

Assessment of the innovative freezing-melting technology for desalination of the Mediterranean seawater in the Gaza Strip, Palestine

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ABSTRACT

Although the freezing-melting process is not widely used commercially, perhaps the most significant potential advantage of desalination by freezing is the very low energy required compared with other desalination processes. Five seawater samples of 3,000 mL each were collected from different locations at the Gaza Strip beach. The physicochemical characteristics of the raw seawater samples were tested. The seawater samples were poured into an identical flask connected directly to an external stainless steel single-phase freezer (thermally protected-Sichuan Dandy Co. Ltd. 220 Volt, 50 Hz) with an energy consumption of 0.1 kW/h to be crystallized by direct freezing (at -20°C). Then the physicochemical analysis was undertaken on the water produced from three repeated freezing-melting (FM) cycles for each seawater sample. The average water mineral reduction percentages ranged from 39.0% to 45.5%, (49.7%–52.8%), and (56.0%–59.0%) for the 1st, 2nd, and 3rd FM cycles, respectively. The overall average removal percentage of dissolved minerals and constituents after the 3rd FM cycle for North Gaza, Gaza, Middle area, Khan Younis, and Rafah seawater samples was 84.7%, 85.6%, 87.3%, 86.4%, and 87.6%, respectively. The time of crystallization in the 1st, 2nd, and 3rd freezing cycles was 80, 50, and 30 min, respectively. The consumed energy for produced water after the three cycles of freezing was 0.018, 0.022, 0.018, 0.023, and 0.021 kW/L for the North Gaza, Gaza, Middle Area, Khan Younis, and Rafah seawater samples, respectively. The FM technique could be used as a pretreatment method for other methods of desalination.

Keywords: Desalination; Freezing-melting; Gaza Strip; Palestine; Mediterranean seawater

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1. Introduction

Many nations throughout the world lack natural fresh water. The great majority of people will face acute fresh water scarcity in the next two generations due to pollution, climate change, and overuse of water resources in many areas around the globe. The oceans and seas were formerly the world's largest water reservoirs, with seawater accounting for nearly 97% of the planet's water. As a result, desalination of salt water will be our ideal option for meeting the population's water demands [1–3].

Desalination technology for producing fresh water nowadays may be split into two categories based on the process utilized to remove salts: (a) Membrane separation methods, such as electrodialysis (ED) and reverse osmosis (RO), rely on electrical and mechanical forces. (b) Thermal processes, such as distillation and freezing, cause phase transitions [4–6].

Thomas Bartholinus (1616–1680), a Danish physician, was the first to discover that fresh water could be produced by melting ice formed in salt water. Robert Boyle recorded the same sight almost simultaneously and predicted the phenomenon as a source of fresh water [7]. The Italian scientist Anton Maria Lorgna thereafter proposed a method for purifying salt water and unclean water by freezing and then melting the ice around the end of the eighteenth century [8].

Until the invention of refrigerating machines, the freezing-melting (FM) technique of water purification was only achievable in the coldest places and seasons and was not of practical interest. In the late 1930s, there was renewed interest in the practice of freezing salt water to obtain fresh water. In the 1950s, the FM technique was first employed commercially. Desalination, petroleum, and food processing research in the 1960s and 1970s yielded a slew of technical breakthroughs [9].

Freezing methods are now used in a variety of industries, including fruit juice concentrate, dairy products, wastewater sludge, and desalination. It may also be used as a pretreatment method for desalination of brackish and saline water before being treated further using RO and ED [10].

By freezing and crystallizing water, the freezing process may theoretically separate water from salt water and polluted water. In ideal circumstances, the ice created should be pure and salt-free. Seawater may be frozen, crystals separated, surface washed, and crystals thawed to make fresh water [11–13].

According to a recently published article aimed at understanding the mechanism of salts formation inside the crystallized region, the salt distribution in a concentration gradient flowing from cold to hot outside of the ice surface associated with the temperature gradient in salt ice is exponentially inversely proportional to the distance axis of the ice phase [14]. Direct contact freezing, non-direct contact freezing, and vacuum freezing are the three types of FM procedures. Crystallization, separation, surface cleaning, and freezing of the crystals are all involved in these processes. Gravity drainage, centrifugal, filtration, and wash columns can all be used to separate ice crystals [15–17].

