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Solid layer freeze crystallization processes for desalting saline waters

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ABSTRACT

The separation performance of solid layer freeze crystallization (SLFC) processes for desalting saline waters under the influences of end-point temperature, cooling rate, feed concentration, and agitation rate was investigated. The investigated SLFC processes are static freeze crystallization (SFC) and three different types of dynamic freeze crystallization (DFC) systems agitated by bubbling process (BP), a mechanically stirred system (MSS), and an ultrasonic process (UP). The NaCl feed solution concentrations used were 0.5, 3.5 and 7 wt%. The SFC system was able to achieve the maximum salt rejection of 3.12%, 14.10%, and 14.26% for feed salinities of 0.5, 3.5, and 7 wt%, respectively. The DFC system agitated by BP achieved 50.34%, 30.70%, and 19.90% maximum salt rejection for feed salinities of 0.5, 3.5, and 7 wt%, respectively. The DFC system agitated by MSS achieved 70.20%, 37.30%, and 14% maximum salt rejection for feed salinities of 0.5, 3.5, and 7 wt%, respectively. The DFC system agitated by UP was able to achieve the maximum salt rejection of 84%, 34%, and 28% for feed salinities of 0.5, 3.5, and 7 wt%, respectively. The experimental results were encouraging and may be used to develop a hybrid system combining the membrane based process (such as reverse osmosis or forward osmosis technology) with the most suitable SLFC system, on a pilot scale, for further research and development.

Keywords: Freeze–melting process; Forward osmosis; Reverse osmosis; Agitation system; Ice crystallization; Static crystallizer; Desalting; Bubbling process; Mechanically stirred; Ultrasonic process

1. Introduction

Seawater desalination process can be accomplished through a number of different technologies that remove either the salt molecules or the water molecules from the saline water [1]. Seawater desalination technologies are usually classified into two main categories which are thermal and membrane separation process. The thermal separation processes are multi-stage flash (MSF) distillation, multi-effect distillation (MED), vapor compression (VC) distillation, and freezing, whereas the membrane separation process are reverse osmosis (RO), forward osmosis (FO), electro dialysis (ED), although there are other approaches (e.g., ion exchange) and hybrid processes (e.g., membrane distillation) that can be utilized for seawater desalination applications [2]. The principles of these desalination technologies and methods are described in detail in the literature [1,3–9].

MSF and RO are used extensively for seawater desalination applications [1,4,10]. However, the MSF process is usually coupled with power generation plants and is affected by high capital and operating costs and low recovery ratios compared with RO [10,11]. Also, RO membrane technology is considered to be an energy intensive process since it requires a pressure that is greater than 50 atm, because of the requirement of a high hydraulic pressure to overcome the osmotic pressure generated by seawater [12,10]. Furthermore, RO has several problems, such as a significant concentration polarization, scaling deposition, and membrane fouling, leading to the reduction of the production rate, that is, water recovery ratio [12,10]. In addition, RO has a limited water recovery ratio since this

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technology recovers only 30%–50% of freshwater from seawater while producing large volumes of undesired waste brines [10,13].

Therefore, intensive research activities on innovative non-conventional desalination technologies are continually being carried out by leading scientists in order to seek the most feasible and sustainable desalting process for seawater applications. Among a variety of innovative non-conventional desalination technologies, the freeze crystallization technology might be an economically and a technically feasible process for such an application.

The fact that the freezing–melting (FM) process can purify and concentrate liquids has been known for many years [14]. The simplest natural example is that sea-ice has a much lower salt content than seawater, a phenomenon used by the inhabitants of the polar regions as a source of drinking water. The first treatment system on water desalination by freezing was introduced by Anton Maria Lorgna in 1786 as reported in the literatures [2]. Lorgna has performed the first experiments on desalination by freezing, through producing a block of fresh water ice from seawater using Venice lagoon. The laboratory apparatus was capable of reducing the TDS of seawater from 36,200 ppm down to traces of salts over a series of successive freezing stages. The apparatus was further developed in order to include a washing process prior to conducting the melting operation to achieve product water at high quality level. After developing the refrigeration systems, the first experimental freezing desalination plant was revived in the late 1930s in Italy by the Institute Superior di Sánita. This pilot plant was utilizing indirect freezing method as reported in the literature [14]. Several approaches using freezing desalination technologies were developed in the period 1950–1970 [1]. According to Johnson [15], the first successful pilot plant was demonstrated by the Carrier Corporation. This pilot plant was utilizing a vacuum freeze process employing an absorption system. The Structures Wells Corporation, on the other hand, was intensively involved in developing a secondary refrigerant freeze technology. A plant with a capacity of 200,000 gpd was built during the early 1960s [15]. Another developer known as Colt industries continued the development of a primary vacuum freeze process, and successfully constructed a pilot plant with a capacity of 100,000 gpd at Wrightville Beach, North Carolina (USA), in the late 1960s. The United Kingdom Atomic Energy Authority (UKAEA) in cooperation with Simon Carves, which is commercial organization, developed a secondary refrigerant process with a plant capacity of 10,000 gpd [15]. The investigated plant was successfully operated and the results were encouraging as reported by Johnson [15]. In addition to these plants, a pilot plant using vacuum freezing vapor compression technology was constructed in Middle East; whereas another plant, utilizing secondary refrigerant freezing, was built in Florida (USA); and a pilot plant, using an indirect freezing process, was built in Yanbu (Saudi Arabia) [16].

The classification of the freezing desalination technologies can be divided into three concepts (based on contact of refrigerant with the solution), which are direct contact freezing, indirect contact freezing, and vacuum freezing [1,17–19]. The most commonly known technologies are indirect freezing process with a secondary refrigerant, vacuum-freezing vapor compression process, vacuum-freezing vapor absorption process, and secondary refrigerant freezing process.

Although the FM process is not widely used commercially [17,1,4], the process has a number of important advantages. It has been reported as being effective process to remove various organic and inorganic impurities from aqueous solutions including saline water and wastewater [20–22]. This technology has high production rate and absence of moving parts [19]. The greatest potential advantage of FM is the very low energy requirement compared with that of distillation processes [18,23]. This is due to the latent heat of fusion of ice is only one-seventh the latent heat of vaporization of water [24,25]. FM separation could achieve 75% to 90% reduction of the energy required by conventional thermal process [26]. In theory, this process has a lower energy requirement when compared with other thermal separation technologies [21,27,28]. In other words, this process requires only 420 kJ/kg of energy in order to produce 1 kg of fresh water, which means that this process requires energy six times less than that of MSF requirement as reported by the literature [29,30]. According to the literatures [16,31], the energy cost of a freezing desalination process is theoretically almost similar to that of a RO membrane plants; however, the investment and operational costs for freezing technologies are less than RO membrane plants, because of the fact that the biological fouling is substantially reduced by low temperature operation. This technology can achieve a very high separation factor. The FM processes minimizes scaling and corrosion problems because of the advantage of a low operating temperature [23,32,33]. Low cost materials, such as inexpensive plastics, can be utilized at low temperature [18,32,34,35]. By using a secondary refrigerant freezing process (i.e., seawater is directly in contact with an immiscible refrigerant), a very high surface area and high heat transfer coefficient can be gained. FM process does not require chemical additives, that is, absence of pretreatment step [36]. The absence of chemical pretreatment means no discharge of toxic chemicals to the environment [36]. In addition, FM is not subject to fouling limitation [34,37] and has low ecological impact [31,35,36].

