Manuscript Details

Manuscript number	DES_2017_2015_R1
Title	Freeze desalination by the integration of falling film and block freeze-concentration techniques
Article type	Full Length Article

Abstract

Block and falling film freeze concentration are two technologies that separate water by freezing, with the potential to desalinate seawater. In this study, the integration of two freeze concentration techniques as an alternative to obtain potable water was analysed. Water with 0.5%–8% NaCl was freeze-concentrated by the falling film technique. The ice from each stage was fractionally thawed to recover the solids retained in the ice. The diluted fractions of the thawing stage were freeze-concentrated using the block technique to increase water purity. Falling film freeze concentration was effective to separate the salt from the solution, even at high salt concentrations. Block freeze concentration was effective to increase the water purity until drinkable water was obtained. A multistage process with the integration of these techniques was proposed to obtain 74% of the amount of the initial solution at 0.05% of salt, and 26% at 13.4% of salt. With this process, a salt removal efficiency of 98.5% was achieved. The energy consumption was analysed. The integration of these techniques results in water that meets the requirements for drinkable water and demonstrates the technical feasibility of the process.

Keywords	cryoconcentration; seawater; freezing; falling film
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Fig 1.docx [Figure]

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Table 1.docx [Table]

Table 2.docx [Table]

Table 3.docx [Table]

January 12th, 2018

Professor
Nidal Hilal
Editor-in-Chief
Desalination

Revised Manuscript: DES_2017_2015

Dear Professor Hilal,

We appreciate the valuable comments that the reviewers made to our paper. We are attaching the revised manuscript and the detailed response to the comments of the reviewers. We hope that the corrections improve the quality of the manuscript.

Sincerely,

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January 12th, 2018

Professor
Nidal Hilal
Editor-in-Chief
Desalination

Revised Manuscript: DES_2017_2015

Dear Professor Hilal,

Thanks for your answer. We appreciate the valuable comments that the reviewers made to our paper. We believe that the comments greatly improved the manuscript. In the following paragraphs you will find all comments and answers that we gave and the description of the changes that we have made to this new version of the paper. The changes are highlighted in the manuscript.

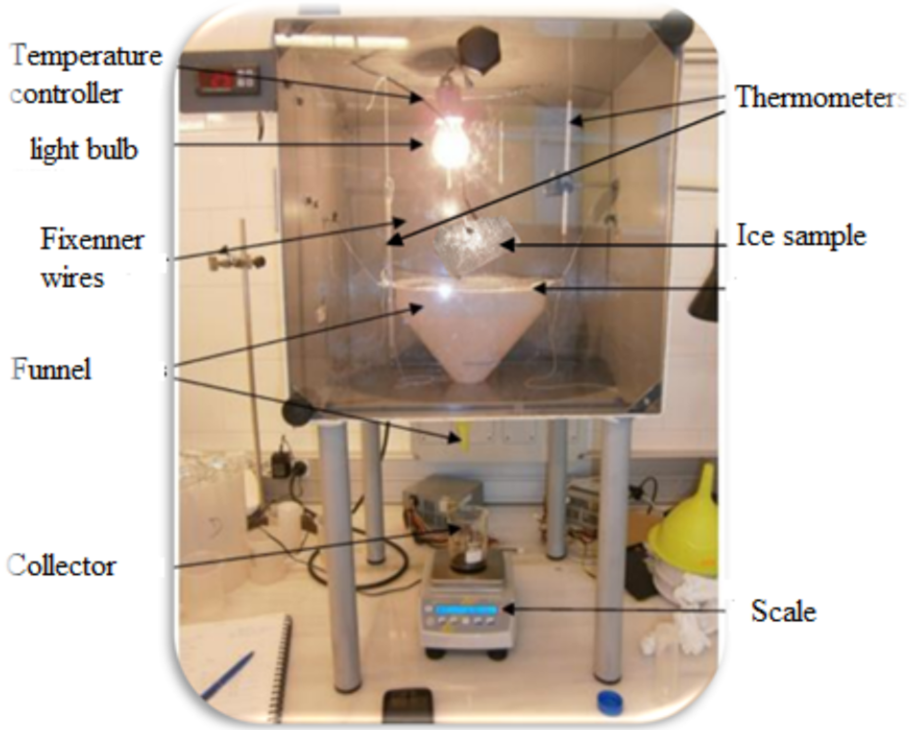
REVIEWER #1.

1. For falling film freeze concentration, the detailed experiment parameters of the experimental setup should be provided, which includes refrigerating machine power, falling film velocity, falling film thickness, ambient temperature and etc

The details of the experimental set-up of the falling film freeze concentration tests were included in lines 133-145.

2. For fractionated thawing, could the photograph of thawing be shown by authors?

Yes, The following is the picture of the set-up of the fractionated thawing tests:



The thawing of the ice plates was performed in a chamber with a temperature control system. The plates were placed vertically. The product of melting ice was collected by a funnel in fractions of 10% of the mass of the plate with a scale. The description of the set-up is shown in the texts in the figure 1 b). For this reason, we don’t think that the picture is necessary in the manuscript.

3. For data analysis, if the indexes, such as removal efficiency and concentration index, reflect the energy consumption, it would be well.

The relation between the concentration index and the energy consumption was calculated for the freeze concentration techniques. This relation indicates the energy required to increase the concentration of the brine and consequently, purify the water. The calculation was performed by the measurement of the experimental electricity consumption. Y this reason is just a comparative measure, because of the scale of the equipment. The following text was included in the manuscript in the lines 321-331. In addition, the lines 145-147 were included with the description of the measurement.

“…This result indicates that BFC is an efficient method for the removal of the occluded salt in the lowest tested concentrations. On the other hand, FFFC is more effective to separate salt faster than BFC. The relationship between the concentration index and the experimental energy consumption of the cooling stage was calculated to compare the behavior of the block and the falling film techniques. This value expressed by CI/Kwh was related to the operational time. The higher its value, the higher the energy efficiency. The FFFC technique obtained values between1.6 and 5 units of concentrations per kwh. Meanwhile, the BFC technique obtained values between 0.1 and 0.2 . This result confirm that FFFC is more efficient to separate the salt than BFC. The BFC requires a higher energy consumption, but with high purity ice separation".

4. For the Fig.2-Fig.5, different concentration should be presented in Figs.

The figures 2-5 were modified to include the concentration of the each test. In addition, the decimal numbers were corrected due to edition mistakes.

5. The references should be written according to requirements of the journal.

We appreciate the comment. The references were revised and adjusted to the requirements.

-REVIEWER 2

Publication is recommended.

Freeze desalination is a new research area.

The three techniques that were evaluated makes a good contribution to the existing knowledge.

Thank you for the comment

We appreciate all the comments. We hope that the corrections improve the quality of the manuscript.

Sincerely,

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Freeze desalination by the integration of falling film and block freeze-concentration techniques

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Abstract

Block and falling film freeze concentration are two technologies that separate water by freezing, with the potential to desalinate seawater. In this study, the integration of two freeze concentration techniques as an alternative to obtain potable water was analysed. Water with 0.5%–8% NaCl was freeze-concentrated by the falling film technique. The ice from each stage was fractionally thawed to recover the solids retained in the ice. The diluted fractions of the thawing stage were freeze-concentrated using the block technique to increase water purity. Falling film freeze concentration was effective to separate the salt from the solution, even at high salt concentrations. Block freeze concentration was effective to increase the water purity until drinkable water was obtained. A multistage process with the integration of these techniques was proposed to obtain 74% of the amount of the initial solution at 0.05% of salt, and 26% at 13.4% of salt. With this process, a salt removal efficiency of 98.5% was achieved. The energy consumption was analysed. The integration of these techniques results in water that meets the requirements for drinkable water and demonstrates the technical feasibility of the process.

Keywords: cryoconcentration, seawater, freezing, falling film

Nomenclature

C	Concentration (%w/w)
CI	Concentration index (unitless)
f	mass fraction of ice or liquid (unitless)
K	Average distribution coefficient (unitless)
m	mass
RE	Removal efficiency (%)
COP	Coefficient of performance

Subindex

0	Initial
ice	Ice (diluted fraction)
liq	Liquid (concentrated fraction)

Superindex

F	Falling Film Freeze Concentration (FFFC)
T	Fractionated Thawing (FT)
B	Block Freeze Concentration (BFC)

1. Introduction.

The availability of drinking water is a global necessity [1-3]. According to a UNICEF report, 780 million people lack access to this resource and about 40% of the population cannot afford sanitation [4]. Potable water and irrigation water are among the basic needs of humans, and unfortunately expected to decline due to population growth and climate change. Meanwhile, approximately 50.5% of the population lives at a distance less than 10 km from the sea. Thus, the desalination of seawater is an interesting alternative to generate potable water from an abundant resource.

