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Novel Inorganic Membrane for the Percrystallization of Mineral, Food and Pharmaceutical Compounds

Julius Motuzas,^a Christelle Yacou,^{a,b} Rasmus S. K. Madsen,^a Weng Fu,^a David K. Wang,^{a,c} Anne Julbe,^d James Vaughan,^a João C. Diniz da Costa^{a*}

^aThe University of Queensland, FIM²Lab – Functional Interfacial Materials and Membrane Laboratory, School of Chemical Engineering, Brisbane Qld 4067, Australia.

^bUniversité des Antilles, Department of Engineering, BP 250, 97157 Pointe-à-Pitre Cedex, Guadeloupe, France.

^cThe University of Sydney, School of Chemical and Biomolecular Engineering, Sydney, NSW 2006, Australia.

^dInstitut Européen des Membranes (UMR 5635 CNRS, ENCM, UM), Université de Montpellier, CC47, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France.

Abstract

This work demonstrates for the first time the phenomenon of continuous percrystallization using a carbon membrane derived from the pyrolysis of food grade sugar. In addition, it is also the first demonstration of membranes separating solute from solvent and delivering dry crystals in a single step. This is contrary to membrane crystallization, which requires two further processing steps to filter crystals from a solution followed by drying the wet crystal particles. The results indicate that carbonised sugar membranes can confer ideal conditions of super-saturation, leading to instantaneous and continuous percrystallization of compounds at the permeate side of the membrane. As a result, very high percrystallization production rates of up to 55,000 kg m⁻² per year are achieved. It is proposed that the percrystallization occurs in a wet thin-film modulated by solution permeation via the mesopores of the membrane, where vapour and crystals are separated at the membrane's solid-liquid-vapour interface. The potential deployment of this novel

technology is further demonstrated for a wide range of crystallization applications in chemical, hydrometallurgy, food and pharmaceutical industries.

Keywords: inorganic membrane; mesopores; percrystallization.

1. Introduction

Crystallization is an important industrial process generating a wide range of products throughout the world. Examples include sugar [1] which is a staple food ingredient, lysozyme [2] which is an antibacterial agent used in food and pharmaceuticals, and nickel sulfate hydrate [3] used in metal electroplating or as a battery precursor material. Essentially crystallization involves evaporating a liquid solvent and concentrating the solute to a sufficient degree of super-saturation at which point it crystallizes into a solid phase. The majority of the technologies used in crystallization are mature and have been optimized based on energy intensive thermal processes to improve the evaporation rate of solvents. To avoid high energy costs, solar evaporation ponds are used in certain applications. The main drawback of solar evaporation is that it is a very slow process, requiring large plant footprint [4] and the performance is highly dependent on weather conditions. A less energy intensive technology compared to traditional evaporation processes is membrane crystallization [5].

Membrane crystallization remained a dormant field for almost a century following the initial observations of Kober in 1917 [6]. It is only in the last 20 years that membrane crystallization has gained practical interest owing to the development of novel polymeric membranes. In one example, Drioli's group used polypropylene membranes to recover sodium chloride, magnesium sulfate hydrate [7] and lithium chloride [8]. In another example, Fane and co-workers [9] used polyvinylidene fluoride membranes to crystallize NaCl from a water desalination reverse osmosis plant to avoid environmental impacts caused by the disposal of brines. Van der Bruggen's group

[10] used polycarbonate/polyurethane membranes for the assisted crystallization of sodium carbonate. To date, membrane crystallization technology is uniquely based on polymeric membranes which allow for the permeation of liquids only, thus causing super-saturation, nucleation and crystallization on the feed side of the membrane [13]. Subsequently, there is a need for two additional processing steps to filter and dry the wet crystal particles [12]. Although membrane crystallization has shown to promote crystal nucleation and growth kinetics [13], crystallization rates reported to date are low [14]. Inorganic membranes have thus far been absent from these technological developments. Therefore, breakthrough technologies are required to address low production efficiencies, sluggish timeframes, high energy consumption and large plant footprint.

This work demonstrates for the first time the phenomenon of continuous percrystallization through porous carbon inorganic membranes. There are differences between membrane crystallization and percrystallization concepts. In the case of the former, crystals nucleate on the feed side of the membrane as the solute concentration increases as the solvent permeates through the membrane. In the case of latter as in this work, both solute and solvent diffuse through the membrane, leading to a combined phenomena of solvent evaporation and solute crystallization on the permeate side of membrane, hence the concept of percrystallization. Porous carbon membranes are generally derived from synthetic polymers [15], following the pioneering work of Koresh and Sofer [16] in early 1980s on the pyrolysis of polymeric hollow fibres. Recently, graphene has also been used to prepare porous carbon membranes [17]. Whilst carbon membranes have been extensively used for gas separation due to pore size tailoring at molecular sieve level, there has been recent applications of carbon membranes for liquid processing [18, 19]. However, this was only achieved by applying a vacuum on the phenolic resin films coated on porous alumina substrates. The vacuum-assisted method resulted in a carbon structure with pores slightly larger upon pyrolysis, thus increasing the water fluxes through the membranes whilst maintaining high levels of salt rejection [18]. In this

work, the membranes were prepared by a vacuum-assisted method by slightly impregnating an α -alumina porous substrate with an aqueous solution containing food grade sugar. As sugars are natural polymers, instead of the traditional synthetic polymers, this is a further novelty of this work as it uses a simple and green chemistry approach to prepare carbon membranes. The membranes were subsequently subjected to pyrolysis treatment in an inert nitrogen rich atmosphere resulting in the formation of a black carbon porous film.