Because of the low operating temperature and lack of harmful chemical discharge, freeze desalination provides

various advantages over other technologies, such as lower energy consumption, scaling, and corrosion resistance [18]. Over the last 40 y, a few FM plants have been built, but the freezing method has yet to be marketed for producing fresh water for municipal use [19].

The current study was conducted in the coastal zone of the Gaza Strip. This area is located in southwest Palestine, and it has a current estimated population of more than 2 million people in an area of around 365 km², making it one of the world's greatest population densities per km². The Gaza Strip is bordered on the east and north by occupied Palestinian areas, Egypt on the south, and the Mediterranean Sea on the west.

The Gaza Strip's drinking water supply systems (DWSSs), like those in other underdeveloped nations, are subjected to a variety of threats. The decline in groundwater quality, the Gaza Strip's primary supply of water, has forced the creation of brackish water small-scale desalination facilities as a strategic alternative to fulfill the community's drinkable water demands. Desalinated water is now used by the great majority of Gaza's inhabitants, mostly for drinking. However, problems with water quality have been noted in Gaza's DWSSs due to the presence of microbiological, chemical, and physical agents, mostly due to nonhygienic practices during water transit or storage [20–23].

The Gaza Strip's coastal aquifer gets an annual average recharge of 55 to 60 million cubic meters (MCM) per year, primarily from rainfall, plus 30 MCM/y from lateral groundwater flow and leakages, for an annual intense abstraction rate of roughly 200 MCM. As a result, the yearly cumulative water deficit is anticipated to be between 90 and 110 MCM/y. As a result of the excessive Total Dissolved Solids (TDS) concentrations, which should not exceed 500 mg/L, groundwater quality is fast decreasing in comparison to World Health Organization (WHO) drinking water regulations. The Palestinian Water Authority (PWA) and the Coastal Municipalities Water Utility (CMWU) reported an increase in nitrate concentrations, particularly in the northern part of Gaza, with high salinity levels of 2,000–10,000 mg/L, high chloride concentrations of 500–3,000 mg/L, and nitrate concentrations of 100–800 mg/L. Furthermore, according to the PWA, per capita daily water consumption in 2019 was 88.3 liters per capita per day (LCD), which is below the appropriate limit of 100 liters per capita per day suggested by the WHO [24].

Persistent power outages are hampering the operation of wastewater treatment and desalination plants, as well as water delivery systems in Gaza. Flooding and pollution are also concerns for many sewage pumping facilities. The Gaza energy grid delivers an average of 208 megawatts per day from power stations in Israel, Gaza, and Egypt, compared to an estimated demand of 350 to 450 megawatts per day. Nonetheless, both optimistic and pessimistic models predict that the gap between power demand and supply in Gaza will widen in future years [25].

To the best of our knowledge, the freezing-melting technology for desalination of the Mediterranean seawater, particularly in the Gaza Strip, Palestine, has not been established yet. Hence, we think that the application of FM technology in an area overlooking the Mediterranean Sea with a sunny sky almost throughout the year would be a vital

solution to the water scarcity in the Gaza Strip, especially since the utilization of solar energy systems has become widespread. Therefore, the current study aims at investigating the effectiveness of such technology in improving the physicochemical characteristics of Mediterranean seawater, such as pH, Electrical Conductivity (EC), TDS, Nitrate, Chloride, Fluoride, Sulfate, Alkalinity, Hardness, Calcium, Magnesium, Potassium, Sodium, Cadmium (total), Copper (total), and Lead (total).

2. Materials and methods

Seawater samples were collected from the beaches of each governorate of the Gaza Strip (five governorates) according to Standard Operating Procedure EAP025, Version 2.0 [26]. For each site, three polyethylene bottles were filled at different depths in the water column and then mixed up in a clean polyethylene bottle (9000 mL) to ensure water consistency; 3000 mL were collected and sent to the laboratory. The reason behind collecting seawater samples from the beach of each governorate in the Gaza Strip is to investigate the potential difference in seawater characteristics due to environmental and anthropogenic activities in each governorate and select the best location for the establishment of a freezing-melting desalination plant.

