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Original Research Article

Roof-Harvested Rainwater Quality Analysis and Freeze Treatment Using Progressive Freeze Concentration

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ABSTRACT

Rainwater can be a safe and sustainable source of drinking water. Progressive freeze concentration has been identified as a suitable freeze treatment process for treating rainwater in drinking water. In this work, the harvested rainwater quality was evaluated based on atmospheric conditions. The subsequent purification process was carried out and reported on the respective supercooling phenomena and the effect of operating parameters. Statistical analysis found the total dissolved solids of rainwater to negatively correlate with rainfall amount ($r = -0.32$), and the range was found to be workable for our progressive freeze concentration system. The supercooling effect in the falling film freeze treatment system was found to be non-existent, showing rainwater can be purified to a relatively high purity without excessive precaution to prevent contamination caused by supercooling. Experimental results and statistical analysis showed that higher circulation time (26 min) and lower rainwater total dissolved solids (6 ppm) improved the purification efficiency of rainwater by giving a higher concentration factor (3.4). A simple energy consumption analysis also signifies that this system consumes significantly lower energy compared to distillation. This work can serve as a preliminary study for future research to explore freeze treatment as a viable process to produce drinking water from rainwater.

KEYWORDS

Water purification, Roof-harvested rainwater, Progressive freeze concentration, Drinking water, Antecedent dry days, Supercooling, Total dissolved solids, Circulation time.

INTRODUCTION

Drinking or potable water can come from various sources, including surface water like rivers and lakes, groundwater from wells and aquifers, treated seawater through desalination and harvested rainwater. This paper will focus on producing drinking or potable water from harvested rainwater. There are numerous methods for purifying rainwater for use in potable (drinking and cooking) and non-potable (irrigation and toilet flushing) applications. Of those methods, only some like media filtration (MF), reverse osmosis (RO) and boiling are suitable for use in a typical household. MF uses media like sand and activated carbon to physically

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remove particles and suspended solids from rainwater at the cost of a large footprint and a high amount of backwash water. In contrast, a semi-permeable RO membrane prevents dissolved solids from passing through and produces pure water on the other side of the membrane. However, RO membranes tend to be more expensive and require more care compared to other techniques. On the other hand, boiling does not remove anything from the rainwater but sterilises it by killing microorganisms. Despite the ease of use, boiling water requires a large amount of energy and does not remove any toxic substances from the water.

In a typical rainwater harvesting system (RWHS), filtration and disinfection are the two processes used to purify rainwater [1]. Turbid water high in TSS usually contains a high level of bacteria. Therefore, filtration can be an efficient way to decrease the level of biological contamination in water. However, filtration does not truly kill the bacteria in water, and without further treatment, it is generally considered not safe to drink water by filtration alone. To ensure water is truly safe for drinking, disinfection is necessary. It can be achieved by either chlorinating the water in conventional water treatment plants or irradiating the water with ultraviolet radiation in household units. In a recent study [2], disinfection of water using solar energy (SODIS) managed to achieve the required effect in 3 hours by raising the water temperature from 24.3 to 66 °C using a SODIS prototype enhanced with a parabolic solar collector to concentrate solar energy onto the feed water and heat storage chamber to buffer the effects of cloudy weather during operation.

Recently, progressive freeze concentration (PFC) has been studied as a potential water treatment technique. Pure ice crystals are produced when the contaminated water is progressively frozen in PFC, due to the formation of the crystal lattice, causing molecules or ions apart from water to be expelled and remain in the liquid fraction. The pure ice (solid phase) can then be easily separated from the liquid fraction and thawed to obtain pure water. As the latent heat of fusion of water is only about one-seventh of the latent heat of vaporisation of water, theoretically only 334 kJ of energy is required to produce 1 kg of water using PFC as compared to 2,260 kJ of energy needed for distillation [3].

For example, PFC was utilised [4] to lower landfill leachate turbidity by as much as 83%. This implies that since turbidity is frequently used as an analogue for TSS, PFC might also be utilised to lower TSS in rainwater. 50 – 70% salt removal efficiency and $K = 0.2 – 0.4$ in brine (10 – 60 g/L) were achieved with higher salt removal efficiency and lower K at lower brine concentration [5], and suggested that PFC is better suited for feed solution with lower concentration. It makes rainwater, a dilute solution of various contaminants, especially suitable for purification using PFC. Rainwater is a unique type of feed compared to other feed solutions studied in the PFC experiment, in the sense that the concentration of the compounds of interest (contaminants) is in ppm range whereas typical feed solutions like fruit juices and brine have solutes that are much more concentrated in percentage range.

Before designing and running experiments using PFC to freeze treat the rainwater, the harvested rainwater quality has to be evaluated based on the atmospheric conditions to decide on the working range of the length of the dry period preceding each rainy event (termed antecedent dry days, ADD) and total rainfall for the PFC design. Typically, the concentration of contaminants on the roof surface increases with ADD, which in turn causes the rainwater runoffs to become more contaminated [6]. Shaheed and Mohtar [7] showed that when using a first flush system to discard the first 3 mm of rainwater in Bandar Baru Bangi, Malaysia, ADD of above 3 days increased concentration of various contaminants like pH, dissolved oxygen, biochemical oxygen demand, chemical oxygen demand, total suspended solids, ammoniacal nitrogen and E. Coli. Thus, it is important to geographically observe the effect of ADD on the quality of the roof-harvested rainwater of the southern region of Malaysia, which will be used in our study.

In terms of total rainfall, a larger rainfall will mostly ensue in a lower pollutant level in the roof-harvested rainwater because there will be a higher volume of rainwater capable of solvating a limited quantity of pollutants on the surfaces of roofs [8]. However, Yan et al. [9]

found that the total rainfall is of negligible importance. Therefore, in this study, the total rainfall was related to the total dissolved solids (TDS) to determine whether the total rainfall actually influences the rainwater quality in this region.

In the designed PFC process as a freeze treatment for rainwater purification, supercooling is a phenomenon that needs to be addressed cautiously to ensure the lowest contaminants in the ice phase. Supercooling of water is defined as water being in the liquid phase below its usual freezing point, even if a more stable state, such as solid ice, may exist [10]. Supercooling can produce impure ice by the inclusion of liquid pockets in the mother liquor during the rapid crystallisation of the metastable subfreezing liquid phase. A study published in 2023 [11] used falling-film PFC to concentrate commercial beer. The study used different freezing temperatures to observe PFC performance, but no temperature data were collected to observe if any supercooling of water occurred during PFC of aqueous solution using a falling-film experimental setup. While supercooling has been shown to occur in solutions agitated with a stirrer, previous works on falling-film PFC have not exhibited conclusive evidence of supercooling. Therefore, this work aims to provide definitive observation (or lack thereof) of supercooling during falling-film PFC experiments by monitoring temperature changes during the PFC process.

