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Progressive Freeze Concentration in Removing Methylene Blue from Dye Wastewater

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Abstract: The dye industry generates huge amount of wastewater and could severely jeopardize environmental quality. This study aimed to purify methylene blue from dye wastewater via progressive freeze concentration (PFC). PFC was introduced as a new approach to purify methylene blue. In this work, PFC technique studied for its effectiveness in removing methylene blue from wastewater of dye industry. In PFC, pure water is produced in the form of ice crystal block and leave behind a higher concentration solution. The effect of coolant temperature, operation time and stirring speed were investigated and evaluated by the value of effective partition constant (K) and percentage of solute reduction. The lowest K value (0.26) was obtained at -8°C with the highest solute reduction (71.55%). Meanwhile, the highest efficiency for stirring speed was determined at 350 rpm with K value and solute reduction were 0.33 and 62.69%, respectively. K value of 0.053 and solute reduction of 93.25% were obtained at the best time of 20 minutes. The results demonstrated that the moderate coolant temperature, moderate operation time and maximum stirring speed resulted in the lowest K value and highest percentage of solute reduction in ice which indicates the highest efficiency of methylene blue removal.

Keywords: Progressive freeze concentration; wastewater treatment; dye wastewater; methylene blue; ice crystal.

1. Introduction

Dyeing is an important process in many manufacturing industries mainly in textile, food, plastic, paper and cosmetics. Despite the impressive growth rate of dye industries, to-date, public are not aware that this industry is harmful to the environment. Dye manufacturing processes produced massive amount of wastewater and liquid effluents [1], which contains high toxic of organic residues with major compounds of phenol derivatives, aniline derivatives, organic acid and benzene derivatives. On the other hand, the dye's color may cause aesthetic problems when discharged without proper treatment [2].

Numerous purification methods have been applied to treat the wastewater and to sustain water supply, including adsorption [3-6], photodegradation [7, 8], reverse osmosis [9-11] and crystallization [12-14]. Crystallization is a solid-liquid separation technique, where solutes from a solution are transformed to a pure solid crystalline phase. In comparison to other techniques, crystallization technology offer many advantages, such as high recovery rate, capability of recovering both high quality water and valuable salts at the same time, no consumption of other supplementary material [15]. In wastewater treatment, cooling crystallization has been applied for solutions that has solubility of solute strongly depending on temperature [16].

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Freeze concentration (FC) is the most recent potential technology for dye wastewater treatment. In principle, FC operates based on the solidification phenomena of water, where the water is removed from solutions by freezing it up to the formation of ice crystals, followed by a separation process to separate the ice crystals from the concentrated solution [17]. There are three types of FC technology: suspension freeze concentration (SFC), progressive freeze concentration (PFC) and block freeze concentration (BFC) [18]. Among the aforementioned techniques, SFC has been widely applied in industrial due to its high efficiencies even though it consumes high operating and investment costs [17-19]. Therefore, the latter methods, PFC [20-22] and BFC [23-25] have been developed to simplify the SFC system, hence reducing its operational cost.

PFC offers numerous advantages over SFC technique, including easier separation process. In the PFC process, the ice formed as a large single ice crystal instead of small particles like those found in SFC. The ice crystal formation takes place on the surface of the heat conducting material where the cooling fluid is supplied. The separation of ice crystal from its mother liquor is much easier to be handled compared to SFC since only a single ice crystal is formed. Due to this reason, the process requires a lower operational cost and less maintenance [26, 27].

PFC is an attentive method used in wastewater treatment. From the viewpoint of device development, PFC seems more advantageous than SFC because the device structure is much simpler [28]. Various types of wastewater have been experimented with, such as polypepton-containing wastewater [29], synthetic wastewater, urban wastewater and cutting oil wastewater [30]. The typical concentrations of wastewater are always very low which only uses a few grams per liter. This is beneficial for PFC as the operating temperature is just a few degrees below zero, which leads to minimum energy costs as well as easily achieving high concentration ratios [30]. Over the years, many kinds of equipment for PFC have been invented, for example a tubular ice system with a circulating flow inside [31], coil crystallizer [32], spiral finned crystallizer [33], and vertical finned crystallizer [22].