The physicochemical characteristics of these five samples such as pH, EC, TDS, Nitrate, Chloride, Fluoride, Sulfate, Alkalinity, Hardness, Calcium, Magnesium, Potassium, Sodium, Cadmium (total), Copper (total), and Lead (total), were measured, in accordance with standard methods for the examination of water and wastewater [27].

The following equation was used to represent the performance of the freezing-melting in terms of reducing the water constituent's concentrations:

$$\text{Removal}(\%) = \frac{P_1 - P_2}{P_1} \times 100 \quad (1)$$

where Removal % is the removal percentage as a performance indicator; P_1 is the initial value of the parameter, and P_2 is the final value of the parameter.

The seawater samples were poured into an identical flask connected directly to an external stainless steel single-phase freezer (thermally protected-Sichuan Dandy Co., Ltd., 220 Volt, 50 Hz) with an energy consumption of 0.1 kW/h to be crystallized by direct freezing (at -20°C). Concentrated water (rejected) was drained from the freezer, then 200 mL of cold (0°C) double-distilled water was used for washing the spherical ice crystals in order to remove the residual deposited salts and pollutants before allowing the ice to melt at room temperature (25°C) in a capped jar to prevent dry deposition and adsorption of gases and particles (Fig. 1). Then the physicochemical analysis was undertaken on the water produced from three repeated freezing-melting (FM) cycles for each seawater sample. The time of freezing was 80, 50, and 30 min for the 1st, 2nd, and 3rd FM cycles, respectively. In the 1st, 2nd, and 3rd FM cycles, 60, 40, and 20 mL of cold distilled water were used for surface washing of the crystals.

3. Results

Table 1 displays the physicochemical characteristics of the five collected raw seawater samples from the beaches of the five governorates of the Gaza strip.

Significant reductions in water dissolved minerals and constituents were noticed after the first, second, and third FM cycles for the seawater samples. The average water mineral reduction percentages ranged from 39.0% to 45.5%, 49.7% to 52.8%, and 56.0% to 59.0% for the 1st, 2nd, and 3rd FM cycles, respectively. For instance, in the North Gaza seawater sample, after the first FM cycle, the reduction of water minerals and constituents ranged between 20% and 57.5% for fluoride and TDS, respectively. In comparison with the raw sample, after the second FM cycle, the average reduction in reduction in water minerals and constituents was 69.9% and ranged between 40% and 91.2% for fluoride and sodium, respectively. Besides, after the third FM cycle, the reduction of water minerals and constituents was 84.7% and ranged between 60% and 98.1% for fluoride and sodium, respectively. The overall average removal percentage of dissolved minerals and constituents after the 3rd FM cycle for North Gaza, Gaza, Middle area Khan Younis,

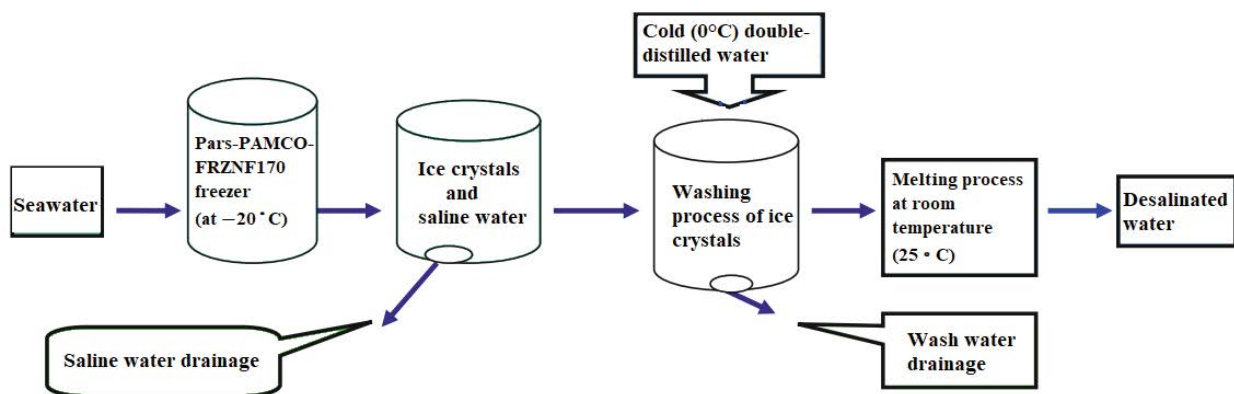


Fig. 1. Flow chart of the freezing-melting process.

