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Development of a New Crystallisation Chamber for a Progressive Freeze Concentration System

Mazura Jusoh, Rosli Mohd. Yunus, Mohd. Ariffin Abu Hassan
*Universiti Teknologi Malaysia
 Malaysia*

1. Introduction

Concentration enhancement of solutions is often a process necessary in many industrial processes, including in liquid food concentration and wastewater treatment. At present, there are three available methods to carry out such a task, namely evaporation, reverse osmosis and freeze concentration. In evaporation, the water vapour from the heating process is removed and a more concentrated liquid is left behind. It is the simplest and commonest method but it uses a large amount of energy to supply for the heat of vaporisation of water which is 1000Btu/lb (Hunter and Hayslet, 2002). It is also not suitable to be engaged if the solution to be concentrated contains volatile organic compounds (VOCs), which would easily turn into dangerous and hazardous vapour when heated. Another increasingly favoured process for solution concentration enhancement is reverse osmosis (RO), which separates the solute and the liquid phase through a water selective membrane. RO uses the least amount of energy because it involves no phase changes and can produce water of very high purity, but clogging of the membrane can easily occur in most cases and replacement of the membrane will definitely involve a high cost. Its efficiency is also sometimes limited by the compatibility of the membrane with the chemical component of the solution, apart from the expensive cost in attaining the osmotic pressure required for the process.

A later introduced method for the purpose of enhancing a solution concentration is freeze concentration (FC). FC is a process where the water component in a solution is frozen and crystallised as ice so that a more concentrated solution will be left behind. The water/ice crystals produced is supposed to be highly pure because the small dimensions of the ice crystal lattice makes the inclusion of any foreign compounds impossible except for fluorohydric acid and ammonia (Lorain, 2001), thus resulting in a highly effective separation of water components from the solution. The energy used in this process is relatively much lower than energy used in evaporation, which is only 143.5Btu/lb. It is also safe to be applied in concentrating solutions containing VOCs, making it a better option in treating wastewater compounded with this hazardous material. As the process do not involve any heating, most volatile components will stay in the concentrated solution, which makes FC favourable in concentration of liquid food such as fruit juices, coffee, dairy products and other food products, where the aroma of the liquid is one of the most important factors to

make it marketable. The highly pure water resulted from FC also has made the process suitable to be engaged for wastewater treatment, which enables the water (thawed ice) produced to be readily disposed off to the water streams. The amount of concentrated solution or wastewater left also leads to reduction of treatment cost as the wastewater volume is also reduced extensively. FC has been recorded to be able to concentrate approximately 80% of the dissolved compounds in 25% of the original volume (Maurer et.al, 2006).

Historically, FC was discovered by a Danish physician, Thomas Bartholinus (1616 – 1680), who reported that water obtained by melting ice formed in seawater was fresh (Rahman et al, 2006). The first paper published on this subject was in 1786 by Lorgna, wondering why no effort was taken in artificial processes, imitating what nature does. Later, an interest in engaging FC in obtaining fresh water from sea water was revived in the late 1930s, when refrigeration process is available.

2. Research Background

Justification of the advantages of FC above has evolved into this research to discover the best FC system design to be employed, which will be focusing on its application for wastewater treatment particularly. In this context, the system should be designed with the attention of producing the purest water possible.

There are two available methods for FC, which are suspension freeze concentration (SFC) and progressive freeze concentration (PFC). In SFC, the ice crystals are formed in a suspension in the mother liquor, which in this case is the concentrated solution, while in PFC the ice crystal is formed as a single block of ice on the refrigerated surface, as illustrated in Fig. 1.

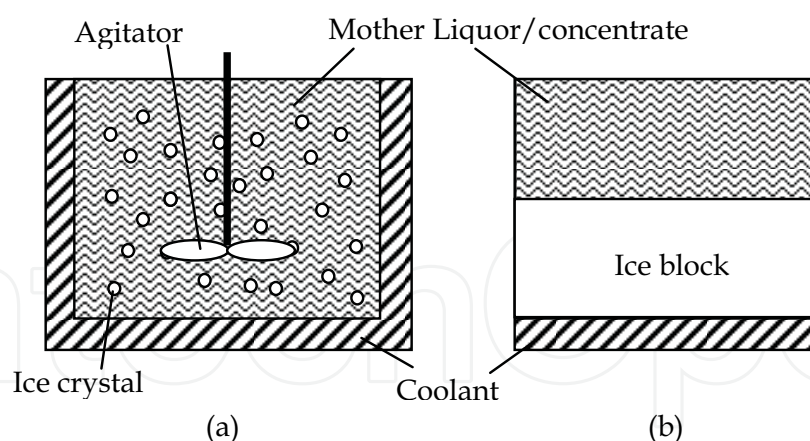


Fig. 1. Illustration of (a) Suspension Freeze Concentration and (b) Progressive Freeze concentration.