Desalination can be achieved using technologies based on the principle of evaporation of water such as multiple-effect evaporation, membrane distillation, pervaporation, or solar distillation. Other technologies are membrane technologies, such as reverse osmosis [5]. Evaporation technologies have some disadvantages such as the high cost associated with the latent heat of evaporation of water. Membranes have a good yield separation but must be periodically changed due to the phenomenon of solute obstruction called ‘fouling’. An alternative that has been explored in an attempt to reduce operating costs is freeze concentration [6].

Freeze concentration is a method of removing water from a solution through the formation and separation of ice crystals of high purity [7]. Maintaining a solution at temperatures below the freezing point generates the phenomena of elution mass transfer and heat that can separate a liquid phase with a higher solute concentration relative to the solid phase; even under suitable conditions, it is possible to remove all the solutes present and have pure water [8]. In terms of water purification, the freeze concentration technique has proved to be viable for removing highly toxic metal ions like Chromium VI present in natural waters such as ocean water [9]. Although the freeze concentration process has several advantages over other techniques of concentration, there are still problems associated with the separation yield that do not yield a highly pure effluent.

Freeze concentration can be carried out by three techniques: suspension, falling film freeze concentration (FFFC), and block freeze concentration (BFC). Suspension is a technology available worldwide in the food industry [10]. Other techniques are being studied, such as block and falling film for food applications, biotechnology, and water treatment processes; these demonstrate high efficiencies compared with the suspension technique and require simple and inexpensive equipment [8], [10-14].

In falling film freeze concentration (FFFC), the solution is in contact with a cooled plate upon which the ice forms as a single layer [15]. Flesland [16] proposed a multi-stage FFFC coupled with reverse osmosis for water desalination, which afforded efficient water elimination. More recently, the recovery of solutes from sucrose solutions retained in ice was attempted by the fractionated thawing of ice [17,18]. In the block freeze concentration technique (BFC), the solution is frozen and partially thawed to separate diluted and concentrated fractions [11]. The viability of this technique was primarily demonstrated for low solid concentrations [7]. However, there are no viable commercial processes for the application of FFFC or BFC to desalination. The future of the freeze desalination depends on the study of new hybrid systems that enables the profitable operation of falling film and block freeze concentration [6]. The aim of this work is to study the use of falling film concentration coupled with block freeze concentration for water desalination and to propose an integrated process of FFFC, fractionated thawing, and BFC to obtain desalinated water.

2. Materials and methods

2.1 Materials

The solutions were prepared from commercial grade salt (Refisal, Colombia) and distilled water at 20°C, and stirred for 10 min at 300 rpm. The samples were refrigerated to achieve a temperature of 0°C. The solid concentration was expressed in mass concentration (C), which is defined as the mass percentage of solute per unit mass of solution. The conductivity of the samples was measured using a portable conductivity meter, CM-135 (Crison, Spain). The relationship between conductivity and C is represented by the equation, $C = 6.69\text{E-}2 * k$ (g/g), ($R^2 = 0.998$). The calibration curve was obtained from the solutions at 1.10, 5.17, 11.17, 16.89, 22.13, 28.43, 34.17, 39.97, 98.97, 162.60, and 231.00 mg/L, and measuring the mass fraction of salt using the method of weight loss proposed by Mandri et al. [19]. The measurements were performed in triplicate.

2.2 Methods

Two techniques of freeze concentration and one technique of solute recovery were studied following the flowchart of freeze concentration tests reported by Moreno et al. [8]. The initial solution was freeze concentrated by the falling film freeze concentration (FFFC) technique, and the resulting ice was melted in ten fractions to study the recovery of the retained solutes. Finally, the diluted fractions obtained during the thawing process were freeze concentrated by the block freeze concentration (BFC) technique in order to increase the amount of pure water. Each technique was studied individually and based on the results a global process was proposed.

2.2.1 Falling Film Freeze Concentration Tests

In each test, 800 mL of saline solutions of different concentrations (0.5, 1.5, 2.5, 3.5, 6.0, and 8.5% (w/w)) was concentrated by the falling film freeze concentration technique according to the protocol reported by Moreno et al. [20]. The experimental setup is shown in Fig. 1a). The solution flows as a falling film on a refrigerated plate (1), inside which circulates an aqueous solution of ethylene glycol at -20°C provided from a circulated bath (Polystat, Cole Parmer, USA). The bath was temperature controlled at an interval from -35 °C to 150 °C ± 0.01 °C. The bath pumped the heat exchange fluid to the plate. The solution was collected in a tank (3) and again circulated by a peristaltic pump, VGC-400 (Seditesa, Spain), with a frequency meter (VFD007L2 Seditesa, Spain) (2) to control the speed of the pump. The saline solutions flux was fixed at 8×10^{-5} $m^3 * s^{-1}$. The ice produced (4) was collected to be later recovered fractionally. Each experiment was performed between 40 and 80 min (less time was spent at lower initial concentrations) to obtain an ice sheet between 290 and 340 g, which correspond to an ice width between 12 and 14 mm. The salinity of the concentrated solution was measured every 20 min during the experiment and at the end of the process, by a portable conductivity meter (CM-135, Crison, Spain). The experiments were carried out in triplicate at room temperature around 20°C. The energy consumption of the cooling stage was measured by a bifilar single phase meter (@meter, Colombia).

2.2.2 Fractionated Thawing Tests

The thawing experiments were performed according to the method described by Gulfo et al. [17]. The plates obtained in the previous step (as the product of the seven different initial concentrations of FFFC in triplicate) were used to carry out the fractional thawing. One sample of 30% of the ice sheets was taken and thawed according to the configuration in Fig. 1b). The experimental configuration consisted of a cubic thermally insulated chamber (volume: 0.5 m^3) (2). The camera had a temperature control system (1) (Pie Electro Dit, model 11551, 0-300 W). Thawing was carried out at 20 ± 1°C and the plates were placed vertically. The product of melting ice was collected by a funnel (3) in fractions of 10% of the mass of the plate with a scale (4) (Ohaus PA3102, USA). The conductivity of each sample was measured and expressed in mass concentration by the calibration equation reported in section 2.1.

2.2.3 Block Freeze Concentration Tests

The process of BFC is shown in Fig. 1c). BFC was carried out with solutions of initial concentration ranging between the diluted fractions obtained in the fractionated thawing tests. The solution (160 g) at concentrations of 0.5 1.5, 2.5, and 3.5% of salt were placed into a cylindrical vessel with a double jacket of 5.2 cm diameter and 8.5 cm high (1). The refrigerant circulating in the inner cylinder and the outer jacket was a mixture of ethylene glycol and water (53% w/w) from two baths (Polystat, Cole Parmer, USA) with temperature control (−35 to 150°C ± 0.01°C). The cooling fluid temperature of the tests was −20°C. This fluid was passed by the inner cylinder to freeze the solution after it reached the cooling temperature. The ice growth occurred from ice formed on the inner wall of the container towards the outer wall. When the sample introduced was completely frozen, the solutes were recovered by pumping fluid from the heating bath (2) at 40°C through the outer jacket. A valve located at the bottom of the container and near the outer wall was opened, and 10 liquid fractions of the same mass were recovered above a scale (Ohaus PA3102, USA) with a precision of 0.01 g. The salt concentration of each fraction was measured by a conductivity meter (900P, Bante, China). The tests were performed in triplicate.

2.2.4 Data analysis

2.2.4.1 Thawing fraction (f). The thawing fraction was defined as the ratio between the thawed mass and the mass of the initial solution, as indicated in Equation 1 [8,18, 21].

$$f = \frac{m_{liq}}{m_0} \tag{1}$$

where f is the thawing fraction, m_{liq} is the mass of the liquid fraction, and m_0 is the initial mass.

2.2.4.2 Removal efficiency (RE). The freeze salt removal efficiency is defined as the percentage of salt removed during freeze desalination. It was calculated by Equation 2 [22]. The removal efficiency is equivalent to the salt rejection or the desalination rate [23, 24].

$$RE = \left(1 - \frac{C_{ice}}{C_0}\right) * 100 \tag{2}$$

where C_{ice} is the salt concentration in the ice fraction and C_0 is the salt concentration in the initial solution.

2.2.4.3 Concentration index (CI). The concentration index was calculated as the concentration of solids in the recovered liquid fraction over the concentration of solids in the initial solution [8, 25].

$$CI = \frac{C_{liq}}{C_0} \tag{3}$$

where CI is the concentration index, C_{liq} is the solid mass percentage in the fraction recovered, and C_0 is the solid mass percentage in the initial solution.

2.2.4.4 Average distribution coefficient ($\overline{K}$). The average distribution coefficient is defined as the proportion of salt mass fraction in ice, relative to the salt mass fraction in the concentrated liquid. It is calculated by Equation 4 [8, 21, 25].

$$\overline{K} = \frac{C_{ice}}{C_{liq}} \tag{4}$$

where K is the average distribution coefficient, C_{ice} is the salt concentration in the diluted fraction, and C_{liq} is the salt concentration in the concentrated fraction.