This first demonstration was observed following a permeation study of a salt brine solution (NaCl 17.5 wt%), where brine diffused through the membrane under vacuum and water and percrystallization of NaCl occurred simultaneously on the permeate side in a continuous process. The evaporated water (>99% pure) was collected in a cold trap and the salt crystals were recovered from the permeate stream. This work further demonstrates that carbonised sugar membranes are flexible by percrystallizing mineral salts, food additives and pharmaceutical compounds.

2. Experimental

2.1 Carbon membranes derived from sugar

Carbon membranes were prepared using supermarket white refined food grade sugar. The sugar was dissolved in deionised water to a 20%wt solution. The solution was coated on the outer shell of commercial α -alumina substrates (tubes of OD = 10 mm; ID=5 mm). The contact time between the substrate and sugar solution was 1 min. The coated substrate was removed from the sugar solution at a withdrawal speed of 10 cm min⁻¹, and vacuum (<10⁻¹ Pa) was applied to the inner shell of the tube for 2 min. Subsequently, the coated tube was dried for 15 hours at 60 °C. Finally, the coated tube was carbonised (i.e., pyrolyzed) in a nitrogen (99.99%) atmosphere at 700 °C for 8 hours with heating and cooling rates of 5 °C min⁻¹. See Fig. A1 (Appendix) for images of membrane substrate and carbonised sugar membrane.

2.2 Other inorganic membranes

A series of membranes were also tested to determine if percrystallization also occurred in different inorganic materials and pore size diameters (d_p). All these membranes have been previously reported in the literature for gas and liquid separation as follows: (i) microporous ($0.3 < d_p < 0.5$ nm) molecular sieve silica membranes [20]; microporous ($d_p \sim 0.5$ Å) carbon molecular sieve membranes [18]; mesoporous ($d_p \sim 3.1$ nm) titania membranes [21]; mesoporous ($d_p \sim 5$ nm) carbon membranes [19]; mesoporous ($d_p \sim 9$ nm) gamma-alumina membranes [22]; macroporous ($d_p \sim 150$ nm) alpha-alumina tube as a commercially purchased substrate.

2.3 Percrystallization experiments

The experimental set-up for the continuous percrystallization study is shown in Fig.1. A carbonised sugar membrane was connected to silicon tubing and placed inside a conical beaker. The silicon tubing was connected to a large beaker containing the feed solution. The large beaker with the solution was placed on a hot plate and the temperature of the solution was measured by a thermocouple placed at the inlet of the carbonised sugar membrane. The feed solution was recirculated through the inner shell of the membrane via a peristaltic pump. The flow rate of the feed solution was 70 mL min^{-1} . The feed side of the membranes was at atmospheric pressure while the permeate side under vacuum $< 10^{-1}$ Pa. A liquid nitrogen cold trap was used to collect the water vapour permeated through the membrane ahead of the vacuum pump.

The water flux (F) was calculated based on the total mass (m) collected in the cold trap for a pre-determined interval (Δt) per area of membrane (A) as $F = m / (A \times \Delta t)$. The solute flux (F) was determined similarly to the water flux as $F = m / (A \times \Delta t)$. A pre-determined volume of water was used to rinse the conical beaker (i.e., vacuum chamber) and the surface of the membrane in order to ensure that all solute in the permeate side of the membrane was collected and analyzed. The

concentration of the substances in the feed (C_f) and permeate (C_p) determined by using a conductivity meter based on standard curves of concentrations vs conductivity. At least 3 permeate collections were taken to ensure the system had reached steady state operating conditions.

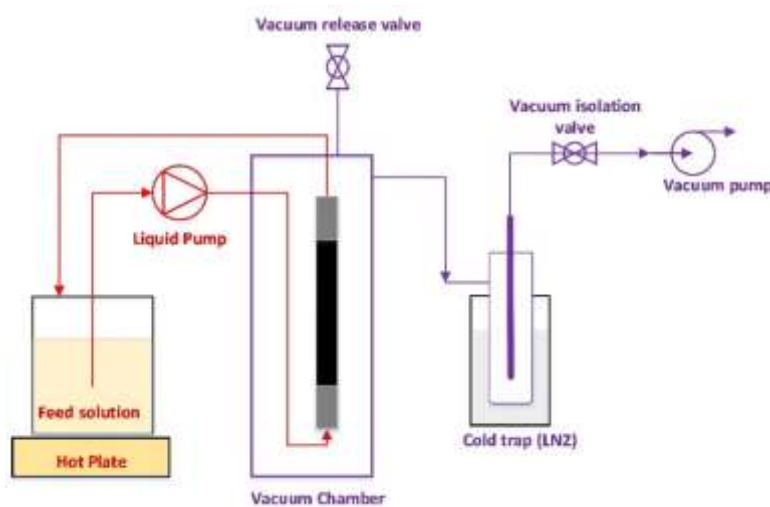


Fig. 1 – Diagram of the percrystallization experimental set up. The carbon membrane tube (black colour) with glazed ends (grey colour) is housed in the vacuum chamber (i.e., conical flask in the experimental work as per video AV1 in the appendix).

2.4 Preparation of feed solutions

All chemicals were used as received without any additional processing. These included NaCl (99.7wt%, Chem-Supply), KCl (99.0wt%, Chem-Supply), $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ (99.7wt%, VWR Chemicals), $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (99wt%, Sigma-Aldrich), ascorbic acid (99.0% wt, Chem-Supply), oxalic acid (99.5 wt%, Chem-Supply) and acetaminophen (paracetamol, 98.0-102.0wt%, Sigma-Aldrich). Bulk solutions were prepared by dissolving the solids in deionized water. In the case of the hydrated salts, their water content was considered in the solution mass balance. The concentration of the substances in the feed solutions were determined by using a conductivity meter based on standard curves of concentrations vs conductivity.

