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EFFECT OF INITIAL CONCENTRATION OF SOLUTION AND COOLANT TEMPERATURE ON A NEW PROGRESSIVE FREEZE CONCENTRATION SYSTEM

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ABSTRACT

Progressive freeze concentration (PFC) is believed to be able to overcome the weaknesses of conventional suspension freeze concentration (SFC), in which among all, can reduce the capital cost involved. PFC produces ice crystals as a single ice block instead of a suspension of small crystals in the mother liquor, hence reducing the number of unit operations to separate the crystals from the concentrated solution. The design of the heat exchanger where crystallization of ice should occur is among important factors in ensuring a PFC process with high efficiency. A new apparatus called crystallisation chamber (CC) for the purpose of crystallisation of ice has been designed in this research, made of copper and helical in shape. The effect of two operating conditions on the performance of the newly designed crystallisation chamber was then investigated, which are the initial concentration of solution and coolant temperature. Effective partition constant, K, was used as an indication of the system efficiency, calculated from the volume and concentration of the solid and liquid phase.

Key Words: Freeze concentration; Freeze wastewater treatment; Ice crystals; Progressive freeze concentration

1.0 INTRODUCTION

There are currently many available methods in concentration enhancement of a solution, with evaporation being the leading technology. In evap oration, the water vapour from the heating process is removed and a more concentrated liquid will be 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 [1]. 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

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crystals produced is supposed to be highly pure because the small dimensions of the ic crystal lattice makes the inclusion of any foreign compounds impossible except fo fluorohydric acid and ammonia [2], thus resulting in a highly effective separation of wate components from the solution. The energy used in this process is relatively much lower tha energy used in evaporation, which is only 143.5Btu/lb. It is also safe to be applied i concentrating solutions containing VOCs, making it a better option in treating wastewate compounded with this hazardous material. As the process do not involve any heating, mos volatile components will stay in the concentrated solution, which makes FC favourable i concentration of liquid food such as fruit juices, coffee, dairy products and other foo products, where the aroma of the liquid is one of the most important factors to make i marketable.

In the case of industrial wastewater which always contain various types of pollutan ranging from chemicals to suspended matters, it is also an advantage if the volume of th wastewater could be reduced extensively before undergoing the appropriate treatment. Thi will result in a reduction in operation cost in terms of the utility. Hazardous wastewater frequently treated by incineration, but to incinerate an aqueous solution with a solid conten of less than 10%, requires tremendous power to 'burn' the water and maintain the hig temperature necessary to destroy the hazardous compound [3]. In addition, the combustio gas produced contributes to the emissions from the process and can rapidly exceed loca limits. To avoid the unnecessary waste of energy, volume reduction through freez concentration is highly recommended.

There are two methods available for freeze concentration, conventional suspensio freeze concentration (SFC) and progressive freeze concentration (PFC). SFC is a process o freeze concentration where the ice crystals are formed in a suspension of the mother liquo and is characterized by the generation of a size distribution of crystal growing isothermally However, in this conventional method, the size of ice crystal is still limited [4]. The smal ice crystals formed has to be transferred to a ripening vessel to be enlarged, then to a washing column and separated from the mother solution after washing with water [5] These steps: ice nucleation, ice crystal growth and ice crystal separation make the whol system very expensive, which has made it unfavourable.

In compensating the disadvantages of SFC, a totally different concept o crystallization, PFC has been introduced. In this method, a large single ice crystal instead a group of small ice crystals suspension is formed. The ice crystal is formed on the surfa of the heat conducting material where the cooling is supplied. As only a single crystal i formed, its separation from the mother liquor is much easier to be handled and at a lowe cost. An illustration of both SFC and PFC is shown in Figure 1. Despite the easie separation in PFC, its productivity is found to be lower than the conventional SFC.

The design of the apparatus where the crystallization of ice is supposed to occur i an important factor in influencing the system efficiency. The selection of material o constructions and the design shape of the apparatus should be carried out carefully in orde to ensure successful operation of freeze concentration. In this particular research a helic copper crystallization chamber was fabricated, where the crystallization of ice should tak place. The newly fabricated chamber was then evaluated in terms of its efficiency accordin to the two parameters, which are the initial concentration of the initial solution and th circulation flowrate during operation. Initial concentration and circulation flowrate a among the important factors that significantly influence the efficiency of the system [6]