Once the rainwater quality and the supercooling phenomenon have been addressed, the investigation of the effect of operating parameters shall be carried out to demonstrate the feasibility and performance of the process. Our previous work in 2023 [12] managed to decrease rainwater TDS by up to 96 % using PFC alone. However, this work did not explain how standard operating parameters like circulation time and initial rainwater quality affect the performance of PFC. The relationship between operating parameters and PFC performance involving other feed solutions cannot be generalised to freeze crystallisation of rainwater. Thus, this study serves to explore the relationship between circulation time, feed rainwater quality and PFC performance in roof-harvested rainwater purification.

MATERIALS AND METHODS

In this study, rainwater was harvested, measured and analysed. The acquired data were then used to determine some statistical characteristics to find relevant relationships. The roof-harvested rainwater was then freeze-treated for drinking purposes using PFC. The overall process flow is shown in Figure 1. The specific methods for each investigation and analysis are detailed in the following sections.

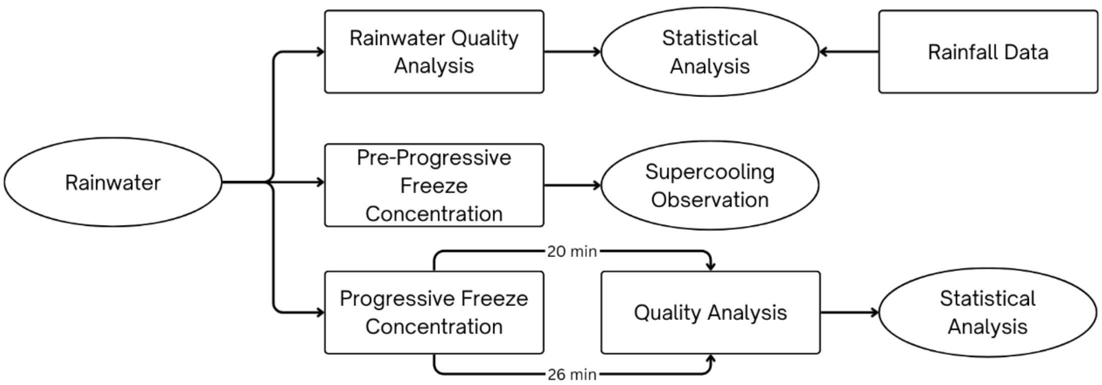

Figure 1. Overall process flow

Rainwater harvesting

Rainfall data and rainwater samples were gathered between October 2023 and May 2024. The roof (clay tiles) of the N12 building at Universiti Teknologi Malaysia (UTM) in Johor Bahru, Malaysia, was used to collect roof-harvested rainwater (Figure 2). For rainfall amount measurement, rainwater was collected using a polypropylene basin (inner diameter of 22.2 cm and catchment area of 387.1 cm^2) and measured using a measuring cylinder to the nearest 5 ml. Serving as a simplified rain gauge in this experiment, the basin must be kept at least 1.35 m above ground to reduce wind turbulence near the ground and away from nearby tall structures or trees to ensure accurate measurement [13]. The rainfall was calculated by dividing the volume of rainwater by the basin area. Each rainfall was tabulated and supplemented with the statistics of the nearest station (JPS Taman Aman) available from the website of Jabatan Pengairan dan Saliran Malaysia [14].

Figure 2. Rainwater harvesting system in the N12 building of UTM

Rainwater quality analysis

Because TDS measurement via the electrolytic conductivity method is inexpensive, simple, and repeatable, it was chosen for this investigation as a function of overall rainwater quality rather than the standard laboratory analysis of the contaminants found in rainwater [15]. Because pure water is very low in conductivity, a high value of TDS derived from a high value of conductivity means a high concentration of dissolved charged species in water. A portable TDS meter and a portable pH meter were used to measure the TDS and pH of rainwater, respectively. The Macherey-Nagel PF-12Plus photometer was used to measure colour and turbidity. All measurements were done at 25 ± 1 °C.

Care must be taken during photometric measurements of the purge water sample, as small air bubbles are formed on the wall of the glass cuvette (Figure 3). These bubbles can affect the readings of the photometer and should be removed by gently swirling the cuvette. Interestingly, no air bubbles formed for thawed ice at room temperature. In addition, two water samples (roof-harvested rainwater and tap water) were sent to an external accredited laboratory for further water quality analysis in order to identify the parameters which were not within the national drinking water standard.

Figure 3. Air bubbles formed on the wall of the glass cuvette

Rainwater statistical analysis

Considering a mass balance on a roof used to harvest rainwater, as the number of antecedent dry days (ADD) increases (i.e., in the longer period of dry days), the amount of contaminant deposited on the roof should increase, assuming the rate of deposition is constant. When a rainfall event does occur, higher rainfall causes a larger volume of rainwater to dissolve a finite amount of contaminant deposited on the roof. Therefore, the hypothesis is that higher rainfall produces rainwater with a lower amount of contaminants and lower TDS. Shorter ADD prior to the rainfall event should also produce rainwater with lower TDS due to shorter time available to deposit contaminant on the roof prior. Thus, Pearson correlation coefficient (r) derived from a simple linear regression (SLR) model calculated using the CORREL function in Microsoft Excel, was used to determine the strength of the relationship between rainfall amount, ADD and rainwater TDS [16]. If the value of r is greater than 0.7, a strong linear relationship exists, whereas if r is less than 0.3, no or a very weak linear relationship exists. The significance of the correlation was calculated using a t-test, shown in eq. (1) where r is the Pearson correlation coefficient and N is the sample size.

$$t = \frac{r \times \sqrt{N-2}}{\sqrt{1-r^2}} \quad (1)$$

In this paper, the *p*-value (T.DIST.2T function in Microsoft Excel) of less than 0.05 was used as a basis to reject the null hypothesis. Distributions of the data were visualised and analysed using box plots. Skewness and excess kurtosis were calculated using the SKEW and KURT functions, respectively, in Microsoft Excel to verify the normality of the distributions. The correlations were re-examined using Spearman's rank correlation coefficient (r_s) for non-normal data. The value of r_s was calculated using the same method as r described earlier, after converting the lists of data into lists of ranks using the RANK.AVg function in Microsoft Excel. By assuming that the amount of pollutant that may be dissolved by rainwater during a storm event relies on the duration of rainfall and the initial concentration of pollutant available, it is possible to approximate the quality of rainwater runoff [17] numerically. Sea salts (Na^+, Cl^-, Mg^{2+} and K^+) accounted for the majority of the dissolved substances in rain [18], and the concentration of these ions drops as one moves farther inland from the shore. However, the majority of Ca^{2+}, NH_4^+, SO_4^{2-}, HCO_3^- and NO_3^- ions originated from terrestrial sources such as dust and human-caused emissions. This observation suggests that the ionic composition of rainwater depends on the geographical location of the rainfall event.

