Purification of Dye Industries Wastewater via Crystallization: Effect of Operation Temperature and Solution Flow Rate

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Abstract**—** Dye industry is one of the industries that generates huge amount of wastewater and contributes to environmental devastation. Various ways have been used in wastewater treatment to make it less harmful. This study aimed to purify dye industries wastewater via a method of crystallization known as progressive freeze concentration (PFC). PFC is a crystallization process that forms only one single block of ice making it easier to be separated with the mother liquor solution. The effect of operation temperature and solution flow rate (stirring speed) was investigated in this study. The performance analysis was carried out by using simulated solution and was evaluated by the value of effective partition constant, K and percentage of ice purity. It was found that at temperature of -8˚C, the K value obtained of 0.2615 was the lowest with the highest percentage of ice purity of 71.55%. It was also notable that the best stirring speed to achieve highest efficiency was at 350 rpm with a K value of 0.3343 and ice purity percentage of 62.69%.

Keywords**—** Freeze concentration, progressive freeze concentration, wastewater treatment, dye wastewater

I. Introduction

Dyeing process has been very crucial towards many industries such as textile, food, plastic, paper, cosmetics and many more. Despite the impressive growth rate of dye industries, not many know that this industry is harmful to the environment. This is due to the fact that dye manufacturing processes produced massive amount of wastewater as well as the liquid effluents from cleaning equipment after each batch operation. What worse is that dye wastewater contains toxic organic residues with major compounds of phenol derivatives, aniline derivatives, organic acid and benzene derivatives. In dye wastewater, the content of pollutants is relatively high. The color of dyes will cause aesthetic problems if the wastewater is being discharged without proper treatment [1].

However, dye wastewater could be purified to recover the valuable water since water resources are limited. There are many purification methods that have and could be applied such as distillation, evaporation, solvent extraction, oxidation, reverse osmosis, precipitation, micro- and ultra-filtration as well as crystallization. Crystallization is a solid-liquid separation technique, in which solute from a solution turns into a pure solid crystalline phase. Comparing with other techniques, crystallization technology has 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 materials [2]. In wastewater treatment, cooling crystallization is typically applied for solutions that its solubility of solute is a strongly depending on temperature [3].

Cooling crystallization can be categorized into solute crystallization, freeze crystallization (freeze concentration) and eutectic freeze crystallization. Freeze concentration (FC) is a process of concentrating liquid products by freezing the water content and subsequently removing the so-formed ice crystals from the solution. In wastewater application, it focuses on the crystallization of water in the waste solution; while concentrating the organic and inorganic compounds in the remaining liquid. FC can be subdivided into two categories which are suspension freeze concentration (SFC) and progressive freeze concentration (PFC).

The mechanism of SFC is that the ice crystals crystallize out from the concentrated solution that is enlarged in size by Ostwald ripening [4]. The size of crystals produced is relatively small resulting in the difficulty to separate them from bulk liquids [5]. This is the reason why SFC is not really a popular method to be used in waste water treatment.

Progressive freeze concentration (PFC) is an attentive method used in wastewater treatment. Unlike SFC, in PFC, only one block of ice forms on the cooling surface. Large ice mass formed and grown making the separation of the crystals from mother liquor relatively easy [6]. From the viewpoint of device development, PFC seems more advantageous than SFC because the device structure is much simpler [7]. Various type of wastewater has been experimented with such as polypepton-containing wastewater [8], synthetic wastewater, urban wastewater and cutting oil wastewater [9]. The typical concentrations of wastewater are always very low which only a few grams per liter are. This is beneficial for PFC as the operating temperature just a few degrees below zero, which lead to minimum energy costs as well as easily achieving high concentration ratios [9]. Over the years, many kinds of equipment for PFC have been invented, for example tubular ice crystallizer with a bubble-flow circulator [8];[7], an aluminium plate heat exchanger system [8] and a tubular ice system with a circulating flow inside [10].