There are several factors affecting the efficiency of the system and the thawed ice quality [34]. Therefore, it is important to study the behaviors of system efficiency at different operating conditions. In the present paper, PFC was applied to purify simulated dye wastewater focusing on coolant temperature, operation time and stirring speed. The objective of this study is to investigate the mentioned parameters on the efficiency of PFC by considering the effective partition constant (K) and the percentage of solute reduction in ice.

2. Materials and method

2.1 Materials

The main material used in simulating dye wastewater was methylene blue or known as basic blue dye with chemical formula of $C_{16}H_{18}N_3SCl$ (M_W = 319.851 g/mol and λmax = 665 nm). This methylene blue powder was diluted with distilled water into desired concentration whereas for the coolant, ethylene glycol was used and mixed with distilled water.

2.2 Experimental Set-up

The experimental set-up in this study is shown in Figure 1. The cooling bath was equipped with a motor stirrer. A cylindrical stainless-steel vessel with 1L of volume was plunged and immersed at a position of ¾ the depth of the cooling bath. The cooling bath was pre-cooled at desired operation temperature and controlled by thermo-controller (HAAKE DL 30).

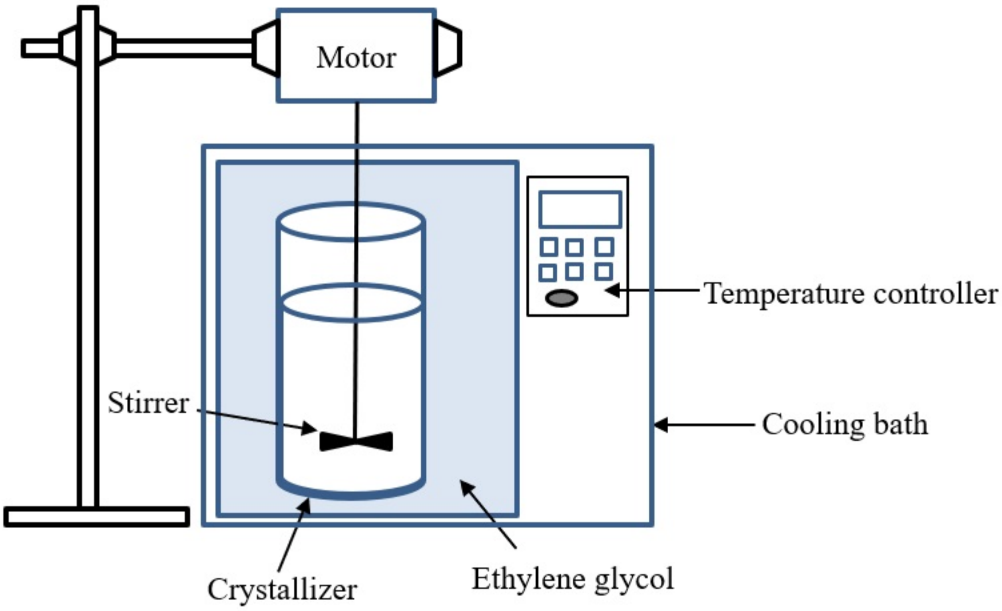

Figure 1. Schematic diagram for PFC system.

2.3 Experimental Procedure

The basic dye, methylene blue powder was weighed accurately at 0.500 ± 0.02 g and diluted in 1 L of distilled water to obtain a solution of simulated dye wastewater with concentration of 500 mg/L [35]. This sample solution was then kept at temperature ranged 2–3°C meanwhile the cooling bath was filled with ethylene glycol/water (50 v/v%) and pre-cooled at desired temperature. A stainless-steel cylindrical vessel was used and equipped with a motor stirrer to control solution flowrate. To prevent initial supercooling, 30 mL of pure water was added into the stainless steel-bottom of the vessel to form as an ice lining. After the formation of ice lining, about 1 L of simulated dye wastewater with temperature of 2°C (near to freezing point of water) was then poured into the sample vessel plunged into the cooling bath. In this work, the coolant temperature, operation time and stirring speed studied were in range of -4°C to -12°C, 5 minutes to 25 minutes and 150 to 350 rpm, respectively.

After the designated time, the stirrer was stopped, the sample vessel was taken out of the cooling bath and the ice crystal was separated from the concentrated mother solution. The volume, V_L and solute concentration, C_L in the mother liquor solution were analyzed using a UV/Vis spectrophotometer. After a few trials were executed to determine the best wavelength for analysis, 630 nm was chosen as the selected wavelength as it produced the most consistent results. Once the concentration and volume of the product was determined, the effective partition constant (K) and the percentage of solute reduction were calculated. The measurements were performed in duplicate.