2.2.4.5 Statistical analysis. The experimental results obtained in this study were fitted to different models with linear and nonlinear regression procedures using Excel 2016 software. The goodness of fit was assessed using the linear regression coefficient, R^2. All experiments were performed in triplicate. Averages, mean values, and standard derivations were also reported. Differences among variables within each test were calculated by the ANOVA method at a significance level of $\alpha = 0.05$.

3. Results and discussion

3.1 Falling Freeze Film Concentration

A concentrated fraction (liquid) and diluted fraction (ice) were obtained after the falling film freeze concentration tests. The salt concentrations of the concentrated and diluted fractions, as a function of the initial solution are presented in Fig. 2. The increase of the final concentration of the concentrated fraction presented a linear behaviour described by the Equation 5. This linear behaviour has already been identified in food matrices such as orange juice, apple juice, pear juice, and coffee [10, 13, 15, 20]. A final diluted solution with 1.66% salt concentration was obtained for a solution with the typical salt concentration of seawater. This reduction represents a salt removing efficiency of 52 %. The concentrated fraction contained remaining water, which also had to be separated. For this reason, It is necessary to understand the behaviour of the concentration of the separated fraction from solutions with higher salt concentration.

$$C^{F}_{liq} = 1.289 * C^{F}_{0} \qquad R^2 = 0.9985 \qquad (5)$$

The main response variables of freeze concentration during the falling film tests are presented in Table 1. The CI and K varied from 1.2 to 1.6 and from 0.11 to 0.44, respectively. Those values are in the same order as those reported for food fluids [10, 20, 26]. The salt concentration increased significantly at each stage of FFFC. The achieved concentration index decreased, the average distribution coefficient increased, and the removal efficiency decreased at the second stage of FFFC. These results indicate that the occlusion of solutes in the ice increases with the initial concentration. Consequently, the salt removal efficiency decreases. Ice growth occurs by the diffusion of water molecules to the ice surface and the counter-diffusion of salts to the liquid phase. The diffusion rate of the salt decreases when the initial concentration increases, due to the interactions between the molecules; consequently, the achieved concentration decreases [20, 23, 27, 28]. This behaviour occurs in food matrices such as coffee [20], whey [15], and fruit juices [10]. However, from the second initial concentration, no statistically significant differences were found. These results indicate that for the highest concentration, which included the typical concentration of seawater, the removal efficiency remains constant. This behaviour is contrary to those reported for food fluids in which the concentration efficiency decreases considerably with the initial solute concentration. It is possible that the size of salt allows relatively easy removal, even at high salt concentrations. On the other hand, the ice fraction decreases with the concentration due to the supercooling required by the high salt concentration solutions. In this sense, a decrease of temperature can be applied to produce more ice.

3.2 Fractionated Thawing (FT)

The fractionated thawing process was evaluated, considering that one of the main advantages of the thawing process is the increase in separation efficiency due to the migration of occluded solutes in the previous stage (FFFC) [17, 20]. The samples obtained from each FFFC experiment were fractionally thawed in ten parts of equal mass. The concentration index (CI) was calculated in order to follow up the separation (Fig. 3). The values of CI greater than 1 indicated that the first thawed fractions are more concentrated than the remaining ice. Consequently, a purification of the ice can be achieved. The largest amount of solutes was occluded in the first layer of ice formed in the freeze concentration process, because the crystalline structure of the first layer was disordered and rapidly formed by subcooling effects [10, 20, 29-31]. In the middle of the ice sheet, the structure was more rigid since the rate of crystal formation was lower; therefore, this ice was the purest. Finally, in the part of the ice sheet farthest from the cooling plate also occlusion of solutes occurs as in the zone of the plate closest to the wall of the cooling plate, but to a smaller extent. The formed ice structure (pore size and crystal distribution) affects the rate of FT. The elution of solute from the frozen ice to the thawed drops recovered during FT allows the recovery of the occluded salt and increases the water purification.

The CI value descended with the thawing fraction. When the CI reaches a value of 1, two fractions, one concentrated and the other diluted, can be separated. The ice can be purified by this procedure. The response variables calculated when the CI reached a value of 1 are shown in Table 2. The concentration of the liquid and ice fractions was statistically different among the FT. As expected, the ice fraction was the same for all the tested concentrations, with the value around 50%. A concentration index from 1.3 to 1.9 was achieved with the FT. The concentration of the liquid fraction after the thawing stage can be predicted by Equation 6.

$$C^{T}_{liq} = 1.62 * C^{T}_{0} \qquad R^2 = 0.920 \qquad (6)$$

This procedure enables the increase in water purification with RE from 35% to 77%. The diluted fraction for the lowest initial concentration was 0.09%, which is close to the requirement for potable water. However, an additional purification step is needed; therefore, block freeze concentration was studied as presented in section 3.3. The results show the fractionated thawing step as a useful technique to increase the purity of the ice obtained in the FFFC stage.

3.3 Block Freeze Concentration

The results of the block freeze concentration tests are presented in Figs. 4 and 5. The highest concentration indices were obtained for the first thawed fractions. During block FC, the elution of the salt to the thawed drops of the solution descending from the ice block during the thawing stage allows separation of the most concentrated fractions initially [7, 21]. The values of CI obtained were in the range 3–7, and show a good salt separation compared to food fluids, in which the CI of BFC were around 3 [7]. This result is due to the lower size of salt than other molecules [32]. The removal efficiency during BFC is shown in Fig. 5. The highest REs were obtained for the lowest salt concentrations. For example, at the lowest initial concentration of 0.4%, 80% of the salt was separated within the two first thawed fractions corresponding to 20% of the initial mass. These results show the suitability of the BFC technique for increasing ice purity at low salt concentrations.

The CI decreased with f, and was less than 1 for f^{B}_{liq} values from 0.2 to 0.4. At this value of CI = 1, two fractions can be separated, one with lower and another with higher concentration than the initial concentration. By this separation, the desalination process is possible. The response variables were calculated at this f when CI = 1 and listed in Table 3. It is remarkable that the concentration of the diluted fraction was lower than the requirements for drinkable water [19, 22, 33]. The RE was around 70%. The concentration of the concentrated liquid fraction can be predicted by Equations (7) and (8).

$$C^{T}_{liq} = 35.26 * C^{T}_{0} + 0.212 * C^{T} + 0.023 \qquad R^2 = 1.000 \quad (7)$$

$$C^{T}_{ice} = -5.125 * C^{T}_{0} + 0.481 * C^{T} - 0.0008 \qquad R^2 = 0.999 \quad (8)$$

This result indicates that BFC is an efficient method for the removal of the occluded salt in the lowest tested concentrations. On the other hand, FFFC is more effective to separate salt faster than BFC. The relationship between the concentration index and the experimental energy consumption of the cooling stage was calculated to compare the behavior of the block and the falling film techniques. This value expressed by CI/Kwh was related to the operational time. The higher its value, the higher the energy efficiency. The FFFC technique obtained values between1.6 and 5 units of concentrations per kwh. Meanwhile, the BFC technique obtained values between 0.1 and 0.2. This result confirm that FFFC is more efficient to separate the salt than BFC. The BFC requires a higher energy consumption, but with high purity ice separation.

3.4. Proposal of an integrated process

An integrated process is proposed based on the results of the three groups of tests performed. The FFFC technique enabled the separation at high initial concentrations [20]. Fractionated thawing allows the separation of salt occluded in the ice. Finally, block freeze concentration was useful to increase the purity of ice and to achieve concentrations lower than the requirements for drinkable water. Therefore, an integration of the FFFC, FT, and BFC techniques was proposed to obtain water at same salinity as required for drinking water. The process is shown in Fig. 6. Equations 5–8 were used to calculate the concentrations of each solution in the process. The process began with 1,000 kg/h of seawater at 3.5% salt concentration as the calculation base. Firstly, five stages of FFFC are used to increase the concentration of the initial water. 256.9 kg/h of a brine with 13.4% of salt is obtained. This technique allows to remove 98.9% of the amount of the salt contained in the initial seawater. Secondly, the ice obtained in the FFFC is thawed partially to recover two solutions, one diluted and the other concentrated. By this step, an effluent with 1% of salt concentration is obtained from a mixture of the diluted fractions of FT. Finally, three block freeze concentration stages can be applied to this solution in order to reduce this concentration until drinkable water requirements are met. At the end of the process, 743.1 kg/h of water with 0.05% of salt can be obtained. This final effluent complies with the standard of salinity for drinkable water [19, 22, 33]. The overall process achieves a salt removal efficiency of 98.46% which is high value compared with other systems [34].