Table 1
Results of the physicochemical characteristics tests of row seawater in the five governorates of the Gaza strip

Test	Unit	Result					Average
		North Gaza	Gaza	Middle area	Khan Younis	Rafah	
pH		7.3	7.2	7.3	7.1	7.2	7.2
EC	Micro mho/cm	59,326	59,152	59,231	58,159	58,243	58,822.2
TDS	ppm	42,714	42,589	42,636	42,456	42,517	42,582.4
Nitrate	ppm as NO ₃ ⁻	8.2	8.3	8.8	7.4	7.2	8.0
Chloride	ppm as Cl ⁻	20,798	20,889.5	20,457.9	19,344.8	19,062.3	20,110.5
Fluoride	ppm as F ⁻	1.5	1.6	1.6	1.4	1.4	1.5
Sulfate	ppm as SO ₄ ⁻	2,958.3	2,963	2,999	2,811	3,680	3,082.3
Alkalinity	ppm as CO ₃ ⁻	118	118	119	116	115	117.2
Hardness	ppm as CaCO ₃	6,951	7,094	7,131	6,981	6,963	7,024.0
Calcium	ppm as Ca ⁺⁺	483	473	491	463	451	472.2
Magnesium	ppm as Mg ⁺⁺	1,455	1,436	1,332	1,283	1,278	1,356.8
Potassium	ppm as K ⁺	448	446	451	412	433	438.0
Sodium	ppm as Na ⁺	12,825	12,775	12,875	11,789	11,679	12,388.6
Cadmium	µg/L as Cd	116	117	117	115	114	115.8
Copper	µg/L as Cu	326	327	341	318	314	325.2
Lead	µg/L as Pb	210	213	217	207	204	210.2

and Rafah seawater samples were 84.7%, 85.6%, 87.3%, 86.4%, and 87.6%, respectively. Despite the levels of some water minerals have fulfilled the WHO standards for potable water, such as the nitrate range of (7.2–8.8 ppm) (WHO standard = 50 ppm), the copper range of (314–341 µg/L) (WHO standard = 1,300 µg/L), and the cadmium range of (114–117 µg/L) (WHO standard = 3 µg/L). However, some water minerals still exceeded the recommendation after the 3rd FM cycle, such as the TDS range of (1,566–1,977 ppm) (WHO standard = 300 ppm), hardness range of (568–608 ppm) (WHO standard = 100–300 ppm), chloride range of (19,062.3–20,889.5 ppm) (WHO standard = 200–300 ppm), sulfate range of (2,811–3,680 ppm) (WHO standard = 500 ppm), potassium range of (412–451 ppm) (WHO standard = 3.6–5.2 ppm), magnesium range of (1,278–1,455 ppm) (WHO standard = 25–50 ppm), calcium range of (451–491 ppm) (WHO standard = 0 to 60 ppm), fluoride range of (1.4–1.6 ppm) (WHO standard = 4 ppm), sodium range of (245–276 ppm) (WHO standard < 20 ppm), alkalinity range of (115–119 ppm) (WHO standard = 20–200 ppm), and lead range of (207–217 µg/L) (WHO standard = 10 µg/L). The percentage of produced water volume in each FM cycle ranged between 25.1% and 33.6%, whereas in comparison with the initial seawater sample, the percentage of produced water volume ranged between 2.2% and 2.9% (Fig. 2).

The time of crystallization in the 1st, 2nd, and 3rd freezing cycles was 80, 50, and 30 min, respectively. Furthermore, the total time of freezing for produced water from the 1st, 2nd, and 3rd freezing cycles was 2.7 h. The consumed energy for produced water after the three cycles of freezing was 0.018, 0.022, 0.018, 0.023, and 0.021 kW/L for the North Gaza, Gaza, Middle area, Khan Younis, Rafah seawater samples, respectively (Table 2).