A concentration process engaging SFC must be equipped with a filtration system for the ice crystals to be separated from the concentrate, along with a washing column to wash out those concentrates entrained in between and on the surface of the small ice crystals. This is indeed a drawback to the system which has subsequently brought about the later PFC process which is deemed simpler and does not require other unit operations for separation of the ice

block from the concentrates, and also eliminated the needs of using a scraped surface heat exchanger to produce ice seeds to facilitate further ice growth in SFC.

Although PFC is reported to be a reasonably better solution for FC, its productivity is found still to be lower than SFC, which leads to many researches to find the most appealing design for the equipment where the ice crystallisation should occur. Many kinds of design have since been investigated to result in high efficiency and higher productivity. Among all, in 2001, Wakisaka et. al. carried out a progressive freeze concentration research using ice maker channels in square pillar shape standing four in a row and eight in a line as a crossbeam in a well and the chamber contained an agitation device. Sample used was glucose solution to represent the wastewater. They found out that on an average 1.4-fold concentrated solution was obtained after the PFC process. It also produced 135kg ice on average from one batch operation of 70min. In 2004, Miyawaki et. al. has conducted a research on PFC with a tubular design and the refrigeration is supplied at the wall of the cylinder. Therefore the ice layer is formed in a cylindrical shape. They concentrated sucrose solution, coffee extract and tomato juice and have proven that tubular ice system is effective as a method for scale up of PFC with an increased productivity and gives a high yield. A current research in 2006 by Habib and Farid from New Zealand utilized a fluidized bed heat exchanger (FBHE) to replace SSHE to eliminate the high capital investment. They used stainless steel particles in the FBHE and the ice layer is formed at the surface of the metal particle. The research was carried out to concentrate an 8% sodium chloride (NaCl) solution and they found out that the ice production rate was 1.1kg/hr. Another research is also carried out in 2006 by Reventos et. al.. In this research the crystallization unit is an indirect contact freezer where the energy for the refrigeration is transferred through the walls of a plate heat exchanger. Consequently, this produces layer crystallization in which the ice forms in thin layers on the surface of the heat exchanger (80cm x 60cm). The experiments were carried out using sugar solutions, which is glucose, fructose and sucrose. The best achievement was, after the PFC process, the 5° Brix sucrose was concentrated to 31.2° Brix in 16.6 hours.

3. Materials and Methods

3.1 Materials

In this research, focus is given to PFC for the purpose of wastewater treatment. As the research is at a very early stage of testing the feasibility of a new design, glucose solution is used as a substitute to actual wastewater. This is a common practice in many PFC research as stated in researches by Miyawaki (2005) and Wakisaka (2001) and many others. The coolant used is ethylene glycol 50%v/v with water, which is capable of withholding its liquid phase when cooled below the freezing point of pure water.

3.2 Experimental set-up

Figure 2 illustrated the apparatus/equipment where the crystallisation of ice should occur termed here and afterwards as crystallisation chamber (CC).

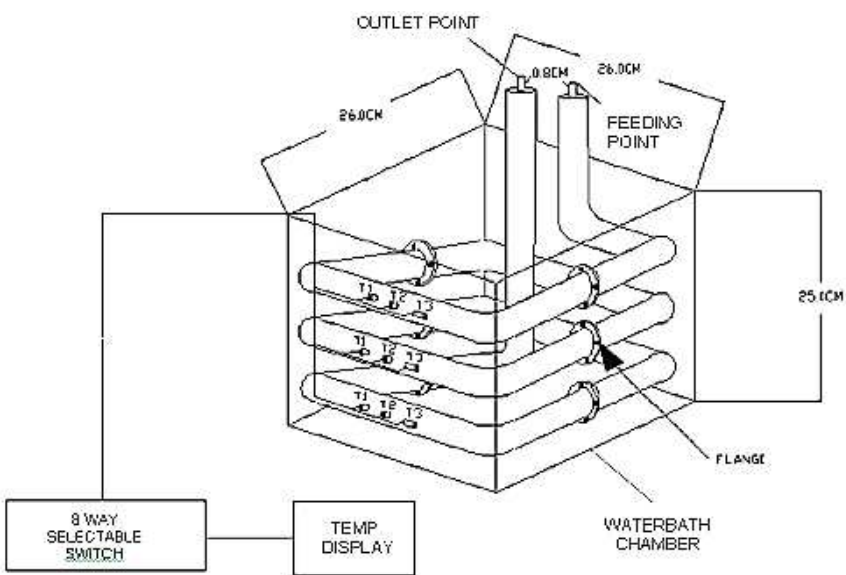


Fig. 2. Crystallisation Chamber (CC)

