Fractional-submerged membrane distillation crystallizer (F-SMDC) for treatment of high salinity solution

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Abstract

Membrane distillation with crystallization (MDC) is an attractive process for high saline seawater reverse osmosis (SWRO) brine treatment. MDC produces additional fresh water while simultaneously recovering valuable resources. This study developed a novel approach of fractional-submerged MDC (F-SMDC) process, in which MD and crystallizer are integrated in a feed tank with a submerged membrane. F-SMDC principle is based on the presence of temperature/concentration gradient (TG/CG) in the feed reactor. The operational conditions at the top portion of the feed reactor (higher temperature and lower feed concentration) was well suited for MD operation, while the bottom portion of the reactor (lower temperature and higher concentration) was favourable for crystal growth. F-SMDC performance with direct contact MD to treat brine and produce sodium sulfate (Na_2SO_4) crystals using TG/CG showed positive results. The TG/CG approach in F-SMDC enabled to achieve higher water recovery for brine treatment with a volume concentration factor

(VCF) of over 3.5 compared to VCF of 2.9 with a conventional S-MDC set-up. Further, the high feed concentration and low temperature at the reactor bottom in F-SMDC enabled the formation of Na_2SO_4 crystals with narrow crystal size distribution.

Keywords: Concentration and temperature gradients; Membrane distillation with fractional crystallization; Resource recovery; Seawater reverse osmosis brine; Sodium sulfate crystal

1. Introduction

Reverse osmosis (RO) based seawater desalination (i.e. SWRO) technology has been widely used to solve global water crisis of fresh water shortage owing to its affordable operation cost and reliability [1-3]. However, one of the major limitations of SWRO is its low recovery (30~50%), resulting in the production of a substantially large amount of concentrated brine that has to be managed [4-6]. The SWRO brine management incurs an additional operating cost to the plant as well as environmental issues when SWRO brine is discharged directly into the environment [7]. SWRO brine contains a variety of chemicals (coagulant, chemical washing agent, and pH adjusting agent) which are employed during SWRO process, Also, SWRO brine contains a high concentration of organic and inorganic matters [8-11]. In recent times, simultaneous brine treatment with extraction/production of valuable resources is favoured to offset the treatment cost rather than the approach of treatment followed by disposal. The formed is also preferred as give than seawater and likewise seawater brine contains a number valuable elements [12, 13].

In this regard, membrane distillation with crystallizer (MDC) shows promising potential in SWRO brine treatment [14-18]. MDC is an integrated process that can achieve high quality fresh water while simultaneously extracting valuable resources from high salinity solution [14]. MDC is attractive compared to traditional crystallization processes because of the following factors: well-controlled saturation rate, faster nucleation rate and reduction of induction time [19]. Moreover, the ability to concentrate solution up to a saturation point with minimal flux decline is an added advantage of MDC [20-22]. Cooling crystallization method is widely used in separation processes for solution having different solubility at different temperatures due to its ease of control and maintenance [23]. However, one of the major limitations is the significant energy consumption due to initial heating (thermal MD operation) followed by cooling for the crystallization.

A number of methods such as submerged MD (SMD) have been evaluated in terms of energy consumption and economic benefits to improve the efficiency of conventional MDC process [3, 24, 25]. For instance, in SMD process, channelling heated feed solution through a pump to the membrane module can be eliminated, which results in lower heat losses through the feed channel [14, 26]. In this case, the feed tank can also act as a crystallizer, achieving an integrated system [3]. Nevertheless, several limitations are still present such as challenging saturated feed concentration effect, and fouling caused by crystal formation in the feed tank as well as on the membrane [27-29]. Previous studies have shown that at elevated feed concentration levels [3], MD performance is affected by flux decline and wetting phenomenon. This decreases the membrane life span, resulting in more frequent membrane replacement, incurring addition operation cost [30].

In view of this, fractional submerged MDC (F-SMDC) based on principle of maintaining a feed concentration gradient (CG) and feed temperature gradient (TG) in the reactor was evaluated in this study. Maintaining CG and TG in the feed reactor can positively influence both MD and crystallization. CG and TG in the reactor enables to reduce feed concentration and increase feed temperature at the top portion of the reactor where the submerged membrane is located. Simultaneously, the bottom portion of the reactor maintains high feed concentration with low feed temperature which enhances crystallization at the bottom portion of the reactor. This is due to the formation of high saturation state at the bottom portion of the reactor where crystals form continuously during F-SMDC operation. This setting potentially promises higher water recovery, with reduced membrane scaling issues. Further, the continuous extraction of crystal from the bottom of the reactor is expected to reduce the salt contents in feed solution [14].

In this study, the feasibility of F-SMDC for the treatment of highly concentrated and saline feed solution was investigated and compared with conventional submerged membrane distillation crystallization (SMDC). The trend of CG/TG in the feed reactor was examined during the operation.

The effect on the flux and crystallization efficiency in the F-SMDC was evaluated. In addition, methods to improve the efficiency of maintaining CG/TG in the feed reactor were investigated.

2. Materials and Methods

2.1 Lab-scale setup

F-SMDC process with direct contact MD (DCMD) configuration based on GC and TG was used in this study (**Figure 1**). The F-SMDC reactor consisted of three cylindrical cells with a height of 150 mm and an inner diameter of 70 mm (volume of the single cell = 580 mL, and total volume of the reactor = 1,740 mL). The reactor is equipped with double wall to enable the control of TG as temperature control of feed solution is essential in the reactor (**Figure 2**). The partition in the shape of funnel (length = 25 mm, and hole diameter = 20 mm) was installed between the top and bottom portion. This partition acts as a barrier that minimized the mixing of solution by natural convection caused by heating or cooling. Feed solution was placed inside of the reactor while heating and cooling water was circulated at the outer wall of the reactor with respective heating and cooling units. This enabled the feed solution at the top portion of the reactor to be maintained at 50.0±1.3 °C, while, the feed solution at the bottom portion of the reactor was maintained at 20.0±1.5 °C. Thermometer was placed in each cell to measure the temperature of feed solution in real-time.

Meanwhile, the permeate temperature (T_p) was maintained at 16.5±0.2 °C, and was measured using temperature sensors placed at the permeate channel. The permeate flow rate of 0.5 L/min was controlled using a gear-pump. Feed solution was fed continuously into the top portion of the reactor by the differential head of water between the reactor and feed tank. Continuous flow of new feed solution to the top portion of reactor enables to maintain a constant feed solution concentration rather than an increasing feed concentration. This systematically minimizes the effect of increased feed

concentration on MD performance. The temperature of feed solution in the feed tank (reservoir) was maintained at room temperature (23.2±0.3 °C).

An external crystallizer was used in the last stage of the F-SMDC operation. Upon attaining super-saturation state at the bottom portion of the reactor, the remaining feed solution (mother liquid) was fed to this external reactor. The external reactor was kept at room temperature (23.2±0.3 °C) with constant stirring (50 rpm) of the mother liquid to enhance crystal growth.

The permeate flux was calculated from on the solution mass difference with time using an electronic balance. The permeate/fresh water quality was evaluated by measuring the conductivity/total dissolved solids (TDS) value in real-time. All the experiments were duplicated to ensure the reproducibility.

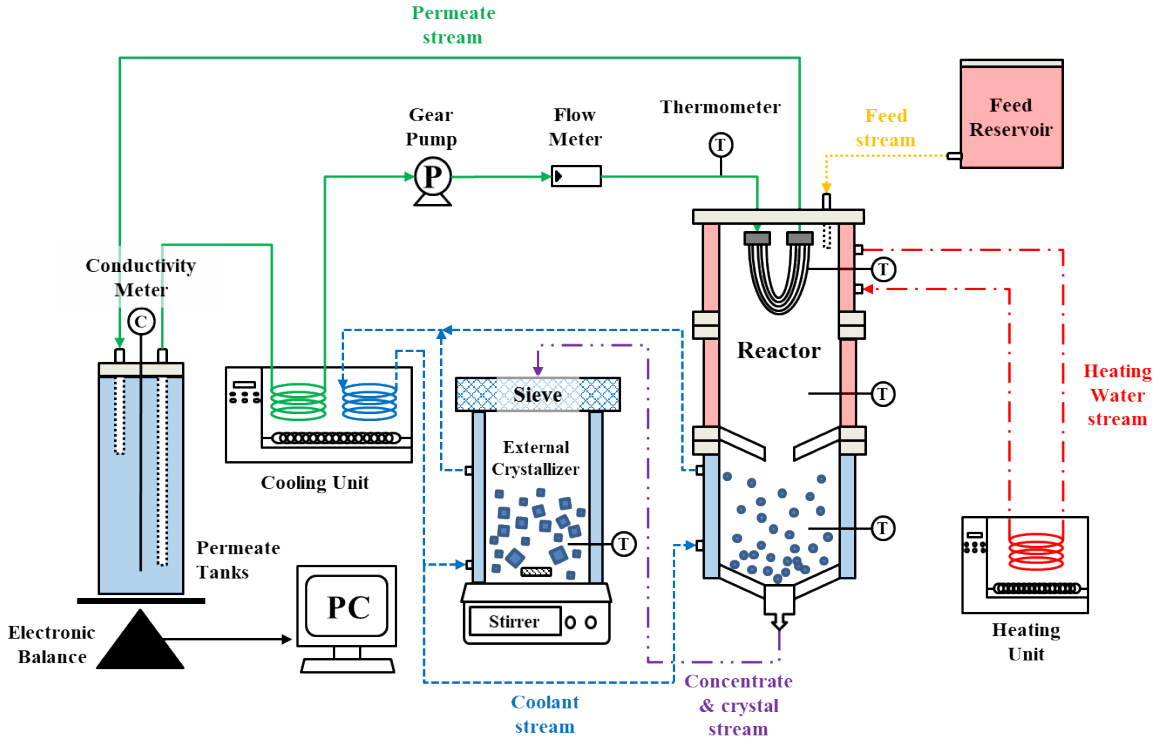


Figure 1 Set-up of F-SMDC process: permeate stream (——), stream of continuous feeding to the reactor (feed solution) (·····), stream of concentrate and crystal generated from the reactor to the crystal

growth cell (—··—), the stream of heating water for the top portion of the reactor (—·—), stream of coolant water for the bottom portion of the reactor and the crystal growth cell (———).

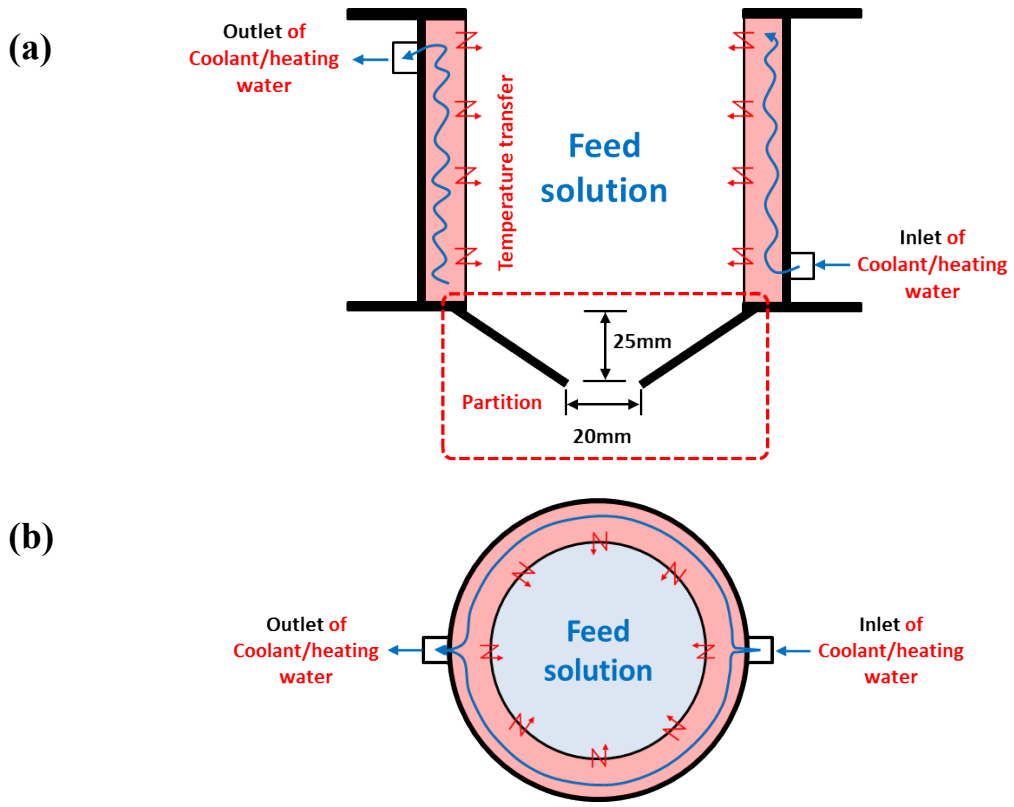


Figure 2 Details of F-SMDC reactor showing the double wall feature for generating FT gradient (heating in the top portion of the reactor and cooling at the bottom portion of the reactor): (a) Cross-sectional view, and (b) Aerial view.

2.2 Feed solution

The performance of F-SMDC process was investigated using 120 g/L Na_2SO_4 solution as feed solution. The solubility of Na_2SO_4 in water varies significantly at different temperature (91 g/L @ 10 °C, 195 g/L @ 20 °C, and 488 g/L @ 40 °C). A mixed solution containing sodium chloride

123 (NaCl) and Na_2SO_4 was then used to examine an effect of salinity on treatment of high concentration
124 Na_2SO_4 solution (
125 **Table** 1). Both feed solutions were prepared using reagent grade salts (Sigma-Aldrich).
126

127 **Table 1** Composition of model solution.

Ions	Concentration (mg/L)
Sodium (Na^+)	58,320
Sulfate (SO_4^{2-})	81,150
Chloride (Cl^-)	30,020

128

129 **2.3 Membrane**

130 A hollow-fiber polyvinylidene fluoride (PVDF) membrane (Econity, Republic of Korea)
131 module was used. The membrane has a nominal pore size of 0.1 μm with an outer and inner diameter
132 of 1.2 mm and 0.7 mm (membrane wall thickness: 250mm), liquid entry pressure (LEP) of 2.0-2.3
133 bar, and contact angle of 106±2° (based on the specifications provided by the manufacturer). A
134 membrane module with an effective membrane area of 0.0136 m^2 was used. The membrane module
135 consisted of 18 fibers, each of 0.2 m in length, which were potted on both ends of membrane fiber.
136

137 **2.4 Analysis**

138 Crystal morphology was characterized by a field emission scanning electron microscopy
139 (FESEM, Zeiss supra 55VP, Carl Zeiss AG). The TDS and conductivity of the permeate were
140 measured with a portable water quality meter (HQ40d multi, Hach). The concentrated feed solution
141 was measured using calibrated conductivity curves made using different concentration of Na_2SO_4

(15, 30, 60, 180 and 300 g/L Na_2SO_4). The concentrated solution was vacuum filtered using a glass microfiber filter (Whatman, Grade GF/C, pore = 1.2 μm) enabling the crystals in the solution to be retained on the filter. The crystals were dried at room temperature (23.2±0.3 °C) for 120 h and the dry weight of crystals was measured using an electronic balance. The crystal form and sizes were evaluated using a microscopy method. In this method, at least 72 crystals were selected randomly, and each crystal was measured using microscope with an image analyser (ImagePro7). The crystal sizes were then quantified with a crystal size distribution (CSD) procedure.

