Fractional Crystallization for Wastewater Treatment from Food Industries: Effects of Operation Temperature and Solution Flowrate

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***Abstract*—In food industry, one of the problems constituent to it is the production of wastewater as by-product, in which this problem contributed to the severeness of the environmental quality, specifically water pollution, as well as to the human health. It is a challenge for researchers around the world to develop effective technology to address this problem. Crystallization technique is seen as one of the potential techniques to deal with this issue. In this work, progressive freeze crystallization (PFC) technique was studied for its effectiveness in wastewater treatment for food industry. In this process, a single layer of ice crystal formed on the surface of the crystallization vessel, making it easier to separate ice crystal from the concentrated solution. The effects of operation temperature and solution flowrate to the effective partition constant, K and solute recovery, Y were investigated to indicate the efficiency of the PFC process on glocose solution as the modeled wastewater sample. It was discovered that lower operation temperature and higher solution flowrate causes K value to decrease while Y value increased, indicating higher efficiency. The highest efficiency was found at the operation temperature of -10°C with K and Y values of 0.4902 and 1.0048 respectively and at solution flowrate of 500 rpm, where K and Y values were 0.6521 and 0.9041.**

Keywords* — *Effective partition constant, Progressive freeze crystallization, Solute recovery,

I. INTRODUCTION

The physical and chemical characteristics of wastewater from food industry has contributed to the destruction of the environment as well as the population. Thus, a proficient wastewater treatment technology need to be developed. Crystallization technique has attracted many attention from researchers around the globe to be implemented in the treatment of wastewater streams from many industries including food industry. In crystallization technique, a pure solid crystalline phase and a concentrated liquid will be formed from the process. [1]. Freeze crystallization (FC) is one of the types of the technique in which it involves the fractional crystallization of water and subsequent removal of the ice [2]. This technique found its potential as a promising procedure in food industry wastewater treatment due to its ability to achieve high purity of water and to operate at low temperature [1] and the process can be scaled up with less of difficulties [3]. Apart from that, the technique is also more advantageous in a way that the energy cost for the technique is lower compared to other crystallization methods [3], as well as the process does not require any addition of accompanying materials like membrane or resins to operate, thus there is no concern about fouling or cleaning.

Freeze concentration is a process in which wastewater will be cooled down to a temperature of below the freezing point, and water will be formed into ice crystals which potentially having an extremely high degree of purity [1]. There are two types of freeze concentration; suspension freeze crystallization (SFC) and progressive freeze crystallization (PFC), in which the later is superior over SFC because of the simpler separation of ice crystals [4]. In SFC, ice crystals formed are small in size and suspended within the liquid, making the separation of these ice crystals from the concentrated liquid complicated [3]. While in PFC, ice crystals formed are growing in a form of layer on the surface of the crystallization vessel and eventually forming only a single large form of ice block instead of many small ice crystals [3]. Thus, the separation of ice for PFC is much easier.

PFC has been applied widely in the food industry to preserve flavors and some precious ingredients in the foods, as well as keeping the chemical and biochemical properties [5]. PFC is also seems to be potentially applicable in the treatment of wastewater from food industry. Therefore, this study was conducted to investigate the performance of PFC process towards the wastewater treatment from food industry. The optimum operating conditions were determined from this experiment, in which the performance of PFC was investigated at varied operation temperature and solution flow rate. The effects of these varied operating conditions were analyzed through the changes in effective partition constant, K and solute recovery, Y.

II. METHODOLOGY

A. Materials

D-(+) Glucose for modeled wastewater sample preparation and ethylene glycol to serve as coolant were purchased from Classic Chemicals, (Selongor).

B. Apparatus set up

The apparatus set up for the PFC process is illustrated in Fig.1. The system consisted of waterbath containing ethylene glycol, sample vessel of stainless steel and a stirrer. The role of the stirrer was to ensure that the concentration of solute in the liquid phase was distributed evenly in the solution phase, as well as to minimize the solute concentration near the ice phase.The waterbath used in this study was an open-bath circulator model from Thermo Haake and the stirrer used was IKA RW 20 digital overhead stirrer. Ethylene glycol was filled into the waterbath in volume of 50% of the waterbath's capacity, and water is also added for another 50% of the volume.

C. *Experimental Procedure*

Simulated wastewater sample was prepared first by dissolving pure glucose powder in distilled water, forming a glucose solution. The glucose solution used in the experiment was at a concentration of 7 mg mL^{-1} [6]. Prior to the feeding step of the process, the sample solutions prepared were stored in a refrigerator to be cooled down to a temperature near the freezing point of water, to avoid supercooling phenomenon from happening during the sample feeding[3]. Thus, the glucose solutions were cooled in a refrigerator with the temperature set at 4℃.