Progressive Freeze Concentration experimental setup

PFC experiments in this work were carried out using a commercial ice maker, the HICON HZB-60FAB, with a standard vapour-compression refrigeration system with R290 refrigerant (propane) to lower the temperature of the cooled surface made from stainless steel to a temperature below the water freezing point. During the PFC experiment, the feed solution was introduced using an on-board pump and circulated using a different pump. Figure 4 shows a schematic diagram of the operation of the ice maker.

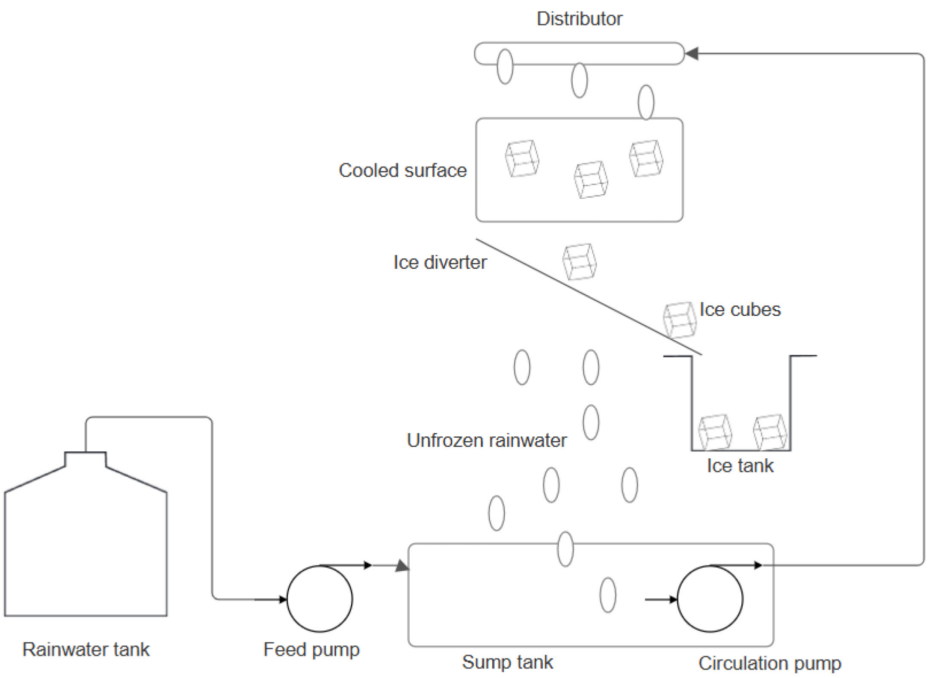

Figure 4. Schematic diagram of the operation of the ice maker

The circulating solution cooled down gradually when flowing down on the cooled surface, eventually reaching the freezing point of water. At that point, ice started to form on the cooled surface while the circulation pump continued running until an internal timer stopped the pump when a cycle was completed. The cooled surface was heated by hot refrigerant to partially thaw the ice and detach it from the cooled surface. The ice cubes were then directed to an ice tank via the ice diverter. Once the cooled surface was free of ice, the circulation pump resumed circulation to initiate the next cycle.

Investigation of the supercooling factor

Water supercooling in PFC is undesired since it will cause fractal or treelike ice dendrites to grow rapidly and contaminants to be trapped and included in the growing ice crystal lattice, lowering the quality of the generated ice. Nonetheless, certain plant and animal species depend on it to keep deadly ice crystals from forming and rupturing their cells so that they can survive the subfreezing temperatures during winter. In the context of this research, supercooling of water is defined as water being in the liquid phase below its usual freezing point, even if a more stable state, such as solid ice, may exist [10]. Lining the cooled surface with pure water to form ice [19] before feed solution is introduced to the surface [20], the use of ice-nucleating protein [21], and holes on the cooled surface [22] are some of the strategies that have been suggested to avoid supercooling in PFC. To the authors' knowledge, no technique for preventing supercooling in falling-film PFC equipment has been put forth to date [23]. This is most likely because the equipment circulating flow is inherently more turbulent compared to other types of PFC setups, thus preventing supercooling.

To monitor temperature change during the experiment, the sump of the circulating fluid housed a calibrated temperature sensor (ISOLAB), which was monitored every 30 seconds. A graph of temperature against time was plotted throughout the experiment. Supercooling was determined to have occurred if the graph showed a characteristic dip below the freezing point of water. Distilled water and roof-harvested rainwater were used as the feed solution to replicate the experiment. After each experimental run, a dilute detergent solution was used to clean the equipment to prevent microbial growth.

Parametric study of Progressive Freeze Concentration

If the roof-harvested rainwater is clean enough and the target use of the rainwater is not in critical applications, it may not require any water treatment prior to using it. In reality, roof-harvested rainwater is usually treated minimally, even for non-potable uses, due to the variability of rainwater quality. The use of green roofs combined with artificially constructed wetlands with aquatic plants was proposed to treat roof-harvested rainwater for non-potable applications [24].

Figure 5. Stainless steel cooled surface

On the other hand, additional purification steps are necessary if the roof-harvested rainwater is intended for drinking. To investigate the effects of circulation time, every batch of rainwater was divided into two portions to be circulated for 20 minutes and 26 minutes, with five cycles in each set.

The stainless steel cooled surface (**Figure 5**) can produce 44 ice cubes every cycle. Purified rainwater, feed rainwater and purge (the concentrated, unfrozen fraction of the rainwater at the end of the experiment) were assessed for TDS, pH, colour, turbidity, and volume. The formed ice was thawed using a hotplate magnetic stirrer (Ingenieurbüro CAT M 6).

Performance analysis of Progressive Freeze Concentration

While longer circulation time produces bigger ice per cycle, the increase in ice size does not increase proportionally to the increase in time. Therefore, it is hypothesised that overall ice output per unit time (yield) is expected to be lower at longer circulation time. Rainwater quality is not expected to affect yield. Previous PFC studies relied on a few common measures to quantify the separation efficiency of PFC, such as effective partition coefficient (K), removal efficiency (RE), and concentration factor (CF). Using PFC for a dilute solution like rainwater, the concentration of ice does not vary as much as the purge does with different feed concentrations. Therefore, K and RE are expected to be very similar for different initial rainwater TDS, unlike CF. Longer circulation time produces higher purge TDS due to more ice formation, concentrating TDS in the purge, resulting in higher CF. The formulae for these three are defined in the next section. Since each batch of rainwater sample was experimented on twice under the different effects of circulation time (20 min and 26 min), the experimental data were analysed using a paired-sample t-test with Analysis ToolPak (t-test: Paired Two Sample for Means) in Microsoft Excel, while the SLR model was used to analyse the effects of feed rainwater quality. Yield, partition coefficient K, removal efficiency RE, concentration factor CF and energy consumption were quantified with equations (2) to (5).