The CC is made of copper and designed to be in three stages, which also could easily be up-scaled when necessary. The thickness of the copper tube is 0.8 mm with internal diameter of 1 inch. It is also equipped with 6 stainless steel flanges where the chamber could be split into two. This is to enable visualisation of the ice layer produced in each experiment. Nine temperature probes (thermocouples type K) were engaged in each stage for temperature profiling purpose, where the solution, copper wall and coolant temperatures are displayed by PicoLog recorder software through a connected computer. This crystallisation chamber was then immersed in a refrigerated waterbath at the desired temperatures. The experimental set-up for the PFC system is shown in Fig. 3. During operation

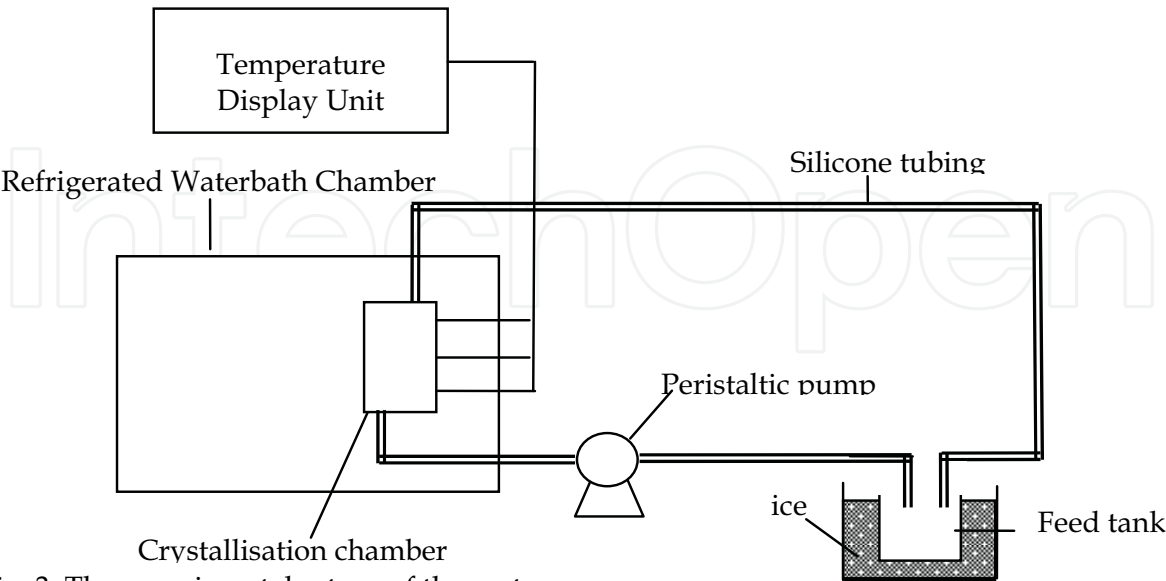


Fig. 3. The experimental set-up of the system

the crystallisation chamber is immersed in a refrigerated waterbath at the desired cooling temperature. The CC is connected via a silicone tube to a peristaltic pump which will circulate the solution from the feed tank and inside the CC for a period of time. A peristaltic pump is selected for this task because of its capability to fluidise the solution with minimal heat generation. The heat generated by the pump should be as minimum as possible to avoid reduction of cooling effects during the freezing process. The flowrate of the solution will be controlled by this pump.

3.3 Experimental Procedure

Glucose solution prepared was first kept in a freezer where the temperature of the solution should be near the freezing temperature of water. The temperature was kept at 3 to 4°C and the solution was mixed with glucose solution ice cubes to maintain the temperature during feeding. The solution was then fed to the chamber using a peristaltic pump through a silicone tube until its full volume was filled. Each end of the silicone tube was then connected to each other.

The filled CC was then immersed in a precooled waterbath at the desired operation temperature, while the pump was run at the desired circulation flowrate. The solution then was left for crystallisation to occur for the desired circulation time. At the designated time, the circulation was stopped and the chamber was taken out of the waterbath to be thawed. The concentrated solution in the silicone tube was then collected as the concentrate sample via flushing with the pump. The flanges were unassembled and the whole volume of the concentrated solution was collected. The ice layer thickness at each flange point was measured and a sample of the ice layer produced was collected. Refractive index of each sample was then measured in order to determine its concentration.

3.4 Evaluation of System Efficiency

The efficiency of such a system depends closely on the intention of the application of the system. In this case, this PFC system is developed for the purpose of a wastewater treatment, therefore, the most important objective is to achieve the highest purity possible of the water to be disposed off. Observation should be carried out on the concentration of glucose in the ice block produced. It is also important to evaluate the volume reduction resulted from this process as the concentrate should be further treated to a certain standard before it is qualified to be channelled to the streams and rivers.