Fig. 1: Apparatus set up for PFC process

During the experiment, prior to the sample introduction into the sample vessel, seed ice lining was first allowed to form in the sample vessel by pouring 30mL of distilled water into the vessel. The vessel was then immersed into the waterbath and the water was allowed to freeze. After the lining had been formed, the refrigerated glucose solution at 1 L volume was introduced into the sample vessel to undergo the PFC process. The vessel containing sample solution was immersed into the coolant, with both the temperature and stirring speed controlled at a desired point. The process was allowed to run for 15 minutes. The process was repeated at operation temperature of -4. -6, -8, -10 and -12 ºC, and at solution flowrate of 100, 200, 300, 400 and 500 rpm, so that their effects on efficiency of the PFC process can be evaluated. When the PFC process had completed the 15 minutes process duration, the sample vessel was taken out, and the volume and concentration for both of the concentrated and melted solutions were measured and recorded.

D. *Analytical Procedure*

Prior to the analysis of samples, a calibration graph of standard glucose solutions was constructed and is shown in Fig. 2. The concentration of samples collected from the PFC process were then analyzed spectroscopically.

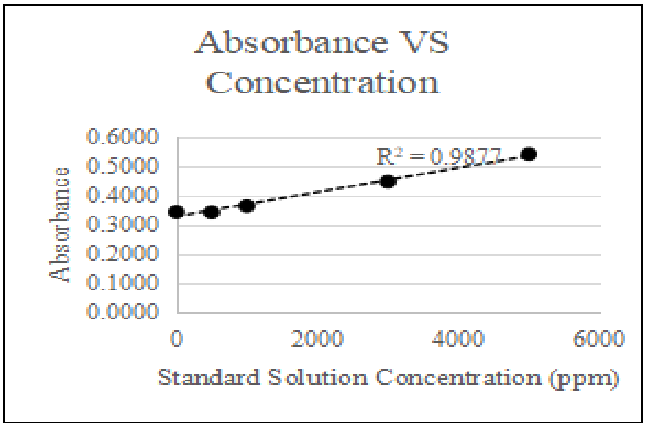

Fig. 2: Calibration Graph of Standard Glucose Solutions

Effective Partition Constant

According to Liu et al. (1997), effective partition constant of a solute, K between the ice phase and the interface is defined as follows;

$$K = \frac{C_S}{C_L} \quad (1.1)$$

where C_S and C_L are solute concentration in ice and solution phase, respectively.

$$\ln\left(\frac{C_0}{C_L}\right) = (1-K)\ln\left(\frac{V_0}{V_L}\right) \quad (1.2)$$

where C_0 and V_0 are the initial solute concentration in the solution phase and initial volume of solution respectively (Fujioka et al., 2013).

Solute Recovery Efficiency

Solute recovery, (Y) is the ration of the glucose concentration in the concentrated solution to that in its initial solution (Samsuri et al., 2015). To calculate the solute recovery;

$$Y = \frac{M_{S,L}}{M_{S,0}} \quad (1.3)$$

in which $M_{S,L}$ is the mass of solute in concentrated solution, while $M_{S,0}$ is the mass of solute in the original solution. Y has a unit of g of glucose/g of initial glucose, and a higher value of Y is preferable, in which it reflects a better efficiency of the PFC process.

III. RESULTS AND DISCUSSION

From the PFC process, ice crystal layer was formed on the inner surface of the cylindrical vessel. Fig. 3 shows the ice crystal formed after the PFC process had ended. The relationship between the PFC operation temperature and the concentration of the liquid phase collected after the process had stopped is illustrated in Fig.4, while the relationship between the stirring speed with the concentration of the liquid phase is illustrated in Fig. 5. It can be observed that glucose concentration in the liquid phase increased with decreasing coolant temperature and increasing solution stirring speed. K and Y values at the varied operation temperature and solution flowrate were evaluated , and the results are tabulated in Table 1.