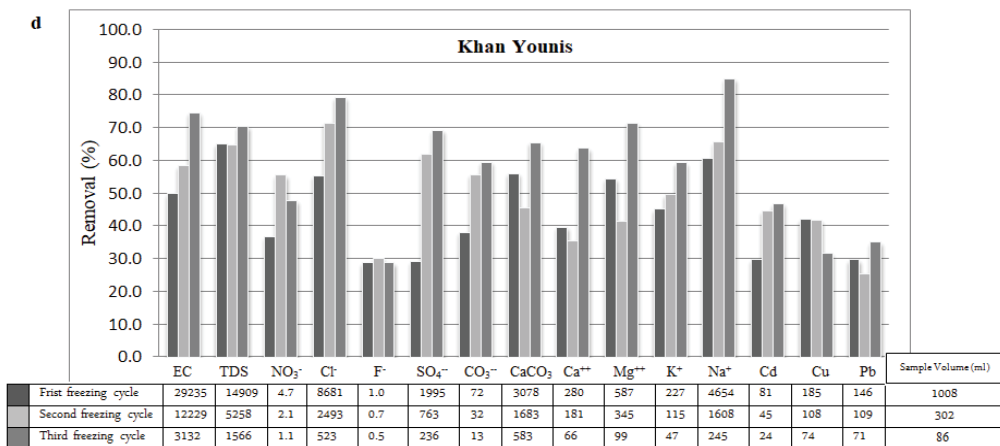
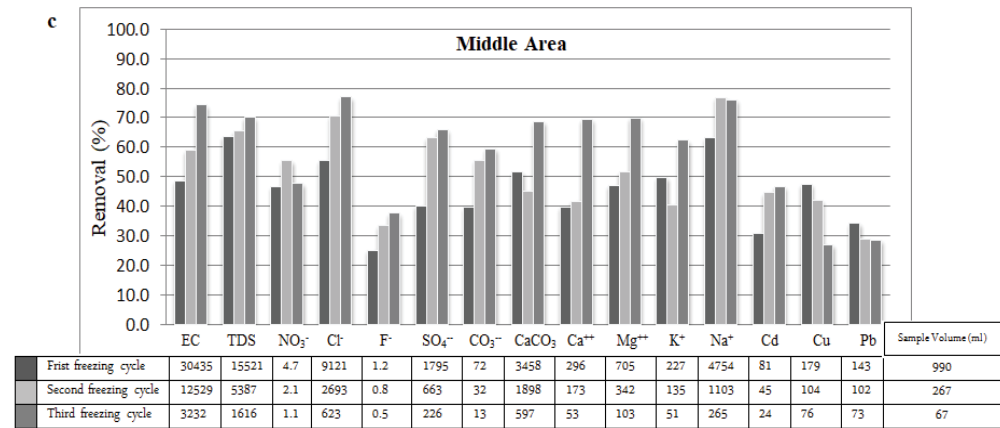
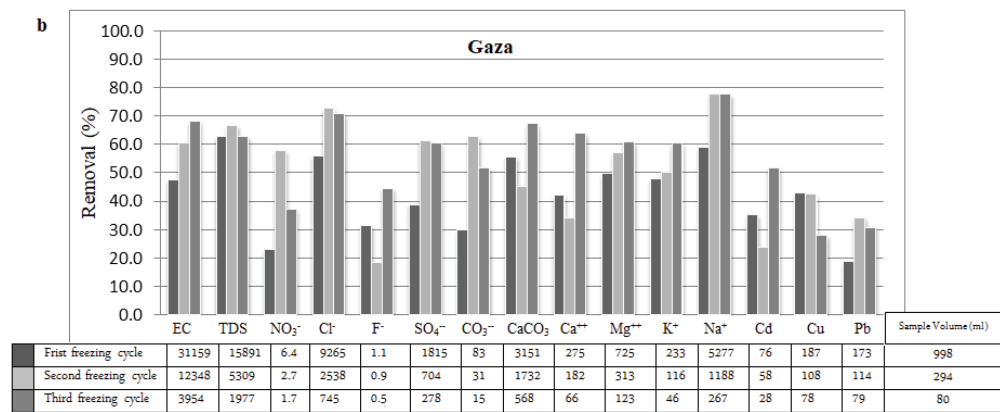
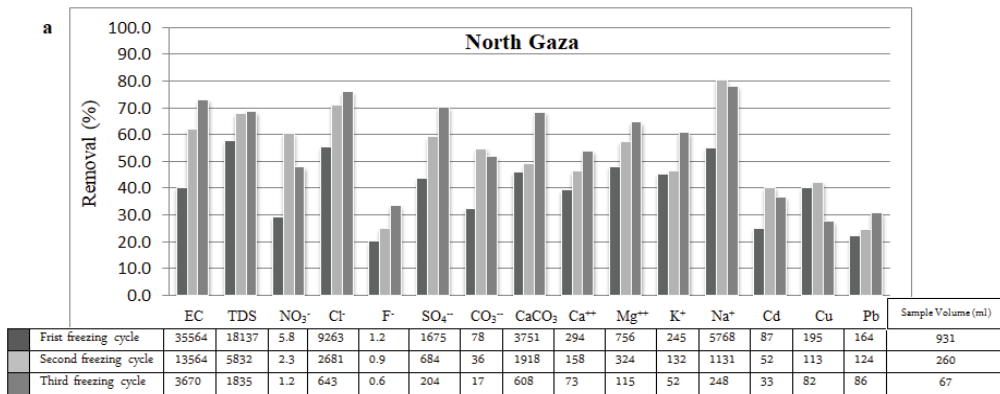
In our study, although direct contact freezing consumed more energy (20 kW h/m³) than the RO (0.4–7 kW h/m³) and