The energy consumption was analysed in terms of the heat transferred and the energy used per kg of feed or per 1,000 kg of water removed. The basic load is the heat consumed to convert 1 kg of feed into an appropriate mixture of ice and residual solution [35]. In the continuous system of FFFC proposed in Fig. 6, the theoretical conversion of 1,000 kg/h of feed (salt solution at 3.5 % w/w) into 743.1 kg/h of desalinated water (0.05%) can produce and melt around 5,126 kg/h of pure ice.
Analysis of the available data showed that energy can be saved in cryoconcentration technology by reducing the temperature difference between the evaporating and condensing refrigerant [36, 37]. In order to save energy by increasing the system COP, ice can be formed to condense at low temperature, typically at 10°C. As the freezing point of the salt solution at concentration of 1 and 10% w/w varies between −0.5 and −7°C, the operating temperature of the refrigerant in the evaporator will be −10°C, while melting ice in a continuous system requires a condensing temperature of 10°C [38]. A Carnot COP of 13.15 was calculated for −10°C evaporation and 10°C condensation temperatures. In practice, real cycles tend to have 60% efficiency compared to the theoretical performance [5]. Therefore, an actual COP of 7.9 is possible for a compressor operating between −10 and 10°C [39. Rodriguez, et al. [40] suggested that a COP above 8 can be reached in the cryoconcentration of wastewater treatment in a FFFC system.
If we assume that the heat of crystallization of ice is 334 kJ/kg, theoretically, 474 kWh of thermal energy is needed in the integrated system proposed in Fig. 6. If a COP of 8 is adopted, the electrical consumption is 59.2 kWh. This value corresponds

to 11.5 kWh per 1,000 kg of ice produced. In similar equipment to that presented in this study, the specific energy consumption of 23.33 kWh for 1,000 kg of ice in a batch falling film CC was reported when coffee and orange juice extract were treated [40]. Other studies in China [41] showed a specific energy consumption of about 21.3 kWh per 1,000 kg of ice removed by cryoconcentration in wastewater treatment. The HybridICE technology [42] applied to desalination has energy consumption between 21 and 26 kWh for 1,000 kg of ice. In addition, some studies suggested that the use of a heat pump can reduce the energy consumption in FFFC, which can reach a value of 10 kWh for 1,000 kg of ice [5, 39]. Finally, another alternative to reduce the energy consumption is to use a process without recirculation. In this case, the concentrated fractions of the fractionated thawing and block FC stages are not recirculated to the process. With this strategy, 269 kg/h of water at 0.05% of salt concentration is obtained. In addition, 99.4 kg/h of brine at 12.4% is obtained, and an effluent of 603 kg/h at 3.7% can be returned to the water source. The energy consumption decreases to 23.1 kWh for the overall the process. This correspond to a reduction of 95% of the energy consumption. Several strategies between the two points of energy consumption, with or without recirculation, can be studied. A further optimization process will be useful to establish the optimal point of recirculation.

Conclusions

A process to desalinate water by the integration of the falling film technique, the fractionated thawing, and the block freeze concentration was proposed. A fraction of 74% of the initial mass can be obtained at a final salt concentration of 0.05%, suitable as drinkable water. The process consists of five stages of FFFC and FT and three stages of BFC. A salt removal efficiency of 98.5% can be obtained with the process. A theoretical energy consumption of 59.2 kWh was calculated for the process, for 1000 kg of initial water. An alternative process without recycling can be used to reduce energy consumption, obtaining 29.6% of the initial water at 0.05% salt with 23.1 kWh of energy consumption for 1000 kg of initial water. An optimization of the process is required to establish an adequate strategy for recycling. FFFC seems to be appropriate to separate salt even at high initial concentrations. The FT method is useful to recover the occluded salt in the ice layers obtained in FFFC and to increase the ice purity. BFC is an effective technique to purify the diluted fractions in order to attain the concentrations of drinkable water.

5. Acknowledgements

This work was supported by the ING-151-2014 project of the Faculty of Engineering of Universidad de La Sabana. Author Moreno F L thanks COLCIENCIAS for its grant for doctoral studies (2013).

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Highlights

A process of freeze desalination was proposed

A final effluent with 0.05% of salt was achieved

Overall salt removal efficiency of 98%

Alternatives for process configuration are analysed

Freeze desalination by the integration of falling film and block freeze-concentration techniques

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Abstract

Block and falling film freeze concentration are two technologies that separate water by freezing, with the potential to desalinate seawater. In this study, the integration of two freeze concentration techniques as an alternative to obtain potable water was analysed. Water with 0.5%–8% NaCl was freeze-concentrated by the falling film technique. The ice from each stage was fractionally thawed to recover the solids retained in the ice. The diluted fractions of the thawing stage were freeze-concentrated using the block technique to increase water purity. Falling film freeze concentration was effective to separate the salt from the solution, even at high salt concentrations. Block freeze concentration was effective to increase the water purity until drinkable water was obtained. A multistage process with the integration of these techniques was proposed to obtain 74% of the amount of the initial solution at 0.05% of salt, and 26% at 13.4% of salt. With this process, a salt removal efficiency of 98.5% was achieved. The energy consumption was analysed. The integration of these techniques results in water that meets the requirements for drinkable water and demonstrates the technical feasibility of the process.

Keywords: cryoconcentration, seawater, freezing, falling film

Nomenclature

C	Concentration (%w/w)
CI	Concentration index (unitless)
f	mass fraction of ice or liquid (unitless)
K	Average distribution coefficient (unitless)
m	mass
RE	Removal efficiency (%)
COP	Coefficient of performance

Subindex

0	Initial
ice	Ice (diluted fraction)
liq	Liquid (concentrated fraction)

Superindex

F	Falling Film Freeze Concentration (FFFC)
T	Fractionated Thawing (FT)
B	Block Freeze Concentration (BFC)

1. Introduction.

The availability of drinking water is a global necessity [1-3]. According to a UNICEF report, 780 million people lack access to this resource and about 40% of the population cannot afford sanitation [4]. Potable water and irrigation water are among the basic needs of humans, and unfortunately expected to decline due to population growth and climate change. Meanwhile, approximately 50.5% of the population lives at a distance less than 10 km from the sea. Thus, the desalination of seawater is an interesting alternative to generate potable water from an abundant resource.

Desalination can be achieved using technologies based on the principle of evaporation of water such as multiple-effect evaporation, membrane distillation, pervaporation, or solar distillation. Other technologies are membrane technologies, such as reverse osmosis [5]. Evaporation technologies have some disadvantages such as the high cost associated with the latent heat of evaporation of water. Membranes have a good yield separation but must be periodically changed due to the phenomenon of solute obstruction called ‘fouling’. An alternative that has been explored in an attempt to reduce operating costs is freeze concentration [6].

Freeze concentration is a method of removing water from a solution through the formation and separation of ice crystals of high purity [7]. Maintaining a solution at temperatures below the freezing point generates the phenomena of elution mass transfer and heat that can separate a liquid phase with a higher solute concentration relative to the solid phase; even under suitable conditions, it is possible to remove all the solutes present and have pure water [8]. In terms of water purification, the freeze concentration technique has proved to be viable for removing highly toxic metal ions like Chromium VI present in natural waters such as ocean water [9]. Although the freeze concentration process has several advantages over other techniques of concentration, there are still problems associated with the separation yield that do not yield a highly pure effluent.

Freeze concentration can be carried out by three techniques: suspension, falling film freeze concentration (FFFC), and block freeze concentration (BFC). Suspension is a technology available worldwide in the food industry [10]. Other techniques are being studied, such as block and falling film for food applications, biotechnology, and water treatment processes; these demonstrate high efficiencies compared with the suspension technique and require simple and inexpensive equipment [8], [10-14].

In falling film freeze concentration (FFFC), the solution is in contact with a cooled plate upon which the ice forms as a single layer [15]. Flesland [16] proposed a multi-stage FFFC coupled with reverse osmosis for water desalination, which afforded efficient water elimination. More recently, the recovery of solutes from sucrose solutions retained in ice was attempted by the fractionated thawing of ice [17,18]. In the block freeze concentration technique (BFC), the solution is frozen and partially thawed to separate diluted and concentrated fractions [11]. The viability of this technique was primarily demonstrated for low solid concentrations [7]. However, there are no viable commercial processes for the application of FFFC or BFC to desalination. The future of the freeze desalination depends on the study of new hybrid systems that enables the profitable operation of falling film and block freeze concentration [6]. The aim of this work is to study the use of falling film concentration coupled with block freeze concentration for water desalination and to propose an integrated process of FFFC, fractionated thawing, and BFC to obtain desalinated water.

2. Materials and methods

2.1 Materials

The solutions were prepared from commercial grade salt (Refisal, Colombia) and distilled water at 20°C, and stirred for 10 min at 300 rpm. The samples were refrigerated to achieve a temperature of 0°C. The solid concentration was expressed in mass concentration (C), which is defined as the mass percentage of solute per unit mass of solution. The conductivity of the samples was measured using a portable conductivity meter, CM-135 (Crison, Spain). The relationship between conductivity and C is represented by the equation, $C = 6.69\text{E-}2 * k$ (g/g), ($R^2 = 0.998$). The calibration curve was obtained from the solutions at 1.10, 5.17, 11.17, 16.89, 22.13, 28.43, 34.17, 39.97, 98.97, 162.60, and 231.00 mg/L, and measuring the mass fraction of salt using the method of weight loss proposed by Mandri et al. [19]. The measurements were performed in triplicate.