Volume concentration factor (VCF) used in this study was based on the reactor volume and the amount of produced fresh water. The total volume of feed solution in F-SMDC reactor was maintained at a fixed volume (1,740 mL) with continuous feeding of feed solution at the same rate of produced fresh water. If the rejection ratio of produced fresh water is 100% over time, the feed solution concentration in the rector would increase while the total volume of feed solution was maintained. In this context, the VCF value was calculated as:

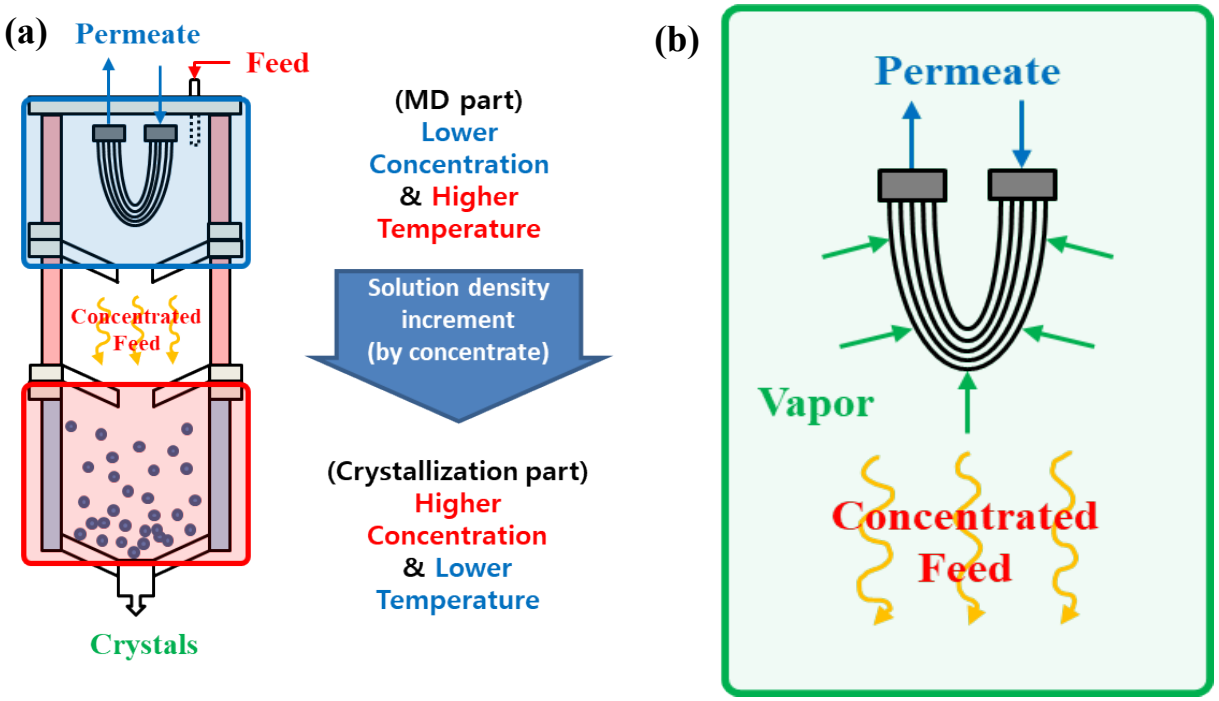
$$\mathrm{VCF} = \frac{V_{reactor} + V_{total,\ permeate}}{V_{reactor}}$$

where $V_{reactor}$ is the reactor volume, and $V_{total,permeate}$ is the total amount of permeate produced.

3. F-SMDC principle

F-SMDC is a combination of two processes: MD and crystallization in a single feed reactor with a submerged membrane (**Figure 3(a)**). The submerged membrane module is placed at the top portion of the feed reactor. In F-SMDC, a CG is generated in the feed reactor as a result of difference in solution density. Upon the increase of feed solution concentration (MD part), the density of the feed solution increases, resulting in the gravitation of concentrated feed solution to the bottom of the reactor (**Figure 3(b)**). In S-DCMD, cooling down of feed solution by the cold permeate stream

164 further enhances this factor as water density is higher at low temperature. Accordingly, CG is
165 generated in the reactor. Simultaneously, TG is generated by external heating and cooling of the
166 outer wall (**Figure 2**).



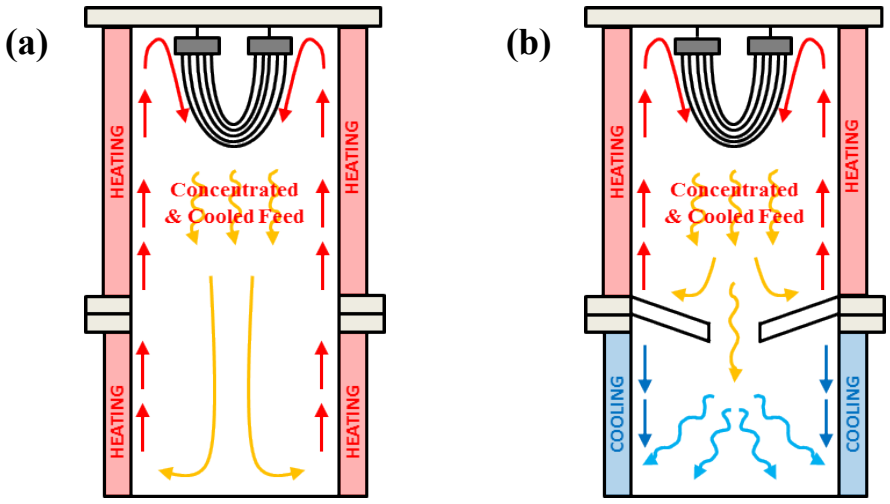
167 **Figure 3** Generation of concentration gradient (CG) in feed reactor of F-SMDC: (a) lower feed
168 concentration at the top portion and higher feed concentration at the bottom portion, and (b) concentration
169 effect at the top portion of the reactor containing submerged membrane.

170

171 The presence of CG in the feed reactor influences both MD and crystallization efficiency of
172 the F-SMDC process. In MD, dissolved ion concentration in the feed solution is increased as the feed
173 solution in concentrated, resulting in decrease of permeate flux. However, in crystallization process,
174 elevated dissolved ion contents are favourable for attaining saturation degree of targeted compounds.
175 Lower concentration at the top portion of the reactor is suitable for MD operation. Higher
176 concentration at the bottom portion of the reactor is favourable for the formation of crystals since
177 super-saturation (above the limits of metastable zone) of target salt should be reached to get a

178 nucleation of crystals. F-SMDC achieves an increase of feed concentration at the bottom portion of
179 the reactor at a faster ratio compared with theoretical concentration ratio in the whole reactor, and
180 crystals are formed when solution concentration exceeds the limits of metastable zone of solution.
181 Moreover, TG is formed in the reactor by the temperature transfer caused by movement of
182 concentrated feed solution to the bottom portion without additional temperature control (using
183 heating or cooling). Temperature at the top portion is higher than the bottom portion. The
184 maintenance of TG in F-SMDC enhances the crystallization phenomenon.

185 Convection current in the reactor occurs differently (**Figure 4(a)).** If feed solution is heated
186 up near the reactor wall, its density decreases with its expansion. As a result, it moves towards the
187 upper portion, and the unheated feed solution moves downwards. Moreover, concentrated and cooled
188 (because of the effect of lower permeate temperature (around 16.5±0.2 °C) of S-DCMD) feed
189 solution by membrane operation favours the above effect. As a result, feed solution is mixed, and
190 therefore CG cannot be maintained in the feed reactor. Even though convection current effect on
191 solution mixing does not significantly affect CG, it should still be controlled to ensure that CG is
192 well controlled/maintained throughout the operation. In our design of F-SMDC, the incorporation of
193 a partition in the feed reactor enables to maintain convention current effect within the respective cells
194 (top and bottom portion of the reactor) (**Figure 4(b)**). The partition prevented the feed solution
195 mixing by convection current, resulting in maintaining CG and TG in the reactor.



196 **Figure 4** Convection current in reactor by heating and cooling of (a) conventional MDC process
197 (reactor without cooling and partition) and (b) F-SMDC process (reactor with cooling and partition).

4. Results and discussions

In this study, the feasibility of F-SMDC was examined for the treatment of feed solution containing Na_2SO_4 alone and with NaCl.

4.1. Performance comparison of F-SMDC and SMDC

The performance of conventional submerged MDC (SMDC) (reactor without cooling and partitioning) was compared with F-SMDC (reactor with cooling and partitioning) under the same operating conditions (reactor, feed temperature and feed solution) and same sampling points at the top and bottom portion of the reactor. The initial flux of both SMDC and F-SMDC mode was 2.8 and 2.7 LMH respectively. The initial flux of S-MDC was slightly higher than F-SMDC, while the feed solution concentration trend varied. Up to a feed solution VCF 2.5, a similar concentration variation was observed for both SMDC and F-SMDC mode. However, in SMDC, above VCF 2.5, a rapid increase of concentration from VCF 2.5 to 2.8 accompanied by a rapid flux decline was observed (**Figures 5** and **6).** Both processes maintained 99% ion rejection ratio until the end of the experiment. Comparatively, F-SMDC was able to maintain a stable concentrate (without rapid increase) up to VCF 3.0 and sustained the operation up to VCF 3.5. The results indicated that in F-SMDC, the partition between the top and the bottom portion of the reactor prevented the mixing of feed solution by natural convection current, emulating a trap. This enabled to create a CG in the reactor, with a higher concentration at the bottom portion of the reactor. In F-SMDC, the presence of CG in the feed reactor was beneficial for both the MD and crystallization processes. Maintaining a low feed concentration closer to the membrane in F-SMDC enabled to achieve a higher VCF (around VCF 3.5) with smaller flux decline compared to the SMDC (around VCF 2.8). In SMDC, concentrated feed solution interferes with the transportation of vapour through the hydrophobic membrane, decreasing its performance (reduced flux decline).

In F-SMDC, the presence of CG in the feed reactor was well reflected by the CG variation between the top and bottom portion of the reactor (

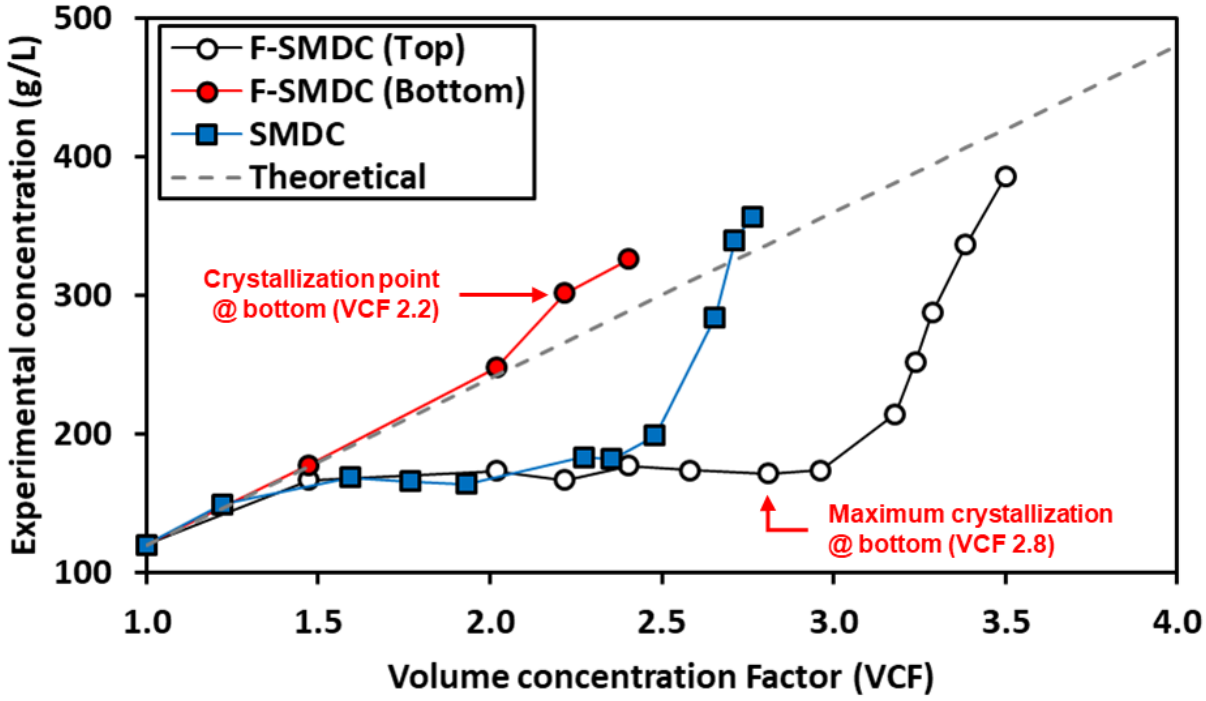


Figure 5). The CG effect was especially apparent from VCF 1.5 onwards. The feed concentration at the top portion (MD part) of the reactor did not change rapidly while a rapid increase of feed concentration at the bottom portion of the reactor was observed. At the top portion, the feed solution concentration was maintained (range: 171.8±5.1 g/L, 1.4 times of initial feed concentration) below the theoretical feed concentration increment (initial feed concentration × VCF). Above VCF 2.0, feed concentration at the bottom portion of the reactor showed higher increment than the theoretical feed concentration level. Over time, the feed concentration at the bottom portion of the reactor greatly varied to the theoretical feed concentration. The results reflected the capacity of F-SMDC to maintain a stable CG in the feed reactor.

In the F-SMDC mode, higher feed concentration at the bottom portion of the reactor than the top portion made it suitable for the formation of target crystals. Also, lower temperature (around 20.0 ±1.5 °C) at the bottom portion of the reactor, which was generated by the cooling as well as the movement of concentrated/cooled feed solution from the top portion (heated up) was favourable for the stimulation of crystals.

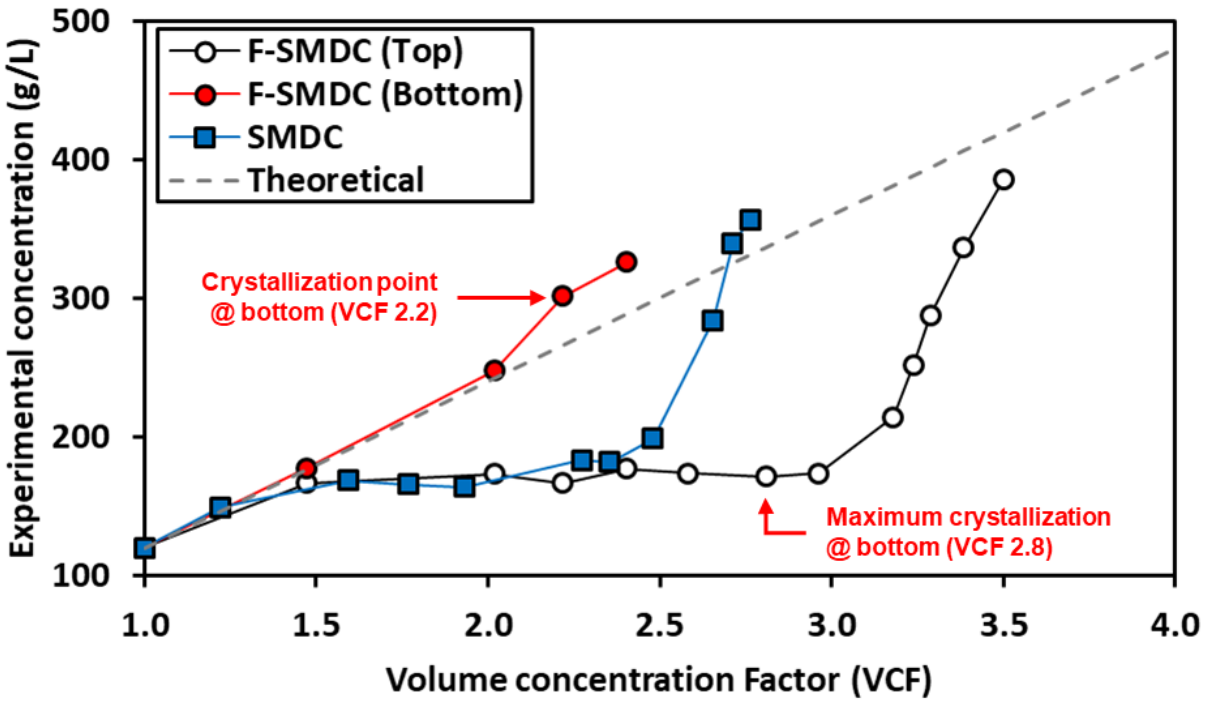


Figure 5 Variation of feed concentration in the reactor during the operation in F-SMDC and SMDC modes (feed: Na_2SO_4).