Despite a number of previous and currents patents and peer-reviewed papers published for different freezing-desalination methods and systems, all these processes are still in their infancy due to serious limitations and challenges [24]. These limitations are as follows: (i) the capital and operating costs for the freeze desalination system are higher than that of conventional distillation processes and RO technology [38]. For normal seawater (3.45% salt) at a temperature of 25°C, the minimum work has been analytically calculated and is equal to 0.86 kWh/m^3 [39]. The current power consumption for seawater RO membrane desalination is between 3 and 4 kWh/m^3, and in the case of brackish waters and groundwater, the energy is usually less than 50% of that in seawater application [40]. However, the energy consumed by RO for seawater desalination is still about four times greater than that of the minimum work. The previously mentioned Colt industries' plant, at Wrightville Beach, North Carolina (USA), was tested over 2,000 h of operation, and the power consumption was less than 10.34 kWh/m^3, which was encouraging for a non-optimized system as reported in the literatures [11,15]. According to Spiegler [41], Colt industries predict that the power consumption by their technology has a potential of being decreased down to 6.60 kWh/m^3. However, these values are only about 12 to 8 times higher than that of the required minimum work; (ii) undesirable flavors and aromas (which are initially accompanied with feed seawater) may be present in the final product [42]; (iii) freeze desalination system requires several complicated steps including ice nucleation, ice growing, ice separation and handling, and ice washing as well as ice melting [36]; (iv) freeze desalination system needs for mechanical vapor compressors, which energy intensive process. Accordingly, the operating cost of running the crystallizer at lower temperatures is an energy-intensive process [23]. The power consumption of freeze crystallization to separate seawater into freshwater and brine at given rate of production is directly proportional to the crystallization temperature. Accordingly, the operating cost of running the crystallizer at lower temperatures will be substantially increased; (v) the greatest challenge of this freezing technology is the fact that this process cannot be designed and optimized for commercial scale applications with confidence, owing to the process complexity of the main unit operations involved in the crystallizer and wash-separation system as well as melting unit [36]; (vi) during the crystallization process, the ice crystals are impure because the appearance of the brine pockets trapped inside of the ice crystals, and, thus, ice crystals may require crushing and re-crystallization of ice [36]; (vii) a progressive increase in the concentration levels of the dissolved substances and non-condensable gases [36]; (viii) wash-separation system needs certain amount of the product water in order to be used for washing the ice crystals and lowering the salt content in the final product [36].

Therefore, these processes have been utilized only to a very limited extent in commercial applications. Because of the limited knowledge in the ice nucleation and growth as well as lack of practicalities of handling and separating ice slurries, innovative methods for effective and complete separation process of ice crystals from the residual liquid have not yet been developed [36].

Freezing and subsequent removal of residual liquid as well as melting process of the ice crystalline is an alternative physical process which can be employed for seawater desalination and brine concentration applications. It has been reported that this process is effective for purifying water from various organic and inorganic impurities in the feed-water including saline water and wastewater as reported by the literatures [20,43,44]. Two different types of freeze crystallization methods are available: suspension and solid layer freeze crystallization (SLFC) [27,45]. According to Melak et al. [21], in both methods, the presence of the different compounds cannot be found in the ice crystal lattice because the ice crystal lattices are produced in small dimensions. In SLFC, the separation of ice crystals formed from the concentrated mother liquor is much easier than in the conventional suspension crystallization, in which many small ice crystals are formed [46,47].

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 SLFC processes as alternative techniques to seawater desalination. This is due to the important advantages of SLFC over the conventional freezing desalination technologies. According to Ulrich and Glade [48], the important advantages of solid layer crystallization technologies are as follows: (i) incrustation problems are avoided, as these incrustations represent the solid layer, which will eventually be separated, melted, and recovered as final product water; (ii) easily controllable 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. Furthermore, no moving parts are involved in the process equipment (apart from circulation pump); (iv) the operation of the post-crystallization treatments, such as washing and sweating, are simple; and (v) multistage process design can easily be applied. On the other hand, the limitations of these technologies are summarized as follows [48]: (a) the surface area of the refrigerated plate is limited; (b) the crystal layer adhered on the heat transfer surface requires an increase in temperature driving force to maintain the constant growth rate; otherwise, a reduction in production rate will occur with increasing thickness; (c) the crystallization and post-crystallization operations are limited in batch operating mode. This is because the desired crystal layer has to be completely melted and separated from the crystallizer, before starting the subsequent crystallization operations. This method requires additional energy for the melting process and partial heating up of the whole apparatus; (d) in the case of a multistage process, the operational cost is dramatically increased due to the repetition of the crystallization process, while the production rate of the overall multistage process is decreased. The last two points may be avoided at some point, when the solid layer crystallization technology is operated in continuous mode.

The primary concern of this paper is to seek the most feasible and applicable solid layer freeze crystallization technologies that are potentially capable of concentrating the dissolved ionic content of the liquid streams, especially for those causing severe pollution problems, or drawing solutions using NaCl solutes. Therefore, the performance of a static crystallization technique with various forms of agitated crystallization processes was experimentally investigated and assessed for treating a range of liquid streams, using aqueous solutions of sodium chloride (NaCl). The investigated saline waters ranged from low salinity simulating brackish water up to high concentration typical of those causing the most severe pollution problems, such as reject brine of desalination plants. Post-treatment processes, such as washing and sweating, were not considered in this study. By eliminating post-treatment (e.g., sweating process), a number of considerable advantages can be rendered to the freezing process; these are (a) the total amount of final product water will be increased since there is no certain amount of product water will be removed either by rinsing or sweating process. As a result, the mass of the crystal layer will be maintained at maximum level; (b) the time retention of the freezing stage will be substantially reduced, since the rinsing or sweating process will be eliminated, so the total melting process can be immediately performed in the fastest possible way, leading to dramatically increasing the production rate; and (c) additional energy consumption of the sweating process will be avoided.

A laboratory bench-scale experimental setup was used for investigating and verifying the performance of a static crystallizer with different types of agitation systems for desalting NaCl solutions at different salt concentrations ranging from 0.5 to 7 wt%. These laboratory investigations were carried out using a thermo-stated double wall reaction vessel with a capacity of 200 mL. The crystallization process was investigated in batch mode with three agitation systems: a bubbling system (BS), a mechanically stirred system (MSS), and an ultrasonic system (US). These were examined individually, and the results were analyzed and compared with the results of the performance of the crystallizer when no agitation was applied, that is, the static crystallization process.

The main objective of this study is to assess the viability of the static freeze crystallization and various forms of dynamic freeze crystallization processes for introducing future hybrid system combining the semi permeable membrane technology and freeze separation process. The specific aims of this laboratory-scale experimental investigation are to verify the influence of the initial salt concentration of the feed, crystallization temperature, crystallization time, and agitation rate (such as air pressure for the BS, stir rate for the MSS, and amplitude rate for the US), upon the salt rejection and water recovery.

2. Material and methods

Four experimental setups were prepared, constructed, and tested for investigating and verifying the performance of a static crystallizer with different types of agitation systems for treating aqueous solutions of NaCl at different salt concentrations. The principal unit operations that have been considered for the laboratory study are crystallization, separation, and total melting. The applied crystallization process is characterized as the secondary-refrigerant indirect freezing method, and utilizes a solid layer crystallization concept.

2.1. Experimental setup description

Fig. 1 shows the equipment for the crystallization experiments using a static and agitated crystallization processes.