In the present paper, PFC was applied to purify simulated dye wastewater. The principal aim is to study the effect of operation temperature and solution flow rate on the efficiency of PFC. The efficiency of PFC will be discussed based on the effective partition constant (K) and the percentage of ice purity.

II. METHODOLOGY

A. Materials

The main material used in simulating dye wastewater was methylene blue or also known as basic blue dye with chemical formula of $C_{16}H_{18}N_3SCl$. It has a molecular weight of 319.851 g/mol and λ_{max} = 665 nm. This methylene blue was diluted with distilled water into desired concentration. As for coolant, ethylene glycol was used and mixed with distilled water.

B. Experimental Set-up

The real experimental set-up in this study is shown in Fig. 1. The cooling bath was equipped with a motor stirrer. A cylindrical stainless steel vessel 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).

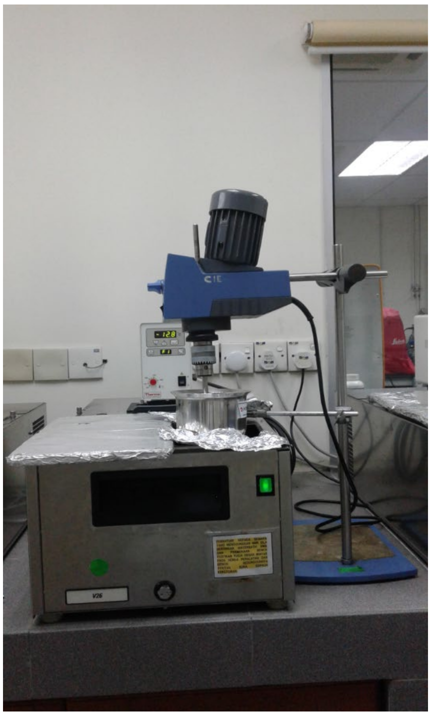

Fig. 1: Real experimental set up for progressive freeze concentration

C. Experimental Procedure

The basic dye, methylene blue powder was weighed accurately at 0.500 g and diluted in 1L of distilled water. This is to create a solution of simulated dye wastewater with concentration of 500 mg/L [11]. This sample solution was then kept at temperature of 4˚C to 5˚C.

The cooling bath was filled with ethylene glycol (50% volume) and water (50% volume) and was pre cooled at -12˚C. A stainless-steel cylindrical vessel was used as sample vessel and equipped with a motor stirrer to control solution flow rate.

In order to prevent initial supercooling, 30 mL of pure water was applied on the stainless steel-bottom of the vessel to provide an ice lining. Then, 1L of simulated dye wastewater was poured into the sample vessel which was then plunged into the cooling bath. The stirrer which was equipped with motor was set at a speed of 350 rpm. The range for operation temperature studied was from -4˚C to -12˚C while the stirring speed was ranging from 150 rpm to 350 rpm. The first set of experiment was run at operation temperature of -12°C for 15 minutes.

After 15 minutes, the stirrer was stopped and the sample vessel was taken out of the cooling bath. 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. The solute concentration, C_L was analyzed at a wavelength of 630 nm by using a UV/Vis spectrophotometer. The absorbance value was recorded and used to obtain concentration from the standard curve. Once the value of C_L and V_L has been determined, the effective partition coefficient, K and the percentage of ice purity, was calculated.

D. Analytical Procedure

The concentration of concentrated mother solution was measured analytically by using UV/Vis spectrophotometer (Perkin Elmer). This analytical method gave the absorbance value at a wavelength of 630 nm which then 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 Fig. 2. The curve was obtained by making few standard solutions which have the concentration range of 5 ppm to 100 ppm.