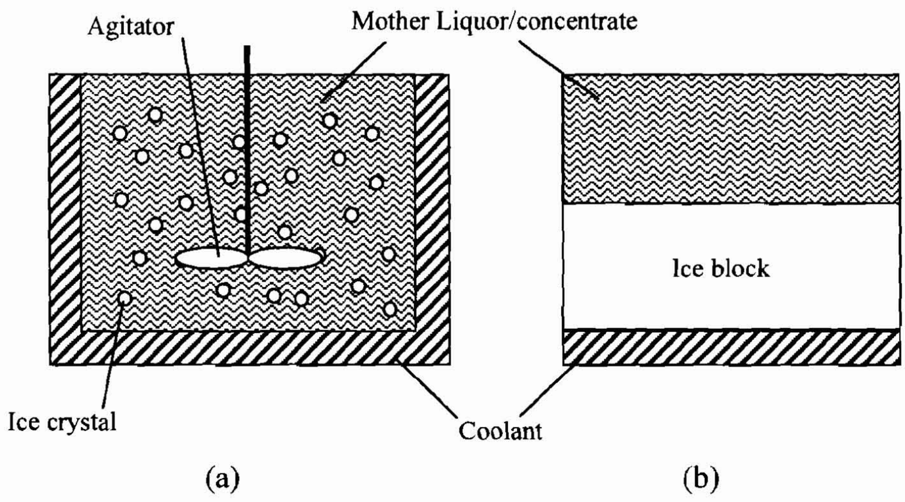

Figure 1 Illustration of (a) Suspension Freeze Concentration and (b) Progressive Freeze concentration.

2.0 MATERIALS AND METHODS

2.1 Materials

Glucose solutions at various concentrations ranging from 2-8 mg/ml were used to represent the simulated wastewater. It is very common that glucose be used in assessing the performance of a wastewater treatment system. Glucose used was 99.9% pure.

2.2 Equipment

Figure 2 shows the crystallization chamber (CC) fabricated using copper as the material. The thickness of the copper tube is 0.8 mm with internal diameter of 1 inch. The chamber has three layers or stages and is also equipped with 6 stainless steel flanges where the chamber could be split into two. This is to enable visualization 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 crystallization chamber was then immersed in a refrigerated waterbath at the desired temperatures. The coolant used was ethylene glycol at 50% volume with water.

2.3 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 of the same concentration to maintain the temperature during feeding.

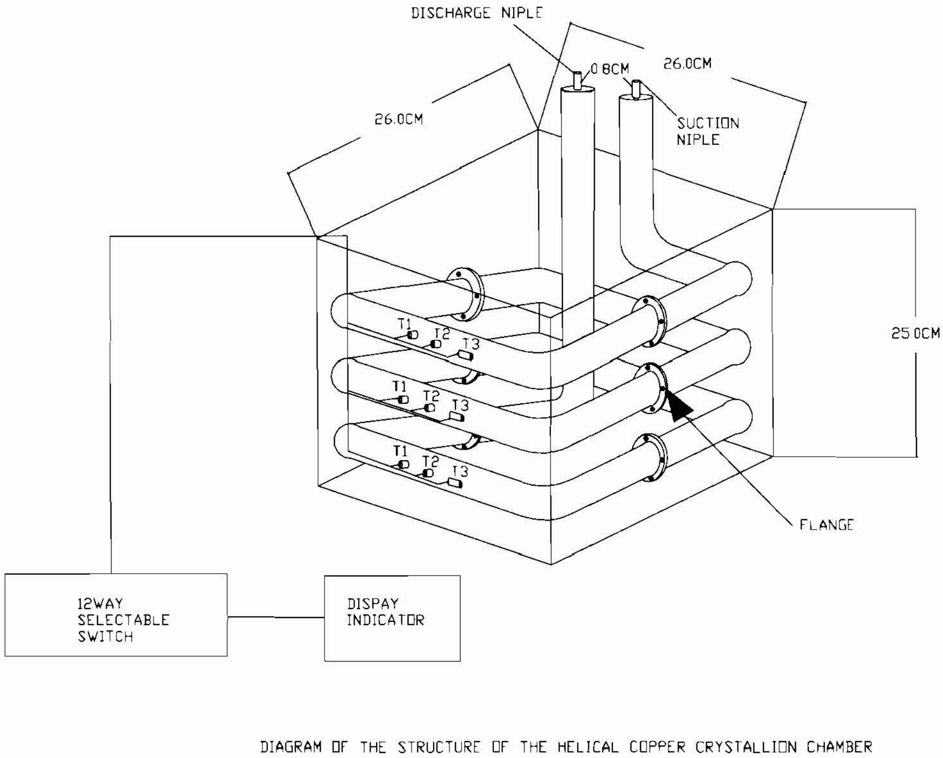

Figure 2 Diagram of the helical copper crystallization chamber (CC) structure

The solution was then fed to the chamber using a peristaltic pump through a silicon tube until its full volume was filled. Each end of the silicone tube was then connected. Th filled CC was then immersed in a precooled waterbath at the -8°, while the pump was run the desired circulation flowrate. The solution then was left for crystallization to occur for 1 minutes. After the designated time, the circulation was stopped and the chamber was tak out of the waterbath to be thawed. The concentrated solution in the silicone tube was the collected as the concentrate sample via flushing with the pump.