2.2 Methods

Two techniques of freeze concentration and one technique of solute recovery were studied following the flowchart of freeze concentration tests reported by Moreno et al. [8]. The initial solution was freeze concentrated by the falling film freeze concentration (FFFC) technique, and the resulting ice was melted in ten fractions to study the recovery of the retained solutes. Finally, the diluted fractions obtained during the thawing process were freeze concentrated by the block freeze concentration (BFC) technique in order to increase the amount of pure water. Each technique was studied individually and based on the results a global process was proposed.

2.2.1 Falling Film Freeze Concentration Tests

In each test, 800 mL of saline solutions of different concentrations (0.5, 1.5, 2.5, 3.5, 6.0, and 8.5% (w/w)) was concentrated by the falling film freeze concentration technique according to the protocol reported by Moreno et al. [20]. The experimental setup is shown in Fig. 1a). The solution flows as a falling film on a refrigerated plate (1), inside which circulates an aqueous solution of ethylene glycol at -20°C provided from a circulated bath (Polystat, Cole Parmer, USA). The bath was temperature controlled at an interval from -35 °C to 150 °C ± 0.01 °C. The bath pumped the heat exchange fluid to the plate. The solution was collected in a tank (3) and again circulated by a peristaltic pump, VGC-400 (Seditesa, Spain), with a frequency meter (VFD007L2 Seditesa, Spain) (2) to control the speed of the pump. The saline solutions flux was fixed at 8 x10^{-5} m^3*s^{-1}. The ice produced (4) was collected to be later recovered fractionally. Each experiment was performed between 40 and 80 min (less time was spent at lower initial concentrations) to obtain an ice sheet between 290 and 340 g, which correspond to an ice width between 12 and 14 mm. The salinity of the concentrated solution was measured every 20 min during the experiment and at the end of the process, by a portable conductivity meter (CM-135, Crison, Spain). The experiments were carried out in triplicate at room temperature around 20°C. The energy consumption of the cooling stage was measured by a bifilar single phase meter (@meter, Colombia).

2.2.2 Fractionated Thawing Tests

The thawing experiments were performed according to the method described by Gulfo et al. [17]. The plates obtained in the previous step (as the product of the seven different initial concentrations of FFFC in triplicate) were used to carry out the fractional thawing. One sample of 30% of the ice sheets was taken and thawed according to the configuration in Fig. 1b). The experimental configuration consisted of a cubic thermally insulated chamber (volume: 0.5 m^3) (2). The camera had a temperature control system (1) (Pie Electro Dit, model 11551, 0-300 W). Thawing was carried out at 20 ± 1°C and the plates were placed vertically. The product of melting ice was collected by a funnel (3) in fractions of 10% of the mass of the plate with a scale (4) (Ohaus PA3102, USA). The conductivity of each sample was measured and expressed in mass concentration by the calibration equation reported in section 2.1.

2.2.3 Block Freeze Concentration Tests

The process of BFC is shown in Fig. 1c). BFC was carried out with solutions of initial concentration ranging between the diluted fractions obtained in the fractionated thawing tests. The solution (160 g) at concentrations of 0.5 1.5, 2.5, and 3.5% of salt were placed into a cylindrical vessel with a double jacket of 5.2 cm diameter and 8.5 cm high (1). The refrigerant circulating in the inner cylinder and the outer jacket was a mixture of ethylene glycol and water (53% w/w) from two baths (Polystat, Cole Parmer, USA) with temperature control (−35 to 150°C ± 0.01°C). The cooling fluid temperature of the tests was −20°C. This fluid was passed by the inner cylinder to freeze the solution after it reached the cooling temperature. The ice growth occurred from ice formed on the inner wall of the container towards the outer wall. When the sample introduced was completely frozen, the solutes were recovered by pumping fluid from the heating bath (2) at 40°C through the outer jacket. A valve located at the bottom of the container and near the outer wall was opened, and 10 liquid fractions of the same mass were recovered above a scale (Ohaus PA3102, USA) with a precision of 0.01 g. The salt concentration of each fraction was measured by a conductivity meter (900P, Bante, China). The tests were performed in triplicate.

2.2.4 Data analysis

2.2.4.1 Thawing fraction (f). The thawing fraction was defined as the ratio between the thawed mass and the mass of the initial solution, as indicated in Equation 1 [8,18, 21].

$$f = \frac{m_{liq}}{m_0} \tag{1}$$

where f is the thawing fraction, m_{liq} is the mass of the liquid fraction, and m_0 is the initial mass.

2.2.4.2 Removal efficiency (RE). The freeze salt removal efficiency is defined as the percentage of salt removed during freeze desalination. It was calculated by Equation 2 [22]. The removal efficiency is equivalent to the salt rejection or the desalination rate [23, 24].

$$RE = \left(1 - \frac{C_{ice}}{C_0}\right) * 100 \tag{2}$$

where C_{ice} is the salt concentration in the ice fraction and C_0 is the salt concentration in the initial solution.

2.2.4.3 Concentration index (CI). The concentration index was calculated as the concentration of solids in the recovered liquid fraction over the concentration of solids in the initial solution [8, 25].

$$CI = \frac{C_{liq}}{C_0} \tag{3}$$

where CI is the concentration index, C_{liq} is the solid mass percentage in the fraction recovered, and C_0 is the solid mass percentage in the initial solution.

2.2.4.4 Average distribution coefficient ($\overline{K}$). The average distribution coefficient is defined as the proportion of salt mass fraction in ice, relative to the salt mass fraction in the concentrated liquid. It is calculated by Equation 4 [8, 21, 25].

$$\overline{K} = \frac{C_{ice}}{C_{liq}} \tag{4}$$

where K is the average distribution coefficient, C_{ice} is the salt concentration in the diluted fraction, and C_{liq} is the salt concentration in the concentrated fraction.

2.2.4.5 Statistical analysis. The experimental results obtained in this study were fitted to different models with linear and nonlinear regression procedures using Excel 2016 software. The goodness of fit was assessed using the linear regression coefficient, R^2. All experiments were performed in triplicate. Averages, mean values, and standard derivations were also reported. Differences among variables within each test were calculated by the ANOVA method at a significance level of α = 0.05.

3. Results and discussion

3.1 Falling Freeze Film Concentration

A concentrated fraction (liquid) and diluted fraction (ice) were obtained after the falling film freeze concentration tests. The salt concentrations of the concentrated and diluted fractions, as a function of the initial solution are presented in Fig. 2. The increase of the final concentration of the concentrated fraction presented a linear behaviour described by the Equation 5. This linear behaviour has already been identified in food matrices such as orange juice, apple juice, pear juice, and coffee [10, 13, 15, 20]. A final diluted solution with 1.66% salt concentration was obtained for a solution with the typical salt concentration of seawater. This reduction represents a salt removing efficiency of 52 %. The concentrated fraction contained remaining water, which also had to be separated. For this reason, It is necessary to understand the behaviour of the concentration of the separated fraction from solutions with higher salt concentration.

$$C^F_{liq} = 1.289 * C^F_0 \qquad R^2 = 0.9985 \qquad (5)$$

The main response variables of freeze concentration during the falling film tests are presented in Table 1. The CI and K varied from 1.2 to 1.6 and from 0.11 to 0.44, respectively. Those values are in the same order as those reported for food fluids [10, 20, 26]. The salt concentration increased significantly at each stage of FFFC. The achieved concentration index decreased, the average distribution coefficient increased, and the removal efficiency decreased at the second stage of FFFC. These results indicate that the occlusion of solutes in the ice increases with the initial concentration. Consequently, the salt removal efficiency decreases. Ice growth occurs by the diffusion of water molecules to the ice surface and the counter-diffusion of salts to the liquid phase. The diffusion rate of the salt decreases when the initial concentration increases, due to the interactions between the molecules; consequently, the achieved concentration decreases [20, 23, 27, 28]. This behaviour occurs in food matrices such as coffee [20], whey [15], and fruit juices [10]. However, from the second initial concentration, no statistically significant differences were found. These results indicate that for the highest concentration, which included the typical concentration of seawater, the removal efficiency remains constant. This behaviour is contrary to those reported for food fluids in which the concentration efficiency decreases considerably with the initial solute concentration. It is possible that the size of salt allows relatively easy removal, even at high salt concentrations. On the other hand, the ice fraction decreases with the concentration due to the supercooling required by the high salt concentration solutions. In this sense, a decrease of temperature can be applied to produce more ice.