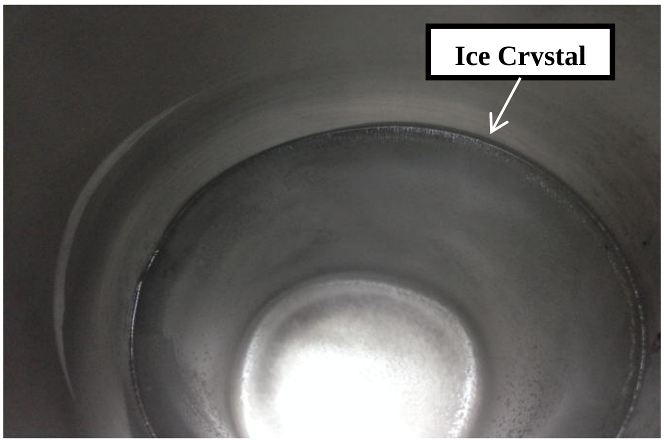

Fig. 3: Ice Crystal Lining Formed after PFC Process

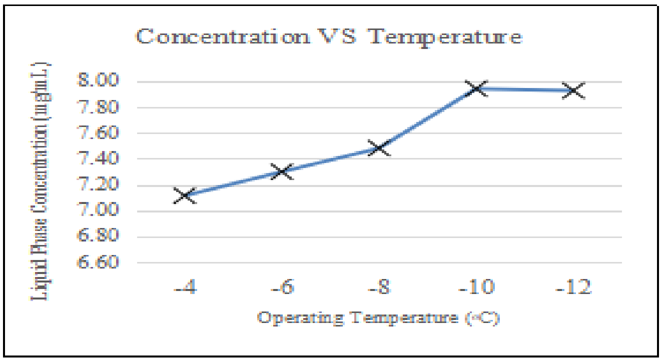

Fig. 4: Graph of Concentration of Concentrated Liquid Phase Against Operating Temperature

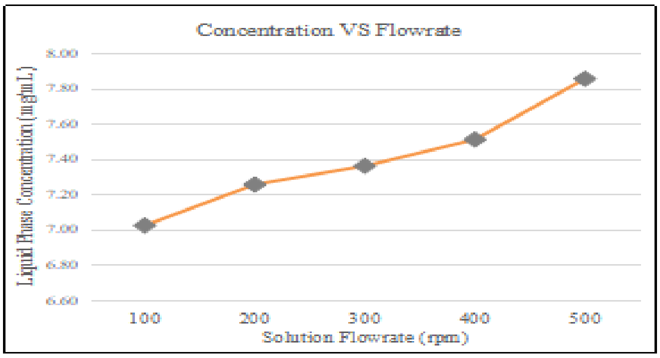

Fig. 5: Graph of Concentration of Concentrated Liquid Phase Against Solution Flowrate

A. Effects of Operation Temperature

The operation temperature of PFC process refers to the coolant temperature, in which the temperature was regulated through the digital controller equipped to the waterbath. Heat transfer occurred between the coolant and sample solutions through the surface of the vessel wall due to the temperature difference between the coolant temperature, surface temperature and the temperature of glucose solution [5]. Heat transfer rate is directly proportional to the temperature difference between the coolant temperature and glucose solution [7]. This means that; lowering the coolant temperature causes the heat transfer rate to increase, since the temperature difference has increased. Thus, it is preferable that the coolant temperature to be lower, as this condition enhance the heat transfer between the coolant and the glucose solution. Lower surface temperature is obtained at lower temperature, in which this is an adequate initial supercooling condition for ice nucleation.

The effects of operation temperature on the performance of PFC process was analyze through the calculation of K and Y values, by implementing equations 1.2 and 1.3, respectively. Fig. 6 illustrate the relationship between K and Y with the operation temperature of PFC process. It can be observed that K decreases as the coolant temperature decreases from -4ºC to -10ºC, while Y on the other hand increases. However, when the coolant temperature was further decreased from -10ºC to -12ºC, the value of Y dropped while the K value increased slightly. This outcome agrees with the the findings by Samsuri et al. (2015)[7] and Amran et al. (2016)[8], which also found that lower temperature will results in lower K value and higher Y value.

The effect of heat transfer rate between coolant solution and the sample solution explains the decrease in K value and increase in Y value with decreasing temperature. As the coolant temperature decreased, the temperature difference between coolant and glucose solutions became larger, thus increased the heat transfer rate which lead to a higher efficiency of the PFC process performance. For this analysis, it can be observed that at the

Effects of Operation Temperature		
Coolant Temperature (ºC)	**K**	**Y**
-4	0.8828	0.9011
-6	0.8065	0.8765
-8	0.7148	0.9049
-10	0.4902	1.0048
-12	0.5131	0.9934
Effects of Solution Flowrate		
Stirrer Speed (rpm)	**K**	**Y**
100	0.9797	0.8592
200	0.8186	0.8819
300	0.7631	0.8946
400	0.7140	0.9001
500	0.6521	0.9041

operation temperature of -10ºC, K and Y values were at the lowest and highest, respectively. K was 0.4902 and Y was 1.0048 at -10ºC, which portrays that the efficiency of the PFC process was the best at this temperature. The highest amount of glucose was also recovered at this temperature.