$$Yield\ [\frac{ml}{h}] = \frac{Volume\ of\ purified\ rainwater\ [ml]}{Time\ taken\ [h]} \tag{2}$$

$$K = \frac{TDS\ of\ purified\ rainwater\ [ppm]}{TDS\ of\ purge\ [ppm]} \tag{3}$$

$$\mathrm{RE}\ [\%] = \frac{(TDS\ of\ feed - TDS\ of\ purified\ rainwater)}{TDS\ of\ feed} \times 100\ \% \tag{4}$$

$$\mathrm{CF} = \frac{TDS\ of\ purge\ [ppm]}{TDS\ of\ feed\ [ppm]} \tag{5}$$

$$Energy\ consumption\ [\frac{kJ}{kg}] = \frac{Rated\ power\ [W] \times 3.6\ kJ/Wh}{Rated\ capacity\ [\frac{kg}{h}]} \tag{6}$$

RESULTS AND DISCUSSION

Upon completion of the methodologies, the data were collected and analysed to generate relevant findings. The rainfall data and the respective analysis, as well as the findings from the PFC of the roof-harvested rainwater into drinking water, are presented in this section.

Distribution of rainfall data

Partial rainfall data are shown in Table 1 and displayed as box plots in Figure 6. The ADD for the majority of rainfall occurrences was relatively brief, with a mean of 2.4 days and a median of 1 day. Given that Malaysia is a tropical nation, this is hardly unexpected. The rainfall amount was 17.4 mm on the median and 23.6 mm on the mean. With a median and mean of 14.5 ppm and 16.2 ppm, respectively, the TDS of each rainwater sample were below 50 ppm, which was the municipal water TDS.

Table 1. Snippet of rainfall data

Date	From	To	Rainfall (rain gauge) [mm]	Rainfall (DID data) [mm]	Rainfall (average) [mm]	TDS [ppm]	ADD
30/12/23	0630H	2000H	1.7	5	3.4	27	2
31/12/23	1630H	1700H	2.1	2	2.1	29	1
1/1/24	1230H	2300H	7.2	55	31.1	35	1
3/1/24	1530H	1600H	1.6	3	2.3	18	2
4/1/24	0330H	2200H	40.8	48	44.4	14	1

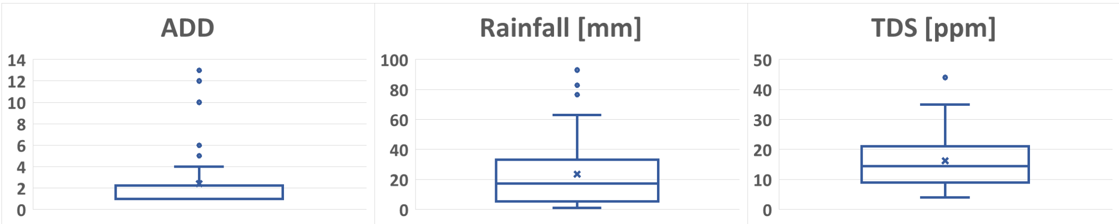

Figure 6. Box plots of rainfall data (ADD, rainfall and TDS)

All three distributions of ADD, rainfall and TDS showed positive skewness (skewness > 0) and leptokurtic distribution (excess kurtosis > 0). Graphically, the box plots show that the value of the mean (cross) was greater than the median (horizontal line inside the box). As a normal distribution has skewness and excess kurtosis of 0 [25], all three distributions were not normally distributed, with ADD and TDS showing the most and the least deviation, respectively.

Effects of Antecedent Dry Days and Rainfall on the quality of roof-harvested rainwater

Table 2 shows the summary of rainfall data analysis. TDS was found to be not correlated ($r = 0.076$ and $r_s = 0.001$) with ADD (Figure 7) and weakly negatively correlated ($r = -0.320$, $p = 0.013$ and $r_s = -0.386$, $p = 0.002$) for Pearson r and Spearman r_s, respectively, with rainfall amount (Figure 8). The relationship between TDS and the rainfall amount was considered significant as the p-values were less than 0.05.

Table 2. Summary and analysis rainfall data

Parameter	Median	Mean	Skewness	Excess kurtosis	Pearson r	Spearman r_s	Remark
ADD	1	2.4	2.63	6.57	0.076	0.001	No correlation with TDS
Rainfall	17.4 mm	23.6 mm	1.28	1.64	−0.320	−0.386	Weak correlation with TDS

TDS	14.5 ppm	16.2 ppm	0.82	0.38	-	-	-

Overall, the relationships were weak, and other factors such as the location and nature of roof surfaces and storage tanks, length and intensity of the rainfall events, concentration of greenhouse gases and air pollutants in the atmosphere may affect the quality of the roof-harvested rainwater to various degrees. The list of these factors was not exhaustive and beyond the scope of this study.

