \) is higher, it indicates better efficiency for the PFC performance. As the result, higher purity of ice crystal layer is formed. For this part of the experiment, the lowest effective partition constant of 0.63 and the highest solute recovery of 0.58 were obtained at the fixed coolant temperature which is at \(-12^\circ C\) within 30 minutes.

3.1.3. Effect of Cooling Time
For this experiment, the range of cooling time is 15 to 35 minutes. This range is selected to study the effect of cooling time for PFC method. Based on the preliminary test, the range of the cooling time is selected because the ice layer started to form firmly at the surrounding wall of the stainless-steel vessel. This process is repeated by using different cooling time with the fixed stirring rate which is 300 RPM and coolant temperature, \(-12^\circ C\).

Figure 5 shows the effective partition constant starts to decrease while solute recovery increase from 15 minutes to 35 minutes. This trend is similar compared to the effect of stirring rate previously discussed. Cooling time give significant impact to the rate of solute concentration form compared to the ice crystal formation [24]. Besides, there is a combination of the mass and heat transfer in the freeze concentration method. Due to the high mass diffusion coefficient, heat transfer rates in directional freezing are normally faster compared to the mass transfer. Thus, when more cooling time is available, mass transfer in the rate of sodium chloride solution is higher. The longer the circulation time, the better the efficiency of the system. This can be proven when the crystallization time is longer, thicker ice crystal is produced and more concentrated solution obtained by the end of the process [9].
Figure 5. Graph of effective partition constant (K) and Solute Recovery (Y) vs Cooling Time (min)

In this part of the process, the highest concentration of ice crystal is when the cooling time is at 15 minutes. Thus, the pure ice crystal was not fully formed as it still contains the solute from the concentrated solution. In the meantime, longer cooling time help to separate the water from the liquid phase and increase the salt formation. Nevertheless, if the time taken for freezing is too long, the trend of effective partition constant and solute recovery will be shift because there might be some solute from concentrated solution transfer to the ice crystal. When cooling time is too long, there is a chance that the solute trap inside the ice crystal formation due to the smaller area in the vessel [24]. The efficiency of time-dependent was analyzed from the value of concentration in the ice crystal phase [25].

3.1.4. Effect of Coolant Temperature

From the preliminary experiment, the suitable range for coolant temperature is between -8°C and -16°C. The range for the coolant temperature is acceptable because the eutectic temperature for the sodium chloride solution is -21°C. This process is fixed at 30 minutes and 300 RPM. One of the important parameters for the experiment is the coolant temperature as it influences the freeze concentration process [26].

From Figure 6, it shows that -8°C is the best coolant temperature as it has the lowest effective partition constant value (0.52) and highest solute recovery value which is 0.89. The trend for effective partition constant decrease and solute recovery increase from -16°C to -8°C. The trend that involved in the graph between the effective partition constant and solute recovery is inverse to each other. When the temperature difference between the stainless-steel vessel and the sodium chloride solution is higher, there are more solute will be trapped in the ice crystal because the rate of ice growth is higher. Thus, the pure ice crystal is failed to form as the concentration of ice crystal increase [27].
3.2. Eutectic Freeze Crystallization

For the Eutectic method, there will be no repetition of experiment because the cooling temperature is fixed at the eutectic temperature which is -21℃ and the time for freezing is taken when there is two layers of ice are formed in a stainless steel vessel. For the EFC, the stirring rate used is 300 RPM as it is the best stirring rate for progressive freeze concentration. The cooling time for the EFC is 60 minutes because after 60 minutes there are two layers of ice are formed which are pure ice crystal and the salt concentrated crystal. For the eutectic freeze crystallization method, the effective partition constant is 0.59 and solute recovery is 0.66.

The eutectic freeze crystallization method can be explained based on Figure 7. When the stainless-steel vessel is immersed at the temperature 0℃ the solution is cooled down until it reached -10℃. At that point, only ice crystal starts to form, and the salt is still in the liquid phase. When the solution is further cooling to the -21℃ (point A), another ice crystal which is salt (sodium chloride) starts to form.

Figure 6. Graph of effective partition constant (K) and Solute Recovery (Y) vs Coolant Temperature (℃)

Figure 7. Phase Diagram for Sodium Chloride solution

Figure 7 shows that at -21℃ with the eutectic concentration of salt, the phase that happens in that part is where the pure ice crystal and salt crystal happen. In this experiment, the salt crystal is settled.
down to the bottom while ice crystal float at the surface. This is because the density of salt is heavier compared to the density of pure ice crystal. When the equilibrium temperature is reached, the crystallization will stop immediately, but the sodium chloride solution will be turned into the supersaturated solution first. After a few minutes of cooling time, the supersaturated solution will slowly form a salt crystal [28].

4. Conclusion
In this study, the performance of PFC and EFC on salt recovery was investigated. The objective of this paper is to study the efficiency of both methods. The resultant of ice crystal and concentrate of the solution had been tested on the effective partition constant, K and solute recovery, Y. PFC method performs the best at stirring rate of 300 RPM, cooling time of 35 minutes and coolant temperature of -12°C and the highest efficiency represented by the K of 0.284 and Y of 0.883 was achieved. From the EFC setup for this study, EFC performs the best by achieving K of 0.59 and Y of 0.66.

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