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Assessment of freeze melting technology for brine concentration

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ABSTRACT

High saline waters are produced in large volumes in Kuwait from various industrial applications, including desalination and petroleum sectors. These types of waters as a waste have a significant impact on the surrounding environment, and some of which may pose a number of threats to human health. Freeze melting (FM) technology is considered a novel desalting process that can be further developed for innovative saline water desalination. This paper aimed at evaluating the viability and efficiency of FM process under static and dynamic influences for brine concentration. The dynamic crystallization process was investigated with three agitation systems, which are: a bubbling system, a mechanically stirred system, and an ultrasonic system. The results of dynamic crystallization process were compared to the results of the static crystallization process. The results of the experimental works showed that the most effective crystallization processes was the mechanically stirred agitation system followed by bubbling agitation process and the ultrasonic system using a single-stage of freeze crystallization. The promising results obtained, will lead to a future hybrid system of near zero liquid discharge that combine reverse osmosis and FM process to concentrate the volume of brine to the minimum level possible and simultaneously produce high quality product water, which will eventually lead to enhance the overall permeate water recovery of the integrated technologies.

Keywords: Freeze-melting process; Nucleation; Melt crystallization; Freezing desalination; Ice crystallization; Static freeze crystallization

1. Introduction

To date, intensive research activities on innovative nonconventional desalination technologies are continually being carried out by leading scientists in order to seek the most feasible and sustainable desalting process for brine concentration applications. Among a variety of innovative nonconventional desalination technologies, the freeze crystallization technology might be an economically and a technically feasible process for such an application. This process has a number of important advantages such as low energy requirement, low biological fouling challenges, very high separation factor, minimizes scaling and corrosion problems, low-cost materials can be used, absence of chemical pretreatment and chemical additives [1], low ecological impact [1–3]. Despite these advantages, all these processes are still in their infancy due to serious limitations and challenges [4]. To eliminate the limitations of handling and separating ice slurries in the conventional freezing desalination technologies, this paper will look at static solid layer freeze crystallization and various forms of dynamic solid layer freeze crystallization processes as alternative techniques to seawater desalination. This is due to the important advantages of solid layer freeze crystallization over the conventional freezing desalination technologies. According to Ulrich and Glade [5], the important advantages of solid layer crystallization technologies are (i) incrustation problems are avoided, as these incrustations represent the solid layer, which will eventually be separated, melted, and recovered as a final product water; (ii) easily controllable

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crystal growth rates, due to the driving force being dependent on the temperature difference at the refrigerated surface area of the plate; (iii) a simplified separation process because of the absence of an ice slurry. Thus, complicated ice separation and washing equipment, usually used in conventional desalination through freezing processes and melt suspension crystallization technologies, is avoided.

The paper's main objective is to develop and demonstrate the viability of four different freeze melting (FM) processes, on a laboratory bench-scale, for brine desalination and concentration. The specific aims of this paper are to assess the viability of a static and three dynamic FM processes to concentrate brines; compare experimental data of the proposed FM technologies; and propose a conceptual design of pilot-scale system for desalting and concentrating high saline waters.

2. Experimental

2.1. Preparation of feed samples and physicochemical analysis

Since aqueous solutions of sodium chloride give results in the desalting process very close to process brines [6], salt concentrations of 7% by mass of NaCl salt were prepared, used, and examined as feed material in this experimental investigation. The physical and chemical analysis of the proposed water samples is tabulated in Table 1.

2.2. Experimental setup

Fig. 1 shows the equipment for the crystallization experiments using a static and agitated crystallization processes. The experimental setup for the static crystallization process comprises of a laboratory jacketed beaker with a capacity of 500 mL, refrigerated immersion cooler attached to the cooling coil, refrigerated thermostatic bath, circulator, and flexible tubing.

Table 1
Physical and chemical analyses of feed samples

Feed	NaCl
Feed salinity (wt.%)	7.0
Electrical conductivity (mS/cm)	84.8
Volume (mL)	500
Freezing point (°C)	–4.8

The experimental setup for the static and agitated crystallization processes are identical apart from the agitation system used. In the case of the mechanically stirred crystallization process, the setup consists of overhead stirrer assembly, which includes an overhead stirrer and stirring paddle. As for the experimental setup for the crystallization process using a bubbling system, an air pump assembly that includes an air pump with a ball type ceramic air-stone diffuser was utilized in this study. The experimental setup for the crystallization process using an ultrasonic radiation system was provided with the ultrasonic radiation assembly that consisted of an ultrasonic processor device and an ultrasonic probe.