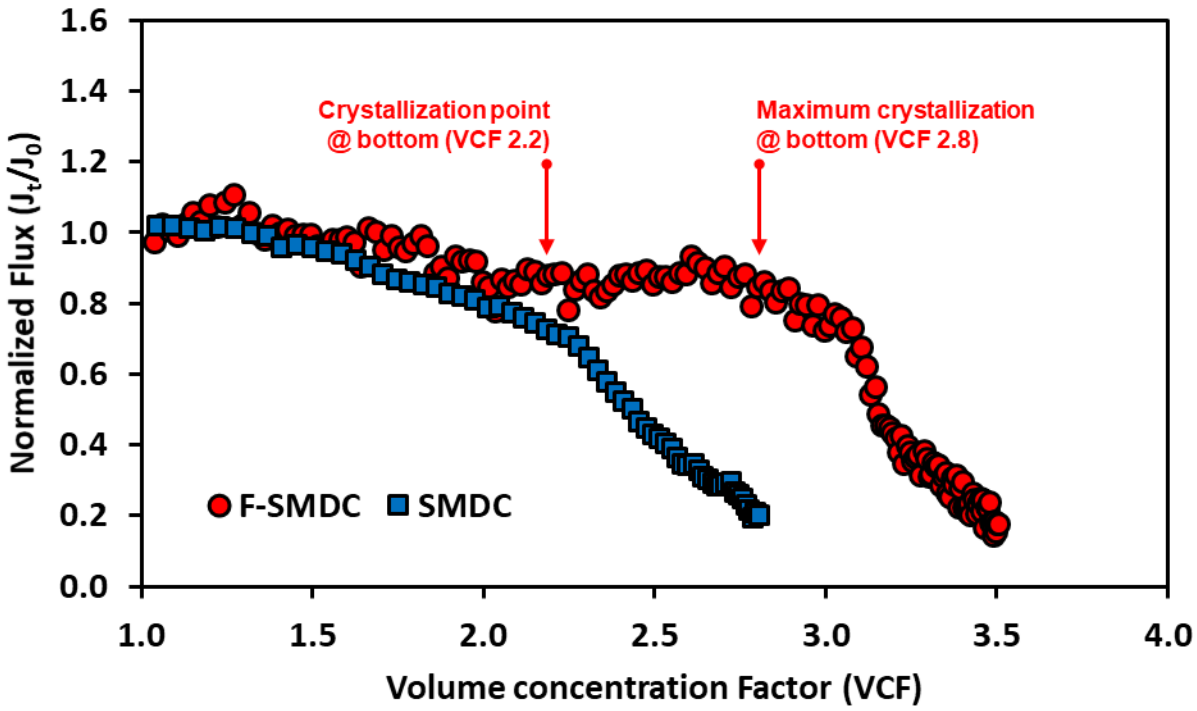


Figure 6 Comparison of flux in F-SMDC and SMDC mode (without crystal extraction).

The F-SMDC was carried out using S-DCMD configuration. The feasibility of different submerged MD configurations (submerged vacuum direct contact MD called as S-VDCMD) in F-SMDC process was examined under the same operational condition. The motivation for using S-VDCMD is the potential of achieving higher permeate flux. In line with this, S-VDCMD achieved a 25% higher initial permeate flux than S-DCMD. However, the CG in F-SMDC with S-VDCMD configuration was not observed. Higher flux decline was also observed with S-VDCMD compared to F-SMDC with S-DCMD configuration (**Figure 7**) with slightly lower feed concentration at the bottom portion than at the top portion of the reactor. This was attributed to the application of vacuum. In a previous S-MD study [3], it was found that the deposition and adhesion of crystals on the membrane surface was intensified by the presence of vacuum pressure in the MD, resulting in more prevalent fouling. In S-VDCMD, concentrated ions were captured in the membrane boundary

layer due to stronger driving force (vacuum pressure) compared to S-DCMD [3]. This restricted the movement of concentrated feed solution, and it stagnated close to the membrane surface. The increase in diffusion potential of concentrated feed solution at the top portion rather than the precipitation downward, resulted in the formation of higher concentration at the top portion than the bottom portion of the reactor. The results highlighted that S-MD using vacuum was not suitable for F-SMDC process.

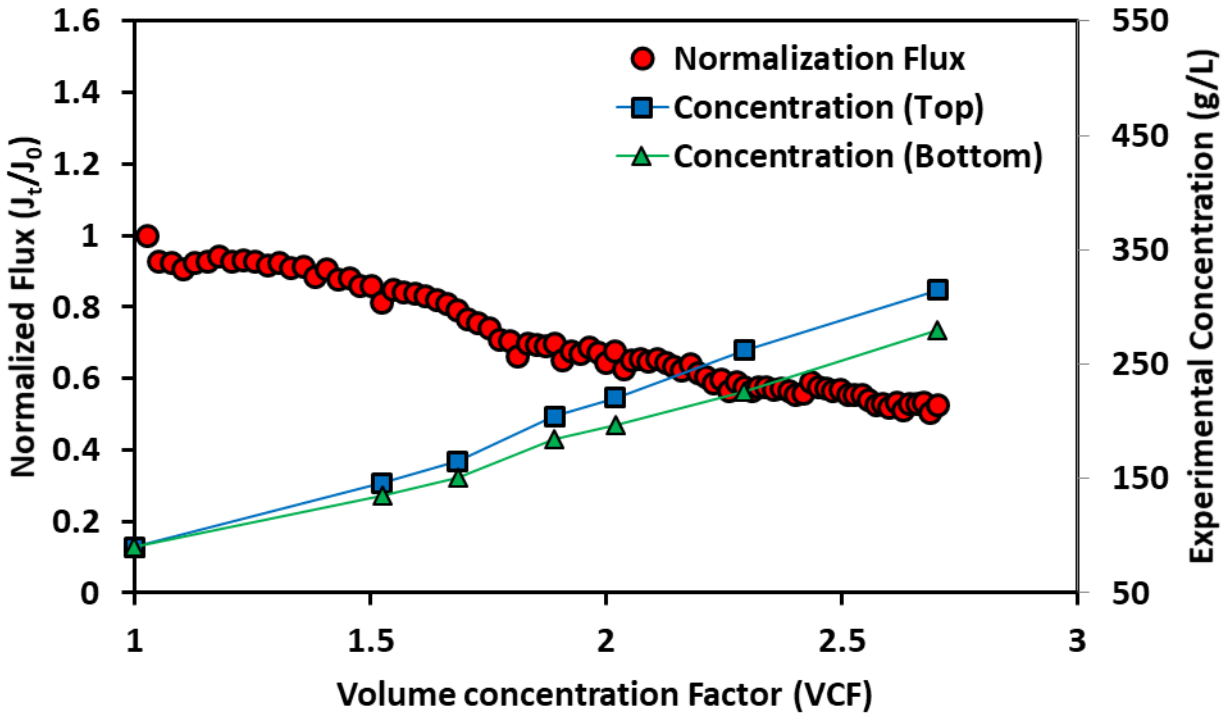


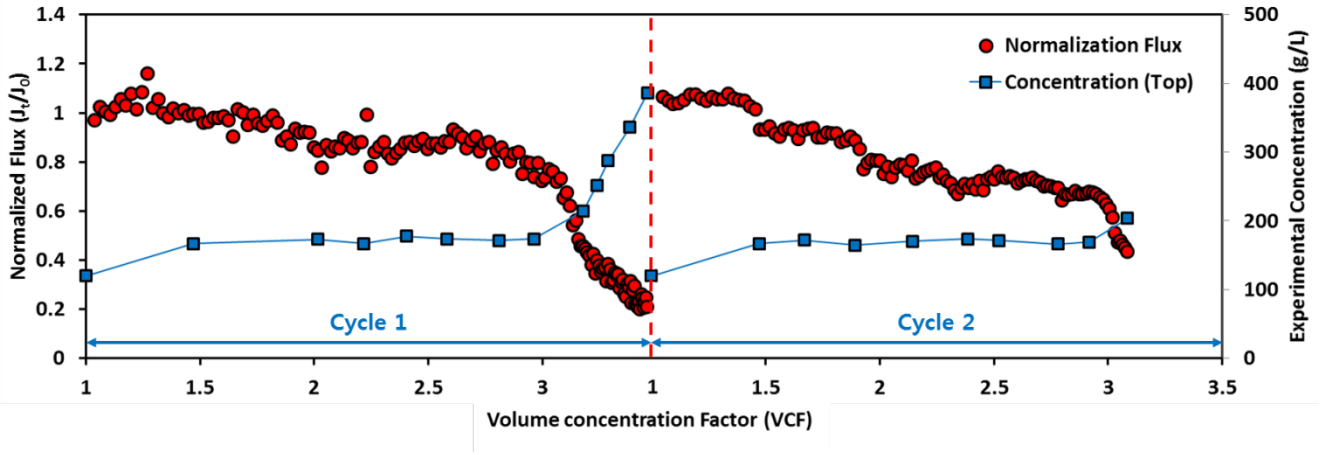
Figure 7 Normalized flux and concentration tendency in F-SMDC comparing with S-VDCMD.

4.2. Continuous F-SMDC operation

The stability of F-SMDC in treating high concentration solution was examined by carrying out two repeated cycles of operation using the same membrane. At the end of each cycle, used membrane was submerged in DI water and stirred at 200 rpm for 10 mins to rinse/clean the membrane before the subsequent operation.

In S-DCMD configuration, generally, the membrane surface feed temperature is lower compared to bulk feed temperature due to direct contact with cold permeate on the membrane surface. This factor plays a prevalent role in the solubility of certain crystal salts that are especially influenced by the effect of temperature. One such salt is Na_2SO_4, which exhibits lower solubility at low temperature (91 g/L @ 10 °C, and 195 g/L @ 20 °C) and higher solubility at increased temperature (488 g/L @ 40 °C). This characteristic of Na_2SO_4 can lead to higher saturation state on the membrane surface, and aggravate the formation of crystals. This results in the non-continuity of MDC process.

The effect of this phenomenon can be mitigated in F-SMDC by creating and maintaining CG in the reactor. The feed concentration (under 195 g/L) was lower at the top portion of the reactor which contains the submerged membrane. Here, the direct contact with the permeate solution (16.5±0.2 °C) lowered the feed solution temperature which was set at 50.0±1.3 °C. Specifically, the feed concentration at the top portion of the reactor was maintained at 171.8±5.1 g/L in cycle 1 and 169.2±3.0 g/L in cycle 2. At these concentration ranges of Na_2SO_4, super-saturation was not reached at 16.5±0.2 °C (feed temperature at bottom portion). As such, salt precipitation followed by crystal deposition on the membrane surface was delayed up to around VCF 3.0 as shown in **Figure 8**. In both cycles 1 and 2, fouling on the membrane surface was not detected due to the lower concentration at the top portion. However, in cycle 1, the fouling phenomenon on the membrane surface was detected after VCF 3.0 (**Figure 9**). This was due to rapid increase of concentration (214.4 to 385.5 g/L) upon reaching VCF 3.0. Rapid flux decline occurred beyond this point (**Figure 8**).



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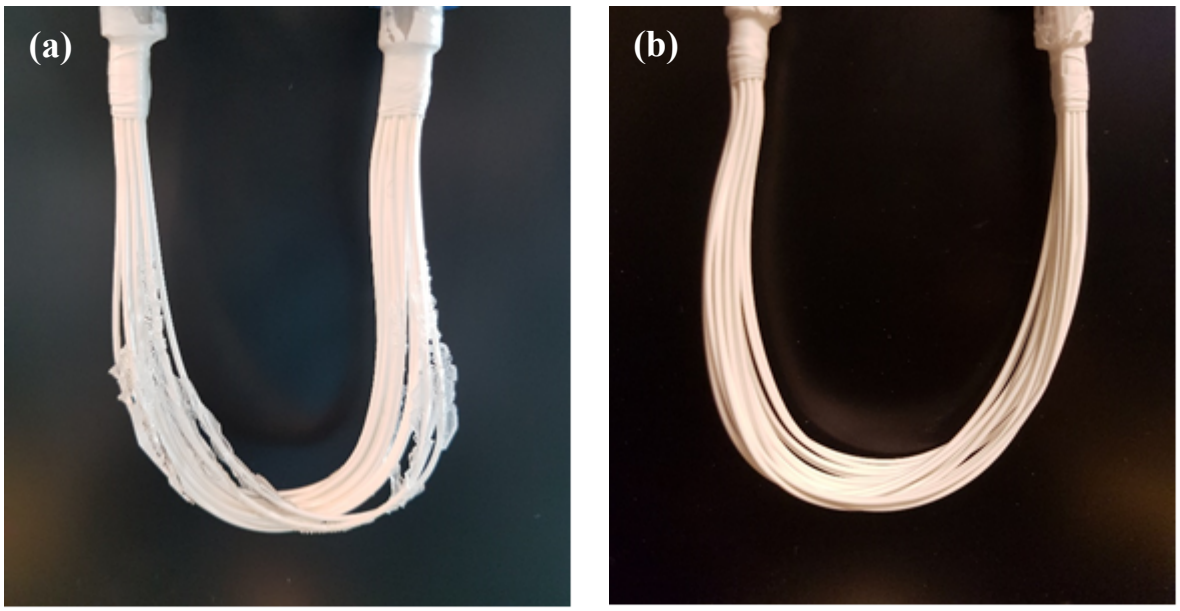
292 **Figure 8** Flux and concentration variation in continuous F-SMDC (without crystal extraction until the
293 completion of each cycle).



294 **Figure 9** Used membrane with Na_2SO_4 treatment at the end of (a) cycle 1, (b) cycle 2.

295

296 Initial crystal formation at the bottom portion of the reactor occurred at around VCF 2.2 in
297 both cycles. At VCF 2.8 and above, the bottom portion of the reactor was completely filled with
298 crystals. At this point, the feed concentration at the top portion of the reactor increased rapidly, and
299 CG in the F-SMDC feed reactor was no longer maintained. As such, it is essential to continuously

300 extract crystals generated at the bottom portion of the reactor to maintain a feed concentration
301 gradient in the F-SMDC process. For this reason, an external crystallizer was used in this study as
302 described in section 2.1.

