

Purification of Dye Industries Wastewater via Crystallization: Effect of Operation Time and Solution Concentration

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Abstract—The high capacity of water consumption also results in high amount of wastewater produced and released to ecosystem and will affect the ecology. Purification of dye wastewater using crystallization, specifically freeze concentration technique provides more width to any process plants towards waste management. It is essential to introduce a new method of freeze concentration to overcome the weaknesses of conventional method, and therefore to enhance the wastewater purification development for a better quality of water treatment.

Keywords— *Colour removal; Simulated dye wastewater; Solute recovery; Effective partition coefficient; Freeze concentration*

I. INTRODUCTION

In textile industry, dying processes are the most polluted waste water affecting process regarding to the formation amount and the pollutants which are involved. The main characteristic parameter of the wastewater that appears at the end of the dying process is colour and the sources of that decomposed and colloidal formed colour are the dying substances used in those processes[1]. Effluents produced by textile industries are often strongly coloured and their disposal into receiving waters causes environmental damage, including significant impacts on the photosynthetic activity of aquatic plants due to reduced light penetration[2]. Today's technology has benefitted us to help reducing the pollution of the unwanted waste to the environment. Physical-chemical process such as adsorption, photocatalytic degradation and coagulation/flocculation–sand filtration as well as nanofiltration process have been demonstrated for purification of dye wastewater[2-4]. Purification of dye wastewater using crystallization, specifically freeze concentration technique provides more width to any process plants towards waste management. 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[5]. Freeze concentration of waste water increases the caloric value, resulting in much smaller downstream incineration units with corresponding reductions in energy consumption[6]. However, the disadvantages of conventional freeze concentration are that, it uses high investment cost besides the associated crystallization equipment is rather complex than other processes' equipment. Therefore, it is essential to introduce a new method of freeze concentration to overcome the weaknesses of conventional method. In this study, the effect of operation time and solution concentration towards the effective partition coefficient, K-value, and solute recovery, Y were determined on purification of methylene blue solution as simulated dye wastewater via progressive freeze concentration (PFC).

II. METHODOLOGY

A. Chemicals and materials

Methylene blue (B.B 9) and ethylene glycol were obtained from R&M Chemicals and distilled water was used for the preparation of simulated industrial dye wastewater. All chemicals used for the study were obtained in highest degree of purity.

B. Experimental Set-up

The laboratory equipment for PFC as shown in Figure B.1 was made up of water bath, stirrer, motor, and cylindrical vessel. A cooling medium, ethylene glycol solution were put into the water and were kept constant at -8°C . A stirrer was positioned near the ice front to stir the solution. The purpose of using the stirrer was to decrease the concentration near the ice front, and thus balance the whole concentration of the liquid. Other equipment needed for the experiments were UV-vis spectrophotometer with cuvette, beaker, measuring cylinder, and weighing scale.

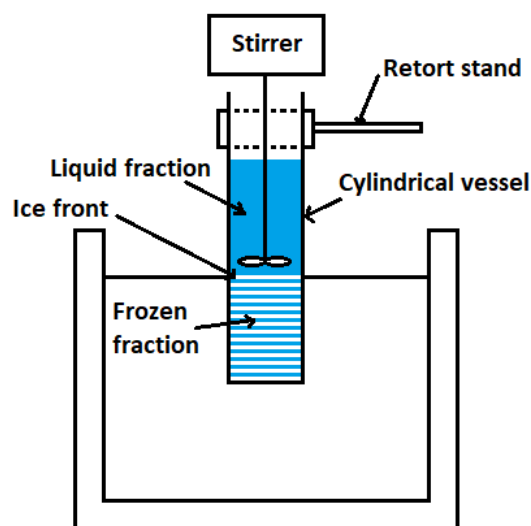


Figure II-1 Experimental set-up of progressive freeze concentration

C. Experimental Procedure

Sample of simulated dye wastewater solution were prepared using methylene blue dye to be dissolved into distilled water. A 50wt% (v/v) ethylene glycol solution used as the coolant was prepared by mixing ethylene glycol with distilled water. The coolant was put into the water bath and cooled to -8°C . It was set to low temperature because of the capability of the ethylene glycol to remain in liquid phase when being cooled below the freezing temperature of pure water.