2.3. Experimental procedure

The operating procedure is presented in Fig. 2. All experiments were conducted in batch mode. Referring to the simplified block diagram in Fig. 2, prior to conducting any experiment, the feed sample was prepared, and then the physiochemical analysis was performed on the feed sample. The jacketed beaker was filled with a constant mass of feed material, that is, 500 g. For all the experiments, the temperature of the heat transfer medium (HTM) was initially reduced via operation of the refrigerated immersion cooler. The circulator was manually turned on when the temperature of HTM reached the specified crystallization cooling rate. The operational cycle of precooling was started to lower the temperature of the jacketed beaker containing the feed sample. For all experiments using the agitated crystallization process, the agitator system used, such as; stirring paddle, air-stone diffuser, or an ultrasonic probe, was dipped into the jacketed beaker. The agitation system was turned on prior to beginning the pre-cooling operation. The agitation rate was set at the predetermined value that remains constant for the duration of the experiment.

For all the experiments, once the temperature of the feed sample reached the freezing point of the feed, a seed ice crystal was added to achieve the nucleation of ice crystals,

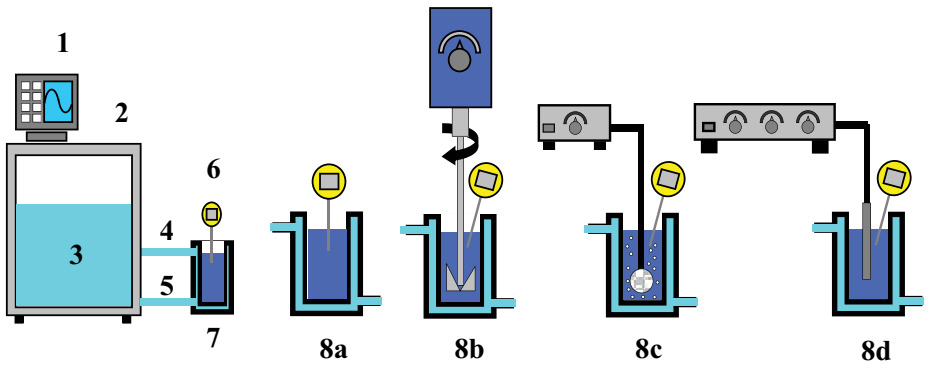

Fig. 1. Scheme of experimental setup. (1) Heating and cooling PID controller, (2) Heating and cooling bath thermostatic bath, (3) Heat transfer medium (HTM), (4 and 5) Inlet and outlet HTM flexible tubes, respectively, (6) Digital thermometer, (7) Jacketed beaker, (8a) Static crystallizer and agitated crystallizer using; (8b) Mechanical stirring, (8c) Air-pump, (8d) Ultrasonic device.

which was then gradually grew over the duration of the experiment. The ice crystals progressively crystallized on the refrigerated surfaces of the jacketed beaker perpendicularly outward to the surfaces leading to the formation on an evenly thin crystal coat on the refrigerated surface. After running the experiment for a predetermined time, the operation of the circulator was terminated, and simultaneously the residue (that is, brine) was drained and retained for further analysis, as shown in Fig. 2. After draining the brine from the system, the ice crystal layer was melted. Following sampling, physiochemical analyses was carried out on the residue and product water samples as per standard procedure.

3. Results and discussion

For all tests, Table 2 presents, concentrating and treating NaCl solution with a salt concentration of 7 wt.% using static crystallization process. The total time duration to reach the lowest temperature of crystallization was 70 min. In each test, the influencing parameter, that is, cooling rate was examined upon the performance indicators, including water recovery, permeate concentration, and salt rejection. These experiments were carried out in a feed stage process, that is, single freezing stage.

3.1. Static freeze crystallization process

In the first series of experiments, the potential of the static crystallization process was investigated for desalinating. Fig. 3 shows the experimental data on the salt concentration of feed of 7 wt.%. Results of the water recovery ratio and salt rejection ratio as a function of the cooling rate are shown in Fig. 3. It can be seen that at cooling rates of –0.004 and –0.061°C/min the water recovery is 24.52 and 44.70, respectively. Fig. 3 shows a dramatic decrease in water recovery ratio when the crystallization temperature was increased. This is due to the fact that growth rate of ice layer decreased as a result of increasing the crystallization temperature. For all experiments, the total time duration to reach the lowest temperature of crystallization was 70 min. The experiments were run for 5 min after attaining the lowest temperature. This trend observation has been demonstrated in earlier study conducted by Rich et al. [7], which was first thoroughly investigated by Burton et al. [8], and later reported by Wilson [9] and Rosenberger [10]. The trend of the graph was found more likely linear. The results indicate that the salinity of product water is very

Table 2
Investigated crystallization temperatures, cooling rates and crystallization time for static crystallization process

Feed concentration (wt.%)	7
Crystallization temperature (°C)	–6 to –10
Cooling rates (°C/min)	–0.004 to –0.061
Crystallization time (min)	70