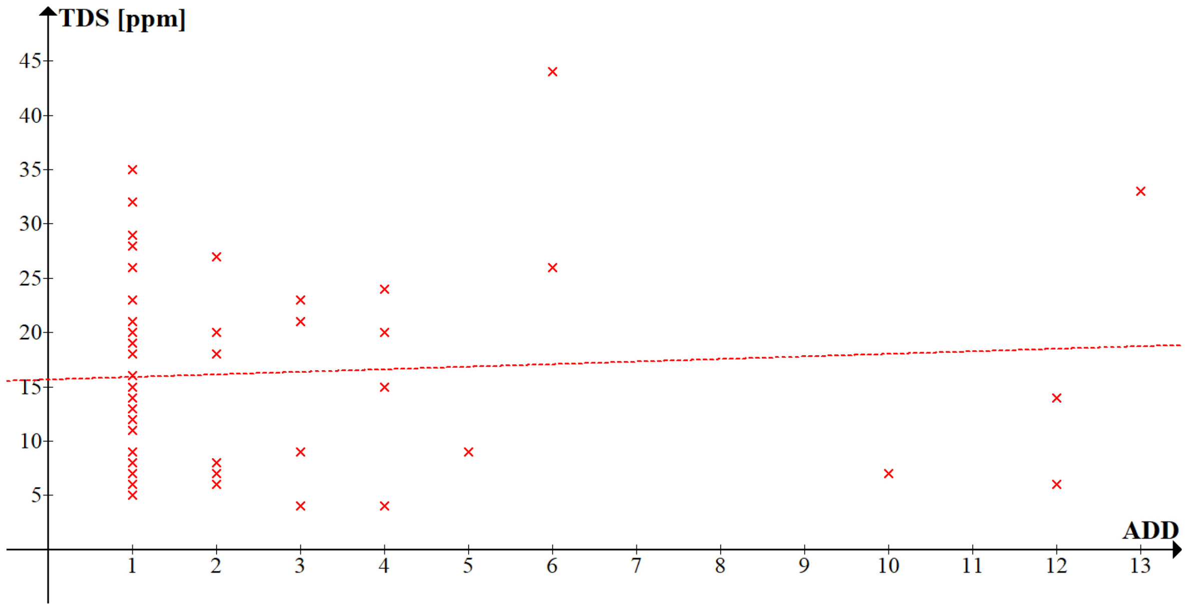

Figure 7. Graph of TDS of rainwater against ADD

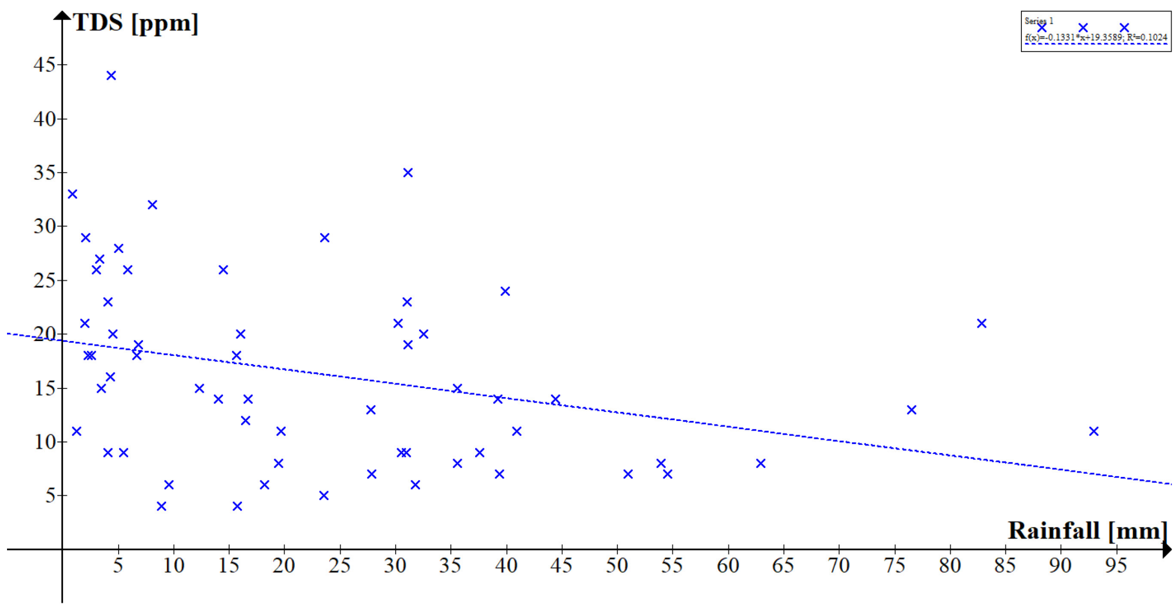

Figure 8. Graph of TDS of rainwater against rainfall amount

Table 3 shows the partial results of the water quality analysis of rainwater and tap water in comparison with the national drinking water standard **[26]**. From the results, the quality of roof-harvested rainwater and tap water is within the water standard, except for free residual chlorine in rainwater and fluoride in tap water. Tap water generally has a higher concentration of dissolved ions, notably chloride, sodium and sulphate, compared to rainwater (**Figure 9**).

Bacterial growth is absent in tap water due to the presence of residual chlorine. No toxic heavy metal was detected in either of the water samples.

Table 3. Partial results of the water quality analysis

Parameter	Rainwater	Tap water	Standard
pH	6.9	7	6.5-8.5
Colour [TCU]	10	<5	15
Turbidity [NTU]	1.1	0.1	2
Aluminium [mg/L]	0.03	0.03	0.2
Chloride [mg/L]	1	17.7	250
Copper [mg/L]	0.01	0.01	1
Fluoride [mg/L]	<0.1	1.1	0.6
Free residual chlorine [mg/L]	<0.1	0.6	> 0.2
Hardness as $CaCO_3$ [mg/L]	39.2	32.7	500
Iron [mg/L]	0.02	0.02	0.3
Magnesium [mg/L]	0.56	1.1	150
Manganese [mg/L]	0.01	0.01	0.1
Mercury [mg/L]	<0.001	<0.001	0.001
Nitrate as N [mg/L]	1.5	2	10
Sodium [mg/L]	1.6	5.8	200
Sulphate [mg/L]	2.4	6.4	250
Zinc [mg/L]	0.05	0.02	3
Total coliform (multiple tube)	2	<1.8	10
Total E. coli	<1.8	<1.8	Absent