The flanges were unassembled and the whole volume of the concentrated solutio was collected. The ice layer thickness at each flange point was measured and a sample of th ice layer produced was collected. Refractive index of each sample was then measured i order to determine its concentration.

3.0 RESULTS AND DISCUSSION

A calibration curve for the concentration of glucose via refractive index (RI) was firs constructed by making several standard solution of glucose with concentration in the rang of 1 to 10mg/ml. The calibration curve is shown in Figure 3 which agrees with previou calibration curves produced previously by other researchers [7].

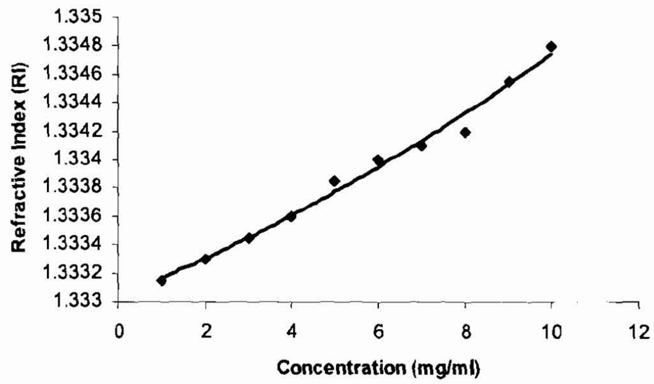

Figure 3 Calibration curve

During freezing, ice crystals were formed on the inner surface of the copper tube wall. Figure 4 and 5 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.

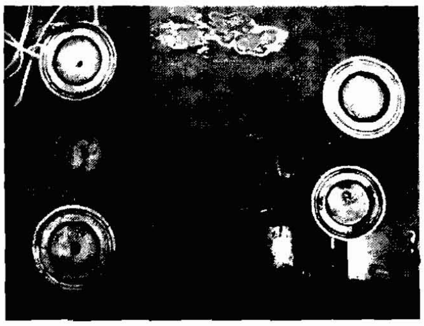

Figure 4 Ice layer formed

Figure 5 A close-up of the ice layer formed

Effect of Initial Concentration of Solution

Solute concentration was investigated for the range of 2-8mg/ml. Other parameter kept constant was the circulation flowrate at 1000 ml/min and circulated for 15 minutes for crystallization. The coolant temperature was kept at -8°C.

The effect of the solution initial concentration on the efficiency of the system is portrayed by the effective partition constant of the system which can be calculated through Equation (1).

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

where C_s is and C_L are solute concentrations in ice and solution phase, respectively [8].

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The experimental value of K is measured by equation (2), where V_0 and C_0 are the volum and solute concentration at the beginning in the solution phase, respectively. V_L is th volume of concentrate produced.

$$(1-K) \log (V_L/V_0) = \log (C_0/C_L) \quad (2$$

After examining the samples and determination of its concentration, the effect o initial concentration on K is depicted in Figure 6. It can be observed that higher initi concentration resulted in higher K, which means lower efficiency for the system, and vic versa. This also means that the efficiency can be affected by the initial amount of solute i the solution to be concentrated and K is dependent on it. In the solidification process, th solution concentration increases at the ice-liquid interface because the solutes accumulate this region [8]. This causes constitutional super-cooling, which strongly affects the dendriti structure at the interface. Higher initial concentration means higher amount of solutes in th initial solution, which will cause higher accumulation of solutes at this interface, causing t ice layer concentration to be higher. This causes an increase in the effective partitio constant, K. Therefore, it can be concluded that the initial concentration affects th efficiency of the process through constitutional supercooling, which causes a change in K [9].

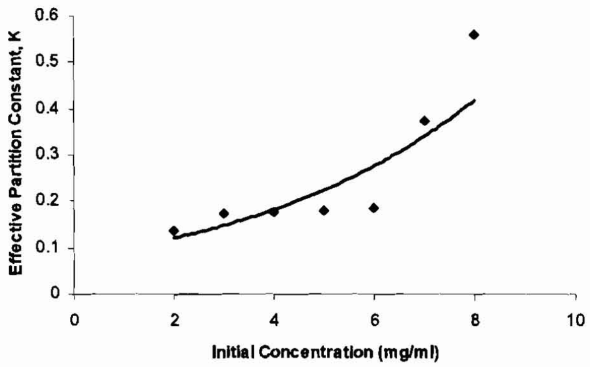

Figure 6 Effect of initial concentration on K

Effect of coolant temperature

The same experimental procedure was also used to observe the effect of coolant temperature on the efficiency of this system. Other parameter kept constant was the circulation flowrate at 1000 ml/min and circulated for 15 minutes for crystallization.