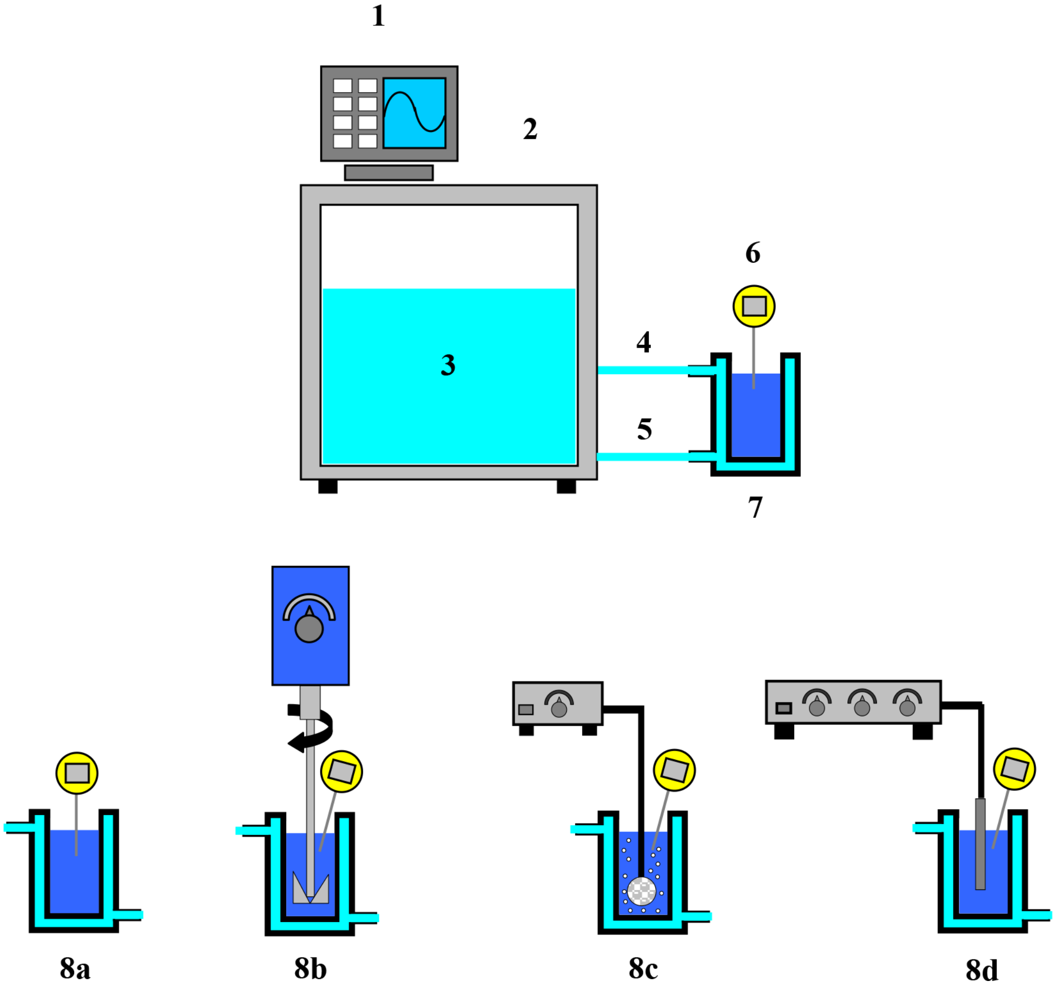


Fig. 1. Scheme of experimental setups, with (1) heating and cooling PID controller, (2) heating and cooling bath thermostatic bath, (3) heat transfer medium (HTM), (4) and (5) inlet and outlet HTM flexible tubes, respectively, (6) digital thermometer, (7) jacketed beaker, (8a) static crystallizer and agitated crystallizer using, (8b) mechanical stirring, (8c) air-pump, (8d) ultrasonic device.

The experimental setup for the static crystallization process comprises of a laboratory jacketed beaker (borosilicate glass jacketed reaction vessel with hose connectors) with a capacity of 200 mL, refrigerated immersion cooler attached to the cooling coil, refrigerated thermostatic bath, circulator, and flexible tubing.

The refrigeration system used for all the laboratory setups was identical, which involves the use of a refrigerated immersion cooler connected to a cooling coil. The latter is immersed in a heat transfer medium (HTM) that is stored in a thermostatic bath. The circulator is installed above the thermostatic bath, so the cooling coil and suction line of the circulator are immersed in an HTM.

The circulator and jacketed beaker are connected by means of flexible tubes. The jacketed beaker was thermodynamically insulated by using foam pipe insulation, while the top surface of the jacketed beaker was entirely open. The thermostatic bath contains 4 L of HTM. The HTM represents a mixture of an antifreeze solution and deionized water. The antifreeze solution was diluted at a weight ratio of 2:1.

The experimental setups 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.

All experimental setups utilized two digital thermometers, where the first one was used for monitoring the operating temperature of HTM, while the second one was used to track the temperature of feed/residue during the operational period of the experiment. This was achieved by immersing the semiconductor measuring elements of the digital thermometers into the mentioned solutions by means of supporting equipment.

2.2. Preparation of feed samples and physicochemical analysis

Since aqueous solutions of sodium chloride give results in the desalting process very close to process brines [49], different salt concentrations of NaCl solutions were prepared, used, and examined as feed material in this experimental investigation. The initial salt concentration of the feed streams used ranged from 0.5% to 7% by weight of NaCl salt. Sodium chloride solutions were made by dissolving a weighed amount of NaCl in a known weight of distilled water.

The physical and chemical analysis of all water samples included measurements of total dissolved solids (TDS), electrical conductivity, weight, volume, and temperature. The physicochemical analysis of the tested feed samples is tabulated in Table 1.

2.3. Experimental procedure

The operating procedure for the experiments is presented in Fig. 2. These experiments were carried out 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, 200 g. For all the experiments, the temperature of the HTM was initially reduced via operation of the refrigerated immersion cooler. When the temperature of HTM reached the desired crystallization temperature, the circulator was manually turned on, and then simultaneously the operational cycle of pre-cooling takes place to decrease the temperature of the jacketed beaker, which includes the feed sample. This is achieved by pumping the HTM from the thermostatic bath to the jacketed beaker at flow rate of 0.8 L/min. The HTM temperature was controlled and set at a desired value through a temperature control knob on the circulator.

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 and set at distance of 12.5 mm above the lower surface of the jacked beaker in order to avoid ice encasing of the agitator. The agitation system was turned on prior to beginning the pre-cooling operation. The agitation rate (such as air pressure for the bubbling process (BP), stir rate for the MSS, and amplitude rate for the ultrasonic process [UP]) was set at the predetermined value that remains constant for the duration of the experiment.

For crystallization experiments using a static approach, the overhead stirrer assembly was devoted only to the pre-cooling process at a rotational speed of 400 rpm, so

Table 1
Physical and chemical analyses of feed samples

Feed	Feed salinity (wt%)	Electrical conductivity (mS/cm)	Mass (g)	Freezing point (°C)
NaCl	0.5	9.2	200	–0.4
	3.5	49.6	200	–2.2
	7.0	84.8	200	–4.7

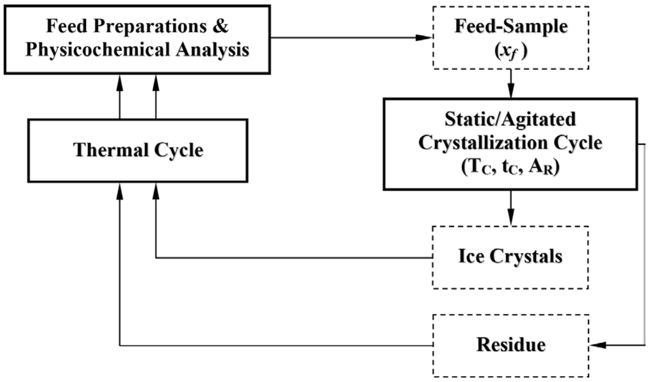


Fig. 2. Simplified block diagram of the operational process for the experiments, where x_f is the feed concentration (wt%), T_C is the temperature of crystallization process (°C), t_C is the running time of crystallization process (minute), and A_R is the agitation rate.

when the feed temperature reached the freezing point, the operation of overhead stirrer assembly was terminated and the impeller was rapidly removed from the jacketed beaker. This procedure enhanced and accelerated the pre-cooling process. When the flowing HTM circulates around the jacketed beaker's surfaces, the HTM absorbs heat from the feed sample through the refrigerated surfaces of the jacketed beaker. Consequently, the feed temperature was gradually reduced. By continuously circulating HTM around a jacketed beaker, the temperature of the feed sample decreased until the freezing point of the feed was reached.

According to Randall et al. [50], the aqueous solutions have the potential to begin the nucleation process but will remain free of ice crystals until either a maximum level of supersaturation is reached or a "seed" ice crystal is added to the aqueous solution. This means that the crystallization process can be occurred if the metastable limit is reached or if the aqueous solution is seeded with ice. Accordingly, 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 (and to avoid nucleation at high super-cooling), which then gradually grew over the duration of the experiment. By continuously circulating HTM around a jacketed beaker, 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. This process simultaneously leads to reduce the mass of residue. After running the experiment for a pre-determined time, the operation of the circulator was terminated, and simultaneously the residue (i.e., 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 inside the jacketed beaker by flowing hot water through the jacketed vessel. Following sampling, physiochemical analyses were carried out on the residue and product water samples as per standard procedure.

All of the tests were performed according to the predetermined values shown in Table 2. The crystallization experiments were conducted under different conditions and operating modes. This was done by changing the mode of crystallization, and operating conditions, such as initial feed concentration, agitation rate, crystallization time, and crystallization temperature.