2.5 Molecular weight (MW) cut-off test

MW cut-off tests were carried out using an aqueous solution containing a single compound such as 36 or 400 kDa polyvinyl pyrrolidone (PVP), or 0.34 kDa sucrose (Sigma), used as received. PVP or sucrose was mixed with deionized water to solutions of 0.3 wt%. A pressure vessel was used to maintain a pressure of 5 bar. Permeation testing was conducted in a cross-flow set-up where the solution was fed via the inner shell of the tube. The permeate stream via the outer shell of the tube was collected in a beaker and the mass was continuously recorded using an electronic scale. The collected permeate solution was analysed using a Shimadzu UV-2700 UV-Vis spectrometer to determine the concentration of PVP against calibrated curves. The MW cut off was determined by the rejection (R) of substances as $R=[1-(C_p/C_f)]\times 100\%$, where C_p and C_f are the concentration of PVP or sucrose in permeate and feed streams, respectively. Measurements were recorded at steady state conditions with a minimum three measurements for each test.

2.6 Materials characterisation

Carbonised sugar xerogels were prepared by dispensing a sugar solution into a petri dish. The samples were then placed inside a closed desiccator where a vacuum was applied for 120 s. Subsequently, the samples were dried in an oven at 60 °C for 1 hour. The xerogel samples were pyrolysed following the same methods as used to prepare the carbonised sugar membranes. The samples were analysed using a Tristar 3020 apparatus (Micromeritics Instrument Corporation) to determine their structural features. The samples were degassed at 200 °C for 24 hours under high vacuum prior to nitrogen adsorption at 77 K. The crystals were analysed by X-ray diffraction (XRD) in a Rigaku Smartlab X-ray diffractometer at 45 kV, 200 mA with a step size of 0.02° and speed of 4 °min⁻¹ using a filtered Cu Ka radiation ($\lambda=1.5418$ Å). Morphological features of the powder samples were examined using a Jeol JSM-7001F SEM with a hot (Schottky) electron gun at an acceleration voltage of 5 kV.

3. Results

Video AV1 (see web link in the Appendix) demonstrates for the first time the instantaneous and continuous percrystallization process observed for all substances tested in this study. In this example, small white crystals were formed on the surface of a carbonized sugar membrane. Subsequently, the white crystals were ejected off the membrane surface into the conical flask, which is under vacuum. At the same time, water evaporated from the membrane surface which was collected in a cold trap as schematically shown in Fig. 1. The salt crystals were recovered from the permeate stream. Fig. 2 shows a SEM image of the percrystallized salt where the particles were characterized by 10 to 20 μm cubic NaCl crystals. These crystals are very small with a narrower size distribution in comparison to those reported for polymeric membrane crystallization with sizes in the range of 20-200 μm [14] and 30-1000 μm [9]. These results strongly suggest that membrane percrystallization is a process that confers superior control of small crystal sizes.

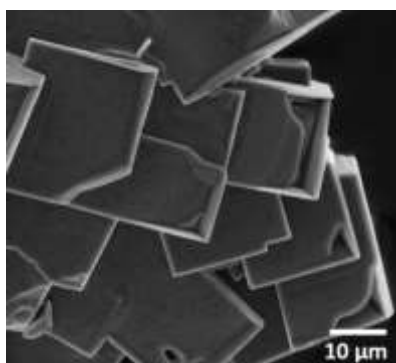


Fig. 2 SEM image of percrystallized NaCl (NaCl 17.5 wt% at 37 °C).

In addition, this study is also the first demonstration of membranes separating solvents (i.e., water) from solutes (i.e., solid crystals) in a single step, contrary to membrane crystallization which requires three processing steps. Fig. 3A shows that the fluxes of NaCl and water increased as a function of the feed brine temperature. At the highest tested temperature of 37 °C and 20 wt% NaCl feed concentration (Fig. 3B), the salt flux reached 5.5 $\text{kg m}^{-2} \text{h}^{-1}$. At these conditions, one square metre of membrane area could produce up to 48,000 kg of NaCl per year. What is more remarkable is that the membrane delivered a water flux of 20 $\text{L m}^{-2} \text{h}^{-1}$ for a hyper saline NaCl brine solution of 20 wt% (Fig. 3B). This performance is within the range of reverse osmosis membranes of 19.7-28.0

$\text{L m}^{-2} \text{h}^{-1}$ reported by Mattia and co-workers [23] though for much lower NaCl feed concentrations of 3.5 wt%. Although the intention of this work is percrystallization membranes, an added benefit is dewatering hyper saline brines well beyond the capabilities of reverse osmosis membranes which is the golden standard technology for desalination.