3.2 Fractionated Thawing (FT)

The fractionated thawing process was evaluated, considering that one of the main advantages of the thawing process is the increase in separation efficiency due to the migration of occluded solutes in the previous stage (FFFC) [17, 20]. The samples obtained from each FFFC experiment were fractionally thawed in ten parts of equal mass. The concentration index (CI) was calculated in order to follow up the separation (Fig. 3). The values of CI greater than 1 indicated that the first thawed fractions are more concentrated than the remaining ice. Consequently, a purification of the ice can be achieved. The largest amount of solutes was occluded in the first layer of ice formed in the freeze concentration process, because the crystalline structure of the first layer was disordered and rapidly formed by subcooling effects [10, 20, 29-31]. In the middle of the ice sheet, the structure was more rigid since the rate of crystal formation was lower; therefore, this ice was the purest. Finally, in the part of the ice sheet farthest from the cooling plate also occlusion of solutes occurs as in the zone of the plate closest to the wall of the cooling plate, but to a smaller extent. The formed ice structure (pore size and crystal distribution) affects the rate of FT. The elution of solute from the frozen ice to the thawed drops recovered during FT allows the recovery of the occluded salt and increases the water purification.

The CI value descended with the thawing fraction. When the CI reaches a value of 1, two fractions, one concentrated and the other diluted, can be separated. The ice can be purified by this procedure. The response variables calculated when the CI reached a value of 1 are shown in Table 2. The concentration of the liquid and ice fractions was statistically different among the FT. As expected, the ice fraction was the same for all the tested concentrations, with the value around 50%. A concentration index from 1.3 to 1.9 was achieved with the FT. The concentration of the liquid fraction after the thawing stage can be predicted by Equation 6.

$$C^{T}_{liq} = 1.62 * C^{T}_{0} \qquad R^2 = 0.920 \qquad (6)$$

This procedure enables the increase in water purification with RE from 35% to 77%. The diluted fraction for the lowest initial concentration was 0.09%, which is close to the requirement for potable water. However, an additional purification step is needed; therefore, block freeze concentration was studied as presented in section 3.3. The results show the fractionated thawing step as a useful technique to increase the purity of the ice obtained in the FFFC stage.

3.3 Block Freeze Concentration

The results of the block freeze concentration tests are presented in Figs. 4 and 5. The highest concentration indices were obtained for the first thawed fractions. During block FC, the elution of the salt to the thawed drops of the solution descending from the ice block during the thawing stage allows separation of the most concentrated fractions initially [7, 21]. The values of CI obtained were in the range 3–7, and show a good salt separation compared to food fluids, in which the CI of BFC were around 3 [7]. This result is due to the lower size of salt than other molecules [32]. The removal efficiency during BFC is shown in Fig. 5. The highest REs were obtained for the lowest salt concentrations. For example, at the lowest initial concentration of 0.4%, 80% of the salt was separated within the two first thawed fractions corresponding to 20% of the initial mass. These results show the suitability of the BFC technique for increasing ice purity at low salt concentrations.

The CI decreased with f, and was less than 1 for f^{B}_{liq} values from 0.2 to 0.4. At this value of CI = 1, two fractions can be separated, one with lower and another with higher concentration than the initial concentration. By this separation, the desalination process is possible. The response variables were calculated at this f when CI = 1 and listed in Table 3. It is remarkable that the concentration of the diluted fraction was lower than the requirements for drinkable water [19, 22, 33]. The RE was around 70%. The concentration of the concentrated liquid fraction can be predicted by Equations (7) and (8).

$$C^{T}_{liq} = 35.26 * C^{T}_{0} + 0.212 * C^{T} + 0.023 \qquad R^2 = 1.000 \quad (7)$$

$$C^{T}_{ice} = -5.125 * C^{T}_{0} + 0.481 * C^{T} - 0.0008 \qquad R^2 = 0.999 \quad (8)$$

This result indicates that BFC is an efficient method for the removal of the occluded salt in the lowest tested concentrations. On the other hand, FFFC is more effective to separate salt faster than BFC. The relationship between the concentration index and the experimental energy consumption of the cooling stage was calculated to compare the behavior of the block and the falling film techniques. This value expressed by CI/Kwh was related to the operational time. The higher its value, the higher the energy efficiency. The FFFC technique obtained values between1.6 and 5 units of concentrations per kwh. Meanwhile, the BFC technique obtained values between 0.1 and 0.2. This result confirm that FFFC is more efficient to separate the salt than BFC. The BFC requires a higher energy consumption, but with high purity ice separation.

3.4. Proposal of an integrated process

An integrated process is proposed based on the results of the three groups of tests performed. The FFFC technique enabled the separation at high initial concentrations [20]. Fractionated thawing allows the separation of salt occluded in the ice. Finally, block freeze concentration was useful to increase the purity of ice and to achieve concentrations lower than the requirements for drinkable water. Therefore, an integration of the FFFC, FT, and BFC techniques was proposed to obtain water at same salinity as required for drinking water. The process is shown in Fig. 6. Equations 5–8 were used to calculate the concentrations of each solution in the process. The process began with 1,000 kg/h of seawater at 3.5% salt concentration as the calculation base. Firstly, five stages of FFFC are used to increase the concentration of the initial water. 256.9 kg/h of a brine with 13.4% of salt is obtained. This technique allows to remove 98.9% of the amount of the salt contained in the initial seawater. Secondly, the ice obtained in the FFFC is thawed partially to recover two solutions, one diluted and the other concentrated. By this step, an effluent with 1% of salt concentration is obtained from a mixture of the diluted fractions of FT. Finally, three block freeze concentration stages can be applied to this solution in order to reduce this concentration until drinkable water requirements are met. At the end of the process, 743.1 kg/h of water with 0.05% of salt can be obtained. This final effluent complies with the standard of salinity for drinkable water [19, 22, 33]. The overall process achieves a salt removal efficiency of 98.46% which is high value compared with other systems [34].

The energy consumption was analysed in terms of the heat transferred and the energy used per kg of feed or per 1,000 kg of water removed. The basic load is the heat consumed to convert 1 kg of feed into an appropriate mixture of ice and residual solution [35]. In the continuous system of FFFC proposed in Fig. 6, the theoretical conversion of 1,000 kg/h of feed (salt solution at 3.5 % w/w) into 743.1 kg/h of desalinated water (0.05%) can produce and melt around 5,126 kg/h of pure ice.
Analysis of the available data showed that energy can be saved in cryoconcentration technology by reducing the temperature difference between the evaporating and condensing refrigerant [36, 37]. In order to save energy by increasing the system COP, ice can be formed to condense at low temperature, typically at 10°C. As the freezing point of the salt solution at concentration of 1 and 10% w/w varies between −0.5 and −7°C, the operating temperature of the refrigerant in the evaporator will be −10°C, while melting ice in a continuous system requires a condensing temperature of 10°C [38]. A Carnot COP of 13.15 was calculated for −10°C evaporation and 10°C condensation temperatures. In practice, real cycles tend to have 60% efficiency compared to the theoretical performance [5]. Therefore, an actual COP of 7.9 is possible for a compressor operating between −10 and 10°C [39. Rodriguez, et al. [40] suggested that a COP above 8 can be reached in the cryoconcentration of wastewater treatment in a FFFC system.
If we assume that the heat of crystallization of ice is 334 kJ/kg, theoretically, 474 kWh of thermal energy is needed in the integrated system proposed in Fig. 6. If a COP of 8 is adopted, the electrical consumption is 59.2 kWh. This value corresponds

to 11.5 kWh per 1,000 kg of ice produced. In similar equipment to that presented in this study, the specific energy consumption of 23.33 kWh for 1,000 kg of ice in a batch falling film CC was reported when coffee and orange juice extract were treated [40]. Other studies in China [41] showed a specific energy consumption of about 21.3 kWh per 1,000 kg of ice removed by cryoconcentration in wastewater treatment. The HybridICE technology [42] applied to desalination has energy consumption between 21 and 26 kWh for 1,000 kg of ice. In addition, some studies suggested that the use of a heat pump can reduce the energy consumption in FFFC, which can reach a value of 10 kWh for 1,000 kg of ice [5, 39]. Finally, another alternative to reduce the energy consumption is to use a process without recirculation. In this case, the concentrated fractions of the fractionated thawing and block FC stages are not recirculated to the process. With this strategy, 269 kg/h of water at 0.05% of salt concentration is obtained. In addition, 99.4 kg/h of brine at 12.4% is obtained, and an effluent of 603 kg/h at 3.7% can be returned to the water source. The energy consumption decreases to 23.1 kWh for the overall the process. This correspond to a reduction of 95% of the energy consumption. Several strategies between the two points of energy consumption, with or without recirculation, can be studied. A further optimization process will be useful to establish the optimal point of recirculation.

