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EFFICIENCY STUDY ON A NEW PROGRESSIVE FREEZE CONCENTRATION SYSTEM FOR FREEZE WASTEWATER TREATMENT

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Abstract. A newer method of freeze concentration, progressive freeze concentration (PFC) was used on glucose solution as simulated wastewater to concentrate and treat it. PFC is hoped to be able to compensate for the disadvantages of the conventional suspension freeze concentration. In PFC, ice crystals were formed as a layer on the designed heat exchanger surface instead of in a suspension. In this particular research, a helical structured copper crystallisation chamber was designed and fabricated. The effect of three operating conditions on the performance of the newly designed crystallisation chamber was then investigated, which are the initial circulation flowrate, concentration of solution and coolant temperature. The performance of the design was evaluated by the effective partition constant, K, calculated from the volume and concentration of the solid and liquid phase. The system was also monitored by a data acquisition tool in order to see the temperature profile throughout the process. On completing the experimental work, it was found that higher flowrate resulted in a lower K, which translated into high efficiency. The efficiency is the highest at 1000 ml/min. It was also discovered that the initial concentration of solution highly affected the purity of the final ice crystals formed. The process also gives the highest efficiency at a coolant temperature of –6 °C.

Keywords: Freeze concentration; freeze wastewater treatment; ice crystals; progressive freeze concentration

Abstrak. Satu cara baru dalam pemekatan pembekuan, iaitu pemekatan pembekuan progresif (PFC) digunakan ke atas larutan glukosa sebagai simulasi air sisa untuk memekatkannya dan sekali gus merawat. PFC diharapkan dapat mengatasi masalah-masalah yang dihadapi oleh proses pemekatan pembekuan yang konvensional, iaitu pemekatan pembekuan terapai (SFC). Dalam PFC, kristal ais dihasilkan dalam bentuk lapisan di permukaan pemindah haba berbanding sebagai pepejal terapai dalam SFC. Di dalam kajian ini, satu alat pengkristalan yang berbentuk helikal dan diperbuat daripada kuprum telah direkabentuk dan dihasilkan. Kesan daripada tiga keadaan operasi telah dikaji untuk menilai kebolehan alat pengkristalan tersebut, iaitu kadar alir larutan, kepekatan awal larutan glukosa dan suhu cecair penyejuk. Kecekapan alat pengkristalan ini dilihat melalui pemalar pemisahan efektif, K, yang dikira menggunakan isipadu dan kepekatan fasa pepejal dan cecair yang dihasilkan. Sistem ini juga dipantau oleh satu alat pemantauan data untuk melihat profil suhu semasa proses ini berjalan. Daripada keputusan eksperimen yang dijalankan, didapati

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bahawa kadar alir yang tinggi memberikan nilai K yang rendah, yang mana bermaksud lebih efisien. Efisiensi adalah paling tinggi pada 1000 ml/min. Kepekatan awal juga didapati memberi pengaruh yang kuat ke atas ketulenan kristal ais yang dihasilkan. Efisiensi didapati paling tinggi pada suhu cecair penyejuk –6 °C.

Kata kunci: Pemekatan pembekuan; rawatan pembekuan air sisa; kristal ais; pemekatan pembekuan progresif

1.0 INTRODUCTION

Industrial wastewater can contain various types of pollutant ranging from chemicals to suspended matters and the type of treatment depends on the type of the pollutants. Regardless of the type of treatment that will be applied to the wastewater, it is such an advantage if the volume of the wastewater could be reduced extensively. Reduced volume of wastewater will result in a reduction in operation cost in terms of the utility. Hazardous wastewater is frequently treated by incineration. But to incinerate an aqueous solution, with a solid content of less than 10%, requires tremendous power to 'burn' the water and maintain the high temperature necessary to destroy the hazardous compound [1]. In addition, the combustion gas produced contributes to the emissions from the process and can rapidly exceed local limits.

In concentration of a solution, there are three methods available: reverse osmosis, evaporation and freeze concentration. Every process has their specific energy and among those three, the energy cost is the highest for evaporation (2.26 kJ/g-water), intermediate for freeze concentration (0.33 kJ/g-water), and the lowest for reverse osmosis because phase transition is not needed [2]. Evaporation is the simplest method which is worth the energy consumed, but it is very dangerous when hazardous volatile organic compounds (VOCs) are involved [3]. Despite of the low energy consumed in reverse osmosis, it is not a favourable method of concentration because clogging can easily occur, and the high cost involved to attain the osmotic pressure required.