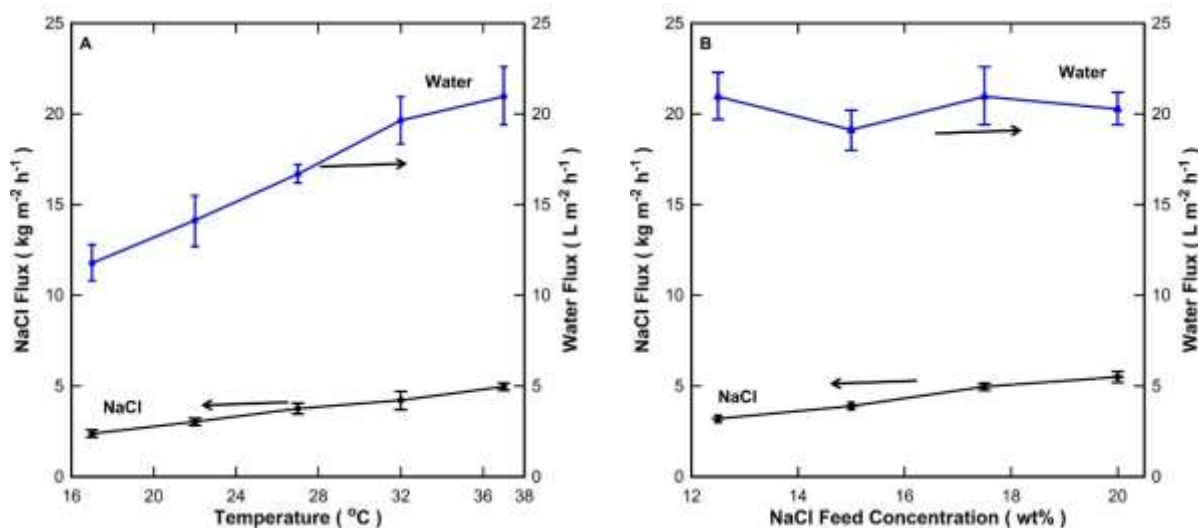


Fig. 3. Water and percrystallized NaCl flux as a function of (A) temperature with a feed solution of NaCl 17.5 wt% and (B) NaCl feed concentration at feed solution temperature of 37 °C.

The structural characterization of carbonized sugar xerogels proved to be difficult resulting in dense carbon structures from nitrogen sorption analysis. The characterization of xerogels generally offer a semi-quantitative analyses between xerogel structure and film structure. This is not the case here as the carbonized sugar membranes delivered high water fluxes (Fig. 3), indicating porous membranes contrary to the dense xerogels. These results are in line with reports that impregnation using an assisted-vacuum method causes oligomers to get entrained with solvent and diffuse into porous substrates to form porous structures [18, 19, 24]. Therefore, molecular weight (MW) cut-off tests were carried out as the best approach to determine pore sizes. Fig. 4 shows that the carbonized sugar membranes had a MW cut-off of around 360 kDa. This value correlates to mesopores of 5 nm for carbonized phenolic resin membranes [19]. Subsequent investigations showed that the pore diameter (d_p) and membrane materials were the key parameters enabling the desired percrystallization properties to be obtained. Salt crystals could be formed through mesoporous

($3 \leq d_p \leq 9$ nm) titania, gamma-alumina and carbon membranes only, but not for other membranes such as microporous ($d_p < 0.5$ nm or 5 Å) silica and carbon molecular sieves, nor macroporous α -alumina substrates ($d_p \sim 150$ nm). Micropores were too small to effectively allow the permeation of hydrated salt ions with radius of $\text{Cl}^- \cdot \text{H}_2\text{O}$ (6.64 Å) and $\text{Na}^+ \cdot \text{H}_2\text{O}$ (7.16 Å) [25, 26], whilst flooding occurred with macropores membranes as the salt solution flowed through.

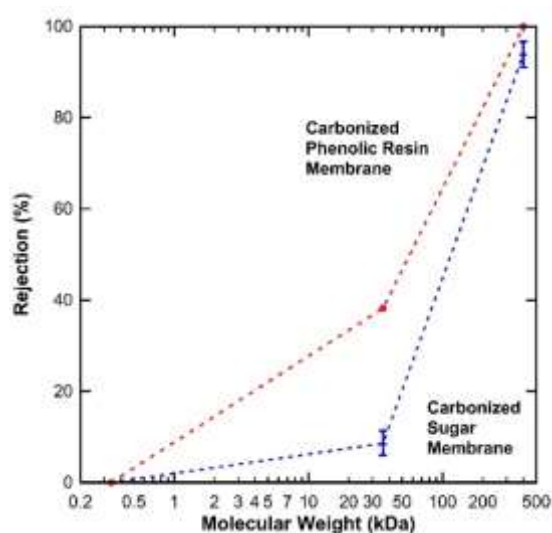


Fig. 4 – Molecular weight cut-off for the carbonized sugar membrane including a comparison to a carbonized mesoporous phenolic resin membranes [19]. Both membranes were prepared under the same conditions and also tested under the same conditions.

The percrystallization phenomenon in this work occurred under vacuum conditions only. In the case of tests under pressure, this phenomenon was not observed. For instance, the mesoporous carbonised sugar membrane delivered high flux as a function of pressure and NaCl concentrations where salt rejection was insignificant (see Appendix Fig. A2A). Further, the pressurised solution fluxes as a function of NaCl concentration (Fig. A2B) varied within experimental error only. These results suggest a bulk diffusion mechanism for the permeation of the solution containing hydrated ions through the mesopores of the membrane. In addition, adsorption tests of NaCl solutions (Fig. A3) shows that hydrated ions did not adsorb on the surface of carbonised sugar powders. As carbon imparts hydrophobicity for contact angles $\geq 90^\circ$, as evidenced by the contact angles (107°) in Fig. 5

for water and various NaCl solutions, these results further support the absence of hydrated ions surface adsorption. Contrary to hydrophilic inorganic membranes, which adsorb hydrated ions [27] leading to significant fouling [28], the hydrophobic carbonised sugar membranes counteracted this effect by repelling hydrated ions similar to other carbon membranes [29, 30]. Therefore, the diffusion of water and hydrated ions via the mesopores of the membranes was dominated by the bulk diffusion mechanism.



Fig. 5 – Contact angle measurements on the carbonised sugar membrane surface (permeate side) as a function of NaCl concentration from 0 to 20 wt%.