Table 2
Operating parameters and conditions during crystallization experiments

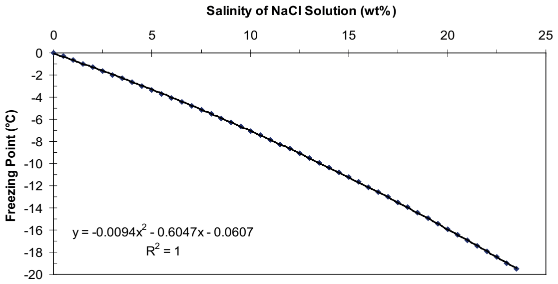
Crystallization mode	Feed salinity (wt%)	Freezing time (min)	HTM temp. (°C)	Agitation rate (rpm), (L/min), or (amplitude)
Static	0.5–7	15–60	–11.5	0
Static	0.5	60	–4.8 to –11.5	0
Bubbled	0.5–7	30	–11.5	0–13.5 L/min
Mechanically stirred	0.5–7	30	–11.5	0–900 rpm
Ultrasonic	0.5–7	30	–11.5	0–100

3. Results and discussion

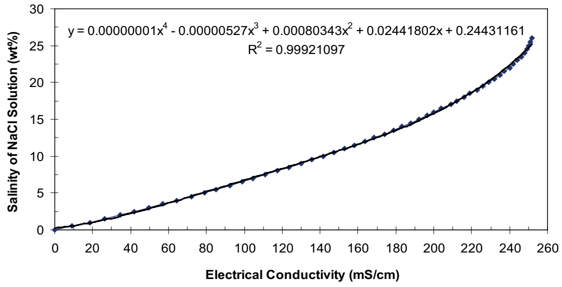
For the purpose of establishing a phase diagram for the aqueous solutions of sodium chloride (NaCl), the parameter of freezing point depression was determined theoretically over a wide range of salt concentrations, ranging from 0 up to 23.5 wt%. Furthermore, the relationship between the electrical conductivity and salt concentration (measured in wt%) was determined by experimentally measuring the salinity of NaCl solution over a wide range of electrical conductivity values, ranging from 0 to 252 mS/cm.

The variations of the mentioned theoretical and experimental results of the key parameters were plotted on graphs as shown in Figs. 3(a) and (b). Based on the experimental results, the empirical polynomial correlations were derived and fitted for the freezing point as a function of TDS value (wt%), and for the TDS value (wt%) as a function of electrical conductivity (mS/cm). These equations were used to instantly calculate the theoretical results of the main key parameters from the conductivity measurement. Figs. 3(a) and (b) show the theoretical phase diagram, and empirical graphs and equations (including R value) for the NaCl solution.

The important observations that can be made from the phase diagram is that the theoretical freezing points of the investigated NaCl solutions (which have TDS values of 0.5, 3.5, and 7.0 wt%) were –0.3°C, –2.3°C, –4.8°C, respectively. In contrast, the experimental results were –0.4°C, –2.2°C, and –4.7°C, respectively. According to van der Ham et al. [51],



(a) Phase diagram



(b) Salinity vs. electrical conductivity

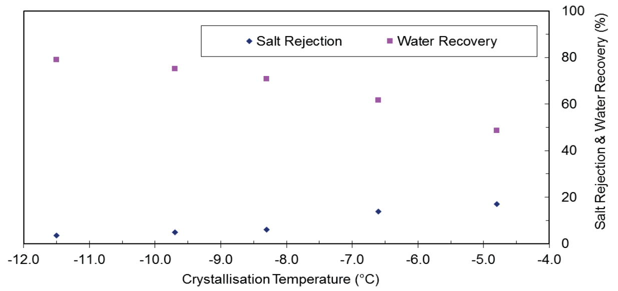
Fig. 3. Summary of the phase diagram and relationships between the main key parameters for the NaCl solution, where y and x are the dependant and the independent variables of the empirical equation, respectively, and R^2 is the polynomial regression correlation coefficient: (a) phase diagram, (b) salinity vs. electrical conductivity.

the eutectic temperature for the NaCl solution is –21.2°C, determined at eutectic chemical composition of 23.3 wt% NaCl salt and electrical conductivity of 246 mS/cm.

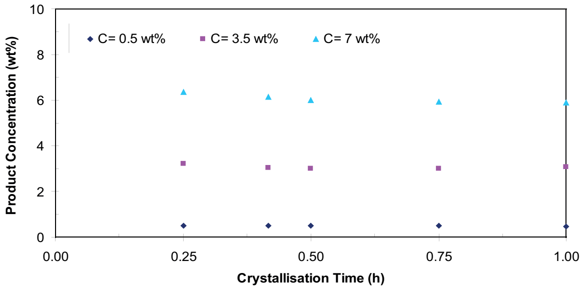
3.1. Static crystallization process

Two sets of experiments were carried out in the static crystallization process. The first set was done at a feed concentration of 0.5 wt%, where the crystallization temperatures ranged from –4.8°C to –11.5°C. The actual operational period of the crystallization process for the experiments was set at 1 h. Results of these experiments are presented in Figs. 4(a) and (b). The second set of the experiments was performed at various feed concentrations ranging from 0.5 to 7.0 wt%. The crystallization temperatures were set at –11.5°C, while the actual operational period of crystallization process for the experiments varied from 0.25 to 1 h.

The effect of crystallization temperature on the salt rejection ratio can be observed in Fig. 4(a). This trend observation has been demonstrated in earlier study conducted by Rich et al. [52]. The trend of the graph was found more likely linear. The results indicate that the salinity of product water is very sensitive to changes in crystallization temperature. The results proved that the slow crystal growth rates, dictated by increasing the crystallization temperature, are of great importance in improving the separation efficiency of the static crystallization process. According to Myerson [53], lower growth rate is leading to increasing diffusivity of the impurity and at the same time it is decreasing diffusion ice crystalline thickness. The maximum and minimum salt concentrations of product water were 0.41 and 0.48 wt%, respectively, where these values were achieved at a crystallization temperature of –4.8°C and –11.5°C, respectively. This gives a clear indication that the salinity of the produced ice layer is improved with lower ice growth rate, which is achieved at a higher cooling rate. In other words, the salt rejection ratio was found to be proportional to the crystallization temperature and cooling rate, and inversely proportional to the feed concentration and average growth rate. This trend observation has been demonstrated in earlier study conducted by Rich et al. [52], which was first thoroughly investigated by Burton et al. [54], and later reported by Wilson [55] and Rosenberger [56]. These previous studies have confirmed that the concentration of crystal increases with increasing growth rates. The aforementioned previous investigations postulated that partial rejection of impurities at the crystal-solution interface cause the concentration of impurities in the interfacial region to increase above its value in bulk solution. Thus, with increasing growth rates, impurities can be rejected at a rate faster than they can diffuse into bulk solution, resulting in their accumulation in the interfacial region, leading to lower the quality of produced ice crystals as reported by Myerson [53].



(a) SR & WR vs. crystallisation temp.(either italics or normal)



(b) Product water conc. vs. crystallisation time.

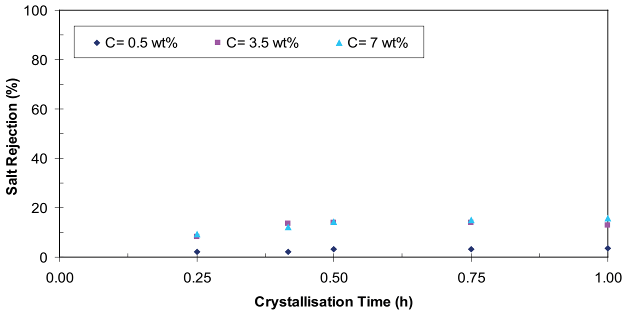
Fig. 4. Experimental data for static crystallization experiments, where SR and WR are the salt rejection and water recovery, respectively, and C is the feed salt concentration: (a) SR and WR vs. crystallization temp. (either italics or normal), (b) product water conc. vs. crystallization time.