2.4 Analytical Procedure

The concentration of concentrated mother solution was measured analytically by UV/Vis spectrophotometer (Perkin Elmer). This analytical method gave the absorbance value at a wavelength of 630 nm and used to determine the concentration from the standard curve. A calibration curve for the concentration of simulated dye wastewater has been constructed and shown in Figure 2. The curve was obtained by making few standard solutions which have the concentration range of 450 mg/L to 750 mg/L.

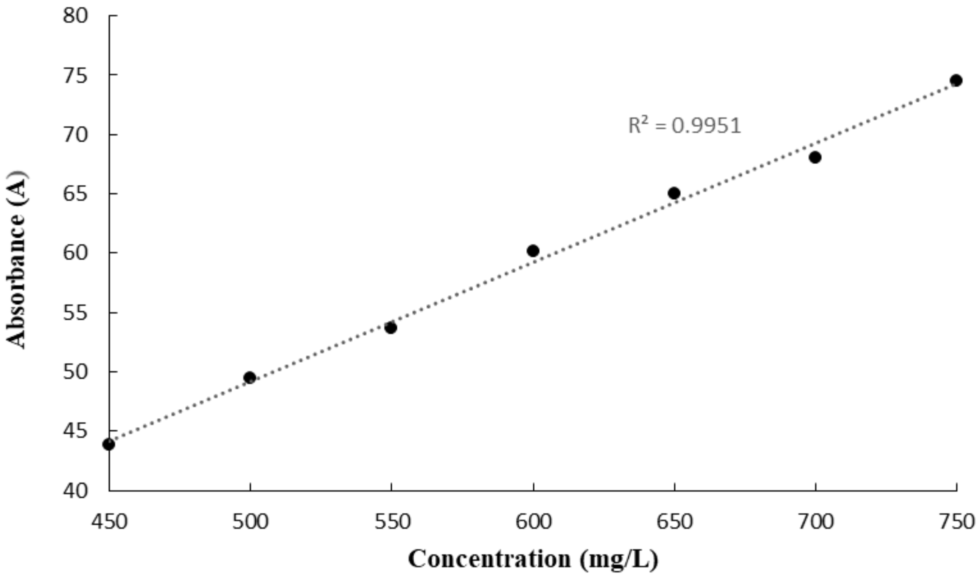

Figure 2. Calibration curve.

The analysis was done based on the value of K and the solute reduction. The K value was calculated by using Equation (1) [31].

$$(1-K) \log (V_L/V_o) = \log (C_o/C_L) \quad (1)$$

where V_o and C_o are the initial volume and concentration of the simulated dye wastewater in liquid phase, respectively meanwhile the V_L and C_L are the volume and concentration of solute in concentrated mother solution, respectively.

The ice purity could be analysed based on the percentage of solute reduction in ice. The ice purity could be determined from the concentration of the solute in ice fraction, C_S. The percentage of solute reduction in ice can be calculated through Equation (2) [36].

$$\text{Percentage of solute reduction in ice} = [(C_o - C_S)/ C_o] \times 100 \quad (2)$$

where C_o is the initial concentration of the solution and C_S is the concentration of ice (solid phase).

3. Results and discussion

Effect of coolant temperature, operation time and stirring speed on the PFC system were discussed by considering K value and the percentage of solute reduction in ice. The changes of concentration for both ice crystal and concentrated solution were evaluated to determine the efficiency of PFC system. The PFC technique was performed for several minutes and afterwards, ice crystal can be observed formed on the wall of the vessel. Table 1 shows the relationship between operation conditions and solute concentration in liquid phase. In the present work, as the investigated parameter was kept varied, the other parameters were kept constant. The coolant temperature range used in this study is -4°C to -12°C with other parameters were kept constant with operation time and stirring speed of 15 minutes and 350 rpm, respectively. In the study of stirring speed effect, the stirring speed was varied from 150 rpm to 350 rpm, while the parameter of coolant temperature and operation time were kept constant at -8°C and 15 minutes. Meanwhile, the investigation on operation time effect, the range of operation time investigated is 5 to 25 minutes with the constant parameter of coolant temperature at -8°C and stirring speed at 350 rpm. From the table, it is clearly shown that the solution is successfully concentrated as the solute concentration in liquid phase is increased as compared to the initial concentration used which is 500 mg/L. In other words, water is significantly frozen out into the ice crystal form and left the solutes in the liquid phase.