ED (1 kW h/m³), it consumed less energy than the multi-stage flash (MSF) desalination (35 kW h/m³) [10,28] and the freezing melting technique using non-direct contact freezing (450 kW h/m³). Moreover, the high TDS of the salt water utilized in this study (42,456–42,714 ppm) has a considerable impact on energy use [28]. However, the established system is still a basic lab-scale one and requires more improvements and to be tested on a larger scale (Table 3).

4. Discussion

When salty water freezes, the pure water crystallizes, leaving the dissolved organic and inorganic particles (such as salt) in liquid pockets in high salinity brine. Precooking the feed water, crystallization of ice into slush, separation of ice from the brine, washing the ice, and melting the ice are all steps in the traditional freezing process. Although fresh water can be easily recovered from ice where seawater naturally freezes, the engineering required to build and operate a freeze desalination plant is highly complex [31].

Previous research has investigated the FM technique using non-direct contact freezing for fluoride removal [32–34], seawater desalination [5,17], synthetic brackish and saline water [35], and nitrate removal [36]. These studies concluded that solar-assisted solutions might have a lot of potential in this instance. The following strategies toward commercial success of the FM process in the desalination business should be considered: (1) Development of a more straightforward and comprehensive FM technique to be used in desalination, in the instance of the vacuum FM technique, several attempts have already been attempted; (2) Desalination should be investigated using commercially accessible FM techniques used in the food and chemical industries; (3) A complete economic analysis of the FM process to uncover clear economic benefits to the desalination



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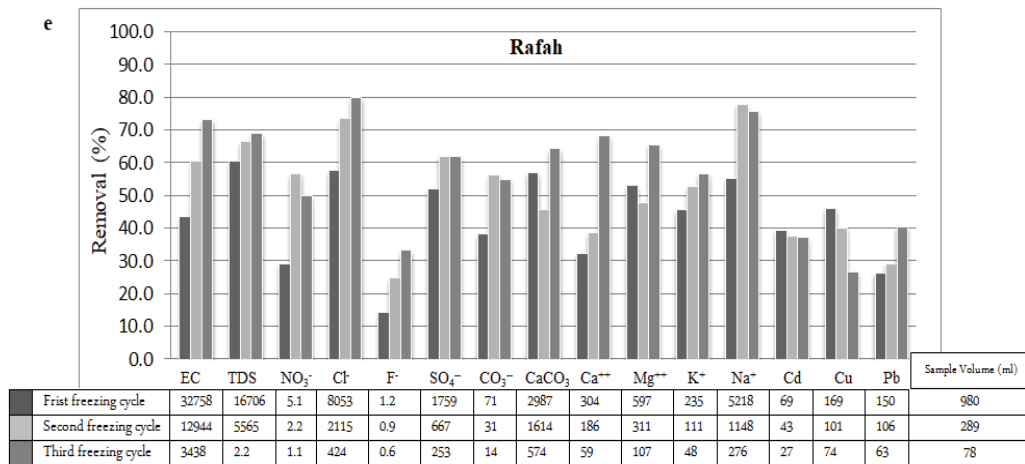