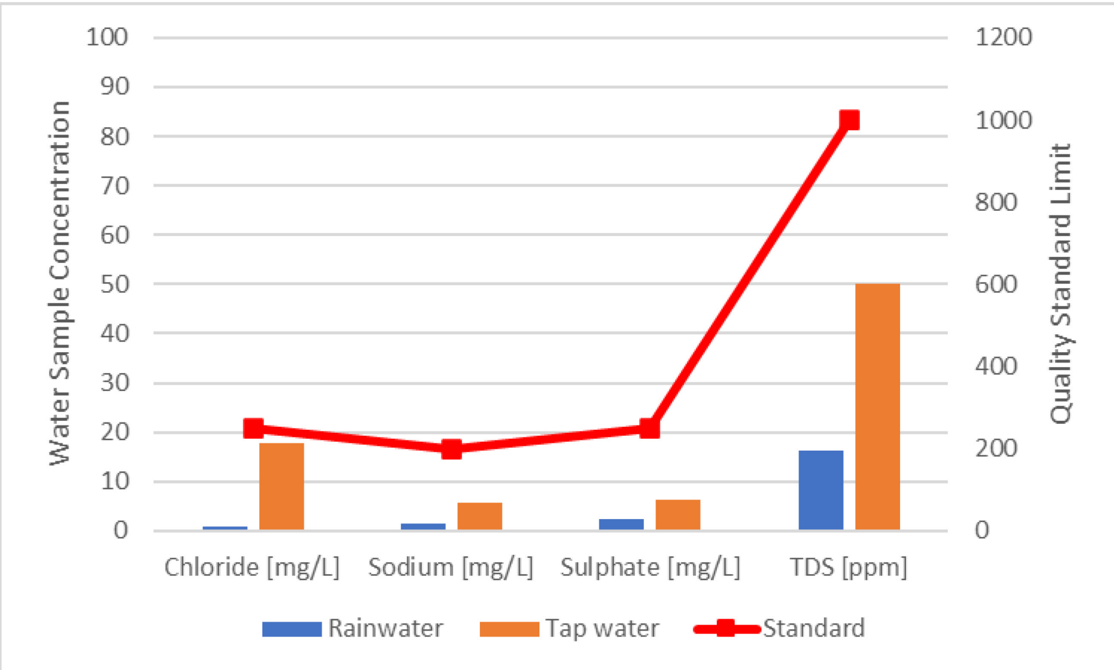

Figure 9. Graph of ionic concentration in rainwater and tap water samples

Provided the roof was in good condition, zinc ion level from roof-harvested rainwater collected from galvanised metal roofs in Austin, United States, was not higher than that of other types of roofs [27], despite the fact that metallic roofs tend to leach metallic ions into roof-harvested rainwater because rainwater is somewhat acidic. Heavy metals such as Cr, Ni, Cu, Pb, Mn, Co, Zn, and Cd ions were detected in roof-harvested rainwater samples collected in Yatta, Palestine, with Pb, Cr, Ni and Zn ions in some samples exceeding WHO limits [28]. Roof-harvested rainwater from concrete and ceramic tile roofs generally has better overall water quality compared to asphalt and galvanised metal roofs [29] in Shanghai, China. Rainfall amount and rainfall intensity have a negative correlation with various rainwater contaminant levels, −0.44 to −0.31 and −0.36 to −0.21, respectively. Simply put, rainwater quality improved with increasing rainfall amount and intensity. Interestingly, there was no significant correlation between ADD and rainwater quality.

Supercooling in falling-film Progressive Freeze Concentration

Solid, clear ice crystallised gradually underneath the falling film of circulating solution as soon as a few minutes after the start of the experiment, as the temperature of the stainless steel cooled surface (Figure 10) reached below the freezing point of water.

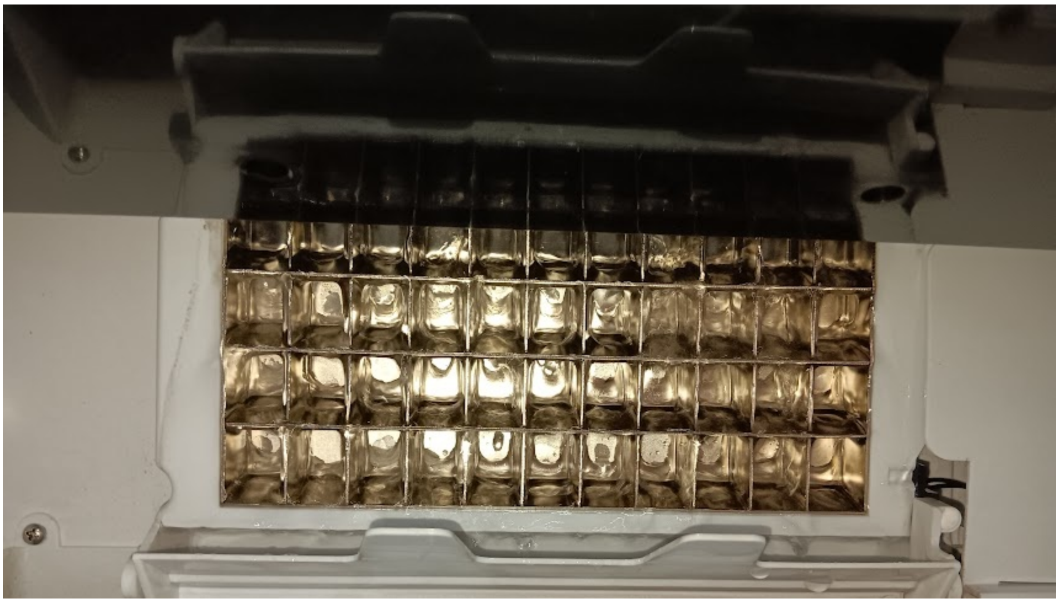

Figure 10. Initial crystallisation of ice

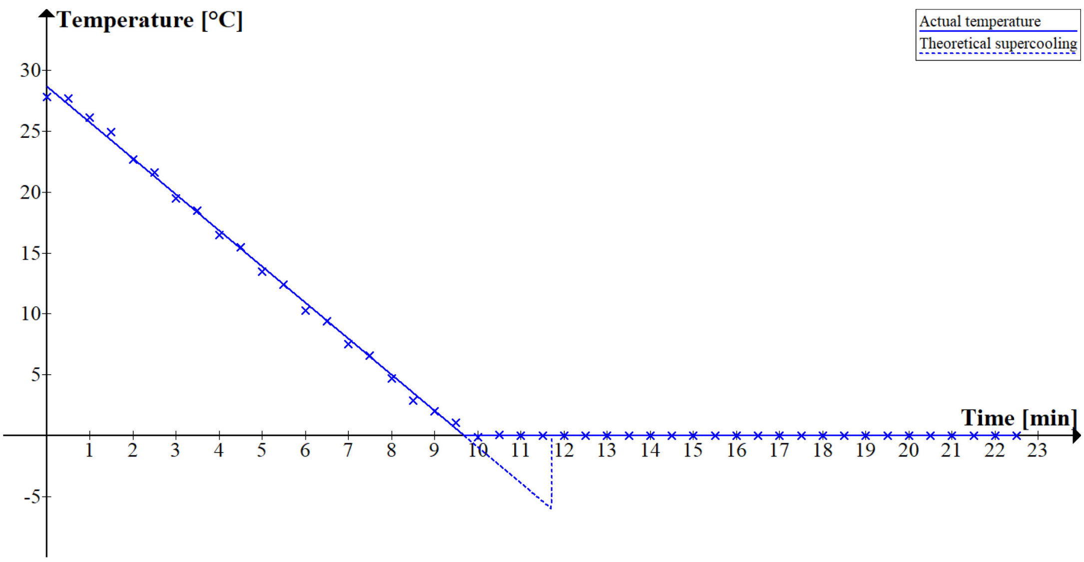

Figure 11. Graph of temperature against time during freezing of distilled water

As seen in **Figure 11**, the temperature of the circulating solution decreased linearly with time. It never fell below the freezing point before ice formed, indicating that neither distilled water nor roof-harvested rainwater experienced supercooling during cooling and ice formation. If supercooling had occurred during the experiment, a characteristic dip (shown in dotted line) would appear in the actual temperature graph. Supercooling might not happen in a falling-film PFC configuration, in contrast to other setups, most likely because of the way the fluid was circulated in the former.

In a falling-film equipment, the circulating fluid became turbulent and aerated when it was forced through the distributor above the cooled surface and flowed in a thin film of a few millimetres, hence the name falling-film. Air bubbles entrapped in the falling film seemed to prevent supercooling by acting as ice-nucleating sites **[30]**. As opposed to the falling-film configuration, the traditional PFC system that uses stirrers was unable to produce enough agitation to encourage heterogeneous nucleation. More PFC studies should be done with falling-film equipment to replicate these observations.