303 At the end of each operation cycle, Na_2SO_4 solution remained at the top and middle portions
304 of the reactor. It must be highlighted that the F-SMDC was carried out in a batch mode. In the
305 scenario of a continuous mode operation, periodic crystal extraction from the bottom portion of the
306 reactor would be possible. This would enable continuous crystal growth simultaneously, while
307 achieving near zero liquid discharge in the reactor. However, in view of the batch mode operation of
308 this study, an external crystallization was used to evaluate the potential of further crystal growth with
309 the remaining Na_2SO_4 solution. This would enable to depict the near zero liquid discharge scenario
310 of a continuous mode. In depth evaluation of F-SMDC operation in a continuous mode will be
311 explored in future studies to establish this scenario.

312 Upon allowing the reactor to stand at room temperature (23.2±0.3 °C) for 3 days (72 h),
313 further salt crystallization occurred due to its super-saturated state (**Table 2**). This step enabled the
314 generation of additional crystals, thereby, increasing the total amount of crystals. Although the initial
315 concentrations in both cycles were different (because of different degree of concentrate: VCF 3.5 in
316 cycle 1 vs. VCF 3.0 in cycle 2), the final concentrations of both cycles were similar. However, the
317 solution volume reduction ratio varied (87% in cycle 1 vs. 47% in cycle 2) (**Table 2**). The simple
318 step of allowing the feed solution to remain at room temperature without additional treatment
319 enabled to decrease the feed concentration and volume by 32% and 46% respectively. Further, the
320 small quantity of remaining solution at the top and middle portions of the reactor can be channelled
321 back to the bulk feed tank for a subsequent F-SMDC operation cycle. This indicated that F-SMDC
322 with external crystallization does have the potential to achieve near zero liquid discharge.

Table 2 Volume and concentration of feed solution extracted from reactor upon F-SMDC and upon external crystallization (standing at room temperature for 24 - 72 h).

	1st cycle		2nd cycle	
Sample	Concentration (g/L)	Amount (mL)	Concentration (g/L)	Amount (mL)
Final F-SMDC feed (Before crystallization)	329.4±6.1	1140	218.1±2.3	1160
Upon external crystallization	160.4±0.2 (24 h) 149.9±2.3 (72 h)	150	160.4±0.7 (24 h) 147±0.3 (72 h)	620

4.3. Crystal production in F-SMDC

In F-SMDC, crystals were generated at the bottom portion of the reactor due to high concentration and lower temperature setting. In this study, the bottom portion of the reactor was cooled down up to 20.0±0.5 °C while the top portion of the reactor was maintained at 50.0±1.3 °C. At the bottom portion of the reactor, the combined condition of higher feed concentration and lower temperature enabled to achieve a faster super-saturation state of Na_2SO_4 compared to the top portion of the reactor. The CG and TG in the F-SMDC (lower concentration and higher temperature at top portion, higher concentration and lower temperature at bottom portion) improved the efficiency of recovering valuable crystals as well as obtaining higher water recovery and better stability (lower scaling) of MD process.

When 120 g/L Na_2SO_4 was treated without using crystals extraction, crystals were generated both at the top and bottom portions of the reactor. The amount of generated crystals formed was

directly proportional to the concentration ratio of feed solution (**Table 3**). High amount of crystals was generated both during cycle 1 (1169.0 g) and cycle 2 (898.0 g). In the case of cycle 1, F-SMDC operation was carried on beyond the point of rapid flux decline in order to obtain a highly concentrated final solution. The rapid permeate flux decline due to fouling and high feed concentration degraded the stability of the process. Therefore, it is not recommended to operate F-SMDC beyond the super-saturation state of the feed solution in the future study.

Table 3 Crystal and fresh water production by F-SMDC operation (feed: Na_2SO_4).

Sources	1st cycle		2nd cycle	
	Produced crystal (g)	Produced fresh water (mL)	Produced crystal (g)	Produced fresh water (mL)
Bottom portion of the reactor	551.3		541.6	
External crystallizer (containing saturated solution from top and middle portion of the reactor)	617.7	4295.5 (99% ion rejection)	356.4	3561.4 (99% ion rejection)
Total	1169.0		898.0	

The crystal production rate can be increased by factors such as temperature control, crystal size and immersion of crystals into saturated solution. As shown in **Table 2**, the volume and concentration of mother liquid decreased due to the formation of Na_2SO_4 crystals with time. For instance, the feed concentration of 160.4±0.2 g/L after 24 h was reduced to 149.9±2.3 g/L after 72 h. This indicated that additional crystals of larger sizes can be produced by the immersion of initial crystals into the mother liquid (**Figure 10(d)**). The morphology of Na_2SO_4 crystals changed from

rectangle shape to spherical shape over time (**Figure 10(a), (b)** and **(c)**). Prevalent growth and change in shape of crystals were detected on crystals that were fully immersed in the mother liquid. The results indicated that direct contact with mother liquid would enhance the growth of crystals. It is therefore essential to have enough contact area and immersion time with mother liquid. By doing so, a narrow size distribution of the crystals can be obtained.

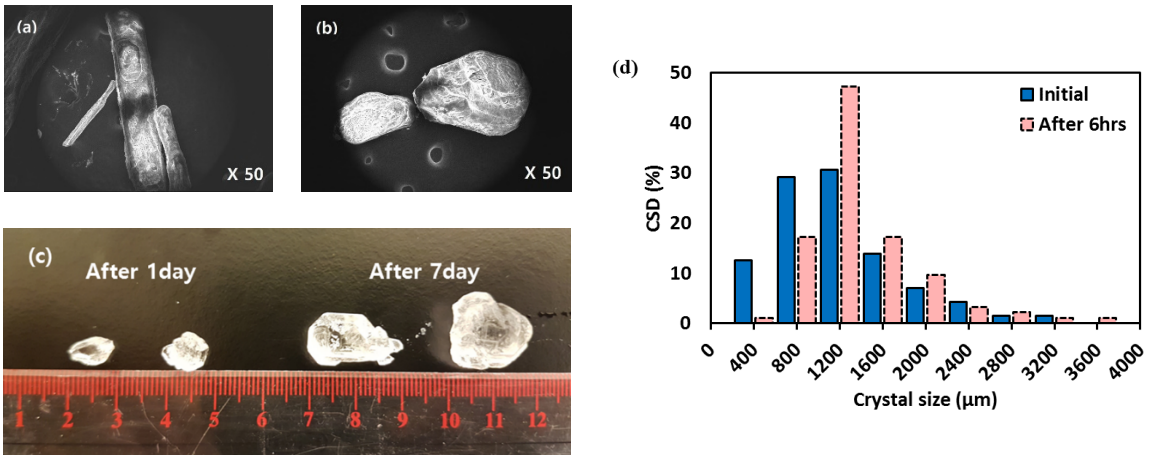


Figure 10 Crystal size distribution (CSD) and change in morphology of produced Na_2SO_4 crystals with time. Images of crystals at (a) initial, and after (b) 60min and (c) 1 day and 7 days, and (d) size distribution of Na_2SO_4.

4.4. Effect of salinity

The effect of salinity in the treatment of Na_2SO_4 solution was examined by adding NaCl. As shown in **Figure 11**, the concentration gradient trend at the initial stage (up to VCF 1.5) was similar with and without the presence of NaCl. In the presence of NaCl, the formation of crystals at the bottom portion of the reactor started from around VCF 1.8, while the concentration at the top portion of the reactor increased (with and without the presence of NaCl), lower VCF was achieved in the presence of NaCl. In the presence of NaCl, from VCF 2.2 onwards, visible presence of crystals was observed. At the same time, rapid flux decline and increase of feed concentration at the top portion

of the reactor occurred. This occurrence was associated to the presence of crystals on the membrane surface. The F-SMDC operation condition, namely concentrated feed solution and cooler membrane surface condition (direct contact with cold permeate) enabled the generation of CG. The crystal deposition on the membrane surface reduced the effective membrane area. This decreased the rate of concentration and degree of cooling by permeate, resulting in reduced crystallization of concentrated solution. Therefore, concentrated solution remained at the vicinity of the membrane boundary layer, and feed concentration at the top portion of the reactor portion increased by diffusion. This caused an increased crystal deposition onto the membrane surface (**Figure 11 (b)**).

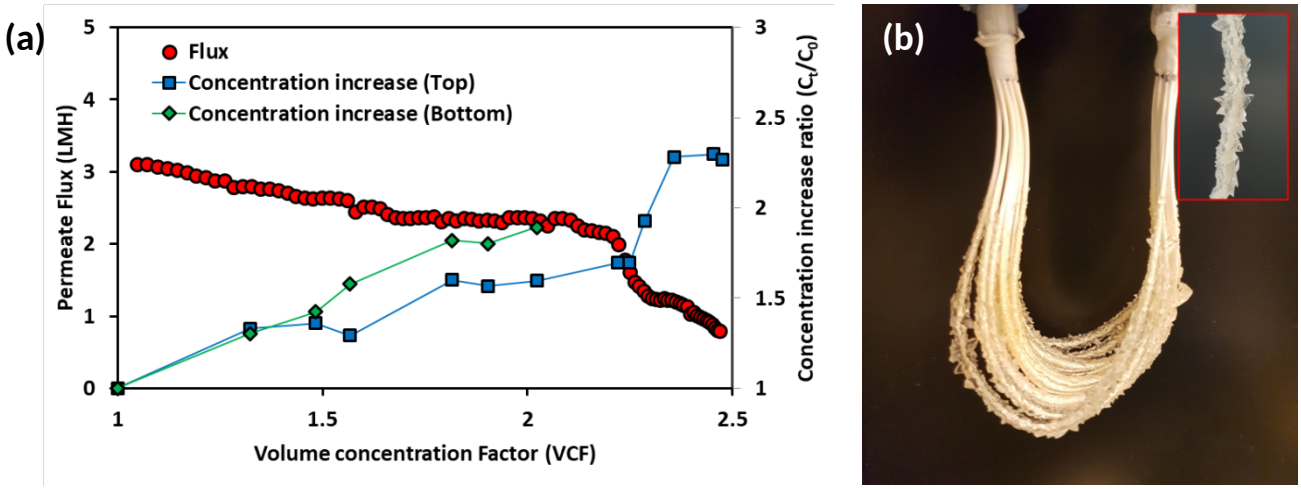


Figure 11 F-SMDC with Na_2SO_4 and NaCl: (a) variation of flux and concentration at the top and bottom portion of the reactor, (b) used membrane at the end of the experiment.

The EDX analysis revealed the presence of sodium, oxygen and sulphur elements on the used membrane surface and at the bottom portion of the reactor (**Figure 12(a)** and **(b)**). On the other hand, chloride ion was detected in crystals generated in feed solution of the top and middle portions of the reactor. The results indicated that a separate generation of crystal from solution can be achieved by a control of concentration and temperature at suitable range. In addition, the concentration of sodium ion in solution seems to influence crystallization phenomenon on the membrane surface and at the

bottom portion of the reactor. The crystallization on the membrane surface was detected at around VCF 3.3 in the absence of NaCl. The crystals formation on the membrane surface became faster (around VCF 2.2) with NaCl. At this point, the concentrations of sodium ion in both feed solutions with and without NaCl were similar (93.08 g/L without NaCl and 93.28 g/L with NaCl). Also, upon crystal formation at the bottom portion of the reactor, similar amount of sodium ion concentration was observed in both the feed solutions (without NaCl: 107.78 g/L in cycle 1 / 106.26 g/L in cycle 2, and with NaCl: 106.08 g/L). The difference in the initial point of crystallization on the membrane surface and at the bottom of the reactor was attributed to temperature difference.

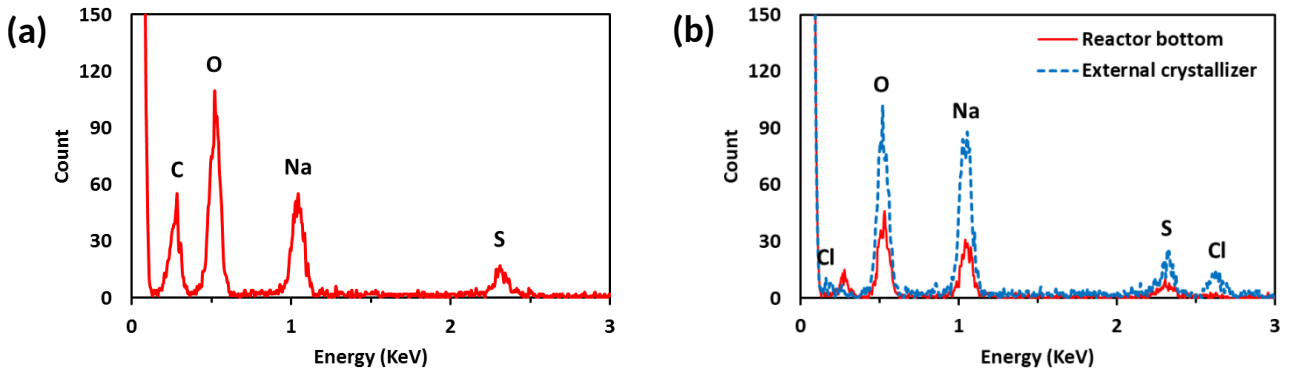


Figure 12 EDX analysis of crystals (a) deposited on the used membrane surface, (b) produced from the bottom portion of the reactor and external crystallizer (saturated feed solution from the top and middle portion of the reactor) (feed solution: Na2SO4 and NaCl).

5. Conclusions

The feasibility of fractional submerged membrane distillation-crystallization (F-SMDC) process was evaluated using a feed solution containing high concentration of Na_2SO_4 without and with NaCl. The following conclusions were made from the experimental investigation:

- F-SMDC setting enabled the creation of CG and TG using a partition and double wall heating/cooling in the feed reactor. A lower feed concentration and higher feed temperature was maintained at the top portion of the reactor. Meanwhile, higher feed concentration and lower feed temperature was maintained at the bottom portion of the reactor.
- The presence of CG/TG in F-SMDC enabled to achieve higher water recovery (VCF 3.5) and lower membrane scaling, compared to SMDC mode (VCF 2.9).
- The condition of elevated feed concentration and lower temperature at the bottom portion of the reactor was favourable for high crystal formation in F-SMDC.
- The presence of salt (NaCl) influenced the crystallization of Na_2SO_4 at the bottom portion of the reactor and on the membrane surface, resulting in higher crystallization in both locations.
- F-SMDC was effective in reducing membrane scaling, producing high quality fresh water and valuable crystals (Na_2SO_4).
- The shape and dimension of F-SMDC reactor are essential factors that influence the formation of CG/TG and the overall F-SMCD performance. Further optimization of the reactor configuration is an important factor that must be explored in detail.

Acknowledgement

This work was funded by Australian Research Council Discovery Research Grant (DP150101377) and two Basic Science Research Programs through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2017R1A6A3A04004335) and the Ministry of Science, ICT, & Future Planning (2017R1A2B3009675).

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Highlights

• Fractional-submerged MDC (F-SMDC) showed promising potential for brine treatment.

• Concentration/temperature gradients (CG/TG) in F-SMDC reactor was beneficial.

• High TG/low CG at reactor top enabled to reduce the scaling on MD membrane.

• Low TG/high CG at reactor bottom was favourable for sodium sulphate crystallization.