The initial solution concentration, $C_0 = 500 \text{ mg/L}$ was measured by dissolving methylene blue powder into distilled water [7, 8]. Initial volume of the solution, $V_0 = 1 \text{ L}$ was measured and put into the cylindrical vessel. The cylindrical vessel was immersed into the water bath which contained precooled coolant at desired temperature of -8°C . The stirrer was run at a desired stirrer circulation velocity, 135 rpm. The solution was then be left for crystallisation to occur at a desired operating time, $t = 5 \text{ min}$, 10 min, 15 min, 20 min, and 25 min. At a designed time, the circulation was stopped and the cylindrical vessel was taken out of the water bath. The ice solid was separated from the concentrated solution. Both sample of concentrated solution and ice layers was collected and tested using UV-vis spectrophotometer to obtain its concentrations, C_L . Volume of the concentrated solution, V_L was measured. For the experiment using operating condition of solution concentration, the procedure is repeated using desired temperature, $T = -8^\circ \text{C}$ and five simulated dye wastewater solutions of different initial solution concentration, $C_0 = 300 \text{ mg/L}$, 400 mg/L , 500 mg/L , 600 mg/L and 700 mg/L respectively.

D. Effective Partition Coefficient, K

One of specific concern in developing freeze concentration is the effective partition coefficient (K) of solute between the ice and liquid phase at the ice-liquid interface, being defined in Eq. (D.1):

$$K = \frac{C_S}{C_L} \quad (\text{D.1})$$

where, C_S and C_L are the solute concentrations in the ice and solution phases, respectively. The concentration of the ice, C_S can be obtained by using Eq. (D.2):

$$C_S = \frac{\rho_L(C_0 V_0 - C_L V_L)}{\rho_S V_S} \quad (\text{D.2})$$

where ρ_L is the solution density, ρ_S is the ice density, C_L are the solute concentrations in the solution, and V_0 , V_L , and V_S is the initial volume, the volume of liquid phase, and the volume of solid phase respectively. The K value is between 0 and 1. When the K value turns out to be small, the effect of dye wastewater purification increases. $K = 0$ means ice is completely purified from dye, while $K = 1$ means the process has no effect on purification of dye wastewater.

The solution volume is known as V_L in the freeze concentration process, and at the moment once the volume of ice increases meaning that the solution volume decreases ($V_L < 0$), and increases the liquid phase concentration by dC_L . The following solute mass balance is developed in Eq. (D.3), assuming the liquid layer is perfectly mixed and that the ice layer is imperfectly mixed.

$$C_L V_L = C_S dV_L + (C_L + dC_L)(V_L - dV_L) \quad (\text{D.3})$$

From Eqs. (D.2) and (D.3), rearranging to get Eq. (D.4):

$$\frac{dC_L}{C_L} = (1 - K) \frac{dV_L}{V_L} \quad (\text{D.4})$$

By integrating both sides of Eq. (D.4) to induce the relationship between the solution volume ratio ($\frac{V_L}{V_0}$) and the solution concentration ratio ($\frac{C_L}{C_0}$), thus creating a linear graph of Eq. (D.5):

$$\ln \frac{C_0}{C_L} = (1 - K) \ln \left(\frac{V_L}{V_0} \right) \quad (\text{D.5})$$

as a function of $Y = mX$. K value can be calculated from the gradient of best fit linear graph. The K value can also be calculated directly using the equation.

E. The solute recovery, Y

The solute recovery, Y is defined as a ratio of the dye concentration in the concentrated solution to that in its initial solution. The equation used to calculate the solute recovery is shown in Eq. (E.1):

$$Y = \frac{C_L m_L}{C_0 m_0} \quad (\text{E.1})$$

where, C_L and C_0 are the concentration of dye in the concentrated and initial solution and m_L and m_0 are mass (mg) in the concentrated and initial solution [9].