The continuous percrystallization of salts via the carbon membrane is schematically idealized in Fig. 6. Under vacuum pressure, a wet thin-film is formed on the surface of the permeate side of the membrane. Under the testing conditions, flooding did not occur suggesting that mesopores were modulating the flow of solution by a bulk diffusion mechanism from the feed side to the wet thin-film on the permeate side. Thin-films are known to improve heat transfer, thus promoting evaporation of water close to the solid–liquid–vapor contact line [31]. The evaporation of water from the wet thin-film results in the permeate side of the membrane cooling up to a temperature 6 °C lower (i.e. measured using a laser thermocouple) as compared to the feed side of the membrane. During evaporation of water, salt grows on nucleation points in the wet thin-film. Upon nucleation and spontaneous crystallization, concurrent separation of solids and liquid occurs in a single step. The lighter water molecules evaporate from the wet thin-film and the heavier NaCl crystals are ejected as dry particles from the membrane surface due to pressure difference and fall under the

effect of gravity. Therefore, solvent (i.e., water) evaporation from the wet thin-film on the permeate side of the membrane is driving the instantaneous percrystallization.

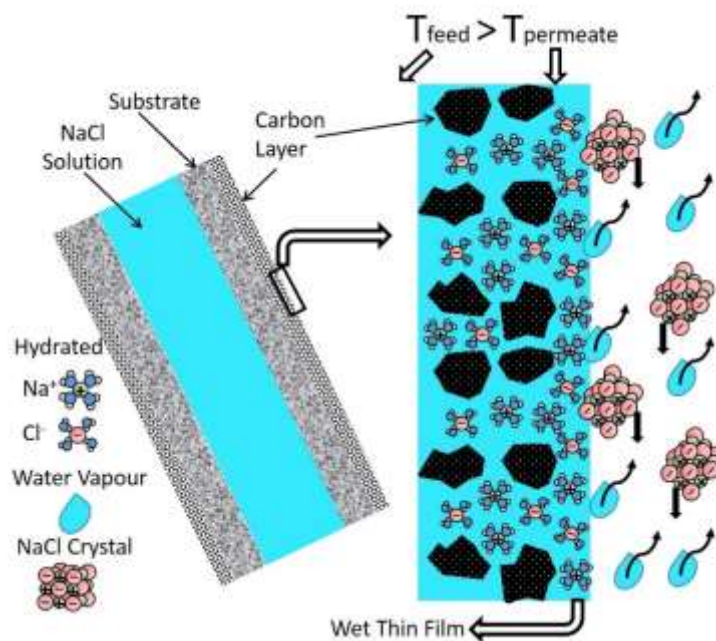


Fig. 6. Idealized schematic of continuous percrystallization via a proposed surface thin-film evaporation/nucleation/crystallization mechanism.

An interesting finding is displayed in Fig. 7A, demonstrating that the separation process conferred by the carbon membrane consistently favoured a higher production of solute rather than solvent. For instance, the mass ratio of NaCl over water in the permeate side of the membrane was always above that of the feed solution. These results strongly suggest that the formation of NaCl crystals at the wet thin-film interface reduces the area available for water to evaporate, thus explaining that the carbonized sugar membranes are slightly selective to NaCl instead of water. Fig. 7B shows an Arrhenius plot of the percrystallized NaCl fluxes as a function of several NaCl feed concentrations. The energy of activation, based on this Arrhenius plot, is listed in Table 1. It is observed that the energy of activation slightly increases as a function of the NaCl feed concentration. This is attributed to the viscosity effect of NaCl solutions, which increases as a function of NaCl concentrations [32]. As viscosity increases, more energy is required for the NaCl solution to

permeate through the pores of the carbonized sugar membrane, and likewise more energy is required for NaCl percrystallization.

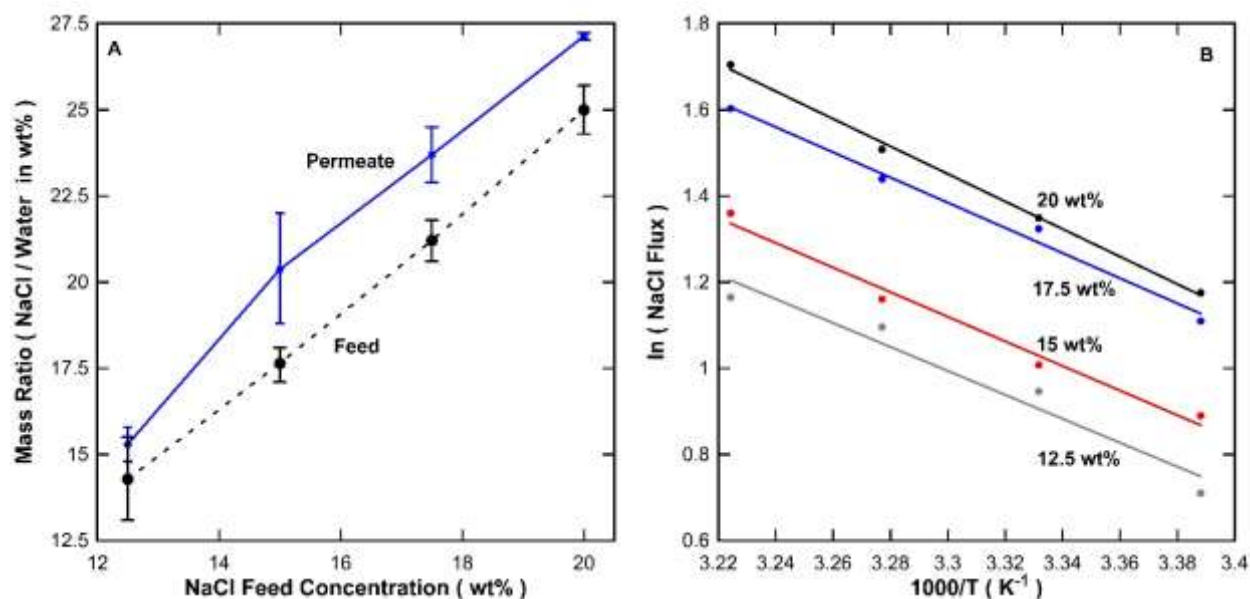


Fig. 6. (A) Selectivity (i.e., ratio of NaCl flux over water flux) at 37 °C and (B) Arrhenius plot of the percrystallization of NaCl for each feed concentration (wt%).