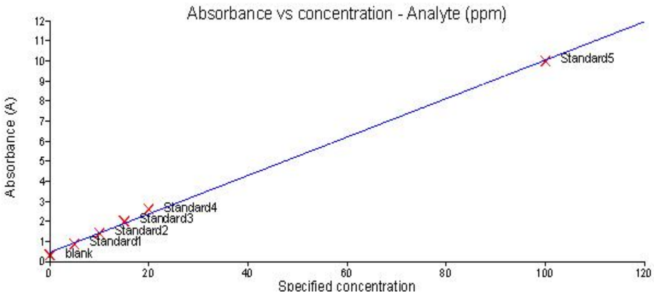

Fig. 2: Calibration curve

The analysis was done based on the value of K and the ice purity. The K value was calculated by using Equation (1).

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

where V_0 and C_0 are the initial volume and concentration of the simulated dye wastewater in liquid phase, respectively. While V_L and C_L are the volume and concentration of solute in concentrated mother solution, respectively.

The ice purity could be analyzed based on the ice purity percentage. The ice purity could be determined from the concentration of the solute in ice fraction, C_S which could be calculated by using Equation (3).

$$K = C_S/C_L \quad (2)$$

$$C_S = K\, C_L \quad (3)$$

The percentage of ice purity can be calculated through Equation (4).

$$\% \text{ of Ice Purity} = [(C_0 - C_S)/ C_0] \times 100 \quad (4)$$

III. RESULTS AND DISCUSSION

The PFC method was run for 15 minutes and afterwards, ice crystal can be seen formed on the wall of the vessel. The ice crystal formed and the melted ice fraction are shown in Fig. 3 and Fig. 4, respectively.

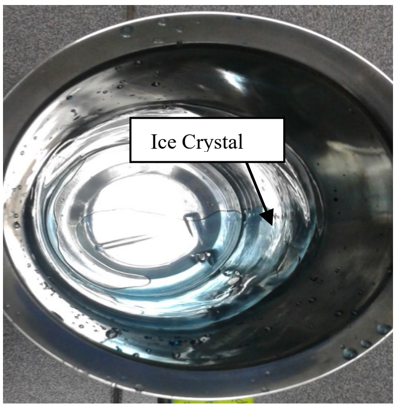

Fig. 3: Ice crystal formed at the wall of the vessel

Fig. 4: Melted ice fraction

A. *Effect of Operation Temperature*

The effect of operation temperature on the progressive freeze concentration 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 operation temperature was plotted as shown in Fig. 5.

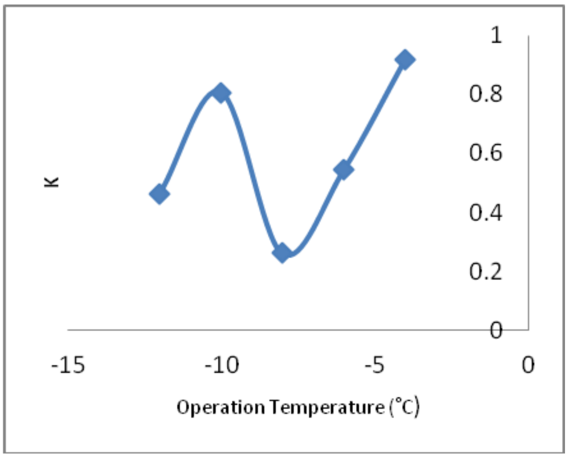

Fig. 5: Graph of K against operation temperature

Based on the graph plotted in Fig. 5, it can be observed that the K value changes according to temperature. This proves that K value is temperature dependant parameter. As observed from the graph, the K value for the highest temperature is 0.9162 then decreasing towards 0.5434 as the operation temperature was reduced to -6˚C. This proves that higher operating temperature yields higher K value. Higher K value indicates lower ice purity [12]. Lower ice purity is due to incomplete crystallization process. This might be related to the high operation temperature which is incapable of forming complete ice crystal within 15 minutes of operation 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 0.2615. Lower K value depicts higher ice purity as well as illustrating higher efficiency of PFC [7]. Hence, -8˚C can be considered as the optimum operation temperature for progressive freeze concentration process. However, the K value suddenly increased to 0.8075 as the temperature was reduced to -10˚C. This might be due to supercooling effect since supercooling has an effect of reducing the ice purity [8]. During supercooling, the ice formed might have contaminants entrained in the ice layer causing higher K value. At the lowest operation temperature, the K value was recorded at 0.4624 which shows an increasing pattern as to be compared with operation temperature of -8˚C. This establishes that the ice purity is low and the efficiency of the system is reducing at too low of operation temperature [13].