III. RESULTS AND DISCUSSION

A. The effect of operation time

The simulated dye wastewater was treated under operation times of 5 minutes, 10 minutes, 15 minutes, 20 minutes and 25 minutes with the same initial concentration of 500 mg/L. Stirring with a range from 135-140 rpm were applied to promote the dye removal. As shown in Table A-1, results showed that the solute concentration increased over time. It showed that the dye removal increases over time of the process as there was an increase of volume of ice formed, leaving the dye particle to accumulate in the concentrated solute. K value was determined from the slope of the graph as shown in Figure A.1. The slopes of the graph at operation time, $t = 5$ minutes, 10 minutes, 15 minutes, 20 minutes and 25 minutes were 0.8616, 0.9335, 0.9358, 0.9469 and 0.9509 respectively.

Figure A.2 illustrated the relationship between effective partition coefficient, solute recovery and operation time. The graph showed that there was a sudden drop of effective partition coefficient, K value between $t = 5$ minutes and $t = 10$ minutes, then followed by constant decrease until $t = 25$ minutes. It was caused by the effect of solute diffusion from cyro-concentrated phase towards the discharge of solute in the ice, resulting in the ice condition to be more concentrated toward the surface of the vessel [9]. A report from Miyazaki [10] have conducted partial melting of sucrose solution in progressive freeze concentration that showed similar results of concentrated solution produced in short time being higher than initial concentration and decreased over time. From the Figure A-2 it also showed the graph of solute recovery, Y along the operation time. The values of Y decreased from 0.95 ($t = 5$ minutes) to 0.70 ($t = 25$ minutes) at an almost linear decrease.

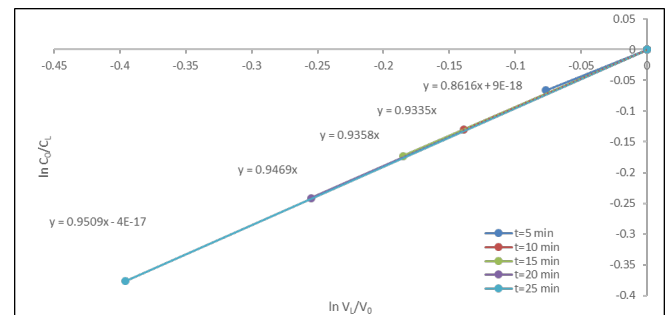


Figure III-1: Effect of operation time on K (Experimental Conditions: C_0 : 500 ppm, U : 135-140 rpm, V_0 : 1000 mL, T : -8°C , t : 5,10,15,20,25 min)

Table A-1: Concentrated solution at different operation time

T (min)	5	10	15	20	25
C_L (mg/L)	534.88	568.96	594.58	637.12	728.94

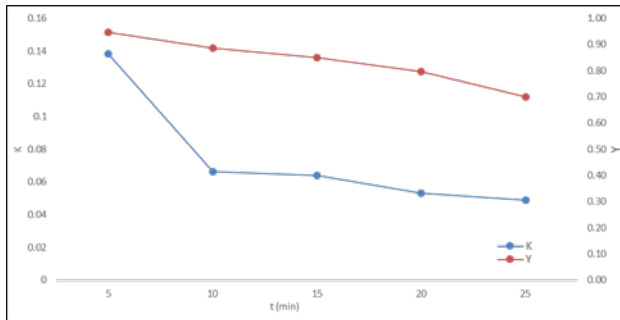


Figure III-2 Relation between partition coefficient (K), Solute recovery (Y) and operation time (t) (Experimental Conditions: C_0 : 500 mg/L, U: 135-140 rpm, V_0 : 1000 mL, T: -8°C , t: 5,10,15,20,25 min)

B. The effect of solution concentration

The simulated dye wastewater was treated under initial concentration of 300 mg/L, 400 mg/L, 500 mg/L, 600 mg/L and 700 mg/L with the same operation time of 15 minutes. Stirring with a range from 135 rpm to 140 rpm were applied to promote the dye removal. From Table B-1, it resulted that concentrated solution fluctuated over initial concentration. It showed that the dye removal are influenced by how concentrated is the initial solution concentration is during the process. K value was determined from the slope of the graph as shown in Figure III-3. The slopes of the graph at initial solution concentration, C_0 = 300 mg/L, 400 mg/L, 500 mg/L, 600 mg/L and 700 mg/L were 0.8102, 0.8989, 0.9358, 0.9597, and 0.9188 respectively.