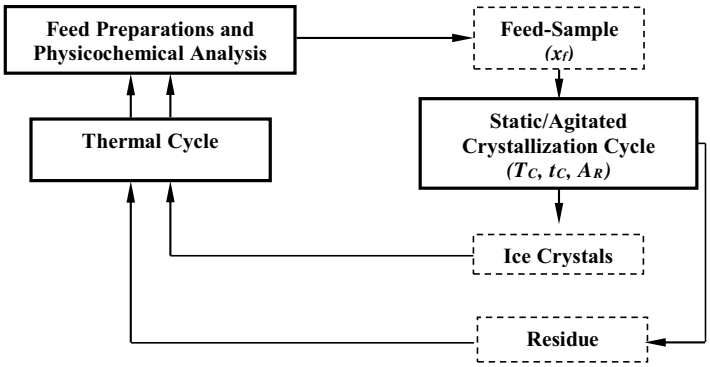

Fig. 2. Simplified block diagram of the experimental set-up. x_f is the feed concentration (wt.%), T_C is the temperature of crystallization process (°C), and t_C is the running time of crystallization process (minute), and A_R is the agitation rate.

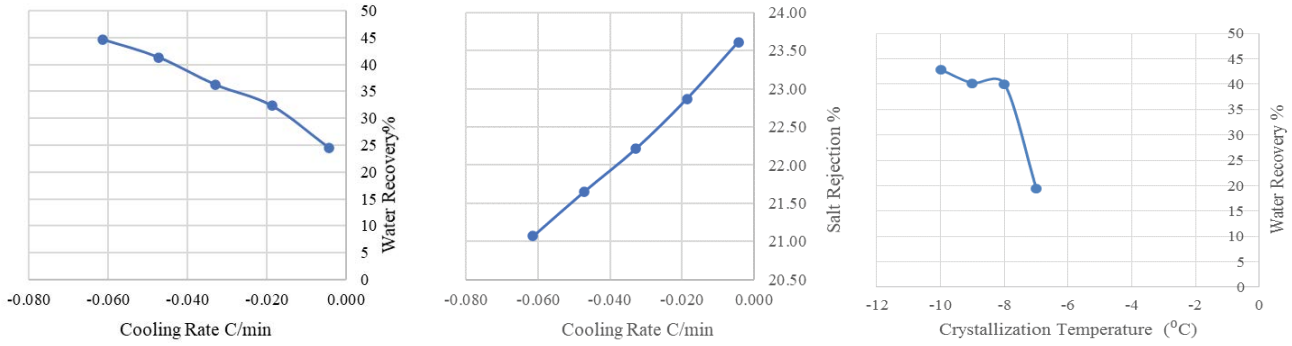

Fig. 3. Water recovery and salt rejection vs. cooling rate and water recovery vs. crystallization temperature at 70 min of crystallization time for 7 wt.% static crystallization.

sensitive to changes in cooling rate. The results proved that the slow crystal growth rates, dictated by increasing the cooling rate, are of great importance in improving the separation efficiency of the static crystallization process. According to Myerson [11], lower growth rate is leading to increasing diffusivity of the impurity and at the same time it is decreasing diffusion ice crystalline thickness. At cooling rates of –0.004, –0.019, –0.033, –0.047, and –0.061°C/min, the salt rejections are 23.61, 22.87, 22.21, 21.66 and 21.07, respectively. The trend of the graph of the salt rejection ratios (shown in Fig. 3) is more or less linear. This trend observation has been demonstrated in an earlier study conducted by Kim et al. [12], and this behavior can be noticed in all dynamic crystallization processes presented in Figs. 5–12.

In general, the water recovery ratio results were found to be inversely proportional to the crystallization cooling rate, whereas the salt rejection was found proportional to the cooling rate.

3.2. Dynamic crystallization process using ultrasonic process

In the second series of experiments, the potential of the dynamic crystallization process using ultrasonic process (UP) was investigated for desalinating, concentrating, and treating different concentrations of NaCl solution ranging from 7 wt.% as indicated in Table 2. The investigated amplitudes of UP were ranged from 20 up to 60%.

Fig. 4 shows the experimental results on feed concentration of 7 wt.% at cooling rates of –0.004 to –0.061°C/min at 80 min of crystallization time and 20%. Results of the water recovery ratio and salt rejection ratio as a function of the cooling rate are shown in Fig. 4. It can be seen that at cooling rates of –0.004 and –0.054°C/min, the water recovery ratio is 8.04% and 38.18%, respectively. At cooling rates of –0.015, –0.032, –0.048, and –0.065°C/min, the salt rejections are 3.17%, 9.77%, 14.43%, 15.94%, and 23.93%, respectively.