Table 1. Relationship of investigated operation conditions and solute concentration in liquid phase.

Coolant temperature (°C)	$C_{L(a)}$ (mg/L)	Stirring speed (rpm)	$C_{L(b)}$ (mg/L)	Operation time (min)	$C_{L(c)}$ (mg/L)
-4	505	150	512	5	535
-6	540	200	516	10	569
-8	544	250	524	15	595
-10	550	300	530	20	637
-12	560	350	538	25	729

*$C_{L(a)}$ – solute concentration in liquid phase for coolant temperature
$C_{L(b)}$ – solute concentration in liquid phase for stirring speed
$C_{L(c)}$ – solute concentration in liquid phase for operation time

3.1 Effect of Coolant Temperature

This study was carried out to determine the effect of coolant temperature on the efficiency of the PFC system. The effect of coolant temperature on PFC can be observed based on the value of effective partition constant (K) obtained. The K value can be calculated by using Equation (1) and a graph of K against coolant temperature was plotted as shown in Figure 3.

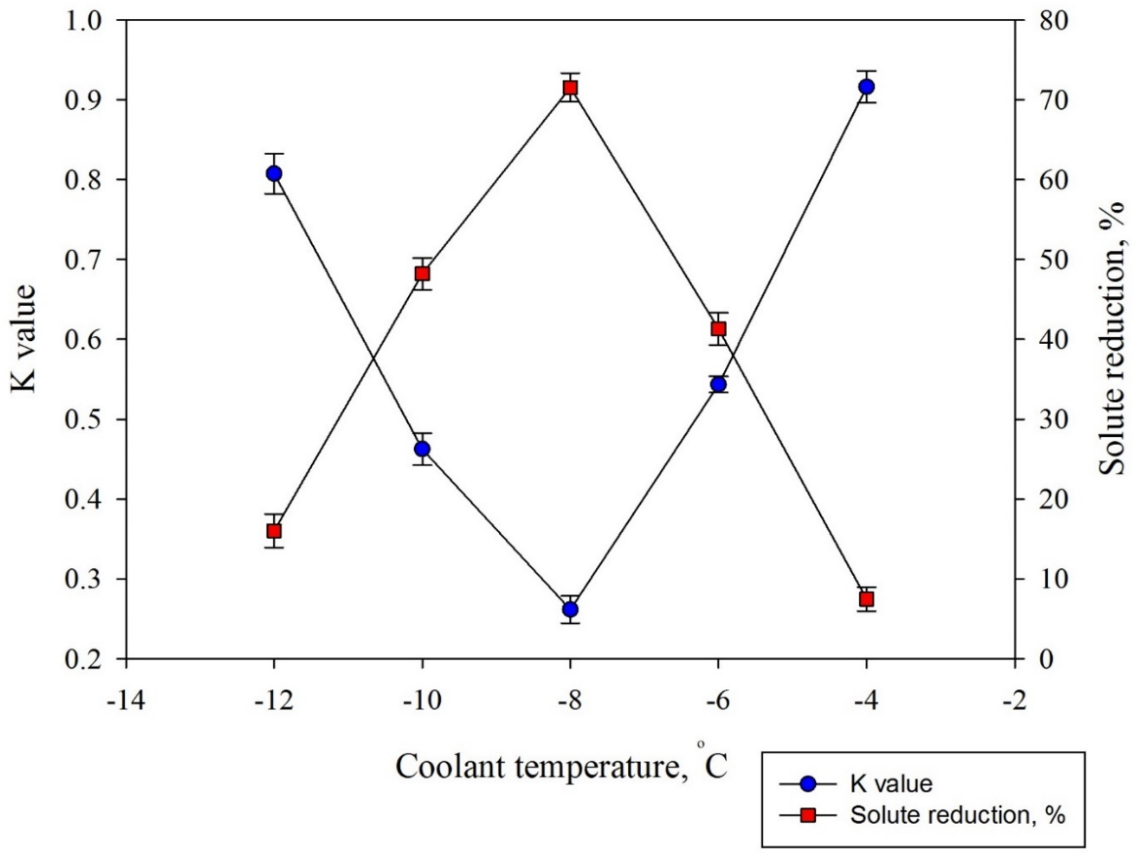

Figure 3. Effect of coolant temperature on K value and solute reduction.