• Stable CG/TG in F-SMDC required periodic crystal extraction from the reactor.

Fractional-submerged membrane distillation crystallizer (F-SMDC) for treatment of high salinity solution

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Abstract

Membrane distillation with crystallization (MDC) is an attractive process for high saline seawater reverse osmosis (SWRO) brine treatment. MDC produces additional fresh water while simultaneously recovering valuable resources. This study developed a novel approach of fractional-submerged MDC (F-SMDC) process, in which MD and crystallizer are integrated in a feed tank with a submerged membrane. F-SMDC principle is based on the presence of temperature/concentration gradient (TG/CG) in the feed reactor. The operational conditions at the top portion of the feed reactor (higher temperature and lower feed concentration) was well suited for MD operation, while the bottom portion of the reactor (lower temperature and higher concentration) was favourable for crystal growth. F-SMDC performance with direct contact MD to treat brine and produce sodium sulfate (Na_2SO_4) crystals using TG/CG showed positive results. The TG/CG approach in F-SMDC enabled to achieve higher water recovery for brine treatment with a volume concentration factor

(VCF) of over 3.5 compared to VCF of 2.9 with a conventional S-MDC set-up. Further, the high feed concentration and low temperature at the reactor bottom in F-SMDC enabled the formation of Na_2SO_4 crystals with narrow crystal size distribution.

Keywords: Concentration and temperature gradients; Membrane distillation with fractional crystallization; Resource recovery; Seawater reverse osmosis brine; Sodium sulfate crystal

1. Introduction

Reverse osmosis (RO) based seawater desalination (i.e. SWRO) technology has been widely used to solve global water crisis of fresh water shortage owing to its affordable operation cost and reliability [1-3]. However, one of the major limitations of SWRO is its low recovery (30~50%), resulting in the production of a substantially large amount of concentrated brine that has to be managed [4-6]. The SWRO brine management incurs an additional operating cost to the plant as well as environmental issues when SWRO brine is discharged directly into the environment [7]. SWRO brine contains a variety of chemicals (coagulant, chemical washing agent, and pH adjusting agent) which are employed during SWRO process, Also, SWRO brine contains a high concentration of organic and inorganic matters [8-11]. In recent times, simultaneous brine treatment with extraction/production of valuable resources is favoured to offset the treatment cost rather than the approach of treatment followed by disposal. The formed is also preferred as give than seawater and likewise seawater brine contains a number valuable elements [12, 13].

In this regard, membrane distillation with crystallizer (MDC) shows promising potential in SWRO brine treatment [14-18]. MDC is an integrated process that can achieve high quality fresh water while simultaneously extracting valuable resources from high salinity solution [14]. MDC is attractive compared to traditional crystallization processes because of the following factors: well-controlled saturation rate, faster nucleation rate and reduction of induction time [19]. Moreover, the ability to concentrate solution up to a saturation point with minimal flux decline is an added advantage of MDC [20-22]. Cooling crystallization method is widely used in separation processes for solution having different solubility at different temperatures due to its ease of control and maintenance [23]. However, one of the major limitations is the significant energy consumption due to initial heating (thermal MD operation) followed by cooling for the crystallization.

A number of methods such as submerged MD (SMD) have been evaluated in terms of energy consumption and economic benefits to improve the efficiency of conventional MDC process [3, 24, 25]. For instance, in SMD process, channelling heated feed solution through a pump to the membrane module can be eliminated, which results in lower heat losses through the feed channel [14, 26]. In this case, the feed tank can also act as a crystallizer, achieving an integrated system [3]. Nevertheless, several limitations are still present such as challenging saturated feed concentration effect, and fouling caused by crystal formation in the feed tank as well as on the membrane [27-29]. Previous studies have shown that at elevated feed concentration levels [3], MD performance is affected by flux decline and wetting phenomenon. This decreases the membrane life span, resulting in more frequent membrane replacement, incurring addition operation cost [30].

In view of this, fractional submerged MDC (F-SMDC) based on principle of maintaining a feed concentration gradient (CG) and feed temperature gradient (TG) in the reactor was evaluated in this study. Maintaining CG and TG in the feed reactor can positively influence both MD and crystallization. CG and TG in the reactor enables to reduce feed concentration and increase feed temperature at the top portion of the reactor where the submerged membrane is located. Simultaneously, the bottom portion of the reactor maintains high feed concentration with low feed temperature which enhances crystallization at the bottom portion of the reactor. This is due to the formation of high saturation state at the bottom portion of the reactor where crystals form continuously during F-SMDC operation. This setting potentially promises higher water recovery, with reduced membrane scaling issues. Further, the continuous extraction of crystal from the bottom of the reactor is expected to reduce the salt contents in feed solution [14].

In this study, the feasibility of F-SMDC for the treatment of highly concentrated and saline feed solution was investigated and compared with conventional submerged membrane distillation crystallization (SMDC). The trend of CG/TG in the feed reactor was examined during the operation.

The effect on the flux and crystallization efficiency in the F-SMDC was evaluated. In addition, methods to improve the efficiency of maintaining CG/TG in the feed reactor were investigated.

2. Materials and Methods

2.1 Lab-scale setup

F-SMDC process with direct contact MD (DCMD) configuration based on GC and TG was used in this study (**Figure 1**). The F-SMDC reactor consisted of three cylindrical cells with a height of 150 mm and an inner diameter of 70 mm (volume of the single cell = 580 mL, and total volume of the reactor = 1,740 mL). The reactor is equipped with double wall to enable the control of TG as temperature control of feed solution is essential in the reactor (**Figure 2**). The partition in the shape of funnel (length = 25 mm, and hole diameter = 20 mm) was installed between the top and bottom portion. This partition acts as a barrier that minimized the mixing of solution by natural convection caused by heating or cooling. Feed solution was placed inside of the reactor while heating and cooling water was circulated at the outer wall of the reactor with respective heating and cooling units. This enabled the feed solution at the top portion of the reactor to be maintained at 50.0±1.3 °C, while, the feed solution at the bottom portion of the reactor was maintained at 20.0±1.5 °C. Thermometer was placed in each cell to measure the temperature of feed solution in real-time.

Meanwhile, the permeate temperature (T_p) was maintained at 16.5±0.2 °C, and was measured using temperature sensors placed at the permeate channel. The permeate flow rate of 0.5 L/min was controlled using a gear-pump. Feed solution was fed continuously into the top portion of the reactor by the differential head of water between the reactor and feed tank. Continuous flow of new feed solution to the top portion of reactor enables to maintain a constant feed solution concentration rather than an increasing feed concentration. This systematically minimizes the effect of increased feed

concentration on MD performance. The temperature of feed solution in the feed tank (reservoir) was maintained at room temperature (23.2±0.3 °C).

An external crystallizer was used in the last stage of the F-SMDC operation. Upon attaining super-saturation state at the bottom portion of the reactor, the remaining feed solution (mother liquid) was fed to this external reactor. The external reactor was kept at room temperature (23.2±0.3 °C) with constant stirring (50 rpm) of the mother liquid to enhance crystal growth.

The permeate flux was calculated from on the solution mass difference with time using an electronic balance. The permeate/fresh water quality was evaluated by measuring the conductivity/total dissolved solids (TDS) value in real-time. All the experiments were duplicated to ensure the reproducibility.

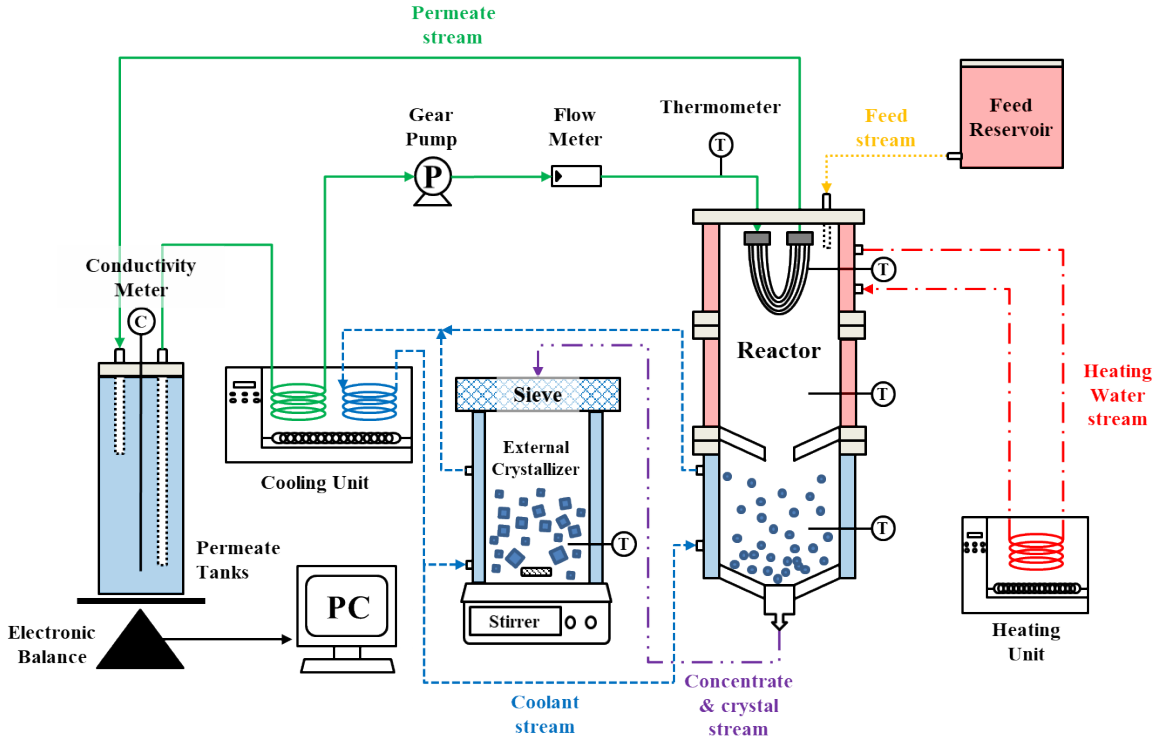

Figure 1 Set-up of F-SMDC process: permeate stream (——), stream of continuous feeding to the reactor (feed solution) (·····), stream of concentrate and crystal generated from the reactor to the crystal

112 growth cell (–···–), the stream of heating water for the top portion of the reactor (–·–), stream of coolant water
113 for the bottom portion of the reactor and the crystal growth cell (–––).

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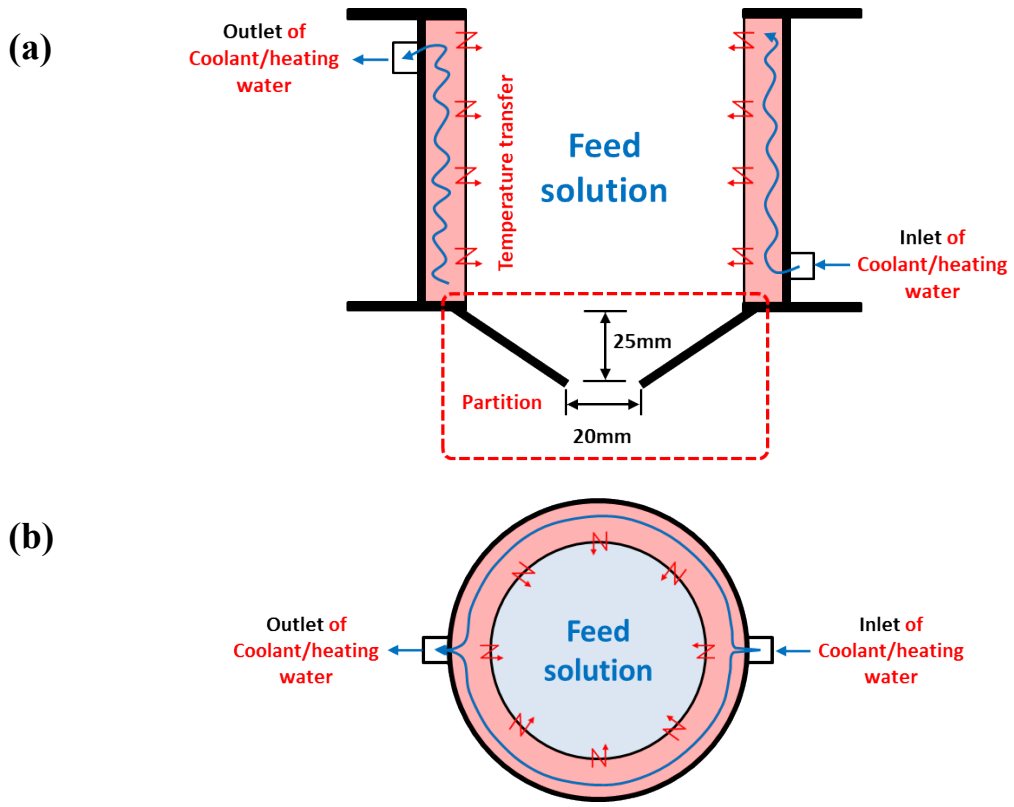


115 **Figure 2** Details of F-SMDC reactor showing the double wall feature for generating FT gradient
116 (heating in the top portion of the reactor and cooling at the bottom portion of the reactor): (a) Cross-sectional
117 view, and (b) Aerial view.

118

119 **2.2 Feed solution**

120 The performance of F-SMDC process was investigated using 120 g/L Na_2SO_4 solution as
121 feed solution. The solubility of Na_2SO_4 in water varies significantly at different temperature (91 g/L
122 @ 10 °C, 195 g/L @ 20 °C, and 488 g/L @ 40 °C). A mixed solution containing sodium chloride

123 (NaCl) and Na_2SO_4 was then used to examine an effect of salinity on treatment of high concentration
124 Na_2SO_4 solution (
125 **Table** 1). Both feed solutions were prepared using reagent grade salts (Sigma-Aldrich).
126

127 **Table 1** Composition of model solution.

Ions	Concentration (mg/L)
Sodium (Na^+)	58,320
Sulfate (SO_4^{2-})	81,150
Chloride (Cl^-)	30,020

128

129 **2.3 Membrane**

130 A hollow-fiber polyvinylidene fluoride (PVDF) membrane (Econity, Republic of Korea)
131 module was used. The membrane has a nominal pore size of 0.1 μm with an outer and inner diameter
132 of 1.2 mm and 0.7 mm (membrane wall thickness: 250mm), liquid entry pressure (LEP) of 2.0-2.3
133 bar, and contact angle of 106±2° (based on the specifications provided by the manufacturer). A
134 membrane module with an effective membrane area of 0.0136 m^2 was used. The membrane module
135 consisted of 18 fibers, each of 0.2 m in length, which were potted on both ends of membrane fiber.
136

137 **2.4 Analysis**

138 Crystal morphology was characterized by a field emission scanning electron microscopy
139 (FESEM, Zeiss supra 55VP, Carl Zeiss AG). The TDS and conductivity of the permeate were
140 measured with a portable water quality meter (HQ40d multi, Hach). The concentrated feed solution
141 was measured using calibrated conductivity curves made using different concentration of Na_2SO_4

(15, 30, 60, 180 and 300 g/L Na_2SO_4). The concentrated solution was vacuum filtered using a glass microfiber filter (Whatman, Grade GF/C, pore = 1.2 μm) enabling the crystals in the solution to be retained on the filter. The crystals were dried at room temperature (23.2±0.3 °C) for 120 h and the dry weight of crystals was measured using an electronic balance. The crystal form and sizes were evaluated using a microscopy method. In this method, at least 72 crystals were selected randomly, and each crystal was measured using microscope with an image analyser (ImagePro7). The crystal sizes were then quantified with a crystal size distribution (CSD) procedure.