Fig. 5 shows the experimental results on feed concentration of 7 wt.% at cooling rates of –0.004 to –0.061°C/min at 80 min of crystallization time and 40%. Results of the water recovery ratio and salt rejection ratio as a function of the cooling rate are shown in Fig. 5. It can be seen that at cooling rates of –0.004 and –0.054°C/min, the water recovery ratio is 4.96% and 42.68%, respectively. For all cases (Figs. 5 and 6), similar to the static crystallization process, a decrease in water recovery ratio with the increase in crystallization temperature was observed due to the decreased growth rate of ice layer. At cooling rates of –0.015, –0.032, –0.048, and –0.065°C/min, the salt rejections are 9.03%, 11.63%, 12.20%, 13.39%, and 20.89%, respectively.

Fig. 6 shows the experimental results on feed concentration of 7 wt.% at cooling rates of –0.004 to –0.061°C/min

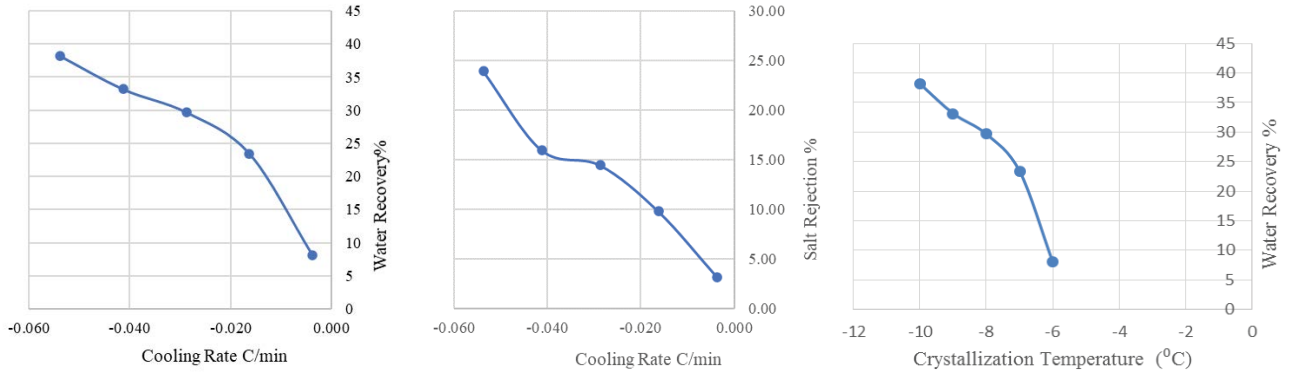

Fig. 4. Water recovery and salt rejection vs. cooling rate and water recovery vs. crystallization temperature at crystallization time of 80 min and amplitude of 20% for 7 wt.%.

Fig. 5. Water recovery and salt rejection vs. cooling rate and water recovery vs. crystallization temperature at crystallization time of 80 min and amplitude of 40% for 7 wt.%.

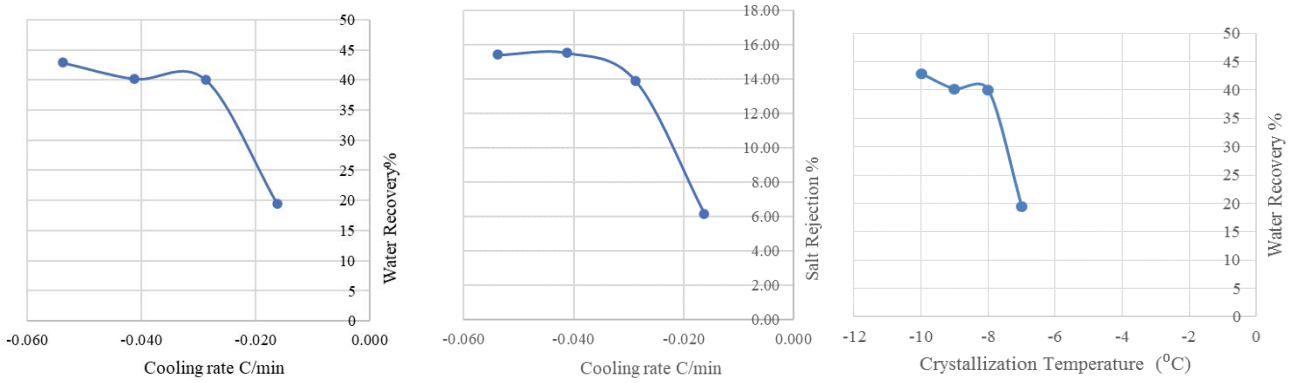

Fig. 6. Water recovery and salt rejection vs. cooling rate and water recovery vs. crystallization temperature at crystallization time of 80 min and amplitude of 60% for 7 wt.%.