Conclusions

A process to desalinate water by the integration of the falling film technique, the fractionated thawing, and the block freeze concentration was proposed. A fraction of 74% of the initial mass can be obtained at a final salt concentration of 0.05%, suitable as drinkable water. The process consists of five stages of FFFC and FT and three stages of BFC. A salt removal efficiency of 98.5% can be obtained with the process. A theoretical energy consumption of 59.2 kWh was calculated for the process, for 1000 kg of initial water. An alternative process without recycling can be used to reduce energy consumption, obtaining 29.6% of the initial water at 0.05% salt with 23.1 kWh of energy consumption for 1000 kg of initial water. An optimization of the process is required to establish an adequate strategy for recycling. FFFC seems to be appropriate to separate salt even at high initial concentrations. The FT method is useful to recover the occluded salt in the ice layers obtained in FFFC and to increase the ice purity. BFC is an effective technique to purify the diluted fractions in order to attain the concentrations of drinkable water.

5. Acknowledgements

This work was supported by the ING-151-2014 project of the Faculty of Engineering of Universidad de La Sabana. Author Moreno F L thanks COLCIENCIAS for its grant for doctoral studies (2013).

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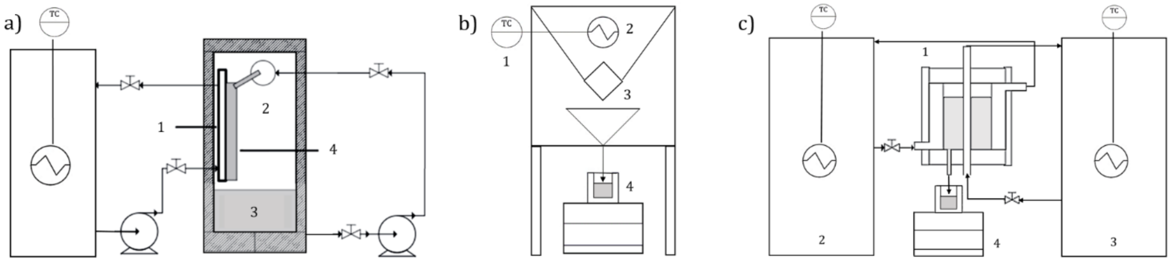

Fig. 1. Experimental setup for Freeze Concentration Tests. (a) Falling Film Freeze Concentration; (b) Fractionated Thawing and (c) Block Freeze Concentration

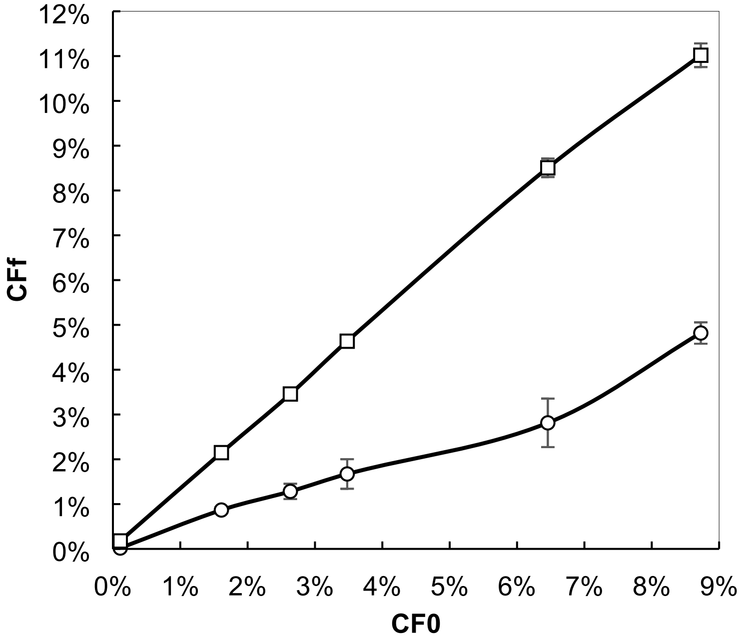

Fig.2. Final solid concentration (C^F_f) in liquid (o) and ice (□) from solutions with different initial salt concentrations (C^F_0) of FFFC.

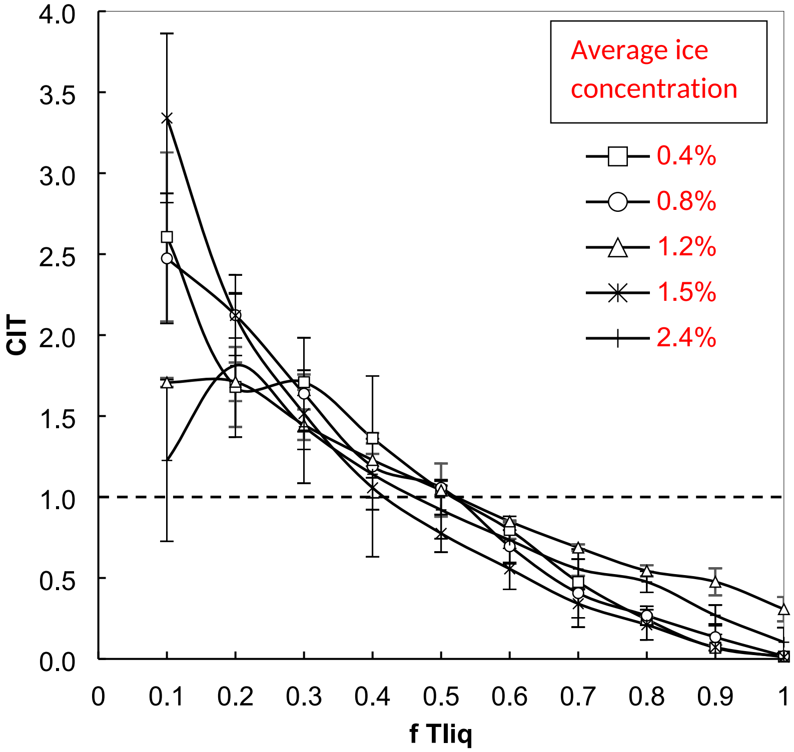

Fig. 3. Concentration index (CIT) as a function of the thawing fraction (f^{T}_{liq}) at different average concentration of the ice: (□) 0.4%; (o) 0.8%; (Δ) 1.2%; (*) 1.5%; and (+) 2.4%.

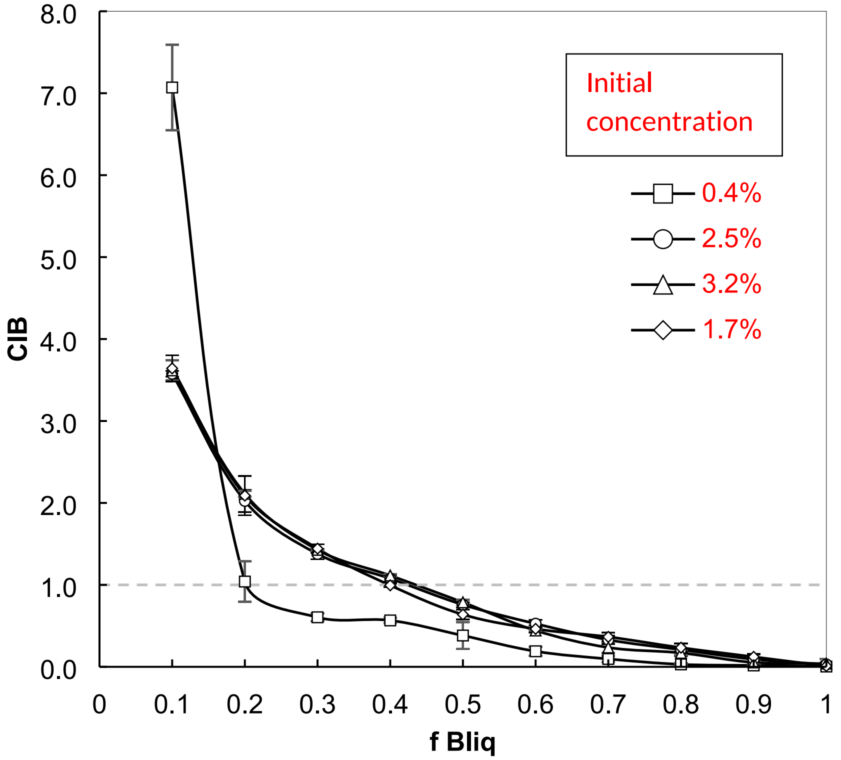

Fig.4. Concentration index (CIB) after block freeze concentration at different initial concentration: (□) 0.4%; (◊) 1.7%; (o) 2.5%; and (Δ) 3.5%.