Wastewater can be treated by separating the ice crystals formed in it, because ice crystals include no components of the wastewater except water, resulting purged water being obtained [4]. This process is called freeze concentration. Freeze concentration is an operation to concentrate an aqueous solution by separating ice crystals produced in the solution [5].

Some other advantages of freeze wastewater treatment are (1) wastewater including toxic compounds [6] or heavy metals [7] can be treated which is difficult to treat biologically; and (2) a smaller facility is required compared to biological wastewater treatment [8].

There are two methods available for freeze concentration, conventional suspension freeze concentration (SFC) and progressive freeze concentration (PFC). SFC is a process of freeze concentration where the ice crystals are formed in a suspension of the mother liquor 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 [9]. The small 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 [10]. These steps: ice nucleation, ice crystal growth and ice crystal separation make the whole system very expensive, which has made it unfavourable.

In compensating the disadvantages of SFC, a totally different concept of crystallization, PFC has been introduced. In this method, a large single ice crystal instead of a group of small ice crystals suspension is formed. The ice crystal is formed on the surface of the heat conducting material where the cooling is supplied. As only a single crystal is formed, its separation from the mother liquor is much easier to be handled and at a lower cost. However, despite of the easier separation, the productivity of PFC is found to be lower than the conventional SFC.

The design of the apparatus where the crystallization of ice is supposed to occur is an important factor in influencing the system efficiency. The selection of material of constructions and the design shape of the apparatus should be carried out carefully in order to ensure successful operation of freeze concentration. In this particular research a helical copper crystallization chamber was fabricated, where the crystallization of ice should take place. The newly fabricated chamber was then evaluated in terms of its efficiency according to the two parameters, which are the initial concentration of the initial solution and the circulation flowrate during operation. Initial concentration and circulation flowrate are among the important factors that significantly influence the efficiency of the system [11].

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 1 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.

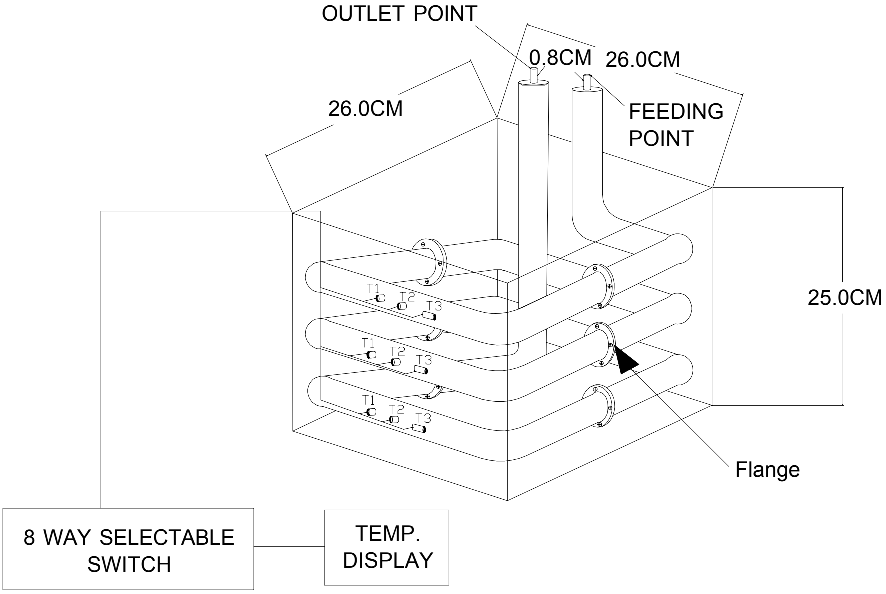

Figure 1 Diagram of the helical copper crystallization chamber (CC) structure

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.

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. The filled CC was then immersed in a precooled waterbath at the –8°, while the pump was run at the desired circulation flowrate. The solution then was left for crystallization to occur for 15 minutes. After 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.

3.0 RESULTS AND DISCUSSION

A calibration curve for the concentration of glucose via refractive index (RI) was first constructed by making several standard solution of glucose with concentration in the range of 1 to 10 mg/ml. The calibration curve is shown in Figure 2 which agrees with previous calibration curves produced previously by other researchers [12].