The water recovery ratio, on the other hand, was found to be inversely proportional to the crystallization temperature, cooling rate, and feed concentration, but proportional to the average growth rate. Fig. 4(a) 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 was decreased as a result of increasing the crystallization temperature. The trend of the graph of the salt rejection ratios (shown in Fig. 4(a)) is more or less linear. This trend observation has been demonstrated in an earlier study conducted by Kim et al. [57]. Fig. 4(b) shows the influence of the crystallization time and feed concentration on the quality of product water, in terms of salinity. During the crystallization process, usually the ice crystal layers are accompanied by undesired impurities that are generated from the brine pockets trapped inside of the ice crystals. Accordingly, the salt concentration of product water was found to be proportional to the feed concentration. This trend observation was demonstrated in an earlier study conducted by Rich et al. [52]. Furthermore, the inclusion of impurities upon progressive freezing has been further described by other author [58], who confirmed that the cooling rate has a strong affect upon the impurity migration. A high rate of growth, achieved by low cooling rate, will contribute to build inclusion of drops within pockets of brine. The purification of the ice layer in a SLFC is depends on the cooling rate and the initial feed concentration as shown in the literatures [59,60]. As a result, the salinity of product water dramatically decreased (i.e., improved) as the feed concentration decreased. In addition to the impurities due to trapped brine pockets, the quality of ice crystals is reduced by the adhered residual liquid in the ice layer after the brine has been drained off the crystallizer. This clearly indicates that the product water quality is sensitive to the variations of the feed concentration. The salinity of product water, on the other hand, was not affected throughout by the variation of crystallization time, as shown in Fig. 4(b). In general, the salinity of product water was on average 0.49, 3.06, and 6.07 wt% for the experiments with NaCl solutions at concentrations of 0.5, 3.5, and 7 wt%, respectively.

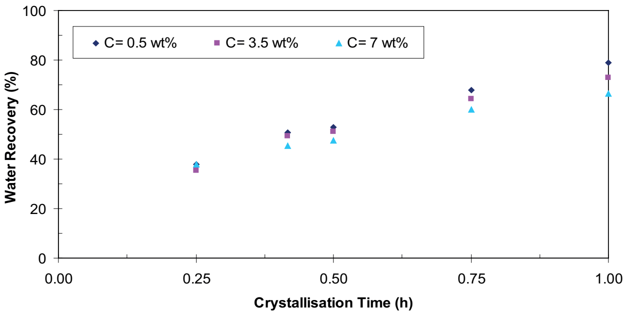
Figs. 5(a) and (b) show the influences of feed concentration and crystallization time on the performance of the static crystallization process, with respect to salt rejection and water recovery ratios. Fig. 5(a) shows that the salt rejection ratio increased slightly as the crystallization time increased. This was because the thickness of the crystal layer, which is a relatively good heat insulator, increased with increasing crystallization time. As a result, reduction in the heat transfer rate, accompanied by a reduction in the growth rate, occurred when the crystallization time increased. As reported by Kim et al. [57], the growth rate decreases as the crystalline layer thickness increases during the ice growth process. This is due to the thermal conductive resistance of crystalline layer that is proportional to the crystalline layer thickness. By comparing the results of the experiments with feed concentrations of 3.5 and 7 wt%, the salt rejection was slightly reduced as the feed concentration decreased. However, the trend is different for feed water with a salt concentration of 0.5 wt% when compared with the results of the experiments with higher feed concentrations. The salt rejection was noticeably reduced for the case of 0.5 wt% feed concentration. The reason behind this was associated with the investigated crystallization temperature, which was set at a constant low value, taking into account that the freezing points of the investigated feed samples are not identical. Thus, the temperature difference between the crystallization temperature and freezing point of feed for the tested feed samples was not the same. As a result, the cooling rate became higher in the case of 0.5 wt% feed concentration. On the other hand, the water recovery was found to be proportional to the crystallization time and inversely proportional to the feed concentration, as shown in Fig. 5(b). For all of the tests, the ice crystal layers, obtained from all static crystallization experiments, were found to be rigid.

The degree of the salt concentration of the product water achieved by the static crystallization process is not within the accepted limits because it is not complying with certified international standards for drinking waters such as the World Health Organization (WHO). The quality of product water obtained by static freeze crystallization (SFC) is not comparable with that obtained from RO membrane technology. Therefore, the investigated process requires a post-treatment process, washing or sweating, to improve the water quality of final product and to keep the salt concentration level within the certified international standards for drinking waters. However, post-treatment process is beyond the scope of this study. Washing process can be achieved by rinsing the external surface of ice crystal layer by using pure water taken from final product. As for sweating process, this technique is defined as a temperature induced purification step based on a partial melting process performed by gradually increasing the temperature of the tube up to a certain level close to the freezing point of the required product [48]. Thus, substantial amounts of impurities adhering to the crystal surface of the crystalline and those brine buckets, contained in pores of the crystalline structure, can be rejected and drained under the influence of gravity [48]. When the temperature of the tube increases, the viscosity of the impurities will be decreased, leading to easy and enhanced draining off [48]. Therefore, the purity of ice crystals can be significantly improved by the sweating process. Based on experimental study, Rich et al. [52] showed that sweating process is effectively capable to lower the salinity of feed and purify the interior of ice crystalline and provide product water that reaches the drinking water quality.

Within the studied domain, the separation performance of the static crystallization process was found to be not efficient in purifying the crystal layer and its quality. Relatively poor quality product water was obtained, even for low feed concentrations, which was due to the inclusion of drops or pockets of brine within the crystal layer. According to Ulrich and Glade [48] and Rich et al. [16], the main reasons for obtaining high impurity crystal layers are usually associated with the following: (i) nucleation achieved at high super-cooling, (ii) high crystal growth rates, and (iii) adherence of contaminated reject brine at the end of the crystallization step. Therefore, further optimizing the crystallization temperature can be suggested for each feed concentration case, in order to improve the salt rejection ratio. This is due to the mentioned parameter greatly influencing the salt rejection as previously proven through experimental investigation. However, the water recovery would be expected to be lower while optimizing the crystallization rate, leading eventually to a negative effect on the production rate. Therefore, the crystallization process with various forms



(a) SR vs. crystallisation time.



(b) WR vs. crystallisation time.

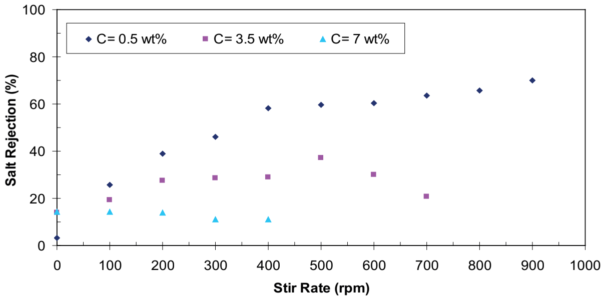
Fig. 5. Experimental data for static crystallization experiments. Operating conditions for crystallization operations are as follows: feed concentration of 0.5 to 7.0 wt%, end-point temperatures of –4.8°C to –11.5°C, and crystallization time ranging from 0.25 to 1 h, where C is the feed salt concentration, and SR and WR are the salt rejection and water recovery, respectively: (a) SR vs. crystallization time; (b) WR vs. crystallization time.

of agitation systems was examined at low crystallization temperature, in order to upgrade the quality of product water without reducing the water recovery ratio by means of crystallization temperature.

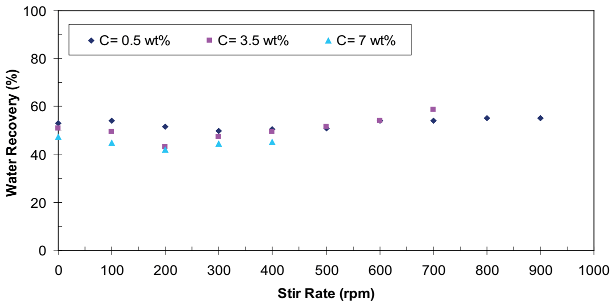
3.2. Crystallization process using MSS

In the second investigation, the performance of the crystallization process using MSS for treating different salt concentrations of feed was investigated. The feed concentrations varied from 0.5 to 7 wt%, while the crystallization temperature was set at –11.5°C. The actual operational period of the crystallization process for the experiments was kept constant at 0.5 h to avoid a high risk of stirrer damage, as the impeller almost reached the crystal layer. The investigated stir rate ranged from 100 up to 900 rpm. Results of salt rejection and water recovery ratios, as a function of the stir rate, are shown in Figs. 6(a) and (b).