The effect of operation temperature on PFC could also be analyzed based on the percentage of ice purity which was calculated using Equation (4). The C_S value was determined from Equation (3).

The effect of operation temperature on percentage of ice purity is shown in Table 1. In term of percentage of ice purity, the highest percentage of ice purity is recorded at temperature of -8˚C with a value of 71.55%. This is parallel to its K value as this temperature yielding ice with highest purity. This indicates that more dye solutes were concentrated in the mother liquor solution leaving the ice fraction almost pure.

Table 1: Effect of operation temperature on percentage of ice purity

Operation Temperature (˚C)	Solute Concentration in Ice Phase, C_S (mg/L)	Percentage of Ice Purity (%)
-4	462.681	7.46
-6	293.436	41.31
-8	142.256	71.55
-10	419.900	16.02
-12	258.944	48.21

B. *Effect of Solution Flow Rate*

The effect of solution flow rate towards the efficiency of progressive freeze concentration can be analyzed based on the K value. Referring to graph plotted in Fig. 6, the K value decreasing with the increment of solution flow rate. This indicates that better efficiency could be achieved at higher stirring speed. This finding is parallel as to previous researcher Miyawaki [10], which proved that higher flow rate yielding ice with higher purity.

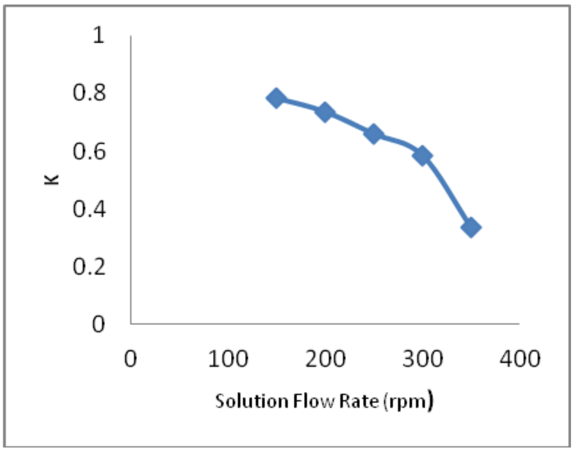

Fig. 6: Graph of K against solution flow rate

The reason of why does the higher flow rate yielding higher ice purity is due to mass transfer occurs at the ice-liquid interface. The solution flow rate actually helps to wash the solute away from the ice fraction and keep them entrained in the liquid fraction. Hence, the higher the solution flow rate, the lower the K value obtained indicating better efficiency for the system.

Table 2 below shows the effect of solution flow rate on the percentage of ice purity. Based on the table, an increasing pattern is observed in the last column. The percentage of ice purity increased from stirring speed of 150 rpm (19.72%) to 350 rpm (62.69%). This depicts that higher solution flow rate yielding ice with higher purity. Higher percentage of ice purity gives a picture of higher efficiency of the system.

Table 2: Effect of solution flow rate on percentage of ice purity

Solution Flow Rate (rpm)	Solute Concentration in Ice	Percentage of Ice Purity (%)

	Phase, C_S (mg/L)	
150	401.408	19.72
200	380.240	23.95
250	345.788	30.84
300	310.103	37.98
350	186.539	62.69

IV. CONCLUSION

PFC was proved to be effective in purifying dye wastewater based on the results obtained. The best operation temperature was obtained at -8˚C with a K value of 0.2615 with the highest percentage of ice purity of 71.55%. The most optimum stirring speed was identified at 350 rpm with a K value of 0.3343 and percentage of ice purity of 62.69%.

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