Fig. 2. Removal efficiency for three FM cycles. (a) North Gaza, (b) Gaza, (c) Middle area, (d) Khan Younis, and (e) Rafah seawater sample.

Table 2
Time for each FM cycle of seawater sample and energy consumption (kW/L)

	Seawater Sample				
	North Gaza	Gaza	Middle area	Khan Younis	Rafah
Time of crystallization in 1st freezing cycle (min)	80	80	80	80	80
Time of crystallization in 2nd freezing cycle (min)	50	50	50	50	50
Time of crystallization in 3rd freezing cycle (min)	30	30	30	30	30
Overall time of freezing for produced water (1st, 2nd, and 3rd freezing cycles) per hour	2.7	2.7	2.7	2.7	2.7
Energy consumption for produced water after three cycles of freezing ^a (kW/L)	0.018	0.022	0.018	0.023	0.021

^a0.1 kW/h × 2.7 h × 0.067 L = 0.018 kW/L

Table 3
Energy consumption for desalination techniques from literature, kW h/m³ [5,29,30]

	Multi-stage flash	Electrodialysis	Reverse Osmosis	Freezing Melting (literature)	Freezing Melting in the current study
kW h/m ³	35	1	0.4–7	450	20
Raw water samples TDS, ppm	30,000–100,000	100–3,000	1,000–45,000	37,650	42,456–42,714

business, and run desalination industry-wide campaigns to foster a positive attitude toward FM technology; (4) Development of hybrid techniques by securing the synergy of the processes.

Our study recommended that the FM technique could be used as a pretreatment method for other methods of desalination. Similarly, according to Ahmed et al. (2007), combining RO with a less expensive FM could be a cost-effective way to desalinate salty liquids [37].

In seawater RO systems running at 40%–45% product water recovery and with energy recovery from the high pressure reject stream, the typical energy consumption is

currently at 3–4 kW/m³ [38]. In parametric evaluations of energy consumption and loss in seawater reverse osmosis (SWRO) plants using energy recovery devices, the average power consumed by the high-pressure pump is in the range 5.56–7.93 kW h/m³ [39]. Electrical energy consumption for SWRO with energy recovery is estimated to be around 5.2 kW/m³ [40]. In comparison, the consumed energy for significantly decreasing Mediterranean seawater salinity after the three cycles of freezing using direct contact freezing was 0.018, 0.022, 0.018, 0.023, and 0.021 kW/L for the North Gaza, Gaza, Middle area, Khan Younis, Rafah seawater samples, respectively.

5. Conclusion

The application of FM technology in an area overlooking the Mediterranean Sea with a sunny sky almost throughout the year would be a vital solution to the water scarcity in the Gaza Strip, especially since the utilization of solar energy systems has become widespread. Significant reductions in water dissolved minerals and constituents was noticed after the 1st, 2nd, and 3rd FM cycles for the seawater samples. Despite the levels of some water minerals having fulfilled the WHO standards for potable water, some water minerals still exceeded the recommendation after the third FM cycle. Although the FM technique using direct contact freezing in this study consumed more energy than the RO and ED, it consumed less energy than the MSF and FM technique using non-direct contact freezing. The high TDS level of the salt water utilized in the current study has a considerable impact on energy use. Therefore, the FM technique could be used as a pretreatment method prior to other methods of desalination. Further investigations of the applicability of the FM technique in seawater desalination on a large scale are recommended.

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Competing interests

The authors declare no competing interests.

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