Table 1 – Energy of percrystallization and coefficient of determination (R^2) for data fitting from Fig. 6B.

NaCl Feed Concentration (wt%)	Energy of Percrystallization (kJ mol^{-1})	Coefficient of Determination (R^2)
12.5	23.1	0.97
15	23.7	0.99
17.5	24.3	0.99
20	26.6	0.99

The percrystallization of NaCl using inorganic membranes is shown to be efficient. For instance, the production of table salt using evaporation ponds is very slow even in a dry continent like

Australia. The Whyalla plant uses 4000 hectares of salt pans to produce 18 kg m^{-2} per year using feed sea water ($\text{NaCl} \sim 3.5 \text{ wt\%}$) [33]. Under the same feed salt concentration of 3.5 wt\% at room temperature operation, carbonized sugar membranes could produce 8400 kg m^{-2} per year. In other words, each 1 m^2 of carbon membranes could replace more than 450 m^2 of evaporation ponds. What is more remarkable about this discovery is the flexibility of the inorganic membranes to process a wide range of substances such as other mineral salts (KCl , NiCl_2 and NiSO_4), organic acids (oxalic acid), ascorbic acid (vitamin C) and an analgesic acetaminophen (paracetamol) as displayed in Fig. 8A, noting the high KCl production rate of up to $55,000 \text{ kg m}^{-2}$ per year. The production rate of NaCl increased as a function of temperature and NaCl feed concentration, reaching best values close to $48,000 \text{ kg m}^{-2}$ per year as shown in Fig. 8B. Long term performance data for 42 days (over 1000 h) displayed in Fig. A4 (Appendix) demonstrates that the carbonised sugar membrane is very stable for all compounds tested in this work. NaCl fluxes increased from the initial to final tests. This could be attributed to structural changes associated with loss of carbonised materials weakly attached to the membrane during the long term testing. In addition, Cicek et al. [34] reported that crystal abrasion on the selective layer of an inorganic membrane led to higher fluxes, in line with the long term effect of flux increase in this work. These results further confirm that fouling did not occur under the percrystallization testing conditions.

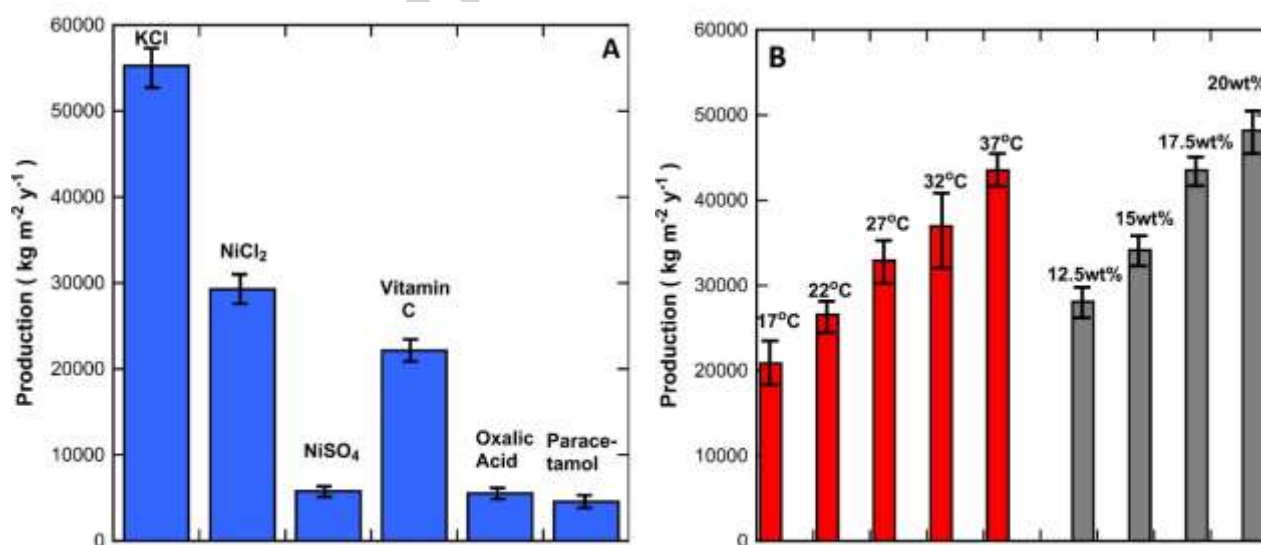


Fig. 8. (A) Percrystallization production rates of KCl, NiCl₂, NiSO₄, oxalic acid (all 17.5 wt% 37 °C), vitamin C (2.5 wt% at 37 °C) and paracetamol (5 wt% at 25 °C), all solutions in water except paracetamol in ethanol; (B) percrytallization production rates of NaCl as a function of temperature (all 17.5 wt%) and NaCl feed concentration (all at 37 °C).

It is interesting to observe the range of crystal shapes and sizes obtained from percrytallization. The SEM images in Fig. 9 show that KCl crystals were similar to NaCl (Fig. 2). The nickel salts, NiCl₂ (as NiCl₂·4H₂O) and NiSO₄ (as NiSO₄·6H₂O), resulted in elongated and large crystals, respectively. Vitamin C formed small crystals almost like needle-geometries, whilst oxalic acid percrytallized as flakes. Paracetamol produced small crystals with various sizes. Fig. 10 (see further details in the appendix) shows the XRD patterns of the crystals obtained in this study, confirming the crystallinity of all samples. For instance, NaCl and KCl formed cubic crystals whilst NiSO₄ tetragonal crystals. Several crystals were characterized by monoclinic space groups such as NiCl₂ (P21/a), Vitamin C (P21), oxalic acid (P21/a) and paracetamol (P21/a).