After examining the samples and determination of its concentration, the effect of coolant temperature on K is depicted in Figure 7. It can be observed that lower coolant temperature resulted in higher K, which means lower efficiency for the system. At -4°C, ice layer formed was not smooth and very thin and in fact was in dendritic form. Therefore, the data collected at this temperature should not be included. Data from the temperature profiling tools shown in Figure 8 shows that even the coolant temperature was set at -4°C, its actual temperature was only -3.1°C at average.

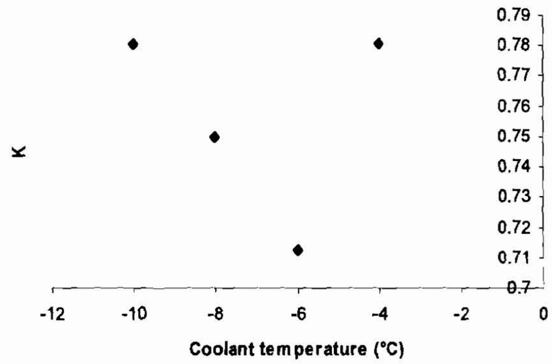

Figure 7 Effect of coolant temperature on K

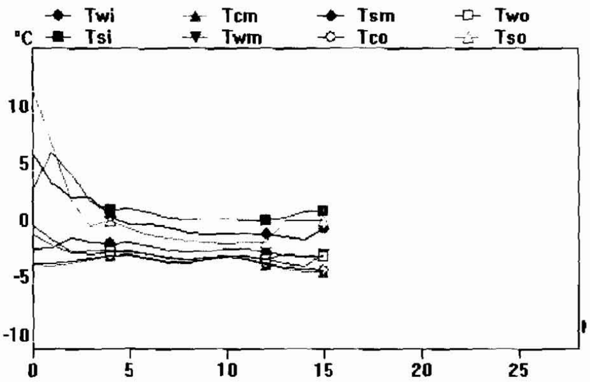

Figure 8 A snapshot of the temperature profiling tool.

Coolant temperature controls the ice crystal front growth rate [8]. Ice growth rate increases with increasing difference between the entering solution and the surface temperatures [10]. Lower 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. [11] and promote solute inclusion in the ice crystals. Low growth rate gives high purity of ice produced [8].

4.0 CONCLUSION

This work has proven that the designed crystallisation chamber is capable of producing ice crystals with good purity. However, those parameter studied should be further investigated in order to discover its best performance in terms of initial concentration used and coolant temperature involved.

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REFERENCES

[1] Hunter, G and R. Hayslet. 2002. Task 2.6: *Mechanical Freeze/Thaw and Freez Concentration of Water and Wastewater Residuals*, California Energy Commissio Sacramento, California.

[2] Lorain, O., P. Thiebaud, E. Badorc and Y. Aurelle.. 2000, Potential Of Freezing i Wastewater Treatment: Soluble Pollutant Applications, *Water Research Journal*, Vol (35), 541-547.

[3] Holt, S. 1999.The Role of Freeze Concentration in Waste Water Disposal, *Filtratio and Separation Journal*, 34 – 35.

[4] Gu, X., T.Suzuki., and O.Miyawaki. 2005. Limiting Partition Coefficient i Progressive Freeze Concentration. *Journal of Food Science*. Vol (70): 546-51.

[5] Widehem P. and N. Cochet. 2003. *Pseudomonas syringae* as an ice nucleator- application to freeze-concentration. *Process Biochemistry*. 39: 405-410.

[6] Kagitani, K. and K. Hayakawa. 2006. Method of controlling pregressive freeze concentration, *US Patent*, US7017367B2.

[7] Vaz, D. and I.Castanheira. 2000, Uncertainty budgets and mpes in refractometry: A project Study, *OIML bulletin Volume XLI* Number 4, 8-11.

[8] Miyawaki O., L.Liu, Y.Shirai,S. Sakashita and K. Kagitani. 2005. Tubular ice system for scale-up of progressive freeze-concentration. *Journal of Food Engineering*. 69: 107-113

[9] Miyawaki, O., T. Abe, and T. Yano. 1992, Freezing and ice structure formed i protein gels. *Bioscience Biotechnology and Biochemistry*, 56: 953-957.

[10] Flesland, O. 1995. Freeze concentration by layer crystallization. *Drying Technology* 13(8-9), 1713-1739.

[11] Chen, P., X.D .Chen X. D. and K.W. Free. 1998 Solute inclusion in ice formed from sucrose solutions on a sub-cooled surface – an experimental study, *Journal of Food Engineering* 38: 1-13.