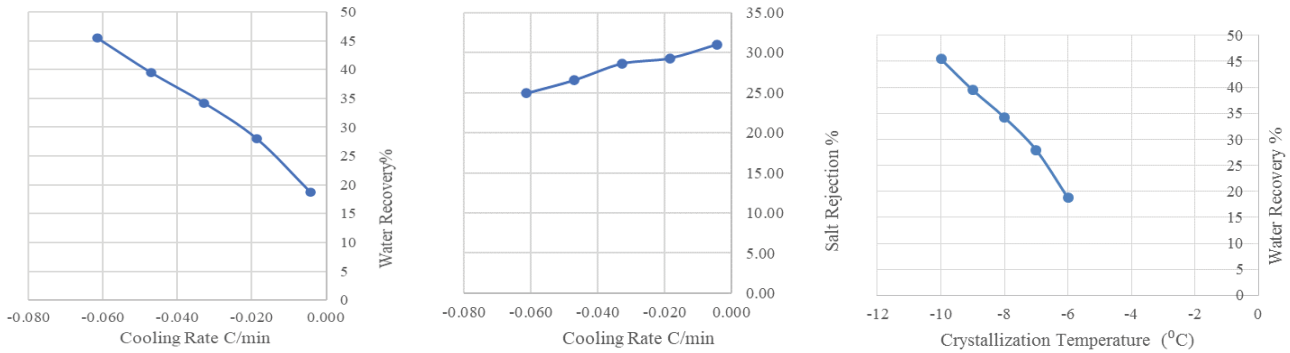

Fig. 7. Water recovery and salt rejection vs. cooling rate and water recovery vs. crystallization temperature at 70 min of crystallization time and flow rate of 10 L/min for 7 wt.%.

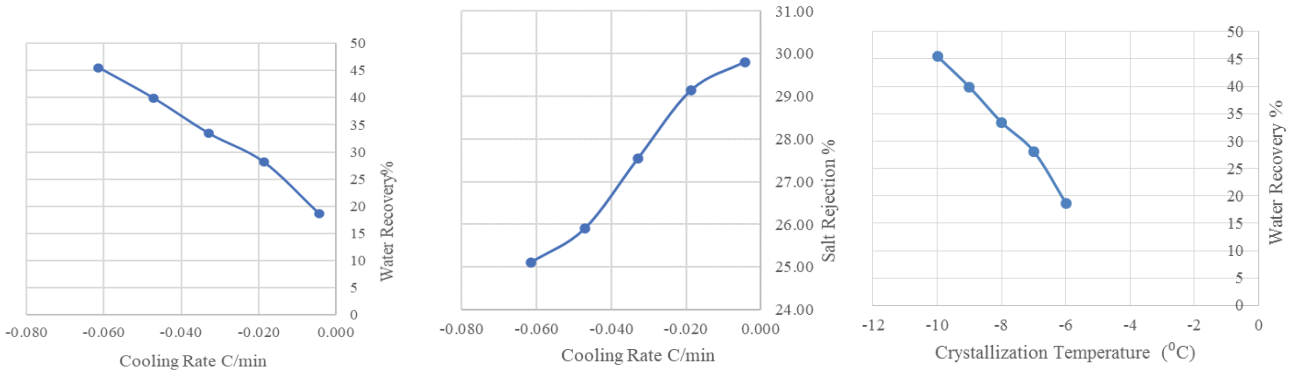

Fig. 8. Water recovery and salt rejection vs. cooling rate and water recovery vs. crystallization temperature at crystallization time of 70 min and flow rate of 20 L/min for 7 wt.%.

at 60 min of crystallization time and 60%. Results of the water recovery ratio and salt rejection ratio as a function of the cooling rate are shown in Fig. 6. It can be seen that at cooling rates of –0.016 and –0.054°C/min, the water recovery ratio is 19.48% and 42.90%, respectively. At cooling rates of –0.016, –0.029, –0.041, and –0.054°C/min, the salt rejections are 6.17%, 13.89%, 15.51%, and 15.40%, respectively.

3.3. Dynamic crystallization process using bubbling process (BP)

In the third series of experiments, the potential of the dynamic crystallization process using BP was investigated for desalinating, concentrating, and treating different concentration of NaCl solution ranging from 7 wt.% as indicated in Table 2. The investigated feed concentrations,