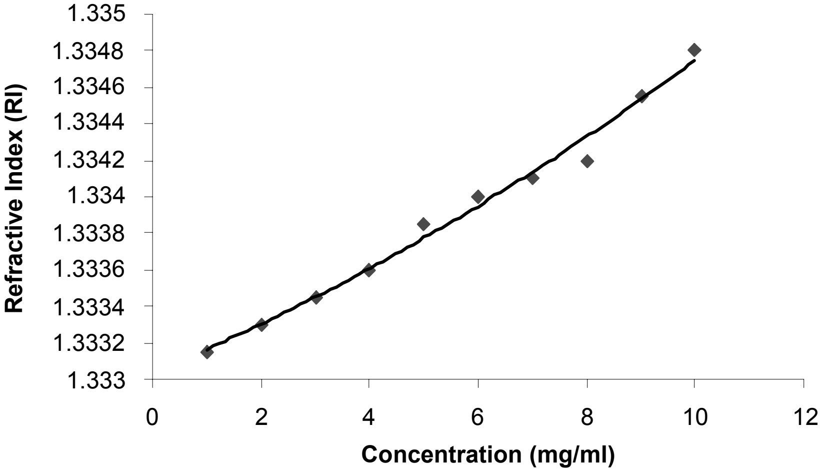

Figure 2 Calibration curve

Figure 3 Ice layer formed

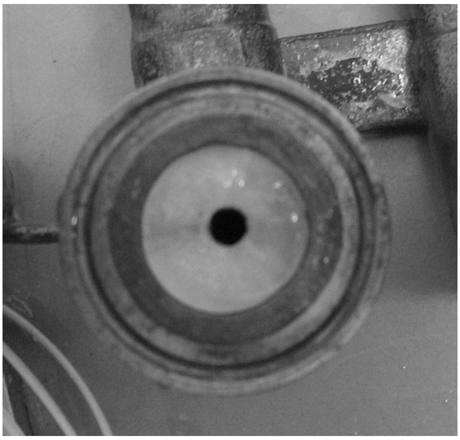

Figure 4 A close-up of the ice layer formed

During freezing, ice crystals were formed on the inner surface of the copper tube wall. Figure 3 and 4 shows 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.

3.1 Effect of Circulation Flowrate

The studied range of circulation flowrate for the newly designed PFC system was 400 to 1000 ml/min, which was chosen based on the existing pump capacity. While the circulation flowrate was varied, the other operating conditions were kept constant. Coolant temperature was kept at –8 °C and the circulation period at 15 minutes.

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

$$K = C_s / C_L \tag{1}$$

where C_s is and C_L are solute concentrations in ice and solution phase, respectively [2].

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

$$(1 - K) \log (V_L/V_0) = \log (C_0/C_L) \tag{2}$$

Figure 5 shows the effect of circulation flowrate on the effective partition constant K.

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.* [2] and Ramos *et al.* [13], higher flowrate will result in a highly pure ice crystal layer.

Increasing the flowrate of solution promotes heat transfer with ice crystals from its tips, hence enhancing the planar ice growth from the cooling wall by keeping contaminants away from the ice-liquid interface [14]. Therefore, higher flowrate will result in ice layer with higher purity. For this system, the K value is predicted to be lower if the flowrate is further increased. Figure 6 shows the effect of circulation flowrate on ice purity from this study which is very similar to the previous findings.