Another factor should be looked into is the value of the effective partition constant, K , which is very synonym to a PFC process and a very common parameter used to evaluate such a system. The effective partition constant is evaluated by the concentration of solutes in the ice and bulk liquid phase (Gu et. al., 2008), as defined by Equation 1:

$$K = C_s / C_L \quad (1)$$

where C_s is and C_L are solute concentrations in ice and solution phase, respectively (Miyawaki, 2005).

According to Miyawaki et.al, the value of K should be calculated experimentally, which is carried out by developing a linear equation from a mass balance of the process. When the volume of liquid is V_L and concentration of solute in the liquid is C_L , a mass balance equation for the process obtained would be expressed as follows, by assuming complete

mixing in the solution phase and no mixing in the ice phase:

$$C_L V_L = -C_S dV_L + (C_L + dC_L)(V_L + dV_L) \quad (2)$$

where $(-dV_L)$ is a small volume increase in the ice phase and dC_L is the solute concentration increase in the solution phase assumed (Miyawaki, 2005).

Combining Equation 4.1 and 4.2:

$$\frac{dC_L}{C_L} / \frac{dV_L}{V_L} = K - 1 \quad (3)$$

When K is assumed constant Equation 3 can be integrated into:

$$(1 - K) \log \left(\frac{V_L}{V_0} \right) = \log \left(\frac{C_0}{C_L} \right) \quad (4)$$

where V_0 and C_0 are the volume and the solute concentration at the beginning in the solution phase, respectively. The value of K is between 0 to 1, where $K=0$ when there is no freeze concentration and $K=1$ for complete freeze concentration. A series of experiment giving samples at consistent sampling times along the full time of circulation should produce a straight line, which K could be calculated from the gradient of a graph of $\log(C_0/C_L)$ against $\log(V_L/V_0)$.

4. Results and Discussions

An array of glucose solutions with different concentration were prepared for the refractive index (RI) to be measured. The range tested was 1 – 10 mg/ml, which is predicted to be the range of concentrations significant for the experiments to be carried out in this investigation. An advanced graphical tool was utilised to ensure a high reliability of the calibration curve produced. Fig. 4 shows the constructed curve with an R^2 value of 0.9904 which portrays an excellent curve fitting of the results to the curve constructed. All values of RI for future experiments were based on this calibration curve, by keying in the value of RI for each sample into the function generated by the curve fitting equation.

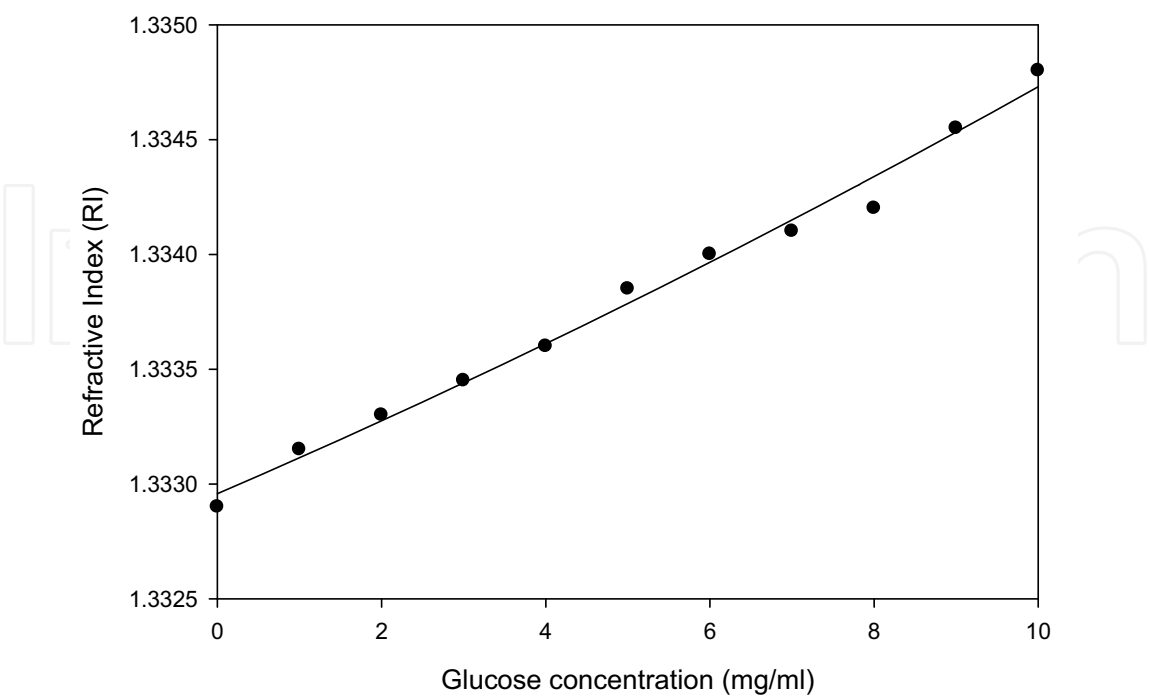


Fig. 4. Glucose calibration curve

During freezing, ice crystals were formed on the inner surface of the copper tube wall. Fig. 5 and Fig. 6 show the ice layer formed in the CC at the end of the experiments. The thickness of the layer varied with the operating conditions varied throughout the experimental works.