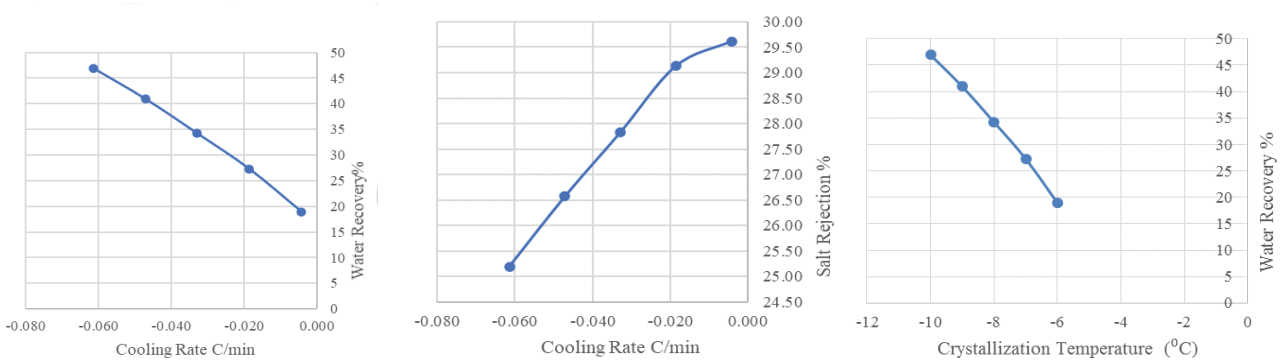

Fig. 9. Water recovery and salt rejection vs. cooling rate and water recovery vs. crystallization temperature at crystallization time of 70 min and flow rate of 30 L/min for 7 wt.%.

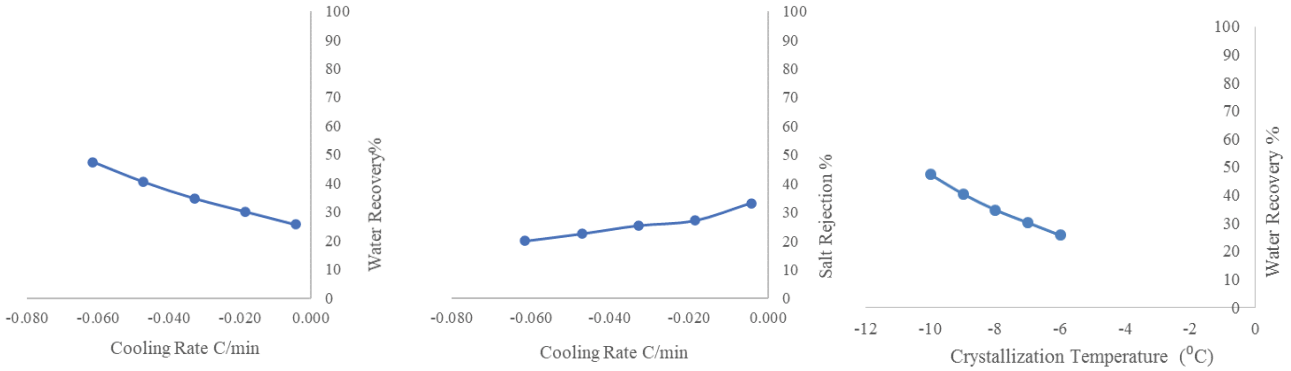

Fig. 10. Water recovery and salt rejection vs. cooling rate and water recovery vs. crystallization temperature at crystallization time of 70 min and stir rate of 200 rpm for 7 wt.%.

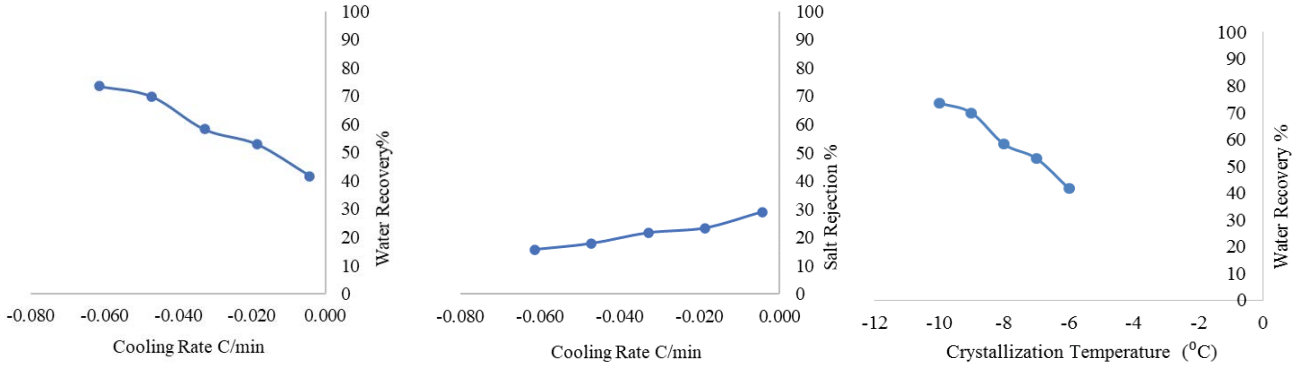

Fig. 11. Water recovery and salt rejection vs. cooling rate and water recovery vs. crystallization temperature at crystallization time of 70 min and stir rate of 400 rpm for 7 wt.%.

cooling rate, and crystallization time are as given previously for the first and second investigation. The investigated air pump flow rates ranged from 10 up to 30 L/min. In each experiment, the influences including: salt concentration, cooling rates and crystallization time were investigated upon concentration as well as the water recovery and salt rejection ratio. The predetermined values for the influences are shown in Table 2. All experiments were carried out in a feed stage process, that is, single freezing stage, without any post-treatment such as rinsing and/or sweating (i.e., partial melting).