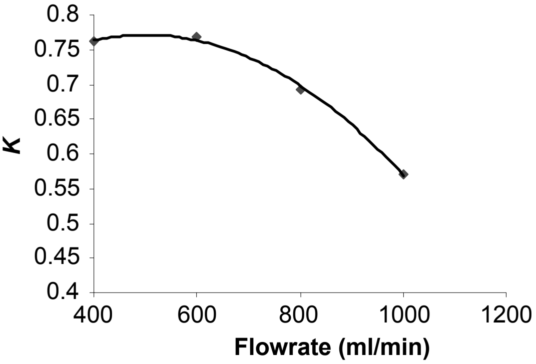

Figure 5 Effect of circulation flowrate on K

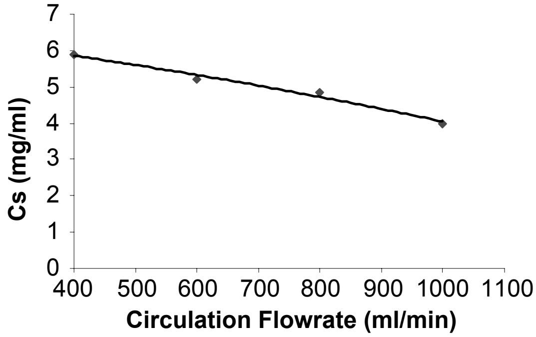

Figure 6 Effect of circulation flowrate on ice purity

3.2 Effect of Initial Concentration

The same experimental procedure was used in order to investigate the effect of initial concentration on the efficiency of this system. Solute concentration was investigated for the range of 2-8 mg/ml. 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 initial concentration on K is depicted in Figure 7. It can be observed that higher initial concentration resulted in higher K, which means lower efficiency for the system, and vice versa. This also means that the efficiency can be affected by the initial amount of solute in the solution to be concentrated and K is dependent on it. In the solidification process, the solution concentration increases at the ice-liquid interface because the solutes accumulate at this region [2]. This causes constitutional supercooling, which strongly affects the dendritic structure at the interface. Higher initial concentration means higher amount of solutes in the initial solution, which will cause higher accumulation of solutes at this interface, causing the ice layer concentration to be higher. This causes an increase in the effective partition constant,

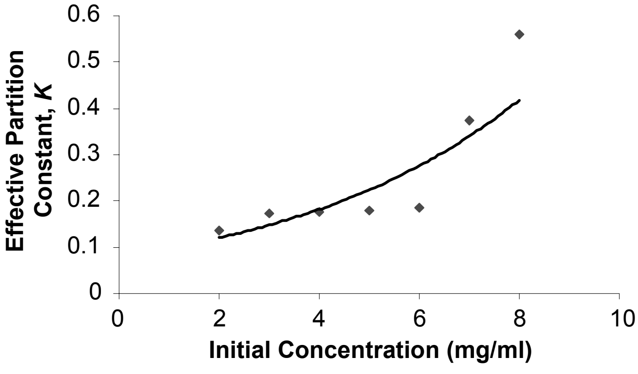

Figure 7 Effect of initial concentration on K

K. Therefore, it can be concluded that the initial concentration affects the efficiency of the process through constitutional supercooling, which causes a change in K [15].

3.3 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 8. 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 9 shows that

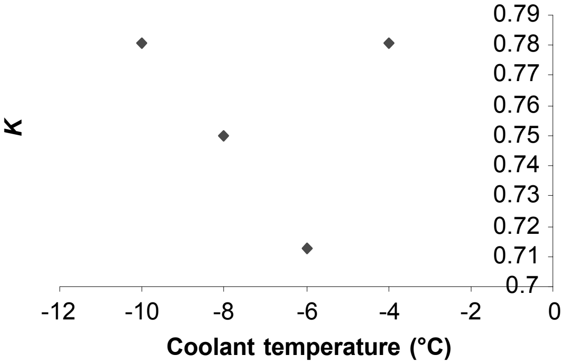

Figure 8 Effect of coolant temperature on *K*

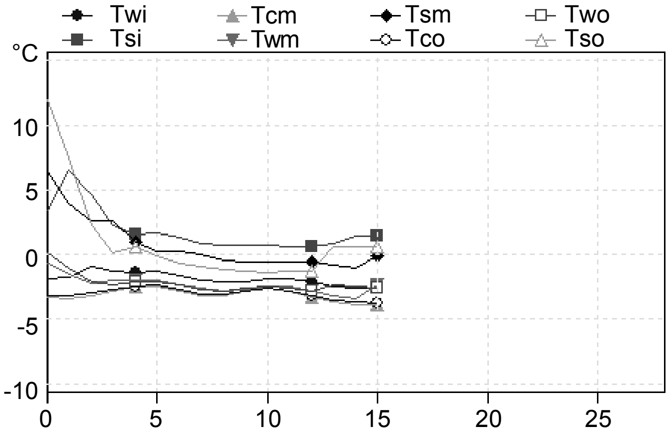

Figure 9 A snapshot of the temperature profiling tool

even the coolant temperature was set at –4 °C, its actual temperature was only –3.1 °C at average.

Coolant temperature controls the ice crystal front growth rate [2]. Ice growth rate increases with increasing difference between the entering solution and the surface temperatures [16]. 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. [17] and promote solute inclusion in the ice crystals. Low growth rate gives high purity of ice produced [2].

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 flowrate and initial concentration used.

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