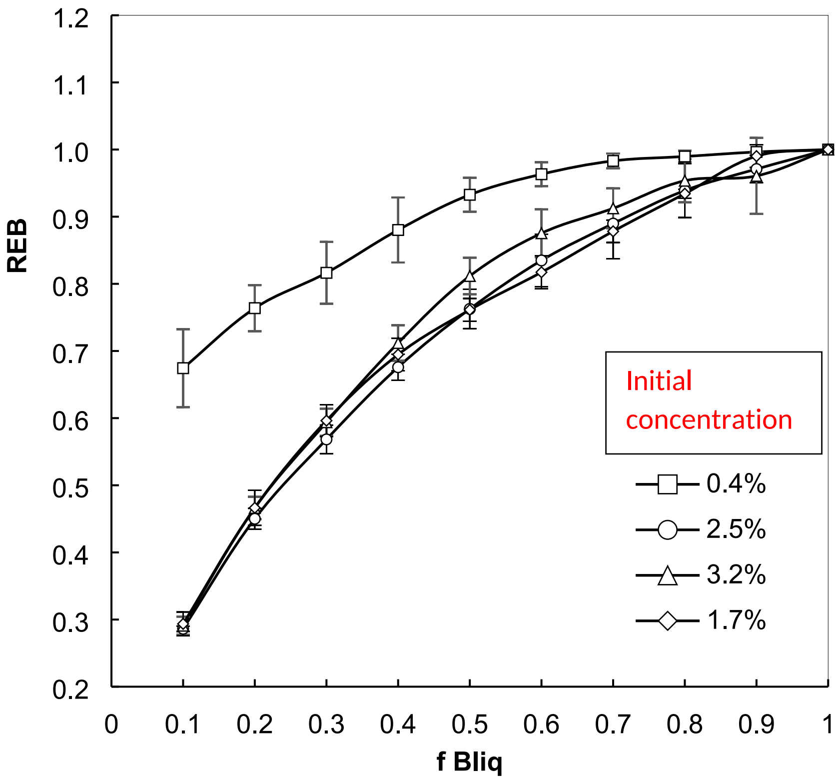

Fig. 5. Removal efficiency (REB) after block freeze concentration at different initial concentrations: (□) 0.4%; (◊) 1.7%; (o) 2.5%; and (Δ) 3.5%.

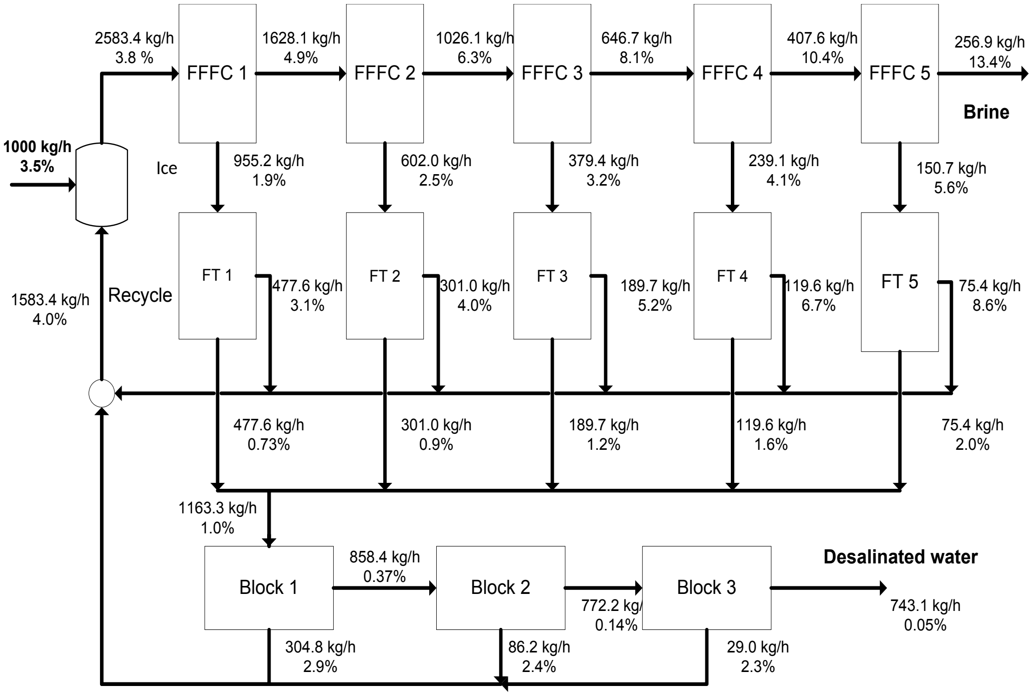

Fig. 6. Flow diagram of the integrated process for the freeze desalination of water using Falling Film Freeze Concentration (FFFC), Fractionated Thawing (FT), and Block Freeze Concentration (BFC) with recirculation.

Table 1. Descriptors of the FFFC performance solutions at different initial concentrations. Initial salt solid concentration (C^F_0), concentration index (CIF), average distribution coefficient (KF), ice fraction (f^F_{ice}), and removal efficiency (REF).

C^F_0 (%)	CI^F	K^F	f^F_{ice}	RE^F (%)
0.11 ± 0.01^{a}	1.63 ± 0.05^{g}	0.11 ± 0.01^{i}	0.43 ± 0.02^{l}	83 ± 2.4^{o}
1.61 ± 0.01^{b}	1.33 ± 0.01^{h}	$0.40 \pm 0.03^{j,k}$	$0.42 \pm 0.03^{l,m}$	$46 \pm 4.4^{p,q}$
2.63 ± 0.02^{c}	1.31 ± 0.04^{h}	$0.37 \pm 0.07^{j,k}$	$0.38 \pm 0.01^{l,m,n}$	$51 \pm 6.1^{p,q}$
3.48 ± 0.11^{d}	1.33 ± 0.06^{h}	$0.36 \pm 0.07^{j,k}$	$0.39 \pm 0.04^{l.m.n}$	$52 \pm 8.1^{p,q}$
6.46 ± 0.08^{e}	1.32 ± 0.03^{h}	0.33 ± 0.07^{j}	0.36 ± 0.02^{n}	56 ± 8.2^{p}
8.73 ± 0.10^{f}	1.26 ± 0.04^{h}	0.44 ± 0.02^{k}	$0.37 \pm 0.05^{m,n}$	45 ± 3.3^{q}

Different letters indicate statistically significant differences ($p < 0.05$).

Table 2. Descriptors of FT performance solutions when CIT = 1 at different initial concentrations. Initial salt solid concentration (CT_0), concentration index of the concentrated fraction (CIT) at CIT = 1, portion of mass recovered in the diluted thawing fraction at CI = 1 (f^{T}_{ice}), salt concentration in the diluted FT fraction (C^{T}_{ice}) at CIT = 1, salt concentration in the concentrated FT fraction (C^{T}_{liq}) at CIT = 1, and removal efficiency (RET) at CIT = 1.

C^{T}_{0} (%)	**CI^{T}**	**f^{T}_{ice}**	**C^{T}_{ice} (%)**	**C^{T}_{liq} (%)**	**RE^{T} (%)**
0.40 ± 0.03^{a}	1.90 ± 0.25^{f}	0.53 ± 0.06^{h}	0.09 ± 0.07^{i}	0.74 ± 0.05^{k}	77.2 ± 15.3^{o}
0.80 ± 0.12^{b}	1.81 ± 0.15^{f}	0.53 ± 0.03^{h}	0.23 ± 0.04^{i}	1.47 ± 0.33^{l}	$71.2 \pm 8.13^{o,p}$
1.17 ± 0.06^{c}	1.30 ± 0.16^{g}	0.45 ± 0.06^{h}	$0.76 \pm 0.14^{i,j}$	1.53 ± 0.24^{l}	35.0 ± 12.4^{p}
1.45 ± 0.15^{d}	1.96 ± 0.33^{f}	0.58 ± 0.04^{h}	0.50 ± 0.25^{i}	2.88 ± 0.73^{m}	$71.8 \pm 29.3^{o,p}$
2.41 ± 0.28^{e}	$1.55 \pm 1.55^{f,g}$	0.50 ± 0.19^{h}	1.47 ± 0.94^{j}	3.70 ± 0.24^{n}	$56.1 \pm 29.0^{o,p}$

Table 3. Descriptors of BFC performance solutions at CI = 1. Initial salt solid concentration (CB0), portion of mass recovered in the diluted thawing fraction (fBice), salt concentration in the diluted T fraction (CBice), salt concentration in the concentrated fraction (CBliq), concentration index of the concentrated fraction (CIB), and removal efficiency (REB).

C^{B}_{0} (%)	f^{B}_{ice}	C^{B}_{ice} (%)	C^{B}_{liq} (%)	CI^{B}	RE^{B}
0.43 ± 0.01^{a}	0.85 ± 0.07^{e}	0.12 ± 0.01^{g}	2.46 ± 1.11^{j}	5.70 ± 2.46^{n}	73 ± 1.7%^{p}
1.65 ± 0.28^{b}	0.63 ± 0.06^{f}	0.57 ± 0.16^{h}	3.62 ± 1.05^{k}	2.17 ± 0.25^{o}	66 ± 3.6%^{q}
2.51 ± 0.02^{c}	0.60 ± 0.00^{f}	0.81 ± 0.04^{i}	5.05 ± 0.11^{l}	2.01 ± 0.03^{o}	68 ± 1.9%^{p,q}
3.24 ± 0.09^{d}	0.60 ± 0.00^{f}	0.94 ± 0.11^{i}	6.70 ± 0.06^{m}	2.07 ± 0.04^{o}	71 ± 2.6%^{p}