Nevertheless, as the operation temperature was lowered further from -10ºC to -12ºC, K value slightly elevated from 0.4902 to 0.5131 and Y also dropped from 1.0048 to 0.9934. This indicates that the efficiency of the process had reduced. Ironically, lowering the temperature should lead to better efficiency. The deviation may due to the supercooling effect which usually occurred at the operation temperature that was too low. Supercooling phenomenon marked down the efficiency of PFC process by lowering the solute recovery, Y and increasing the K value. Higher K value indicates that the ice crystal layer formed has a poor purity. Supercooling effect accelerates the formation of ice crystal layer, which causes higher inclusion of solute in the solid ice phase.

Table 1: K and Y values at Varied Operation Temperature and Solution Flowrate

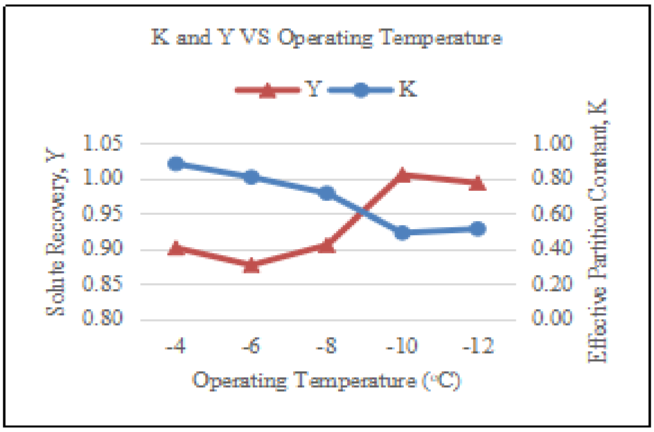

Fig. 6: Effects of operation Temperature on K and Y

B. Effects of Solution Flowrate

The solution flowrate for the PFC process was controlled in order to prevent solutes from being trapped into the ice crystal formation, so that high solute concentration in the concentrated solution can be recovered [8]. The solution flowrate was controlled through the stirring speed at the ice-liquid interface. Miyawaki et al. (2005) [3] explained that the stirring rate was related to the mass transfer of a freezing system. The stirring speed contributed to the advance rate of the ice front as well as the mass transfer between the ice and liquid interface, which eventually contribute to the efficiency of a PFC system. The inclusion of high solutes or contaminants concentration in the solid ice phase can be prevented at higher solution flowrate, as the solutes are continuously stirred away from the ice-solution interface.

The analysis of solution flowrate effects on K and Y values are illustrated in Fig. 7. It was observed that as the solution flowrate, or the stirring speed increased from 100 rpm to 500 rpm, K value decreased, while Y on the other hand, increased. In this study, the best efficiency was found at the solution flowrate of 500 rpm with the lowest K value of 0.6521 and highest Y of 0.9041. The analysis agrees with the outcomes from the studies conducted by Amran et al. (2016) which found that lower K value was obtained with higher solution flowrate. An efficient PFC system is established at higher solution flowrate, at which the rate of the ice growth becomes slower, resulting in a higher purity of the ice crystals formed.

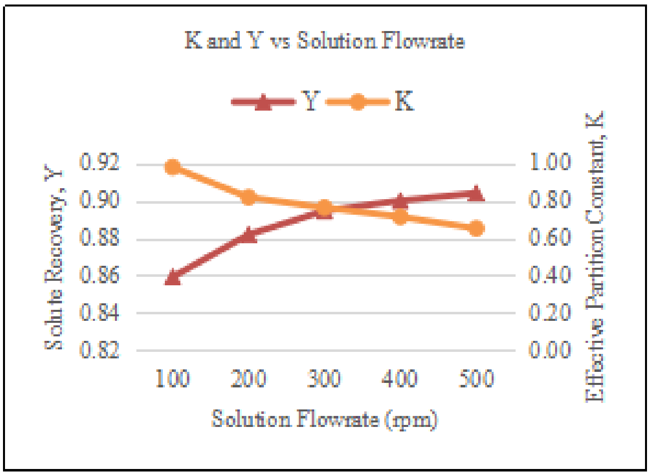

Fig. 7: Effects of Solution Flowrate on K and Y

IV. CONCLUSION

The PFC process is seen as a potential technology in the treatment of wastewater from food industries. In this study, the effects of the operation temperature and solution flowrate on the efficiency of the PFC process was evaluated through the determination of effective partition constant, K and solute recovery, Y. The best operation temperature for this system was found to be at -10ºC with the lowest K value of 0.4902 and highest Y of 1.0048. Meanwhile, for solution flowrate, the optimum condition was determined at 500 rpm with K value and Y of 0.6521 and 0.9041, respectively.

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