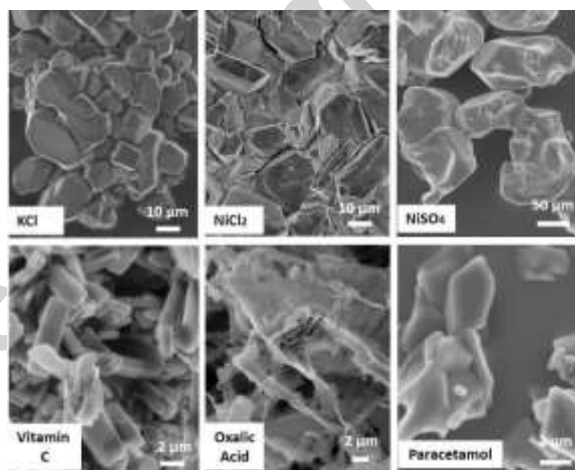


Fig. 9. SEM images of percrytallized KCl, NiCl₂, NiSO₄, oxalic acid (all 17.5 wt% 37 °C), vitamin C (2.5 wt% at 37 °C) and paracetamol (5 wt% at 25 °C) - all solutions in water except paracetamol in ethanol.

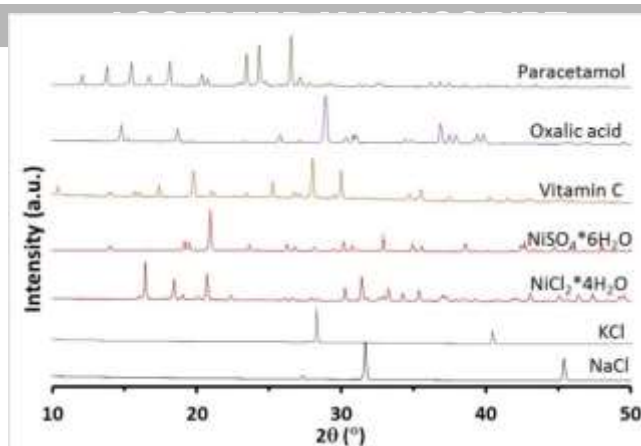


Fig. 10 – XRD patterns of crystals obtained by percrystallization membranes.

Therefore, this novel technology has a broad spectrum of percrystallization application. It can be used in chemical / mining / hydrometallurgical operations to recover substances of interest such as metals or acids, with the added benefit of also recovering water/solvent and complying with new environmental regulations of zero liquid discharge. In addition, inorganic membrane percrystallization can spearhead developments in wide range of fields of interest in the human endeavour, particularly in health and bio-crystallization of proteins, food/flavour additives and pharmaceutical compounds.

4. Conclusions

This work demonstrates for the first time that porous inorganic membranes can be used to percrystallize mineral salts, food and pharmaceutical compounds. A practical aspect of this novel approach is that the dry solute is separated from the solvent in a single step. The reaction appears to take place in a wet thin-film on the permeate side of the membrane. Membrane mesoporosity is a key variable in achieving the ideal process conditions. The wet thin-film under vacuum pressure confers ideal condition of super-saturation, nucleation and crystallization of compounds. As a result, dry crystals are continuously ejected off the membrane surface and production rates are high up to $55,000 \text{ kg m}^{-2}$ per year.

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Appendix

A1 - Photos of prepared membranes



Fig. A1 – Photos of the white porous membrane substrate (α -alumina) and black carbonized sugar membrane. Both substrate and membrane tubes have glazed ends to accommodate seals for experimental work.

A2 – Pressurised permeation tests

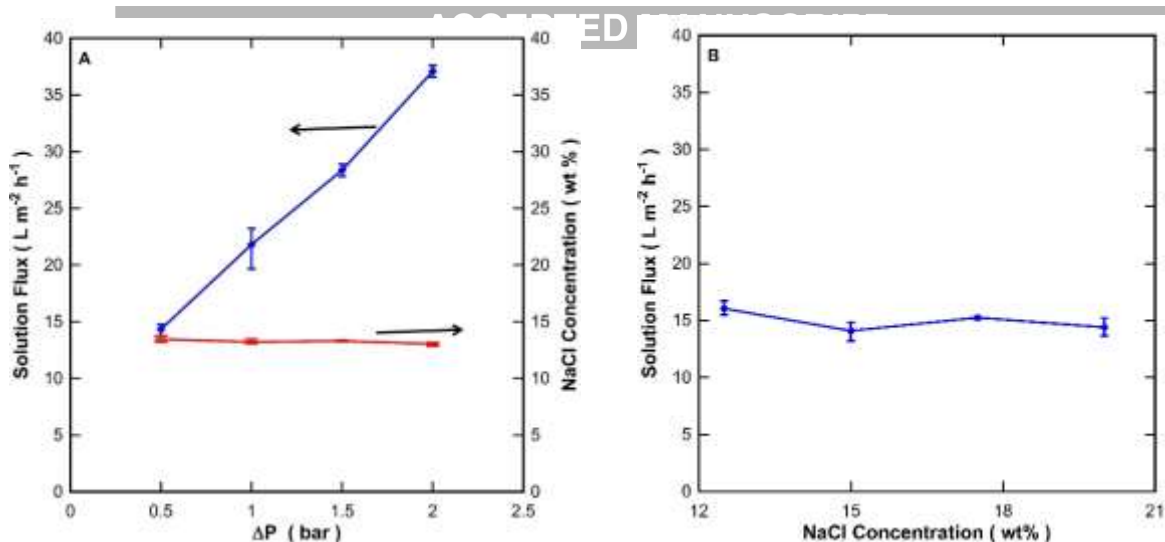


Fig. A2 – (A) NaCl solution flux and NaCl concentration in the permeate stream as a function of pressure difference (Δp) across the membrane for NaCl 12.5 wt%; and (B) NaCl solution flux as a function of NaCl concentration at $\Delta p = 0.5$ bar. All experimental work was carried out at room temperature using the same experimental set up as for the molecular weight cut-off tests.