Volume concentration factor (VCF) used in this study was based on the reactor volume and the amount of produced fresh water. The total volume of feed solution in F-SMDC reactor was maintained at a fixed volume (1,740 mL) with continuous feeding of feed solution at the same rate of produced fresh water. If the rejection ratio of produced fresh water is 100% over time, the feed solution concentration in the rector would increase while the total volume of feed solution was maintained. In this context, the VCF value was calculated as:

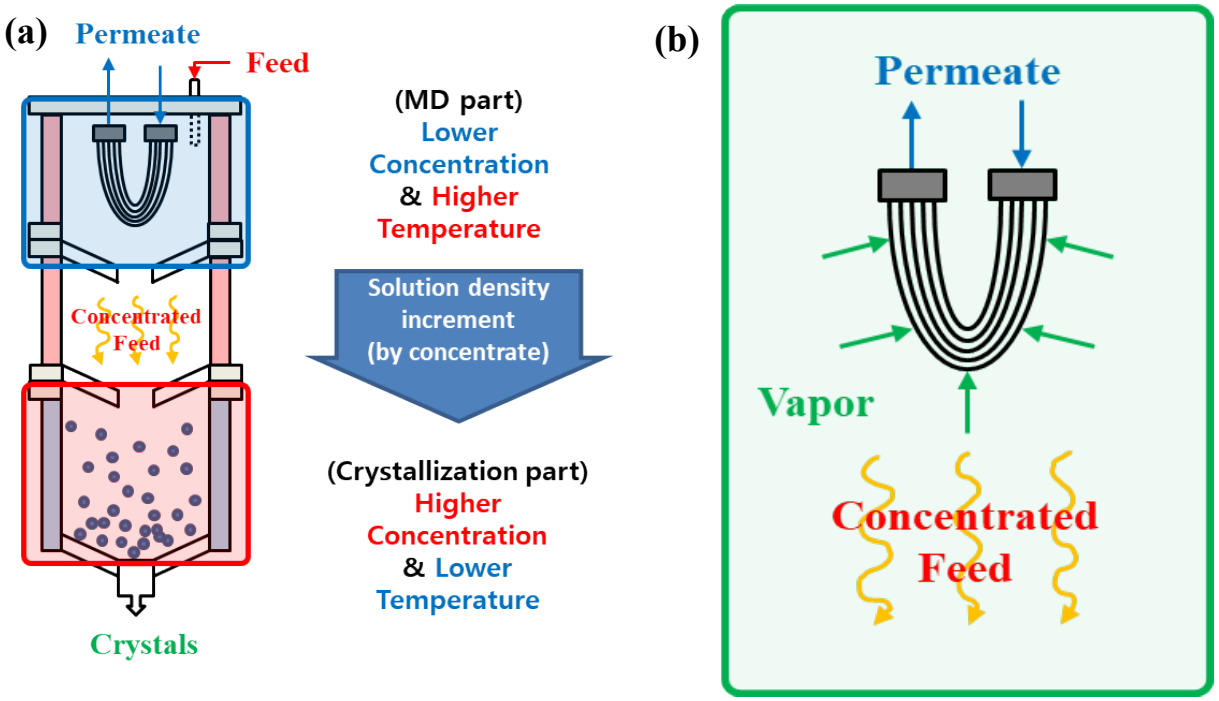
$$\mathrm{VCF} = \frac{V_{reactor} + V_{total,\ permeate}}{V_{reactor}}$$

where $V_{reactor}$ is the reactor volume, and $V_{total,permeate}$ is the total amount of permeate produced.

3. F-SMDC principle

F-SMDC is a combination of two processes: MD and crystallization in a single feed reactor with a submerged membrane (**Figure 3(a)**). The submerged membrane module is placed at the top portion of the feed reactor. In F-SMDC, a CG is generated in the feed reactor as a result of difference in solution density. Upon the increase of feed solution concentration (MD part), the density of the feed solution increases, resulting in the gravitation of concentrated feed solution to the bottom of the reactor (**Figure 3(b)**). In S-DCMD, cooling down of feed solution by the cold permeate stream

164 further enhances this factor as water density is higher at low temperature. Accordingly, CG is
165 generated in the reactor. Simultaneously, TG is generated by external heating and cooling of the
166 outer wall (**Figure 2**).



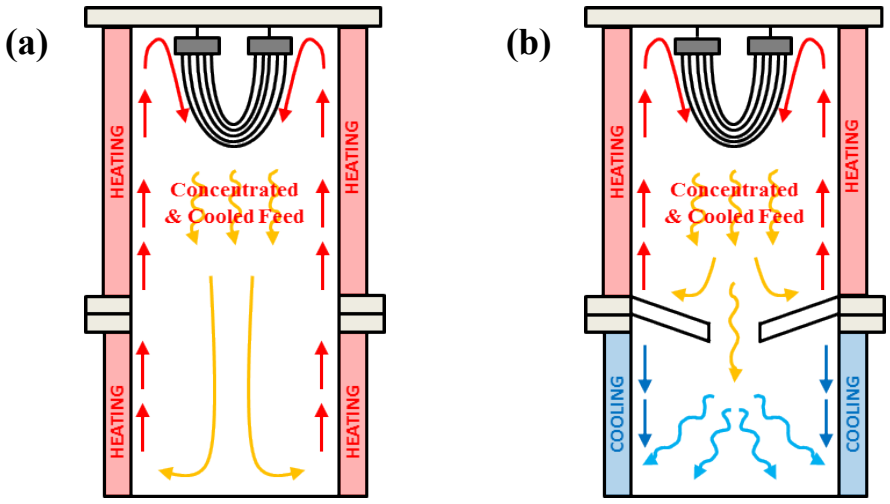
167 **Figure 3** Generation of concentration gradient (CG) in feed reactor of F-SMDC: (a) lower feed
168 concentration at the top portion and higher feed concentration at the bottom portion, and (b) concentration
169 effect at the top portion of the reactor containing submerged membrane.

170

171 The presence of CG in the feed reactor influences both MD and crystallization efficiency of
172 the F-SMDC process. In MD, dissolved ion concentration in the feed solution is increased as the feed
173 solution in concentrated, resulting in decrease of permeate flux. However, in crystallization process,
174 elevated dissolved ion contents are favourable for attaining saturation degree of targeted compounds.
175 Lower concentration at the top portion of the reactor is suitable for MD operation. Higher
176 concentration at the bottom portion of the reactor is favourable for the formation of crystals since
177 super-saturation (above the limits of metastable zone) of target salt should be reached to get a

178 nucleation of crystals. F-SMDC achieves an increase of feed concentration at the bottom portion of
179 the reactor at a faster ratio compared with theoretical concentration ratio in the whole reactor, and
180 crystals are formed when solution concentration exceeds the limits of metastable zone of solution.
181 Moreover, TG is formed in the reactor by the temperature transfer caused by movement of
182 concentrated feed solution to the bottom portion without additional temperature control (using
183 heating or cooling). Temperature at the top portion is higher than the bottom portion. The
184 maintenance of TG in F-SMDC enhances the crystallization phenomenon.

185 Convection current in the reactor occurs differently (**Figure 4(a)).** If feed solution is heated
186 up near the reactor wall, its density decreases with its expansion. As a result, it moves towards the
187 upper portion, and the unheated feed solution moves downwards. Moreover, concentrated and cooled
188 (because of the effect of lower permeate temperature (around 16.5±0.2 °C) of S-DCMD) feed
189 solution by membrane operation favours the above effect. As a result, feed solution is mixed, and
190 therefore CG cannot be maintained in the feed reactor. Even though convection current effect on
191 solution mixing does not significantly affect CG, it should still be controlled to ensure that CG is
192 well controlled/maintained throughout the operation. In our design of F-SMDC, the incorporation of
193 a partition in the feed reactor enables to maintain convention current effect within the respective cells
194 (top and bottom portion of the reactor) (**Figure 4(b)**). The partition prevented the feed solution
195 mixing by convection current, resulting in maintaining CG and TG in the reactor.



196 **Figure 4** Convection current in reactor by heating and cooling of (a) conventional MDC process
197 (reactor without cooling and partition) and (b) F-SMDC process (reactor with cooling and partition).

199 **4. Results and discussions**

200 In this study, the feasibility of F-SMDC was examined for the treatment of feed solution
201 containing Na_2SO_4 alone and with NaCl.

202 **4.1. Performance comparison of F-SMDC and SMDC**

203 The performance of conventional submerged MDC (SMDC) (reactor without cooling and
204 partitioning) was compared with F-SMDC (reactor with cooling and partitioning) under the same
205 operating conditions (reactor, feed temperature and feed solution) and same sampling points at the
206 top and bottom portion of the reactor. The initial flux of both SMDC and F-SMDC mode was 2.8 and
207 2.7 LMH respectively. The initial flux of S-MDC was slightly higher than F-SMDC, while the feed
208 solution concentration trend varied. Up to a feed solution VCF 2.5, a similar concentration variation
209 was observed for both SMDC and F-SMDC mode. However, in SMDC, above VCF 2.5, a rapid
210 increase of concentration from VCF 2.5 to 2.8 accompanied by a rapid flux decline was observed
211 (**Figures 5** and **6).** Both processes maintained 99% ion rejection ratio until the end of the experiment.
212 Comparatively, F-SMDC was able to maintain a stable concentrate (without rapid increase) up to
213 VCF 3.0 and sustained the operation up to VCF 3.5. The results indicated that in F-SMDC, the
214 partition between the top and the bottom portion of the reactor prevented the mixing of feed solution
215 by natural convection current, emulating a trap. This enabled to create a CG in the reactor, with a
216 higher concentration at the bottom portion of the reactor. In F-SMDC, the presence of CG in the feed
217 reactor was beneficial for both the MD and crystallization processes. Maintaining a low feed
218 concentration closer to the membrane in F-SMDC enabled to achieve a higher VCF (around VCF
219 3.5) with smaller flux decline compared to the SMDC (around VCF 2.8). In SMDC, concentrated
220 feed solution interferes with the transportation of vapour through the hydrophobic membrane,
221 decreasing its performance (reduced flux decline).

In F-SMDC, the presence of CG in the feed reactor was well reflected by the CG variation between the top and bottom portion of the reactor (

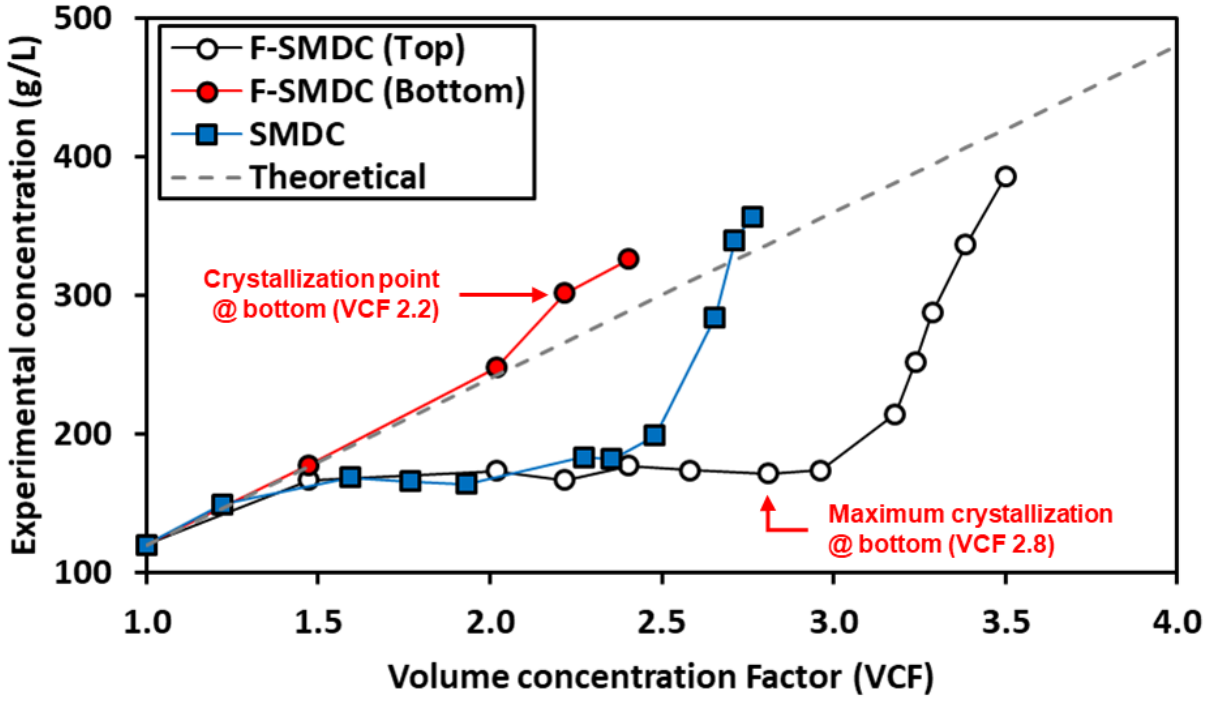


Figure 5). The CG effect was especially apparent from VCF 1.5 onwards. The feed concentration at the top portion (MD part) of the reactor did not change rapidly while a rapid increase of feed concentration at the bottom portion of the reactor was observed. At the top portion, the feed solution concentration was maintained (range: 171.8±5.1 g/L, 1.4 times of initial feed concentration) below the theoretical feed concentration increment (initial feed concentration × VCF). Above VCF 2.0, feed concentration at the bottom portion of the reactor showed higher increment than the theoretical feed concentration level. Over time, the feed concentration at the bottom portion of the reactor greatly varied to the theoretical feed concentration. The results reflected the capacity of F-SMDC to maintain a stable CG in the feed reactor.

In the F-SMDC mode, higher feed concentration at the bottom portion of the reactor than the top portion made it suitable for the formation of target crystals. Also, lower temperature (around 20.0 ±1.5 °C) at the bottom portion of the reactor, which was generated by the cooling as well as the movement of concentrated/cooled feed solution from the top portion (heated up) was favourable for the stimulation of crystals.