Figure III-4 illustrated the relationship between effective partition coefficient, solute recovery and initial solution concentration. The graph showed that there was a decrease of effective partition coefficient, K value from C_0 = 300 mg/L to the lowest K value at C_0 = 600 mg/L (K = 0.0403), then followed by an increase at C_0 = 700 mg/L (K = 0.0812). Currently there is no similar tendency of the result from other studies. According to a report by Fujioka [11], the less initial concentration is, the effect of desalination increases, suggesting that progressive freeze-desalination is much more helpful after some primary treatment to decrease initial concentration. From the Figure III-4, the graph of solute recovery, Y over the initial solution concentration showed fluctuating trend. The values of Y decreased from 0.8483 (C_0 = 300 mg/L) to 0.8260 (C_0 = 400 mg/L) but then started to increase until it reached the peak point at Y = 0.8407 (C_0 = 600 mg/L) and then it decreased again to Y = 0.8051 (C_0 = 700 mg/L).

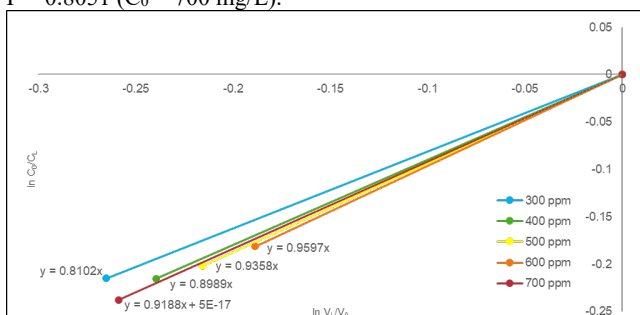


Figure III-3 Effect of solution concentration on K (Experimental Conditions: C_0 : 300, 400, 500, 600, 700 mg/L, U: 135-140 rpm, V_0 : 1000 mL, T: -8°C , t: 15 min)

Table B-1 Concentrated solution at different initial solution concentration

T (min)	5	10	15	20	25
C_L (mg/L)	534.88	568.96	594.58	637.12	728.94

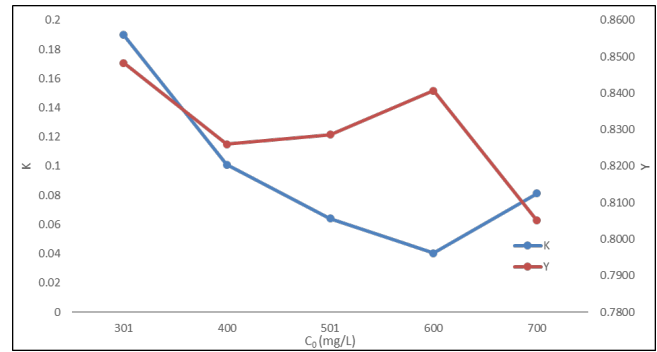


Figure III-4 Relation between partition coefficient (K), Solute recovery (Y) and solution concentration (C_0) (Experimental Conditions: C_0 : 300, 400, 500, 600, 700 mg/L, U: 135-140 rpm, V_0 : 1000 mL, T: -8°C , t: 15 min)

IV. CONCLUSION

This study was initiated in order to look for the new and effective purification technologies for dye wastewater treatment. Hence, progressive freeze concentration, one of crystallization technique being currently used in food processing, was assumed to be applied for dye wastewater purification. The experimental results proved that progressive freeze concentration is useful not only in food processing, but also in desalination process. By using effective partition constant (K) and solute recovery (Y), the effects of operation time and initial concentration were successfully investigated. Effective partition coefficient increases with increasing time. However, the purification efficiency decreases as the solute recovery decreases at increasing operation time. The optimum solution concentration for methylene blue dye solution for effective purification process was at 600 mg/L considering it has the lowest possible partition coefficient and high solute recovery, with K = 0.0403 and Y = 0.8407.

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VI. REFERENCES

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