A3 – Adsorption

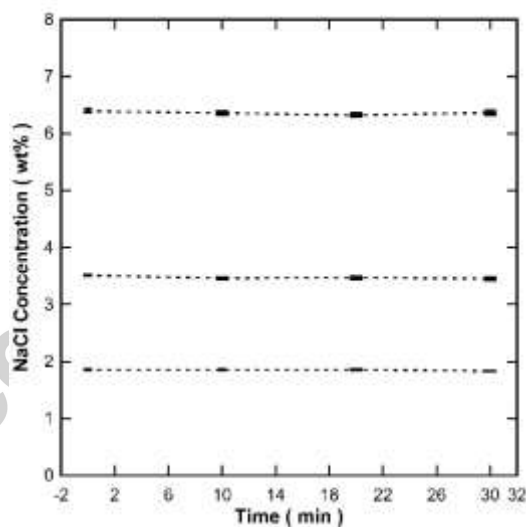


Fig. A3 – Adsorption tests of NaCl solutions as a function of time. The NaCl concentration was constant, thus indicating that hydrated ions were not adsorbing on the surface of carbonized sugar powders. This experimental work was carried out by vigorous stirring of a mixture containing carbonized sugar powders with a desired NaCl solution. Electrical conductivity measurements were taken every 10 min in triplicate and correlated to an NaCl calibration curve.

A4 – Long term results

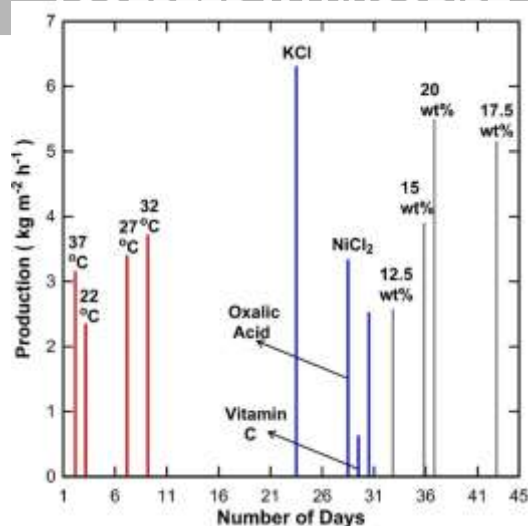


Fig. A4 – Long term crystal fluxes for NaCl (17.5 wt%) as a function of temperature (red bars); KCl and NiCl₂ (17.5 wt% and 37 °C) and oxalic acid and vitamin C (2.5 wt% and 37 °C) (blue bars); and NaCl (37 °C) as a function of NaCl feed concentration (gray bars).

A5 - X-ray diffraction (XRD)

Details of the XRD patterns of the crystallised materials obtained in this study as per Fig. 9:

- Sodium chloride (NaCl) determined as cubic (Fm-3m) space group number 225 pdf file reference number 01-077-2064.
- Potassium chloride (KCl) as cubic (Fm-3m) space group number 225 pdf reference number 01-075-0296.
- Nickel chloride pattern as nickel chloride tetra hydrate (NiCl₂*4H₂O) as monoclinic (P21/a) crystal structure space group 14 with reference number 01-079-2297.
- Nickel sulphate pattern as nickel sulphate (VI) hexahydrate (NiSO₄*6H₂O) as tetragonal (P41212) space group number 92 pdf with reference number 01-079-0106.
- Vitamin C as ascorbic acid as monoclinic (P21) crystal structure space group 4 with reference number 00-022-1560.
- Oxalic acid as monoclinic (P21/a) crystal structure space group 14 with reference number 00-030-0624.

- Paracetamol as acetaminophen as monoclinic (P21/a) crystal structure with space group 14 with reference number 00-027-1902.

A6 - Video of the membrane percrystallization process

This short video displays the instantaneous and continuous per-crystallization process observed for all substances tested in this study. In this example, small white crystals (Vitamin C) are formed on the surface of a carbonized sugar membrane. Subsequently, the white crystals are ejected off the membrane surface into the conical flask, which is under vacuum. Video SV1 – please open the following video file available on (outbox.eait.uq.edu.au/uqjdiniz/J_Membr_Sci_per-



J_Membr_Sci_per-cry
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crystallisation_inorganic_membrane.mp4):

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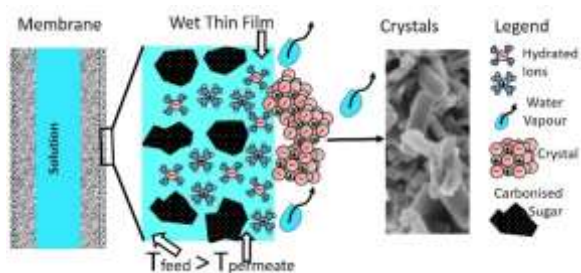
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Graphical Abstract



Highlights

- First demonstration of continuous percrystallization using inorganic membranes.
- Also first demonstration of membranes separating solute from solvent in a single step.
- Very high percrystallization production rates of up to $55,000 \text{ kg m}^{-2}$ per year.
- Percrystallization occurs in a wet thin-film on the permeate side of the membrane.
- Wide application for chemical, hydrometallurgy, food and pharmaceutical industries.