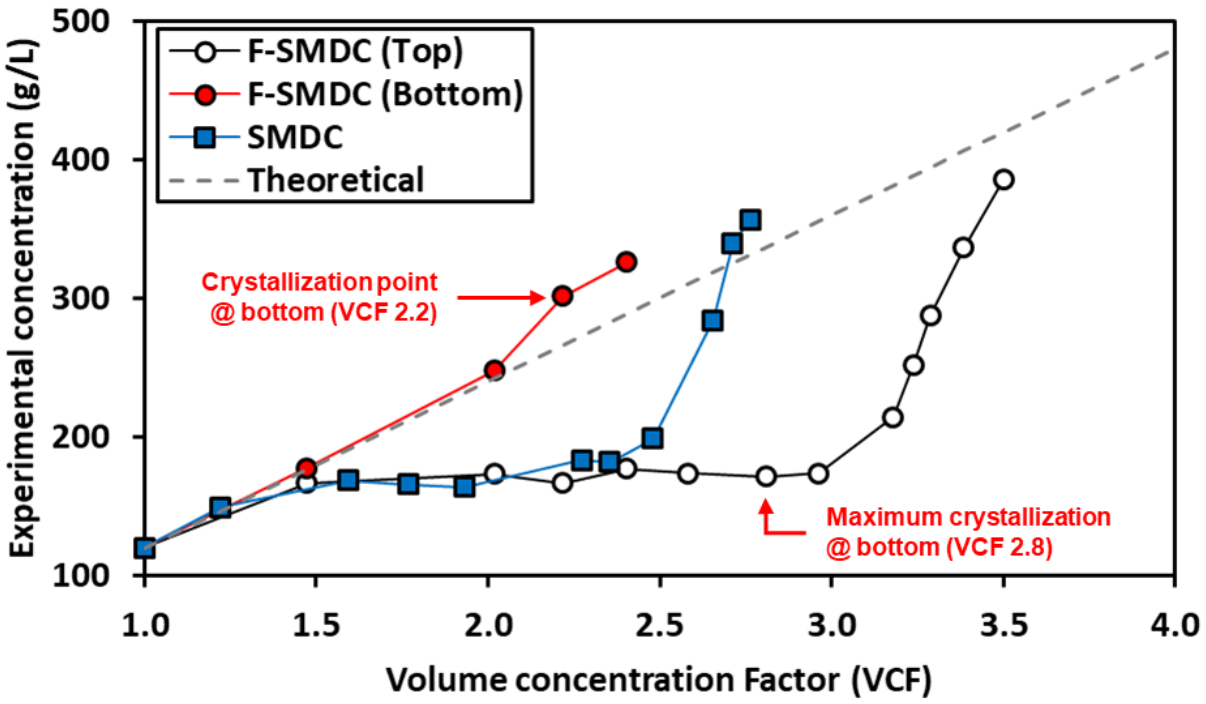
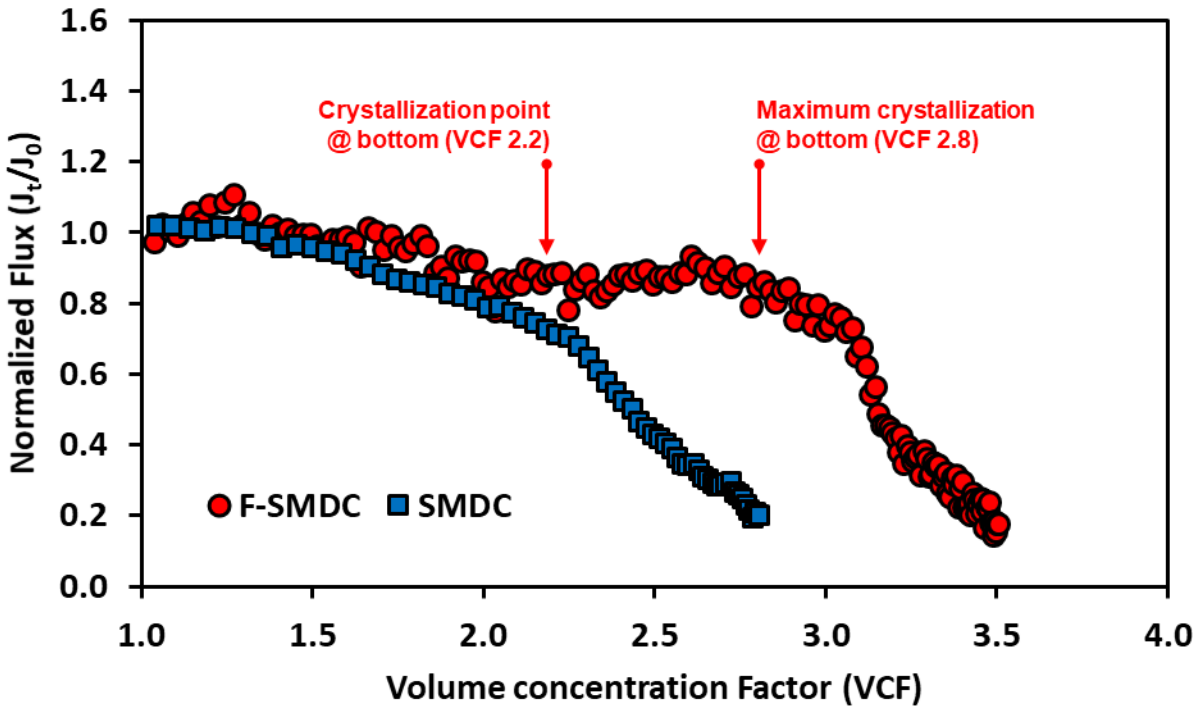


Figure 5 Variation of feed concentration in the reactor during the operation in F-SMDC and SMDC modes (feed: Na_2SO_4).



242

243 **Figure 6** Comparison of flux in F-SMDC and SMDC mode (without crystal extraction).

244

245 The F-SMDC was carried out using S-DCMD configuration. The feasibility of different
246 submerged MD configurations (submerged vacuum direct contact MD called as S-VDCMD) in F-
247 SMDC process was examined under the same operational condition. The motivation for using S-
248 VDCMD is the potential of achieving higher permeate flux. In line with this, S-VDCMD achieved a
249 25% higher initial permeate flux than S-DCMD. However, the CG in F-SMDC with S-VDCMD
250 configuration was not observed. Higher flux decline was also observed with S-VDCMD compared to
251 F-SMDC with S-DCMD configuration (**Figure 7**) with slightly lower feed concentration at the
252 bottom portion than at the top portion of the reactor. This was attributed to the application of
253 vacuum. In a previous S-MD study [3], it was found that the deposition and adhesion of crystals on
254 the membrane surface was intensified by the presence of vacuum pressure in the MD, resulting in
255 more prevalent fouling. In S-VDCMD, concentrated ions were captured in the membrane boundary

layer due to stronger driving force (vacuum pressure) compared to S-DCMD [3]. This restricted the movement of concentrated feed solution, and it stagnated close to the membrane surface. The increase in diffusion potential of concentrated feed solution at the top portion rather than the precipitation downward, resulted in the formation of higher concentration at the top portion than the bottom portion of the reactor. The results highlighted that S-MD using vacuum was not suitable for F-SMDC process.

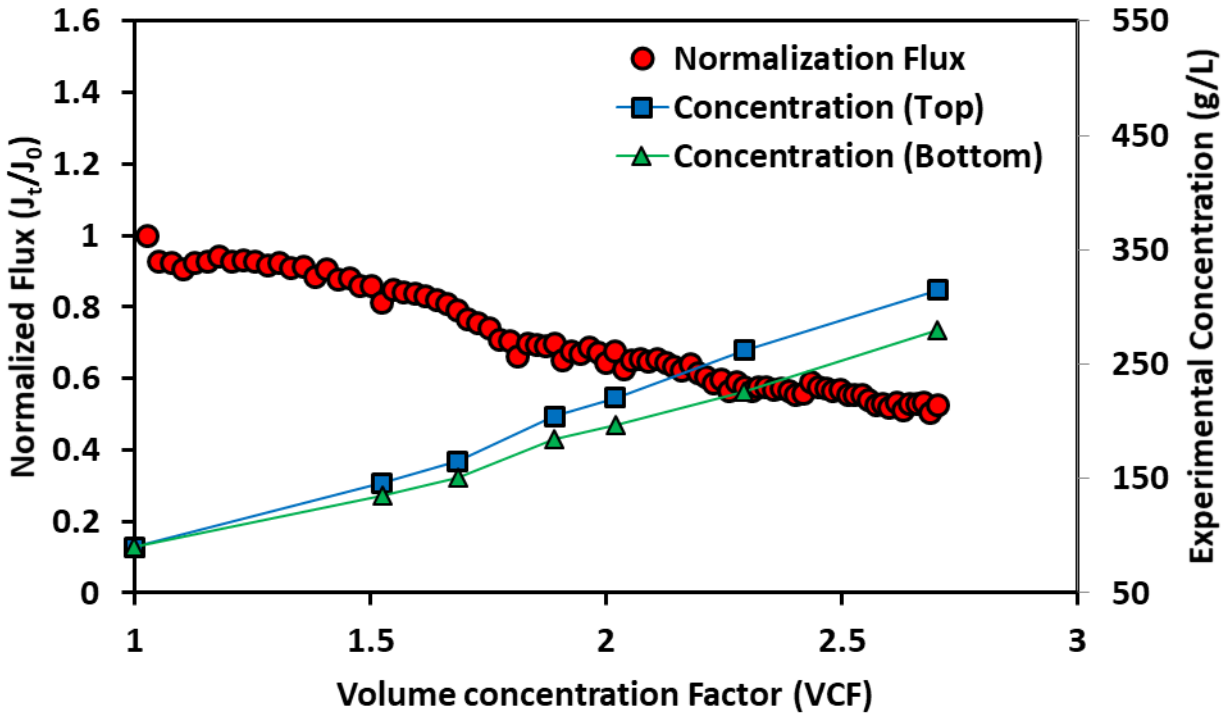


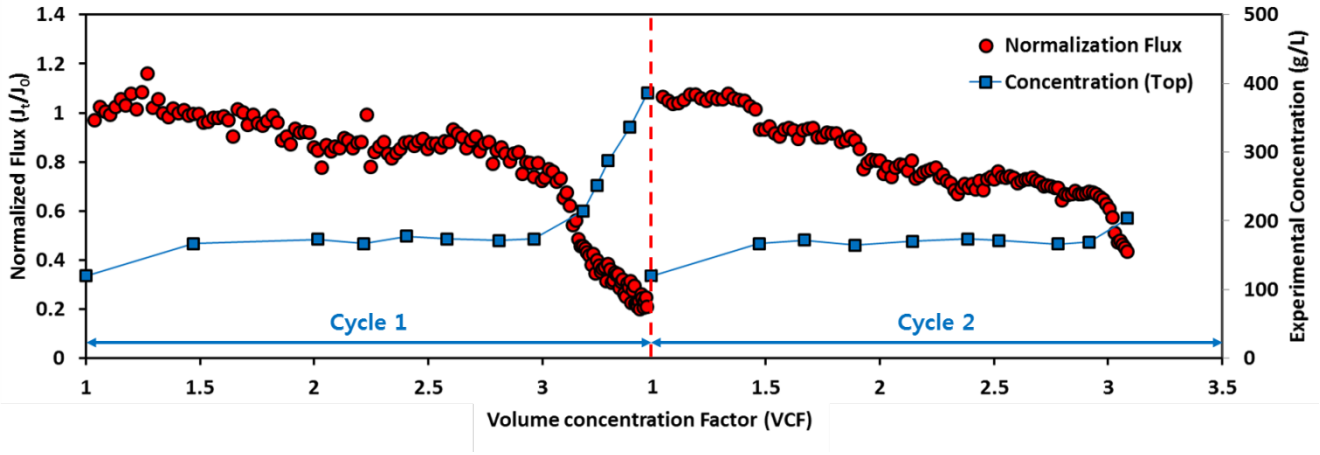
Figure 7 Normalized flux and concentration tendency in F-SMDC comparing with S-VDCMD.

4.2. Continuous F-SMDC operation

The stability of F-SMDC in treating high concentration solution was examined by carrying out two repeated cycles of operation using the same membrane. At the end of each cycle, used membrane was submerged in DI water and stirred at 200 rpm for 10 mins to rinse/clean the membrane before the subsequent operation.

In S-DCMD configuration, generally, the membrane surface feed temperature is lower compared to bulk feed temperature due to direct contact with cold permeate on the membrane surface. This factor plays a prevalent role in the solubility of certain crystal salts that are especially influenced by the effect of temperature. One such salt is Na_2SO_4, which exhibits lower solubility at low temperature (91 g/L @ 10 °C, and 195 g/L @ 20 °C) and higher solubility at increased temperature (488 g/L @ 40 °C). This characteristic of Na_2SO_4 can lead to higher saturation state on the membrane surface, and aggravate the formation of crystals. This results in the non-continuity of MDC process.

The effect of this phenomenon can be mitigated in F-SMDC by creating and maintaining CG in the reactor. The feed concentration (under 195 g/L) was lower at the top portion of the reactor which contains the submerged membrane. Here, the direct contact with the permeate solution (16.5±0.2 °C) lowered the feed solution temperature which was set at 50.0±1.3 °C. Specifically, the feed concentration at the top portion of the reactor was maintained at 171.8±5.1 g/L in cycle 1 and 169.2±3.0 g/L in cycle 2. At these concentration ranges of Na_2SO_4, super-saturation was not reached at 16.5±0.2 °C (feed temperature at bottom portion). As such, salt precipitation followed by crystal deposition on the membrane surface was delayed up to around VCF 3.0 as shown in **Figure 8**. In both cycles 1 and 2, fouling on the membrane surface was not detected due to the lower concentration at the top portion. However, in cycle 1, the fouling phenomenon on the membrane surface was detected after VCF 3.0 (**Figure 9**). This was due to rapid increase of concentration (214.4 to 385.5 g/L) upon reaching VCF 3.0. Rapid flux decline occurred beyond this point (**Figure 8**).



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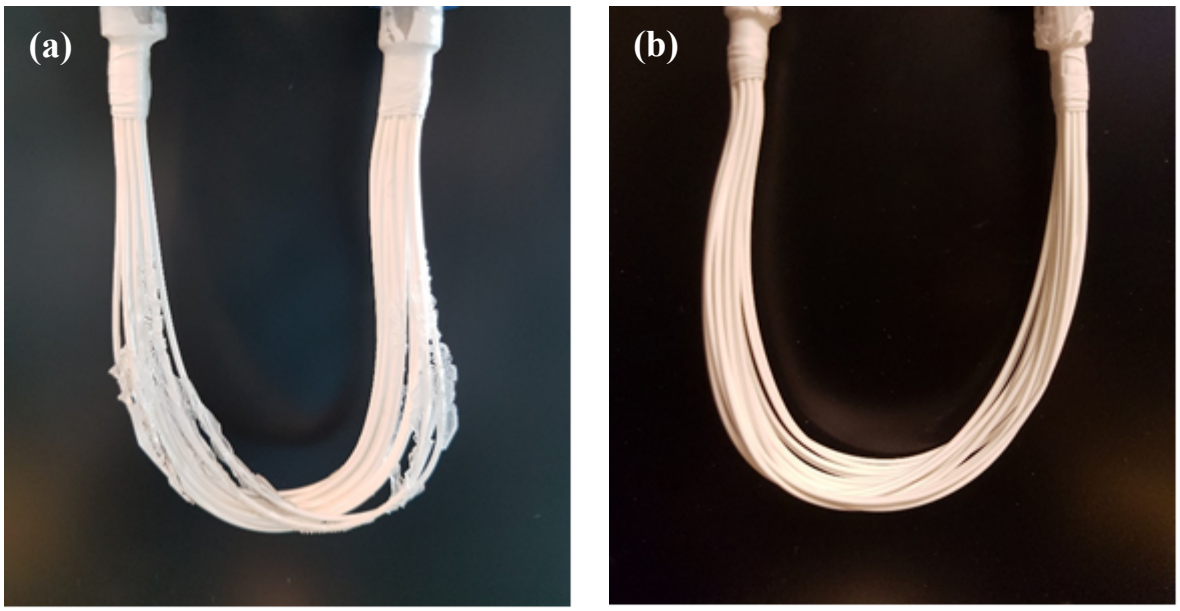
292 **Figure 8** Flux and concentration variation in continuous F-SMDC (without crystal extraction until the
293 completion of each cycle).



294 **Figure 9** Used membrane with Na_2SO_4 treatment at the end of (a) cycle 1, (b) cycle 2.