As can be seen from Figure 3, there are decreasing changes of K value from -4°C to -8°C and the trend is shifted when the temperature of -10°C was applied. This proves that K value is temperature-dependent parameter. The K value for the highest temperature is 0.92 then decreasing towards 0.54 as the coolant temperature was reduced to -6°C. This verifies that higher coolant temperature yields higher K value, which indicates lower ice purity [13]. This situation might be due to incomplete crystallization process since the high coolant temperature was incapable of forming complete ice crystal within 15 minutes of operating time. Higher K value also points to lower efficiency for the system.

It is an obvious notation that the lowest K value was obtained at temperature of -8°C which is 0.26. Lower K value depicts higher ice purity as well as illustrating higher efficiency of PFC. Hence, -8°C can be considered as the optimum coolant temperature for PFC process. However, the K value's trend was shifted as the temperature was reduced to -10°C. The deviation may due to the supercooling effect which usually occurred at the lowest coolant temperature [37]. Supercooling has an effect of reducing the ice purity [29]. Supercooling effect accelerates the formation of ice crystal layer, which causes higher inclusion of solute in the solid ice phase. In addition, according to Zhang and Hartel (1996) [38], lower temperatures resulted in higher ice crystal growth rates, hence poor purity of ice produced. This establishes that the ice purity is low and the efficiency of the system is reducing at too low of coolant temperature [21].

The effect of coolant temperature on PFC could also be seen based on the percentage of solute reduction in ice which was calculated using Equation (2). In terms of percentage of solute reduction, the highest percentage was recorded at -8°C with a value of 71.55%. This result agrees to the K value, as at -8°C the ice was obtained at the highest purity. This also indicates that more dye solutes were concentrated in the mother liquor solution leaving the ice fraction almost pure. As the temperature was further decreased, the percentage of solute reduction is decreased. The incredible drop in the amount of solute reduction below -8°C is also probably because of the dendrites of ice crystals growth, thus causing solutes easily to be trapped between the dendrites [39]. Moreover, when the coolant temperature is lowered, the ice growth rate will be increased. Therefore, the chance for solute to be entrapped in the ice phase becomes higher, resulting low purity of ice produced.

3.2 Effect of Stirring Speed

According to Fukui and Maeda [40], the fluid flow structure of the solution is one of the factors that control the transfer phenomena of heat and mass in PFC. Solution movement plays a role to remove the trapped solute in ice crystals resulting a highly purified ice. This solution movement was introduced to provide a uniform distribution of flow, hence reducing the accumulation of solute near the liquid-ice interface [21]. In this study, solution flowrate was represented by stirring speed. The effect of stirring speed towards the efficiency of PFC system can be analyzed based on the K value. As can be observed in Figure 4, the K value was decreasing with the increment of solution flowrate which indicates, higher efficiency can be achieved at higher stirring speed.