As evidenced in the experimental results shown in Fig. 6(a) the separation of ice crystals from the bulk was improved as the stirring rate is increased. In other words, the stirring rate induced a significant decrease in the salinity of the ice crystal. The sensitivity of the separation to growth rate becomes significantly reduced at the highest agitation levels for the feed salinities of 0.5 and 3.5 wt%. This trend observation was demonstrated in an earlier study conducted by Fujioka et al. [29] and Myerson [53].



(a) Salt rejection vs. stir rate



(b) Water recovery vs. stir rate

Fig. 6. Experimental data for MSS crystallization experiments. Operating conditions for crystallization operations are as follows: feed concentration of 0.5 to 7.0 wt%, end-point temperatures of –4.8°C to –11.5°C, and crystallization time ranging from 0.25 to 1 h: (a) salt rejection vs. stir rate, (b) water recovery vs. stir rate.

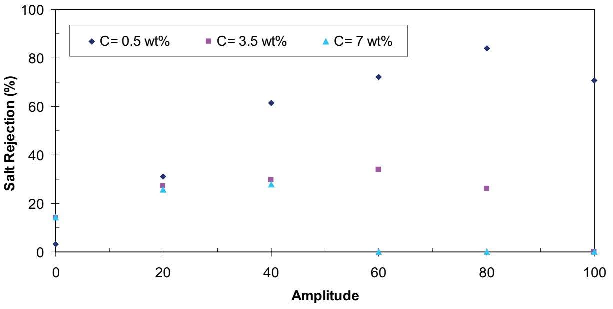
Although the experiments were carried out at a low crystallization temperature, the results of the salt rejection ratio significantly increased (i.e., improved) as the stir rate increased for the cases of treating feed salinities of 0.5 and 3.5 wt%. For instance, when the stir rate was set at 900 rpm, the salt rejection increased substantially from 2.3% to 70.2% for the case of a feed salinity of 0.5 wt%, as shown in Fig. 6(a). When the stir rate was set at 500 rpm, the salt rejection was significantly increased from 13.6% to 37.3% for the case of treating a feed salinity of 3.5 wt%. However, a slight reduction in the salt rejection ratio was observed as the stir rate was increased for the case of treating a feed with a salinity of 7 wt%. This clearly indicates that the effectiveness of stir rate is powerful in improving the quality of product water for the cases of treating feeds with low to moderate salt concentration. A significant increase in salt rejection was also observed as the salt concentration of feed decreased. The water recovery ratio, on the other hand, was not changed by the variation of stir rate, as shown in Fig. 6(b). However, a slight decrease in the water recovery ratio was noted as the feed salinity increased. For the cases of feed salinity of 3.5 and 7 wt%, the maximum investigated stir rates were 400 and 700 rpm, respectively; higher stir rates were not possible, based on visually noting the appearance of an undesired ice suspension (i.e., the ice crystal becomes slushy) inside the crystallizer. The ice suspensions formed in the crystallizer were not considered in this study. The degree of salt concentration of product water is not comparable with that obtained by RO membrane technology and is not within the accepted limits for drinking water. As with static crystallization process, dynamic freeze crystallization (DFC) using MSS also requires a post-treatment process to improve the water quality of final product within the certified international standards for drinking water.

Myerson [53] stated that the DFC technologies improve the mass transfer by mixing rather than circulating the melt. Ulrich and Glade [48] reported that the purpose of utilizing the DFC technologies in front of the boundary layer of the crystallization is to reduce the concentration gradients, which eventually led to decreasing the boundary layer thickness. Ulrich et al. [61] confirmed in their experimental investigations that when the diffusion coefficients are low and the viscosities are high, therefore natural convection is low. This means that the boundary layers are thick and, hence, poor quality of ice crystals will be produced. This is especially true in cases of rapid crystallization rates, that is, rapid growth rate, as reported by Ulrich and Glade [48]. Therefore, in cases of rapid crystallization rates, a dynamic approach by utilizing agitation system can reduce the impurities by as much as threefold when compared with SFC process as reported in the literature Myerson [53] and Ulrich et al. [61]. Ulrich and Glade [48] reported that a dynamic freeze approach is an effective process for low feed concentration applications.

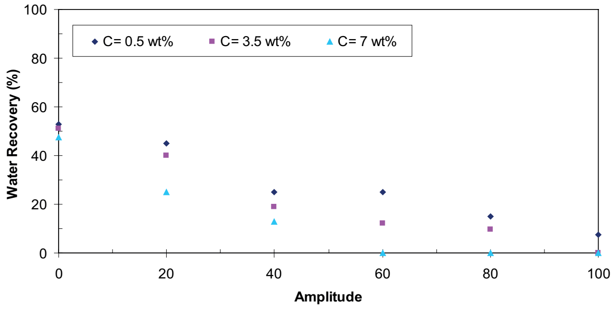
3.3. Crystallization process using ultrasonic agitating system

The third investigation was performed on the crystallization process using an UP. The investigated feed concentrations, crystallization temperature, and crystallization time are the same as given previously for the second investigation. The investigated amplitudes ranged from 20 up to 100.

Figs. 7(a) and (b) shows the salt rejection and water recovery ratios as a function of the amplitude, measured at different feed concentrations. The results indicate that the UP positively enhanced the separation performance of the crystallization process. In the cases of treating feed salinities of 0.5 and 3.5 wt%, a significant increase in the salt rejection ratio was observed as the amplitude value increased. Fig. 7(a) shows that the maximum salt rejection ratios were 84% and 34% for feed salinities of 0.5 and 3.5 wt%, respectively. This means that the product water was at 0.08 and 2.32 wt%, respectively. The salt rejection also improved for the case of a feed salinity of 7 wt%. For instance, the salt rejection increased from 14% to 28%. This clearly indicates that the UP is effective in lowering the salt concentration of product water for treating low to high feed concentrations. The trend of product quality results was found to be in agreement with the previous experimental investigations conducted by Li et al. [62] and Mortazavi and Tabatabaie [63]. Throughout the tests, the crystal layer was not formed on the bottom heat transfer surface of the crystallizer, when compared with the previous experiments with other experimental setups. The reason behind this was that the probe of the ultrasonic system was positioned above the crystallizer. As a result, the ultrasonic waves prevented the formation of the ice crystal on the bottom heat transfer surface of the crystallizer. Therefore, the water recovery ratio was dramatically decreased as the amplitude increased, as shown in Fig. 7(b).



(a) Salt rejection vs. amplitude



(b) Water recovery vs. amplitude

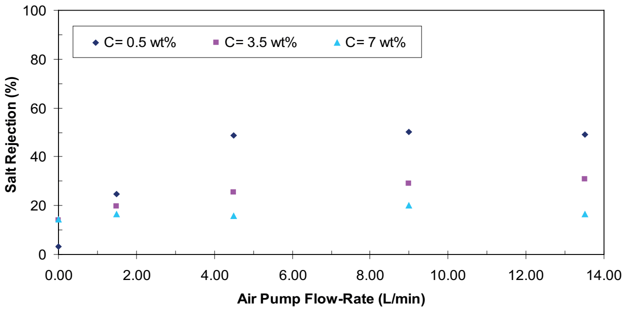
Fig. 7. Experimental data for the ultrasonic crystallization experiments. Operating conditions for crystallization operations are as follows: feed concentration of 0.5 to 7.0 wt%, end-point temperature of –11.5°C, and crystallization time of 0.5 h: (a) salt rejection vs. amplitude, (b) water recovery vs. amplitude.