Fig. 5. Ice layer formed in the detached CC



Fig. 6. A close-up of the ice layer formed

4.1 Effect of Circulation Time

In order to study the effect of circulation time to this process, all other operating conditions were kept constant with circulation flowrate at 1000ml/min, coolant temperature of -8°C and an initial solution concentration of 7mg/ml. A series of screening test carried out previously revealed that the maximum time the CC could withhold before being completely full with ice lining was 23 minutes. Therefore, the range studied for the circulation time effect is 5 – 20 minutes.

The purity of the ice block formed was evaluated by the amount of glucose in the solid phase indicated by the refractive index. Figure 7 shows the concentration of glucose in the ice phase at different circulation time. At 5 minutes, the ice produced seems to have quite a high concentration of glucose with just a reduction of 1.8% of the original concentration. From the observation of the ice layer produced, it could be seen that it is not solid, and more of a dendritic structure, which indicates that the freeze concentration process occurred was incomplete.

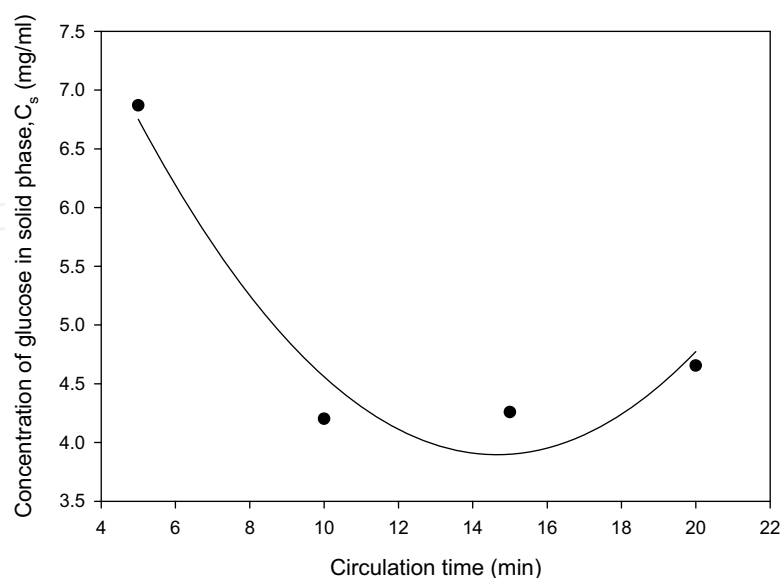


Fig. 7. Concentration of glucose in the solid phase at different circulation time.

Glucose concentration in the solid phase was found to be satisfactorily low at 10 and 15 minutes with a reduction of about 40% of the original concentration. This indicates a good freeze concentration process has occurred at these circulation times. At 20 minutes, the ice layer formed on the inner wall of the CC has nearly filled the entire volume of the chamber. At this point, the concentration of glucose shifted its trend where it starts to increase from a decreasing trend at 10 and 15 minutes. Therefore, it could be concluded that the sampling of the ice layer for the efficiency study should not be taken at 5 and 20 minutes. The range suggested suitable for sampling is between 8 to 16 minutes.

In the volume reduction point of view, from Fig. 8 it could be observed that the liquid phase volume could be reduced up to 76% at 20 minutes.