Fig. 7 shows the experimental results on feed concentration of 7 wt.% at cooling rates of –0.004 to –0.061°C/min at 70 min of crystallization time and 10 L/min. Results of the water recovery ratio and salt rejection ratio as a function of the cooling rate are shown in Fig. 7. It can be seen that at cooling rates of –0.004 and –0.061°C/min, the water recovery ratio is 18.74% and 45.42%, respectively. At crystallization

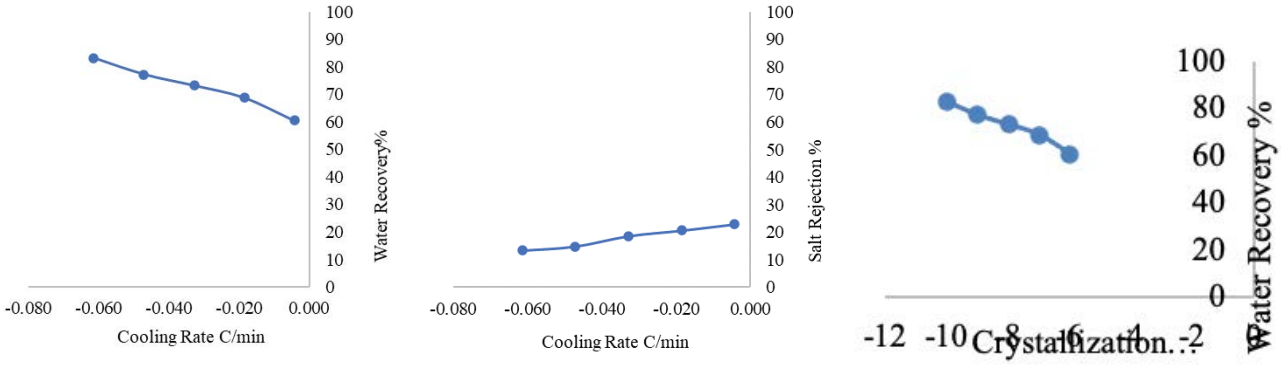

Fig. 12. Water recovery and salt rejection vs. cooling rate and water recovery vs. crystallization temperature at crystallization time of 70 min and stir rate of 600 rpm for 7 wt.%.

temperatures of cooling rates of –0.004, –0.019, –0.033, –0.047, and –0.061°C/min, the salt rejections are 31.04%, 29.30%, 28.63%, 26.56%, and 24.93%, respectively.

Fig. 8 shows the experimental results on feed concentration of 7 wt.% at cooling rates of –0.004 to –0.061°C/min at 70 min of crystallization time and 20 L/min. Results of the water recovery ratio and salt rejection ratio as a function of the cooling rate are shown in Fig. 8. It can be seen that at cooling rates of –0.004 and –0.061°C/min, the water recovery ratio is 18.68% and 45.48%, respectively. At cooling rates of –0.004, –0.019, –0.033, –0.047, and –0.061°C/min, the salt rejections are 29.80%, 29.14%, 27.54%, 25.90%, and 25.11%, respectively.

Fig. 9 shows the experimental results on feed concentration of 7 wt.% at cooling rates of –0.004 to –0.061°C/min at 70 min of crystallization time and 30 L/min. Results of the water recovery ratio and salt rejection ratio as a function of the cooling rate are shown in Fig. 9. It can be seen that at cooling rates of –0.004 and –0.061°C/min, the water recovery ratio is 18.94% and 46.90%, respectively. For all cases (Figs. 7–9), similar to the static and dynamic crystallization using UP process, a decrease in the water recovery ratio with the increase in crystallization temperature was observed due to the decreased growth rate of ice layer. At cooling rates of –0.004, –0.019, –0.033, –0.047, and –0.061°C/min, the salt rejections are 29.61%, 29.13%, 27.83%, 26.57%, and 25.20%, respectively.

3.4. Dynamic crystallization process using mechanically stirred system

In the fourth series of experiments, the potential of the dynamic crystallization process using mechanically stirred system was investigated for desalinating, concentrating, and treating different concentration of NaCl solution ranging from 7 wt.% as indicated in Table 2. The investigated feed concentrations, cooling rate, and crystallization time are as given previously for the first, second, and third investigation. The investigated stir rates ranged from 200 up to 600 rpm. In each experiment, the influences including: salt concentration, cooling rates and crystallization time were investigated upon concentration as well as the water recovery and salt rejection ratio. The predetermined values for the influences are shown in Table 2. All experiments were carried out in a feed stage process, that is, single freezing stage, without any post-treatment such as rinsing and/or sweating (i.e., partial melting).