While supercooling has been widely cited as the leading cause of impure ice, several other theories offer alternative explanations for how impurities get included in ice. In the v/k criterion theory, where v is the maximum allowable growth rate of ice and k is the mass transfer coefficient, pure ice crystals can form provided the value of v is not exceeded **[31]**. The value of v depends on the concentration of impurities in the bulk fluid and the mass transfer coefficient k. This theory also explains that forced convection can improve crystal purity as the value of k increases with stronger circulation of the bulk fluid. However, this theory is limited due to its temperature independence and does not take into account the effects of heat transfer. Various derivations and forms of the theory can be found in **[32]**. On the other hand, in the gradient criterion theory, pure ice crystals can form as long as constitutional supercooling does not occur by having the real temperature gradient higher than or equal to the equilibrium temperature gradient **[31]**. The real temperature gradient is a function of heat transfer coefficient, heat conductivity and temperature of bulk fluid, while the equilibrium temperature gradient is a function of linear gradient in the phase diagram, crystal growth rate and diffusion coefficient.

Like the v/k criterion, these theories do not predict the separation efficiencies given process parameters, as they mainly serve to provide a theoretical framework of how impurities are incorporated during the crystallisation process. Lastly, in the inclusion migration theory, pure ice crystals can form as long as the crystal growth rate is lower than the migration rate of inclusion, which is a function of diffusion coefficient, concentration at the crystallising side of the inclusion and temperature gradient. More detailed explanations of the various theories can be found in **[31]**. The theories described here are not exhaustive and may be helpful in models to describe PFC under different circumstances.

Effects of Circulation Time

Table 4. Overview of experimental data

Parameter	TDS [ppm]	pH	Colour	Turbidity [NTU]	Volume [ml]	Yield [ml/h]	K	RE [%]	CF
Feed	14	6.76	< 25	2					
Purified rainwater (20 min)	< 1	6.19	< 25	1	1,590	970	< 0.024	> 93	
Purified rainwater (26 min)	< 1	6.12	< 25	2	1,830	840	< 0.021	> 93	
Purge (20 min)	42	7.12	28	2	890				3.0

Purge (26 min)	48	7.13	32	2	850	3.4

Table 4 displays a summary of the experimental data. By limiting the incorporation of foreign ions during the growth of ice crystals, PFC significantly reduced the TDS of rainwater.

Purge or concentrate was found to have higher level of TDS and colour, suggesting that the coloured organic materials dissolved in the rainwater were distributed unevenly between solid ice phase and liquid purge phase, attaining separation of contaminants in rainwater according to mass balance, since contaminants must be concentrated in purge phase, even if no discernible change was seen in colour or turbidity between feed and purified rainwater. Since it was not possible to measure the purified rainwater TDS due to the TDS meter detection limit (< 1 ppm), the values of RE and K for both circulation times were given as ranges in Table 4.

Figure 12 shows that the yield of 20 min circulation time is 15.0% higher than 26 min ($p < 0.001$). Although a longer circulation time did increase the mass of ice formed, the increase in mass did not scale proportionally with the increase in time. As ice increased in thickness, the rate of heat transfer decreased, making any increase in circulation time a diminishing return in the increase in mass of ice. Therefore, the yield decreased for longer circulation time. Meanwhile, Figure 13 shows that the CF of 26 min circulation time is 15.0 % higher than 20 min ($p = 0.001$). This result means that longer circulation time can produce a purge with higher concentration but lower yield of ice. Since the ideal circulation time varies depending on the experimental setting and feed solution, it should be assessed case-by-case in pilot experiments before scaling up to industrial applications.

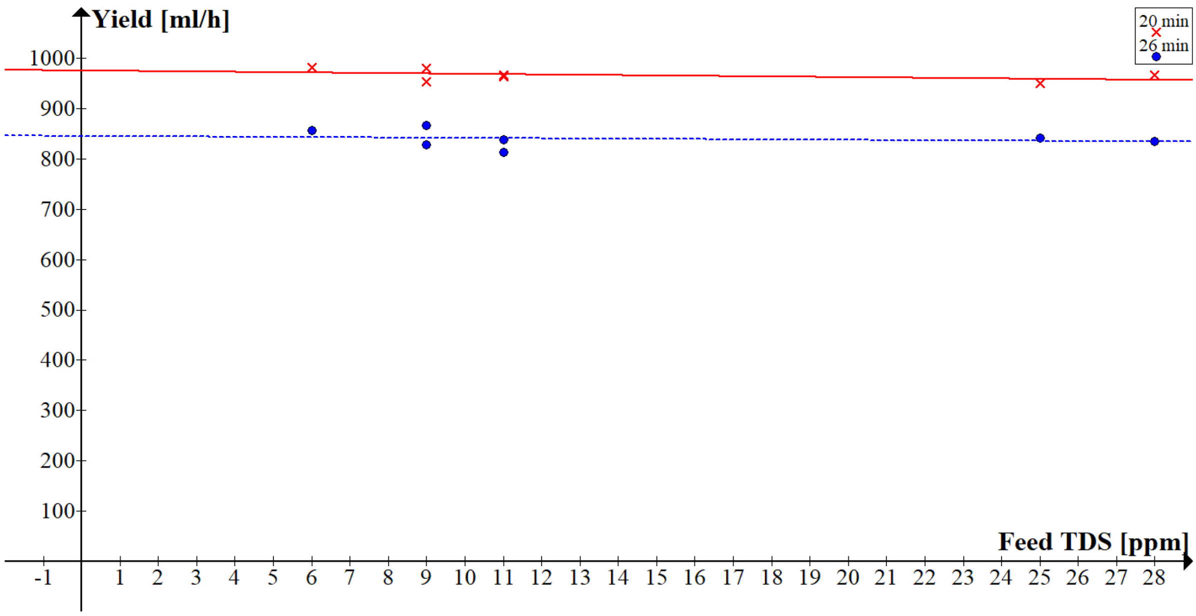

Figure 12. Graph of yield against feed TDS

Effects of feed rainwater quality

Feed rainwater TDS did not significantly influence yield, K, and RE. On the other hand, CF was found to be strongly negatively correlated ($r = -0.766$, $p = 0.045$) and ($r = -0.756$, $p = 0.049$) for 20 min and 26 min, respectively, with feed rainwater TDS (Figure 13). This implies that the TDS concentration effect of PFC weakens as feed TDS increases. No significant correlation was found between yield and feed rainwater TDS (Figure 12). In a sodium chloride solution ranging from 1.75 wt% to 3.5 wt%, K improved (i.e. approached zero) with a more dilute solution [33]. CF of calcium ions increased (1.6 to 2.1) with initial concentration [34] while the performance of PFC did not correlate with the pH of the feed solution. However, CF decreased with increasing concentration of cow cheese whey protein [35]. In glucose solution, when the circulation duration increased from 40 min to 80 min, both K and yield showed a declining trend [36].