It can be seen from Fig. 7(b) that the water recovery ratio declines linearly with the amplitude. This clearly indicates that the water recovery ratio was inversely proportional to the amplitude. This trend observation has been presented in earlier studies conducted by Li et al. [62] and Mortazavi and Tabatabaie [63]. A noticeable decrease in water recovery ratio was also observed as the salt concentration increased. For the case of a feed salinity of 7 wt%, no product water was obtained from the experiment when the amplitude reached 60 and above. A similar situation occurred for the case of 3.5 wt% feed salinity, when the amplitude reached 100. This was because a higher agitation rate results in slushy ice rather than having a rigid crystal layer, where these crystals cannot stick to the heat transfer surface as the waves produced by the ultrasonic system break the ice crystals. The DFC process agitated by UP produced water with salinity level of 800 mg/L for the 0.5 wt% feed, which is within the accepted limits as indicated in certified international standards for drinking waters. However, for higher feed salinities (i.e., 3.5 and 7 wt%), the degree of the salt concentration of product water achieved by this process was not complying with international standards for drinking waters. The investigated process also requires a post-treatment process, such as washing or sweating, which were not considered and investigated in this study.

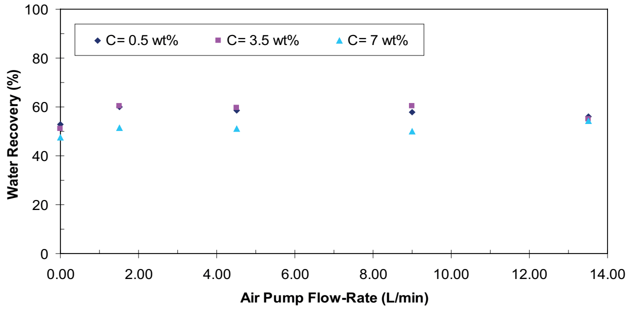
3.4. Crystallization using bubbling agitating system

In the fourth series of experiments, the potential capability of the crystallization step agitated by a BP was investigated. The investigated feed concentrations, crystallization temperature, and crystallization time are as given previously for the second investigation. The investigated air pump flow-rates ranged from 1.5 up to 13.5 L/min.

Fig. 8(a) shows the variation of salt rejection as a function of the air pump flow-rate. The air pump flow-rate also has a strong influence on the quality of product water, where this parameter was found to be effective in removing significant amounts of dissolved salt from the investigated feed concentrations, more specifically feed samples with salt concentrations of 0.5 and 3.5 wt%. Fig. 8(a) shows that the salt rejection ratio was significantly increased as the air pump flow-rate increased for the case of feed sample with concentration of 0.5 wt%. The results showed that the crystallization process agitated by bubbling has a beneficial effect as the other dynamic crystallization processes. The bubbles played a main role in renewing the interface between the ice layer and the bulk and it reduces the salt concentration of the rejected brines incorporated into the ice by mixing it with the bulk as observed by other experimental study [60]. However, the salt rejection was reduced with increasing salt concentration of feed samples, which was noticeable for the experiments with feed concentrations of 7 wt%. In fact, the salt rejection ratio, for such feed concentrations, was not affected by the variation in the air pump flow-rate. In general, the trend of salt rejection results was found to be in agreement with the previous experimental results for the crystallization processes using mechanically stirred and ultrasonic systems. Furthermore, the trend of salt rejection results was found to be in agreement with the previous experimental studies conducted by Rich et al. [60] and Mohamed [64].



(a) SR vs. air pump flow-rate



(b) WR vs. air pump flow-rate

Fig. 8. Experimental data for the bubbled crystallization experiments. Operating conditions for crystallization operations are as follows: feed concentration of 0.5 to 7.0 wt%, end-point temperature of –11.5°C, and crystallization time of 0.5 h where C is the salt concentration, and SR and WR are the salt rejection and water recovery, respectively: (a) SR vs. air pump flow-rate, (b) WR vs. air pump flow-rate.

The degree of salt concentration of product water obtained by this process is also not comparable with that obtained by RO membrane technology and is not within the accepted limits for drinking water. As with previously mentioned crystallization processes, this process also requires a post-treatment process to improve the water quality of final product within the certified international standards for drinking water.

As shown in Fig. 8(b), the water recovery ratio, on the other hand, increased slightly when the air pump flow-rate reached 1.5 L/min, and then the water recovery ratios were stabilized until the air pump flow-rate reached the maximum value. A dramatic decrease in the water recovery ratio was also observed as the feed salinity increased.

4. Conclusions

The results of the laboratory experiments showed that in the case of feed salinities ranging from 0.5 up to 3.5 wt%, the product water quality achieved by the crystallizer had significantly improved through agitation, while the lowest salt rejection was achieved when the static crystallization process was applied. The most effective processes, in terms of salt rejection and recovery, were the BP and MSS. Although the UP gave the highest salt rejection ratio for the cases of low to high feed concentration, the water recovery ratio was relatively poor when compared with the static crystallization process, with and without agitation (i.e., BP and MSS). Apart from the ultrasonic system, the performance of the agitated and static crystallization processes declined for high saline applications (i.e., 7 wt%). In general, the product water quality obtained by the investigated SFC and DFC processes were not comparable with RO and were not complying with certified international standards for drinking waters, except DFC agitated by UP for the case with low feed concentration (0.5 wt%). However, the results of these processes are still promising as the investigated processes were operated as a single-stage of freeze crystallization without the use of post-crystallization treatments such as washing and sweating process. A substantial amount of impurities adhering to the crystal surface of the crystalline and those brine buckets, contained in pores of the crystalline structure, can be rejected under the influence of the multistage configuration of freeze crystallization process and/or the post-crystallization treatments, such as rinsing, diffusion washing, and sweating processes. Therefore, these multistage configurations of freeze crystallization and post-treatment processes are highly recommended as the subject of further research, taking into account that both crystallization and sweating operations has to be well optimized, in order to find out the actual technical and economic feasibility in the field of seawater desalination. For commercial applications, the BP might be the most promising technique, since this method can be easily designed and built for large-scale applications.

References

[1] K.S. Spiegler, Y.M. El-Sayed, A Desalination Primer, Italy: Balaban Desalination Publications, 1994.
[2] P. Williams, M. Ahmad, B. Connolly, D. Oatley, Technology for freeze concentration in the desalination industry, Desalination, 356 (2015) 314–327.
[3] M. Mulder, Basic Principles of Membrane Technology, 2nd ed., Netherlands: Kluwer Academic Publishers, 1996.
[4] O.K. Buros, ABCs of Desalting, 2nd ed. S.I., Topsfield, Massachusetts, United States of America: International Desalination Association (IDA), 2000.
[5] A. Cipollina, G. Micale, L. Rizzuti, Seawater Desalination: Conventional and Renewable Energy Processes (Green Energy and Technology), Springer, Springer-Verlag Berlin and Heidelberg GmbH & Co. KG., 2009.
[6] R. Clayton, Desalination for Water Supply, FR/R0013, Foundation for Water Research, 2011.
[7] A.D. Khawaji, I.K. Kutubkhanah, J.M. Wie, Advances in seawater desalination technologies, Desalination, 221 (2008) 47–69.
[8] J.E. Miller, Review of Water Resources and Desalination Technologies, Sand Report, Sandia National Laboratories, 2003.
[9] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, Reverse osmosis desalination: water sources, technology, and today's challenges, Water Res., 43 (2009) 2317–2348.
[10] M.L. Stone, C. Rae, F.F. Stewart, A.D. Wilson, Switchable polarity solvents as draw solutes for forward osmosis, Desalination, 312 (2013) 124–129.
[11] M. Ahmad, Assessment of Freeing Desalination Technologies, PhD Thesis, Swansea University, 2012.
[12] Q. Ge, M. Ling, T.S. Chung, Draw solutions for forward osmosis processes: developments, challenges, and prospects for future, J. Membr. Sci., 442 (2013) 225–237.
[13] B. Van der Bruggen, L. Lejon, C. Vandecasteele, Reuse, treatment, and discharge of the concentrate of pressure-driven membrane processes, Environ. Sci. Technol., 37 (2003) 3733–3738.

[14] G. Nebbia, G. Menozzi, Early experiments on water desalination by freezing, Desalination, 5 (1968) 49–54.

[15] W. Johnson, State-of-the-art of freezing processes, their potential and future, Desalination, 19 (1976) 349–358.

[16] A. Rich, M. Youssef, B. Nourimane, M. Denis, A. Souad, B. Christine, S. Naoual, K. Jean-Paul, B. Tijani, B. Ahmed, V. Stephane, Freezing desalination of seawater in a static layer crystallizer, Desalination, 269 (2011) 142–147.