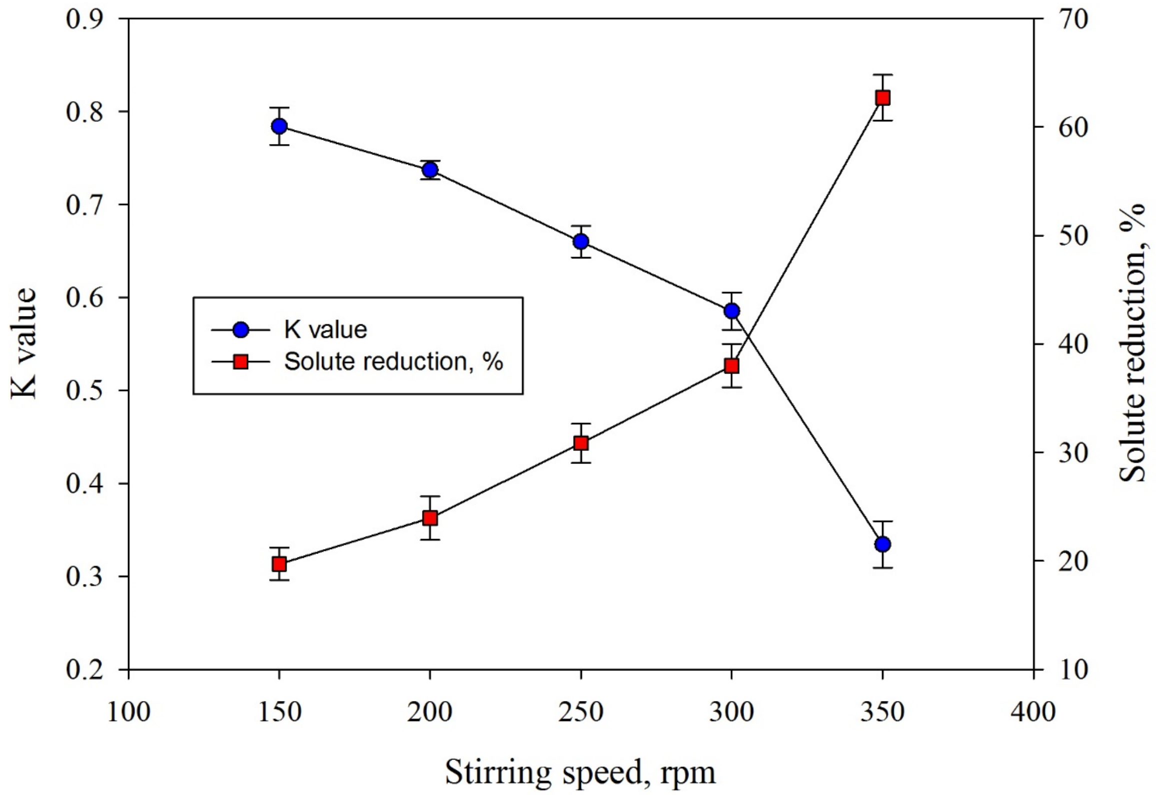

Figure 4. Effect of stirring speed on K value and solute reduction.

Higher flowrate yielding higher ice purity can be explained by the mass transfer resistance at the ice-liquid interface. The stirrer is functioning to lowering the concentration of the ice front, and enhancing the purification ability [41]. In addition, the solution movement helps to wash the solute away from the ice fraction and keep them entrained in the liquid fraction. Hence, the higher the stirring speed, the lower the K value obtained indicating better efficiency for the system.

In another perspective, the ice solute reduction percentage was also investigated to discover the effectiveness of the dye purification process in this system. As presented in Figure 4, an increasing pattern is observed for percentage of solute reduction in ice, portrayed the higher purity of ice crystal. The solute reduction increased from stirring speed of 150 rpm (19.72%) to 350 rpm (62.69%). This depicts that higher solution flowrate yielding ice with higher purity. A higher percentage of solute reduction gives a picture of higher efficiency of the system. Hypothetically, heat transfer rate for ice crystallization will be increased by increasing the solution flowrate [22]. In this situation, ice crystals will be developed in a planar form, hence discarding the impurities away from the solid-liquid interface, resulted in pure ice crystals produced.

3.3 Effect of Operation Time

In PFC system, time is one of the crucial factors that need to be in consideration. In this context, operation time is defined as the time taken for crystallization to occur, in which the feed solution is concentrated, and the pure water will be crystallized into ice form. For this experiment, K value and solute reduction was discovered to determine the effectiveness of PFC system. Generally, higher concentration efficiency can be achieved if the longer time is provided for crystallization to occur [42]. Low ice production is obtained when shorter time was implemented, and it also incorporated with the presence of dendritic structure, which leads to the poor quality of ice crystals.

The effect of operation time towards K value and solute reduction is depicted in Figure 5. From the plotted graph, it is observed that the value of K reduced with operation time until it reaches its minimum point. The graph shows that a suitable crystallization time of 20 minutes is the best condition for the PFC process where the K value is the lowest with 0.053. Consequently, as the operation time progressed further than 20 minutes, higher K can be seen, which is undesirable for this system.