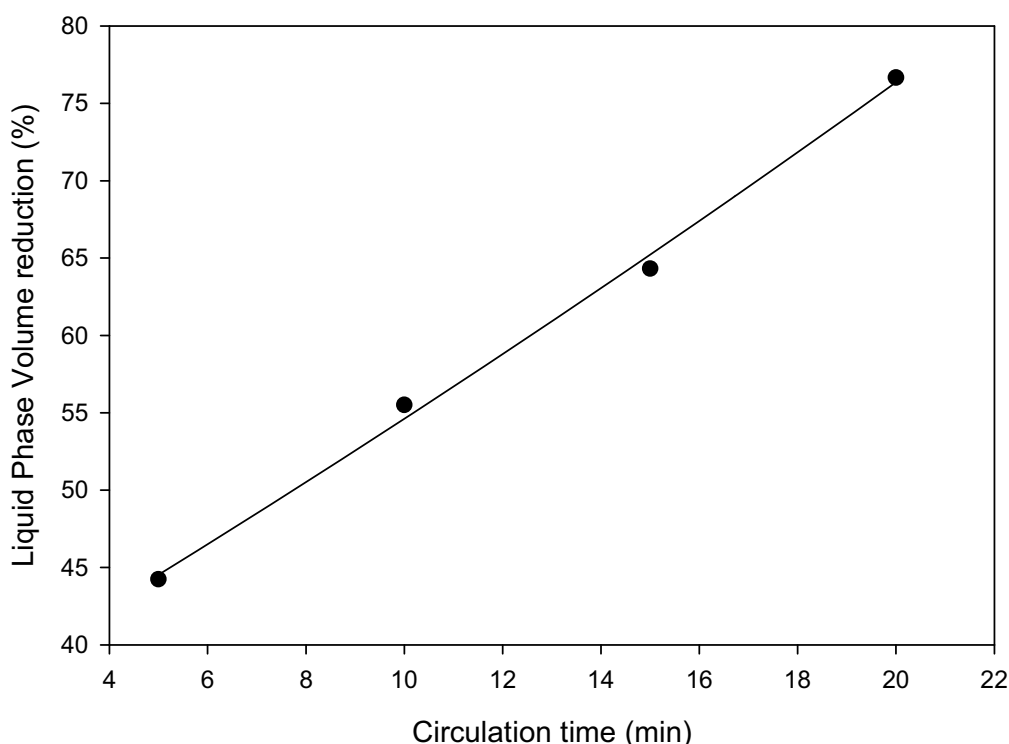


Fig. 8. Liquid phase volume reduction at different circulation time.

4.2 Effect of Circulation Flowrate

The range of circulation flowrate studied was 400 – 1000 ml/min, which is chosen based on the available pump limitation. For the purpose of investigating the effect of circulation flowrate to this process, all other operating conditions were also kept constant with maximum circulation time of 15 minutes, based on the findings mentioned in the previous section. The coolant temperature was kept at -8°C and initial solution concentration at 7mg/ml.

Fig. 9 shows a graph of the effect of the flowrate on the concentration of glucose in the thawed ice. As indicated by the curve, it is evident that higher flowrate produces an ice block with lower glucose concentration. The maximum flowrate of 1000ml/min yielded an ice block with 4mg/ml glucose, which is 43% reduction of solute concentration when compared with the initial concentration (7mg/ml).

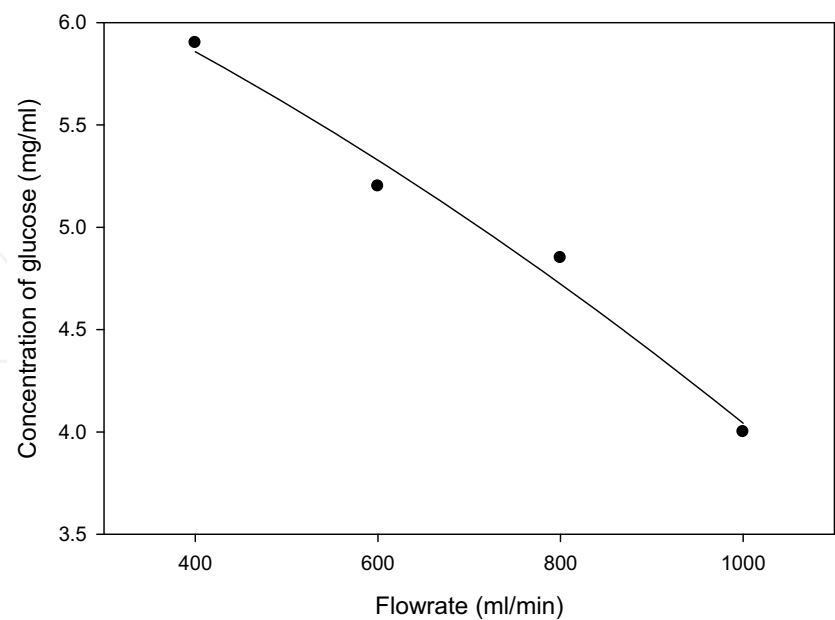


Fig. 9. A graph showing the effect of circulation flowrate on the purity of water produced.

During freezing the temperature of the wall is influenced by the coolant temperature, set at -8°C , which is way below than the freezing point of pure water. As the solution flows inside the chamber, water component of the solution would first be frozen, because the temperature of the solution is lower than pure water.