295

296 Initial crystal formation at the bottom portion of the reactor occurred at around VCF 2.2 in
297 both cycles. At VCF 2.8 and above, the bottom portion of the reactor was completely filled with
298 crystals. At this point, the feed concentration at the top portion of the reactor increased rapidly, and
299 CG in the F-SMDC feed reactor was no longer maintained. As such, it is essential to continuously

300 extract crystals generated at the bottom portion of the reactor to maintain a feed concentration
301 gradient in the F-SMDC process. For this reason, an external crystallizer was used in this study as
302 described in section 2.1.

303 At the end of each operation cycle, Na_2SO_4 solution remained at the top and middle portions
304 of the reactor. It must be highlighted that the F-SMDC was carried out in a batch mode. In the
305 scenario of a continuous mode operation, periodic crystal extraction from the bottom portion of the
306 reactor would be possible. This would enable continuous crystal growth simultaneously, while
307 achieving near zero liquid discharge in the reactor. However, in view of the batch mode operation of
308 this study, an external crystallization was used to evaluate the potential of further crystal growth with
309 the remaining Na_2SO_4 solution. This would enable to depict the near zero liquid discharge scenario
310 of a continuous mode. In depth evaluation of F-SMDC operation in a continuous mode will be
311 explored in future studies to establish this scenario.

312 Upon allowing the reactor to stand at room temperature (23.2±0.3 °C) for 3 days (72 h),
313 further salt crystallization occurred due to its super-saturated state (**Table 2**). This step enabled the
314 generation of additional crystals, thereby, increasing the total amount of crystals. Although the initial
315 concentrations in both cycles were different (because of different degree of concentrate: VCF 3.5 in
316 cycle 1 vs. VCF 3.0 in cycle 2), the final concentrations of both cycles were similar. However, the
317 solution volume reduction ratio varied (87% in cycle 1 vs. 47% in cycle 2) (**Table 2**). The simple
318 step of allowing the feed solution to remain at room temperature without additional treatment
319 enabled to decrease the feed concentration and volume by 32% and 46% respectively. Further, the
320 small quantity of remaining solution at the top and middle portions of the reactor can be channelled
321 back to the bulk feed tank for a subsequent F-SMDC operation cycle. This indicated that F-SMDC
322 with external crystallization does have the potential to achieve near zero liquid discharge.

Table 2 Volume and concentration of feed solution extracted from reactor upon F-SMDC and upon external crystallization (standing at room temperature for 24 - 72 h).

	1st cycle		2nd cycle	
Sample	Concentration (g/L)	Amount (mL)	Concentration (g/L)	Amount (mL)
Final F-SMDC feed (Before crystallization)	329.4±6.1	1140	218.1±2.3	1160
Upon external crystallization	160.4±0.2 (24 h) 149.9±2.3 (72 h)	150	160.4±0.7 (24 h) 147±0.3 (72 h)	620

4.3. Crystal production in F-SMDC

In F-SMDC, crystals were generated at the bottom portion of the reactor due to high concentration and lower temperature setting. In this study, the bottom portion of the reactor was cooled down up to 20.0±0.5 °C while the top portion of the reactor was maintained at 50.0±1.3 °C. At the bottom portion of the reactor, the combined condition of higher feed concentration and lower temperature enabled to achieve a faster super-saturation state of Na_2SO_4 compared to the top portion of the reactor. The CG and TG in the F-SMDC (lower concentration and higher temperature at top portion, higher concentration and lower temperature at bottom portion) improved the efficiency of recovering valuable crystals as well as obtaining higher water recovery and better stability (lower scaling) of MD process.

When 120 g/L Na_2SO_4 was treated without using crystals extraction, crystals were generated both at the top and bottom portions of the reactor. The amount of generated crystals formed was

directly proportional to the concentration ratio of feed solution (**Table 3**). High amount of crystals was generated both during cycle 1 (1169.0 g) and cycle 2 (898.0 g). In the case of cycle 1, F-SMDC operation was carried on beyond the point of rapid flux decline in order to obtain a highly concentrated final solution. The rapid permeate flux decline due to fouling and high feed concentration degraded the stability of the process. Therefore, it is not recommended to operate F-SMDC beyond the super-saturation state of the feed solution in the future study.

Table 3 Crystal and fresh water production by F-SMDC operation (feed: Na_2SO_4).

Sources	1st cycle		2nd cycle	
	Produced crystal (g)	Produced fresh water (mL)	Produced crystal (g)	Produced fresh water (mL)
Bottom portion of the reactor	551.3		541.6	
External crystallizer (containing saturated solution from top and middle portion of the reactor)	617.7	4295.5 (99% ion rejection)	356.4	3561.4 (99% ion rejection)
Total	1169.0		898.0	

The crystal production rate can be increased by factors such as temperature control, crystal size and immersion of crystals into saturated solution. As shown in **Table 2**, the volume and concentration of mother liquid decreased due to the formation of Na_2SO_4 crystals with time. For instance, the feed concentration of 160.4±0.2 g/L after 24 h was reduced to 149.9±2.3 g/L after 72 h. This indicated that additional crystals of larger sizes can be produced by the immersion of initial crystals into the mother liquid (**Figure 10(d)**). The morphology of Na_2SO_4 crystals changed from

rectangle shape to spherical shape over time (**Figure 10(a), (b)** and **(c)**). Prevalent growth and change in shape of crystals were detected on crystals that were fully immersed in the mother liquid. The results indicated that direct contact with mother liquid would enhance the growth of crystals. It is therefore essential to have enough contact area and immersion time with mother liquid. By doing so, a narrow size distribution of the crystals can be obtained.

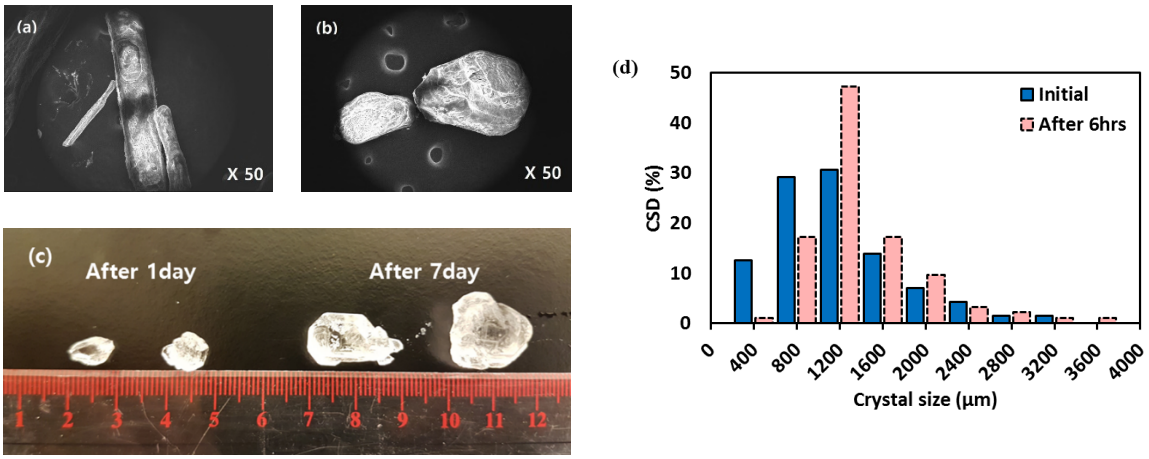


Figure 10 Crystal size distribution (CSD) and change in morphology of produced Na_2SO_4 crystals with time. Images of crystals at (a) initial, and after (b) 60min and (c) 1 day and 7 days, and (d) size distribution of Na_2SO_4.

4.4. Effect of salinity

The effect of salinity in the treatment of Na_2SO_4 solution was examined by adding NaCl. As shown in **Figure 11**, the concentration gradient trend at the initial stage (up to VCF 1.5) was similar with and without the presence of NaCl. In the presence of NaCl, the formation of crystals at the bottom portion of the reactor started from around VCF 1.8, while the concentration at the top portion of the reactor increased (with and without the presence of NaCl), lower VCF was achieved in the presence of NaCl. In the presence of NaCl, from VCF 2.2 onwards, visible presence of crystals was observed. At the same time, rapid flux decline and increase of feed concentration at the top portion

of the reactor occurred. This occurrence was associated to the presence of crystals on the membrane surface. The F-SMDC operation condition, namely concentrated feed solution and cooler membrane surface condition (direct contact with cold permeate) enabled the generation of CG. The crystal deposition on the membrane surface reduced the effective membrane area. This decreased the rate of concentration and degree of cooling by permeate, resulting in reduced crystallization of concentrated solution. Therefore, concentrated solution remained at the vicinity of the membrane boundary layer, and feed concentration at the top portion of the reactor portion increased by diffusion. This caused an increased crystal deposition onto the membrane surface (**Figure 11 (b)**).

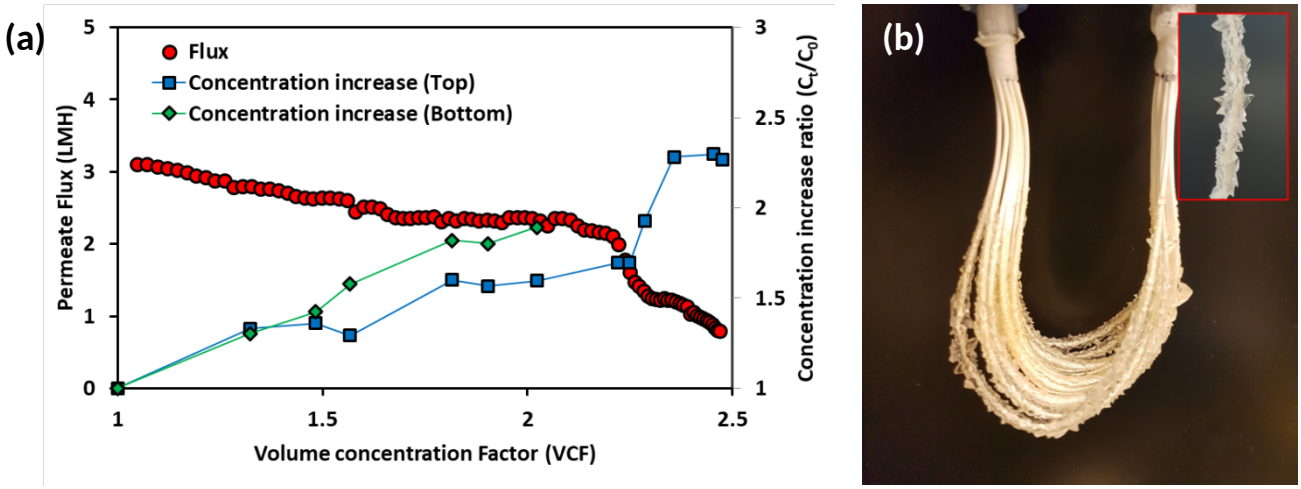


Figure 11 F-SMDC with Na_2SO_4 and NaCl: (a) variation of flux and concentration at the top and bottom portion of the reactor, (b) used membrane at the end of the experiment.

The EDX analysis revealed the presence of sodium, oxygen and sulphur elements on the used membrane surface and at the bottom portion of the reactor (**Figure 12(a)** and **(b)**). On the other hand, chloride ion was detected in crystals generated in feed solution of the top and middle portions of the reactor. The results indicated that a separate generation of crystal from solution can be achieved by a control of concentration and temperature at suitable range. In addition, the concentration of sodium ion in solution seems to influence crystallization phenomenon on the membrane surface and at the

386 bottom portion of the reactor. The crystallization on the membrane surface was detected at around
387 VCF 3.3 in the absence of NaCl. The crystals formation on the membrane surface became faster
388 (around VCF 2.2) with NaCl. At this point, the concentrations of sodium ion in both feed solutions
389 with and without NaCl were similar (93.08 g/L without NaCl and 93.28 g/L with NaCl). Also, upon
390 crystal formation at the bottom portion of the reactor, similar amount of sodium ion concentration
391 was observed in both the feed solutions (without NaCl: 107.78 g/L in cycle 1 / 106.26 g/L in cycle 2,
392 and with NaCl: 106.08 g/L). The difference in the initial point of crystallization on the membrane
393 surface and at the bottom of the reactor was attributed to temperature difference.

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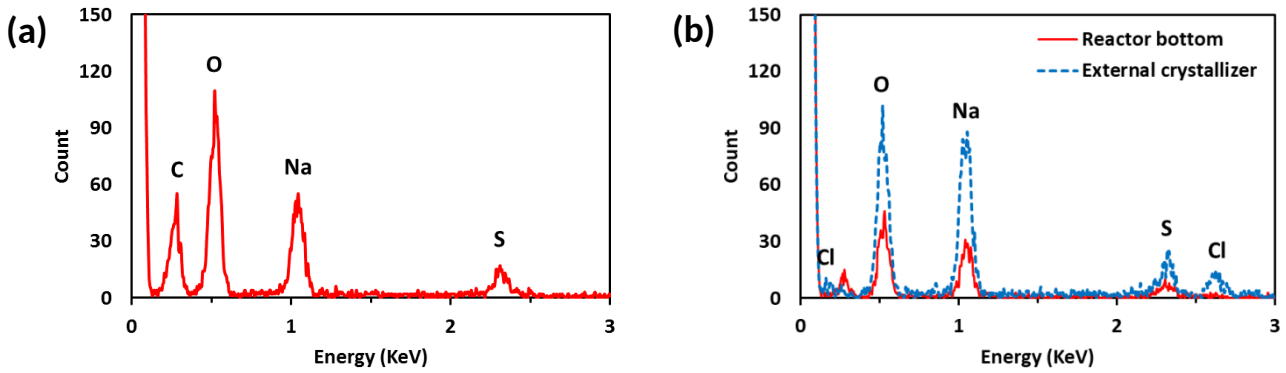

395 **Figure 12** EDX analysis of crystals (a) deposited on the used membrane surface, (b) produced from the
396 bottom portion of the reactor and external crystallizer (saturated feed solution from the top and middle portion
397 of the reactor) (feed solution: Na2SO4 and NaCl).

398

399 **5. Conclusions**

400 The feasibility of fractional submerged membrane distillation-crystallization (F-SMDC)
401 process was evaluated using a feed solution containing high concentration of Na_2SO_4 without and
402 with NaCl. The following conclusions were made from the experimental investigation:

- F-SMDC setting enabled the creation of CG and TG using a partition and double wall heating/cooling in the feed reactor. A lower feed concentration and higher feed temperature was maintained at the top portion of the reactor. Meanwhile, higher feed concentration and lower feed temperature was maintained at the bottom portion of the reactor.
- The presence of CG/TG in F-SMDC enabled to achieve higher water recovery (VCF 3.5) and lower membrane scaling, compared to SMDC mode (VCF 2.9).
- The condition of elevated feed concentration and lower temperature at the bottom portion of the reactor was favourable for high crystal formation in F-SMDC.
- The presence of salt (NaCl) influenced the crystallization of Na_2SO_4 at the bottom portion of the reactor and on the membrane surface, resulting in higher crystallization in both locations.
- F-SMDC was effective in reducing membrane scaling, producing high quality fresh water and valuable crystals (Na_2SO_4).
- The shape and dimension of F-SMDC reactor are essential factors that influence the formation of CG/TG and the overall F-SMCD performance. Further optimization of the reactor configuration is an important factor that must be explored in detail.

Acknowledgement

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