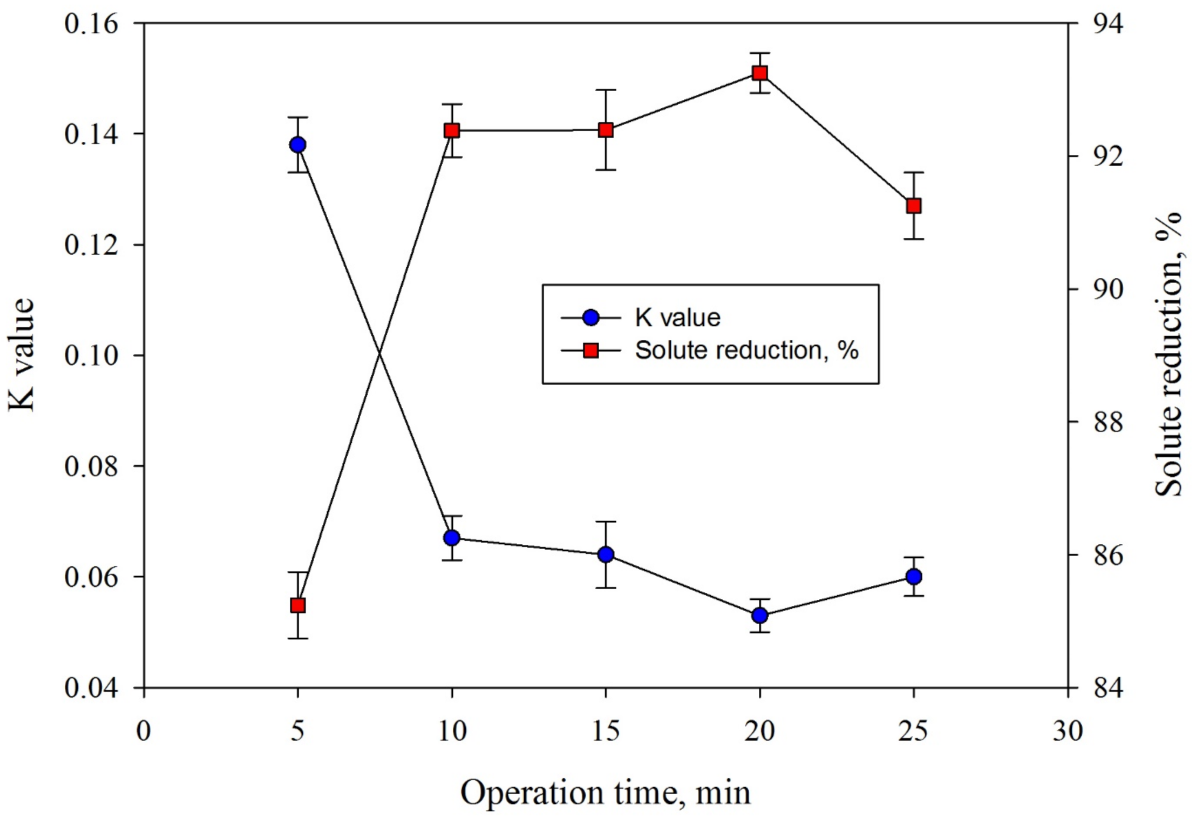

Figure 5. Operation time against K value and solute reduction.

Evidently, above 20 minutes of operation time, the ice formed nearly filled the crystallizer completely, resulting in just a narrow path for the concentrate to pass through thus leaving the contaminants to be trapped in the ice crystal formed on the wall. Obviously, the longer operation time applied will reduce the diameter of the liquid phase path. Consequently, the chance for contamination of ice formed is higher due to the saturation of solute in the solution [17, 39, 43]. This explain the reason of higher K value and lower percentage of solute reduction at 25 minutes.

4. Conclusion

PFC has been a potential technology to be applied for wastewater treatment. Based on PFC fundamental mechanism, this process has a splendid opportunity to be implemented for other industries that required to concentrate solution such as food industry and pharmaceutical, also has been successfully employed for desalination of seawater. In this study, PFC was proved to be effective in removing methylene blue from dye wastewater. The best coolant temperature was obtained at -8°C with a K value of 0.26 and the highest percentage of solute reduction in ice of 71.55%. The most optimum stirring speed was identified at 350 rpm with a K value of 0.33 and percentage of solute reduction of 62.69%. 20 minutes was determined as the best time for PFC system to obtain the high efficiency with K value and percentage of solute reduction in ice are 0.053 and 93.25%, respectively. These conditions are recommended to obtain a high efficiency of methylene blue removal from dye wastewater.

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