Through a concentration polarization model suggested by Miyawaki et. al. (1998), the concentration of solute is the highest at the ice-liquid interface, as depicted in **Fig. 10**. As the concentration is higher, constitutional supercooling would occur, thus encouraging formation of dendritic ice crystals to release the latent heat and deplete supercooling (Williamson & Chalmers, 1966). Solutes are normally trapped between the dendritic structures, which would easily be removed by high fluid flowrate, leaving behind an ice layer with high purity.

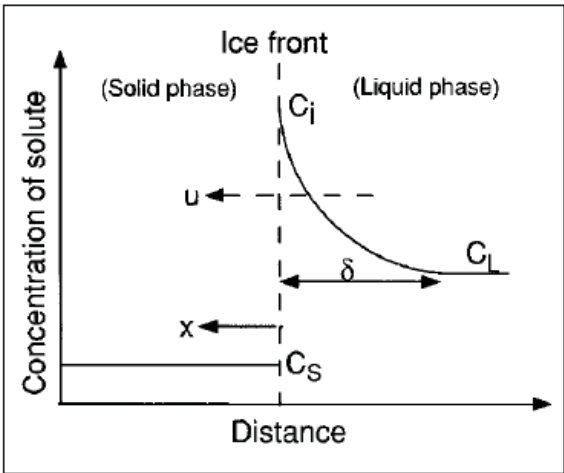


Fig. 10. Concentration polarization at the ice front in PFC

The solute in the solution would also be carried by the shear force of the fluid flow (Rodriguez, 2000). At high flowrates which have high shear force, the solute is brought away from the surface of the stagnant solid ice layer, causing lower contamination of the ice layer produced.

The efficiency of the system was also evaluated from the value of K for each flowrate, which graph is plotted in Fig. 11. From the plotted graph, it can be seen that higher flowrate resulted in a lower K , which means better efficiency. This finding agrees with what was discussed earlier by Miyawaki et.al. (2005) and Ramos et.al. (2005), stating that higher flowrate will result in a highly pure ice crystal layer, giving in low value of K . This could also be explained by the likelihood of the occurrence of a planar ice growth from the cooling wall, which resulted from by a heat transfer with ice crystals from its tips, by keeping away the solutes from the ice-liquid interface (Wakisaka et.al., 2001). A further supporting graph is also provided in Figure 12.

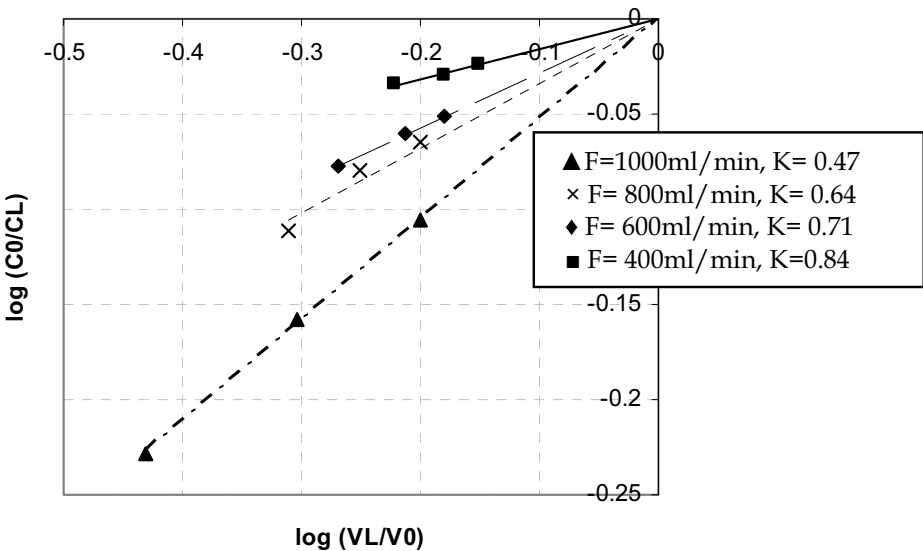


Fig. 11. Graph plotted to see the effect of circulation flowrate on the effective partition constant, K .