[17] K.S. Spiegler, A.D.K. Laird, Principles of desalination "Part A," 2nd ed., London: Academic Press INC., Vol. 1, 1980.

[18] W.E. Johnson, Indirect freezing, Desalination, 31 (1979) 417–425.

[19] D. Randall, J. Nathoo, A succinct review of the treatment of reverse osmosis brines using freeze crystallization, J. Water Process Eng., 8 (2015) 186–194.

[20] W. Goa, Y. Shao, Freeze concentration for removal of pharmaceutically active compounds in water, Desalination, 249 (2009) 398–402.

[21] F. Melak, G. Du Laing, A. Ambelu, E. Alemayehu, Application of freeze desalination for chromium (VI) removal from water, Desalination, 377 (2016) 23–27.

[22] K. Kang, P. Linga, K. Park, S.-J. Choi, J. Lee, Seawater desalination by gas hydrate process and removal characteristics of dissolved ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, B^{3+}, Cl–, SO_4^{2-}), Desalination, 353 (2014) 84–90.

[23] P.L.T. Brian, Potential advantages and development problems in water desalination by freezing, Chem. Eng., 78 (1971) 191–197.

[24] W. Cao, C. Beggs, I. Mujtaba, Theoretical approach of freeze seawater desalination on flake ice maker utilizing LNG cold energy, Desalination, 355 (2015) 22–32.

[25] P. Wang, T. Chung, A conceptual demonstration of freeze desalination membrane distillation (FD-MD) hybrid desalination process utilizing liquefied natural gas (LNG) cold energy, Water Res., 46 (2012) 4037–4052.

[26] J.A. Heist, Freeze crystallization, Chem. Eng., 86 (1979) 72–82.

[27] R. Halde, Concentration of impurities by progressive freezing, Water Res., 14 (1980) 575–580.

[28] N. Fletcher, The freezing of water, Sci. Prog., 54 (1966) 227–241.

[29] R. Fujioka, L. Wang, G. Dodbiba, T. Fujita, Application of progressive freeze-concentration for desalination, Desalination, 319 (2013) 33–37.

[30] A. Attia, New proposed system for freeze water desalination using auto reversed R-22 vapor compression heat pump, Desalination, 254 (2010) 179–184.

[31] M. Rahman, M. Ahmed, Freezing melting process and desalination: I. Review of the state of the art, Separ. Purif. Rev., 35 (2006) 59–96.

[32] C. Agnew, E. Anderson, Water Resources in the Arid Realm, Rutledge, London, 1992.

[33] R.W. Hartel, Evaporation and Freeze Concentration, D.R. Heldman, D.B. Lund (Eds.) Handbook of Food Engineering, New York: Marcel Dekker, 1992, pp. 341–392.

[34] W.E. Johnson, State-of-the-art of freezing processes, their potential and future, Desalination, 19 (1976) 349–358.

[35] J.B. Maguire, Fresh water from the sea, a new process, Desalination, 67 (1987) 155–162.

[36] M. Rahman, M. Ahmed, X. Chen, Freezing–melting process and desalination: review of present status and future prospects, Int. J. Nucl. Desal., 2 (2007) 253–264.

[37] P.J. Schroeder, A.S. Chan, A.R. Khan, Freezing processes – the standard of the future, Desalination, 21 (1977) 125–136.

[38] J.G. Muller, Freeze concentration of liquids: theory, practice and economics, Food Technol., 21 (1967) 49–60.

[39] Energy Requirements of Desalination Processes, Encyclopedia of Desalination and Water Resources (DESWARE). Available at: http://www.desware.net/Energy-Requirements-Desalination-Processes.aspx

[40] M. Ahmad, P. Williams, Assessment of desalination technologies for high saline brine applications – discussion paper, Desalination, 30 (2011) 22–36.

[41] K.S. Spiegler, Principles of Desalination, London: Academic Press, 1966.

[42] R.J. Braddock, J.E. Marcy, Quality of freeze concentrated orange juice, J Food Sci., 52 (1987) 159–162.

[43] S. Lemmer, R. Klomp, R. Ruemekorf, R. Scholz, Preconcentration of wastewater through the Niro freeze concentration process, Chem. Eng. Technol., 24 (2001) 485–488.

[44] G. Lofrano, S. Meriç, G.E. Zengin, D. Orhon, Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: a review, Sci. Total Environ., 461–462 (2013) 265–281.

[45] M. Gunathilake, M. Dozen, K. Shimmura, O. Miyawaki, An apparatus for partial ice melting to improve yield in progressive freeze-concentration, J. Food Eng., 142 (2014) 64–69.

[46] M. Mahdavi, A.H. Mahvi, S. Nasseri, M. Yunesian, Application of freezing to the desalination of saline water, Arab. J. Sci. Eng., 36 (2011) 1171–1177.

[47] Z. Lu, L. Xu, Freezing Desalination Process, Thermal Desalination Process, Vol. II, 2010.

[48] J. Ulrich, H. Glade, Melt crystallisation, Germany: Shaker Verlag, 2003.

[49] A.J. Barduhn, Freezing Processes for Water Conversion in the United States, First International Symposium on Water Desalination, 3–9 October 1965, Washington D.C., USA.

[50] D. Randall, J. Nathoo, F. Genceli-Guner, H. Kramer, G. Witkamp, A. Lewis, Determination of the metastable ice zone for a sodium sulphate system, Chem. Eng. Sci., 77 (2012) 184–188.

[51] F. Van der Ham, G.J. Witkamp, J. de Graauw, G.M. van Rosmalen, Eutectic freeze crystallization: application to process streams and waste water purification, Chem. Eng. Process., 37 (1998) 207–213.

[52] A. Rich, Y. Mandri, N. Bendaoud, D. Mangin, S. Abderafi, C. Bebon, N. Semlali, J. Klein, T. Bounahmidi, A. Bouhaouss, S. Veesler, Freezing desalination of sea water in a static layer crystallizer, Desal. Wat. Treat., 13 (2010) 120–127.

[53] A. Myerson, Handbook of Industrial Crystallization, 2nd ed., Butterworth-Heinemann, USA, 2002.

[54] J. Burton, R. Prim, W. Slichter, The distribution of solute in crystals grown from the melt. Part I. Theoretical, J. Chem. Phys., 21 (1953) 1987–1996.

[55] L. Wilson, A new look at the Burton, Prim and Slichter model of segregation during crystal growth from the melt, J. Crystal Growth, 44 (1978) 371–376.

[56] F. Rosenberger, Fundamentals of Crystal Growth. Macroscopic Equilibrium and Transport Concepts, New York, Springer-Verlag, 1979, ISBN 3-540-09023-1.

[57] K. Kim, S. Lee, J. Ulrich, Experimental thermal conductivity of ice crystalline layer in layer melt crystallization, J. Ind. Eng. Chem., 9 (2003) 111–116.

[58] R. Halde, Concentration of impurities by progressive freezing, Water Res., 14 (1980) 575–580.

[59] W.F. Weeks, S.F. Ackley, The Growth, Structure and Properties of Sea Ice, The Geophysics of Sea Ice, (1986) 9–164.

[60] A. Rich, M. Siniti, D. Mangin, J. Klein, Y. Mandri, T. Bounahmidi, A. Bouhaouss, S. Veesler, M. El-Ganaoui, Study of a melt crystallization process for seawater desalination, J. Mech. Eng. Autom., 5 (2015) 45–52.

[61] J. Ulrich, S.J. Jancic, A.K. Kuszlik, The Effect of Dissipative Mixing on Separation Efficiency of Progressive Freezing of Organic Melts, Proc. 11th Symposium on Industrial Crystallization, A. Mersmann (Ed.), Garmisch-Partenkirchen/Germany, 18, 1990, pp. 815–820.

[62] H. Li, H. Li, Z. Guo, Y. Liu, The application of power ultrasound to reaction crystallization, Ultrason. Sonochem., 13 (2006) 359–363.

[63] A. Mortazavi, F. Tabatabaie, Study of ice cream freezing process after treatment with ultrasound, World Appl. Sci. J., 4 (2008) 188–190, ISSN 1818-4952.

[64] M. Mohamed, Solidification of phase change material on vertical cylindrical surface in holdup air bubbles, Int. J. Refrige., 28 (2005) 403–411.