Fig. 10 shows the experimental results on feed concentration of 7 wt.% at cooling rates of –0.004 to –0.061°C/min at 70 min crystallization time and stirring rate of 200 rpm. Results of the water recovery ratio and salt rejection ratio as a function of the cooling rate are shown in Fig. 10. It can be seen that at cooling rates of –0.004 and –0.061°C/min, the water recovery ratio is 25.68% and 47.32%, respectively. At cooling rates of –0.015, –0.032, –0.048, and –0.065°C/min, the salt rejections are 33.17%, 27.10%, 25.39%, 22.54%, and 20.04%, respectively.

Fig. 11 shows the experimental results on feed concentration of 7 wt.% at cooling rates of –0.004 to –0.061°C/min at 70 min crystallization time and stirring rate of 400 rpm. Results of the water recovery ratio and salt rejection ratio as a function of the cooling rate are shown in Fig. 11. It can be seen that at cooling rates of –0.004 and –0.061°C/min, the water recovery ratio is 41.70% and 73.58%, respectively. For all cases (Figs. 10–12), similar to the static and dynamic crystallization process using UP and BP, a decrease in water recovery ratio with the increase in crystallization temperature was observed due to the decreased growth rate of ice layer. At cooling rates of –0.015, –0.032, –0.048, and –0.065°C/min, the salt rejections are 29.01%, 23.31%, 21.61%, 17.81%, and 15.66%, respectively.

Fig. 12 shows the experimental results on feed concentration of 7 wt.% at cooling rates of –0.004 to –0.061°C/min at 70 min crystallization time and stirring rate of 600 rpm. Results of the water recovery ratio and salt rejection ratio as a function of the cooling rate are shown in Fig. 12. It can be seen that at cooling rates of –0.004 and –0.061°C/min, the water recovery ratio is 60.60% and 83.16%, respectively. At cooling rates of –0.015, –0.032, –0.048, and –0.065°C/min, the salt rejections are 22.86%, 20.60%, 18.57%, 14.83%, and 13.36%, respectively.

3.5. Conceptual design of pilot-scale system for desalting high saline waters

The performance data obtained from Fig. 11, and more specifically run number 10, the feed concentration was 7 wt.% tested at cooling rate and stir rate of –0.004 and

Table 3
Estimation of the annual rates of all water streams of the Kadhmah RO desalination, the freeze crystallization plant, and the combined plants, where (t/y) represents ton per year

Kadhmah RO plant			Freeze crystallization plant			Combined plant		
Feed[a]	Product[b]	Brine[c]	Feed	Product	Residue	Feed[a]	Product[b]	Residue
(t/y)	(t/y)	(t/y)	(t/y)	(t/y)	(t/y)	(t/y)	(t/y)	(t/y)
239.15	34.17	191.84	169.07	70.96	98.11	*168.19*	34.17	98.11

[a]The annual rate of the feed intake.
[b]The first-stage of the RO membrane assembly produces product water at 8 and 6.5 m^3/h of this is fed to the second-stage RO membrane assembly, while the remaining product water from the first-stage (i.e., 1.5 m^3/h which is equivalent to 13.14 t/y) is not used and drained.
[c]The first-stage of the RO membrane assembly produces rejected brine at 19.3 m^3/h, and this value was considered in Table 3.

400 rpm, respectively. Table 3 shows the estimated annual rates of all liquid streams of the combined water desalination plant including conventional reverse osmosis (RO) plant and freeze crystallization commercial plant. The results provided clear evidence that the proposed crystallization process, using a single freezing stage without use of a sweating process, was capable of producing a significant amount of seawater quality level from highly concentrated RO brine, whilst simultaneously minimizing the volume of the waste stream as far as possible.

4. Conclusions

The primary concern of this study was to seek the most feasible and applicable freezing desalination technologies that are potentially capable of desalting and/or concentrating the dissolved ionic content of liquid streams, especially those brines causing severe pollution. Therefore, various forms of melt crystallization processes, namely solid layer crystallization, were considered and experimentally investigated for such an application. These experimental studies were intended to evaluate and validate the separation performance of each treatment process. The overall experimental results showed that the freeze crystallization influenced by the stirring process was effective in concentrating high salinity feed, and more specifically feed with a total dissolved solids of 70,000 ppm, while producing saline water that could subsequently be easily desalted using any type of conventional desalination technology. As a result, the volumes of waste streams, such as RO brine, could be substantially reduced. For such an application, the experimental results were highly encouraging, and proved that the proposed technology was technically feasible and might be competitive with other available commercial brine concentration systems. The recommendation is for the crystallizer capacity to be increased to a suggested range of 50 to 100 L, taking into account that the investigated agitation system might be changed to higher agitation rates corresponding to the crystallizer's capacity. Detailed technical-economic analysis and studies are recommended to be taken into consideration in future research to estimate the actual power consumption of the investigated agitated crystallization process and compare the figures obtained to those for each crystallizer option.

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