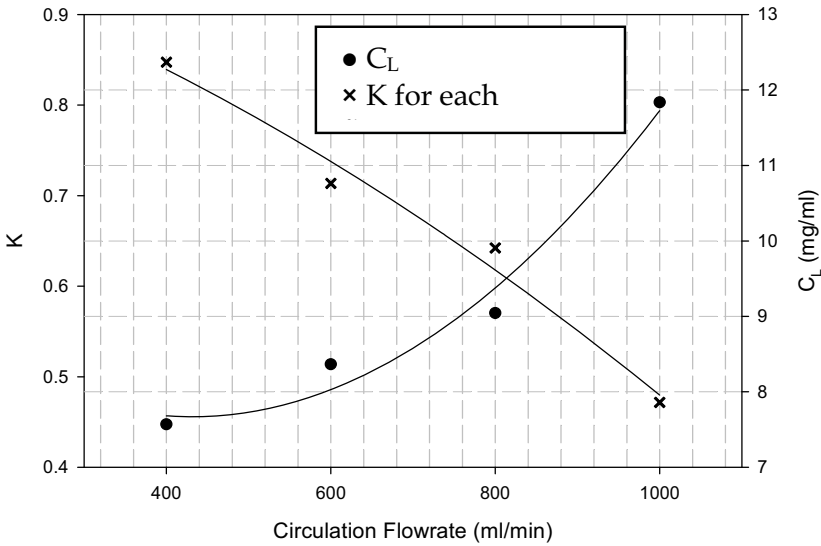


Fig. 12. Effect of flowrate on K and C_L .

4.3 Effect of Coolant Temperature

The same experimental procedure was used in order to investigate the effect of coolant temperature on the efficiency of this system. Other parameters were kept constant with circulation flowrate at 1000 ml/min and initial concentration of 7mg/ml. Upon examining the samples and determination of its concentration, the effect of coolant temperature on K is depicted in Fig. 13.

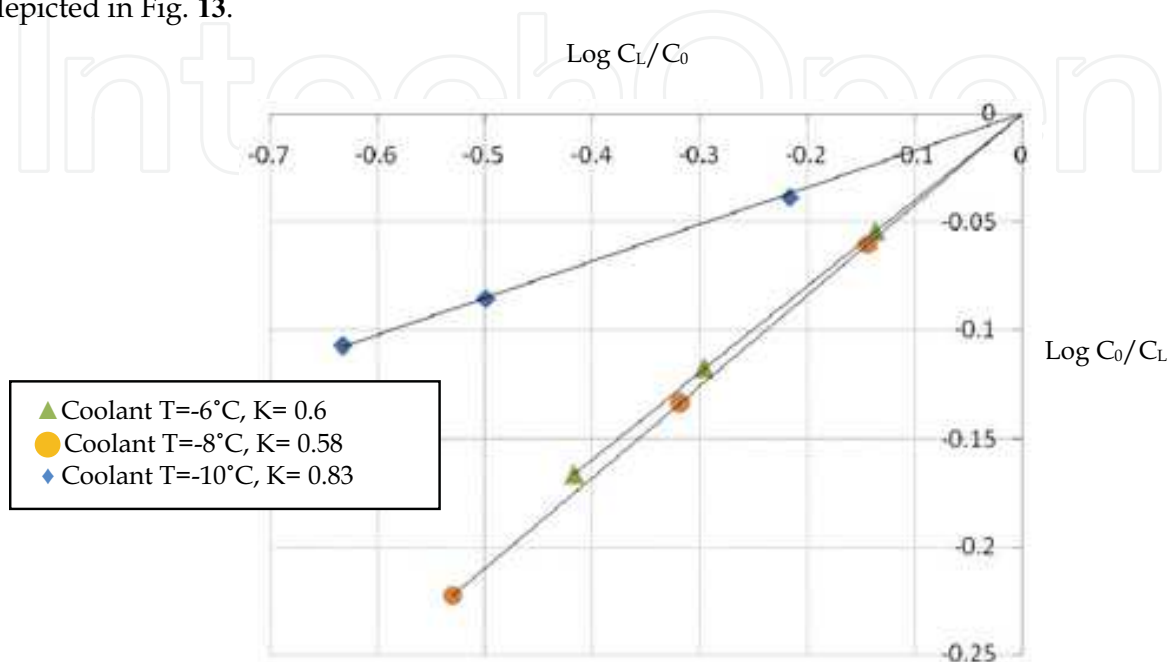


Fig. 13. Effect of coolant temperature on K

Coolant temperature controls the ice crystal front growth rate (Miyawaki). Ice growth rate increases with increasing difference between the entering solution and the surface temperatures (Flesland, 1995). A decrease in the coolant temperature brings a higher growth rate of ice front, which is undesirable to produce a low K for this system. The higher the ice growth rate, the more impurities would be entrained in the ice. This is because the speed of the moving front can become too high to overtake the solute outward movement. (Chen et al, 1998) and promote solute inclusion in the ice crystals. Therefore, low growth rate from suitable coolant temperature gives high purity of ice produced.

5. Conclusion

This work has proven that the designed crystallisation chamber is capable of producing ice layer with decreased concentrations compared to the initial concentration, and is deemed relevant for the purpose of wastewater treatment. The parameter studied should be further investigated in order to discover the most optimum operating condition, where it could produce ice layer with highest purity. Other possible operating conditions should also be investigated, including initial concentration of solution and initial solution temperature.

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51000 Rijeka, Croatia
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