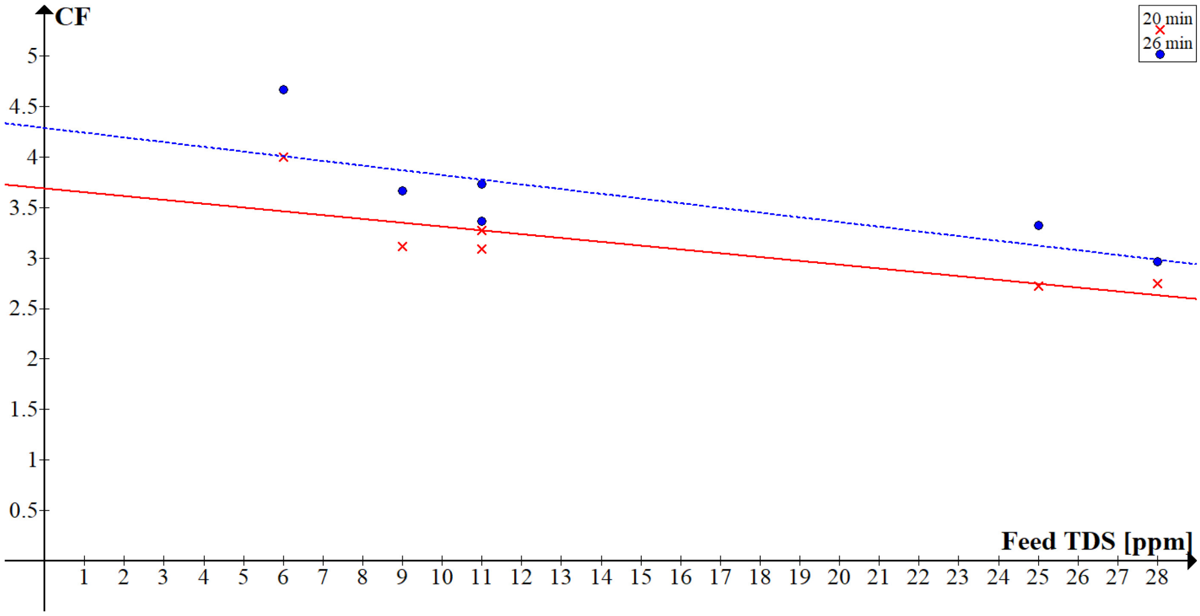

Figure 13. Graph of CF against feed TDS

Nonetheless, the yield of both sets of experiments (840 – 970 ml/h) was far lower than the rated capacity of 68 kg ice production per 24 hours or 2,830 ml/h. This result is due to the rated capacity of the equipment, which was measured by the manufacturer with water inlet temperature and ambient temperature of 20 °C, whereas in this study, the water inlet temperature and ambient temperature were 25 °C. The rate of ice production is dependent on two factors: the amount of heat to be rejected and the rate of heat rejection to the environment. The higher the water inlet temperature, the higher the amount of sensible heat to be rejected and the longer the time required to lower the water temperature to freezing point. Likewise, the higher the ambient temperature, the lower the rate of heat rejection and the less ice is produced per cycle. These two reasons combined resulted in the ice-making equipment yielding less ice compared to the rated capacity. This situation is actual for all refrigeration equipment as their performances are highly sensitive to operating temperatures.

Table 5 shows the comparison of energy consumption and footprint between PFC in the current study and a conventional method for producing pure water. The energy consumption of PFC is 280 kJ/kg water, which is only 10.4% of the energy consumption of a similarly-sized distillation water purifier. PFC energy consumption can be further reduced by scaling up capacity, improving heat recovery (cooling feed rainwater with thawing ice), and improving heat transfer efficiency. The equipment footprints for both methods are similar and require a space of less than 1 m^2 for 1 kg/h water production capacity.

Table 5. Comparison of alternative rainwater treatment methods

Method	Rated power [W]	Rated yield [kg/h]	Energy consumption [kJ/kg]	Energy consumption [kWh/m^3]	Equipment footprint [m^2 per kg/h water]
PFC (current study)	220	2.83	280	78	< 1
Distillation water purifier	3000	4	2700	750	< 1

The main reason the PFC freezing technique was chosen in this research to treat rainwater was that freezing water can produce high-purity ice crystals in a single process with low energy consumption. In contrast, other processes require several different processing steps in series to produce final pure water. Therefore, by furthering research into PFC to overcome its drawbacks, PFC can be used to purify rainwater into drinking water with less costly and complicated equipment.

CONCLUSIONS

All rainfall data were found to have a non-normal distribution from visual representation (box plots) and statistics (skewness and kurtosis). TDS of roof-harvested rainwater had a weak negative correlation ($r = -0.320$) with rainfall amount and no correlation with ADD. In other words, the quality of the roof-harvested rainwater in this study improved with only the total rainfall amount and rainfall after a long rainless period can be harvested with no effect on rainwater quality. Toxic heavy metals were not detected in the roof-harvested rainwater sample. Supercooling was not observed in the falling-film PFC equipment used in this study, which made operation simpler without requiring precautions against supercooling. The absence of supercooling also improved the quality of ice, which is vital for producing safe drinking water from rainwater. CF in this study was 3.0 to 3.4, which was comparable to a similar study of 1.2 to 3.7. CF was also found to depend on circulation time and feed rainwater quality, whereas yield depended on circulation time only. High CF is important to ensure good separation efficiency and rejection of contaminants from pure ice in the PFC process. At the cost of the ice yield, a longer circulation time increased PFC separation efficiency. A lower feed rainwater TDS also improved separation efficiency but did not affect the yield of ice. The process of purifying rainwater into drinking water using PFC has the potential to be both practical and viable. In future comprehensive studies, in order to make sure that treated rainwater is suitable for human consumption, additional water quality parameters should be studied, even if TDS can be used as an overall indicator of pollution in rainwater. Additional research is required to investigate how far PFC can be used to remove other contaminants from rainwater and the relevant optimum operating parameters.

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NOMENCLATURE

Symbols

k	Mass transfer coefficient	[m/s]
K	Effective partition coefficient	
N	Sample size	
p	Probability	
r	Pearson correlation coefficient	
r_s	Spearman's rank correlation coefficient	
t	Student's t distribution	
v	Maximum allowable growth rate	[m/s]

Abbreviations

ADD	Antecedent Dry Days
CF	Concentration Factor

DID	Department of Irrigation and Drainage
MF	Media Filtration
PFC	Progressive Freeze Concentration
RE	Removal Efficiency
RWHS	Rainwater Harvesting System
RO	Reverse Osmosis
SLR	Simple Linear Regression
SODIS	Solar Water Disinfection
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
UTM	Universiti Teknologi Malaysia

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