Stormwater Purification via Progressive Freeze Concentration: Effects of Initial Concentration and Stirring speed

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***Abstract*— Water is one of basic needs and is essential for every living organism on Earth to survive. With increasing population, water has become scarce resource since the water demand is more than water supply. There are several methods to treat water such as evaporation, membrane processes and ultraviolet disinfection. However, these methods have limitations. Thus, researches have to find alternative way and this lead to progressive freeze concentration (PFC) process. This research aims to study the effect of initial concentration and stirring speed in stormwater purification via progressive freeze concentration (PFC) towards effective partition constant (K) value, solute recovery (Y) and concentration efficiency. The range of initial concentration and stirring speed were determined at 2, 4, 6, 8 and 10 ppm and 150, 200, 250, 300 and 350 rpm. Simulated stormwater was created by using zinc chloride instead of actual stormwater to ease the process. Each effect was run at constant coolant temperature and time, -8 ^{o}C and 15 minutes. The results show at lowest initial concentration, the lowest K value obtained is 0.25 and the highest Y value of 0.686. It was found that at stirring speed of 350 rpm produced lowest K value, 0.2305 and utmost value of Y, 0.85. Best efficiency of PFC system achieved at 2 ppm initial concentration which is 75% and 350 rpm stirring speed which is 76.95%.**

Keywords*— *Effective Partition Constant; Progressive Freeze Concentration; Purification; Solute Recovery; Water Treatment

I. INTRODUCTION

Survival of every living things on earth depends on water. For example, plants need water to carry out photosynthesis process, animals and humans to carry out cell activity. For good health, we need a safe, reliable, affordable and easily accessible water supply. However, about a billion people in developing countries have not had a safe and sustainable water supply for several decades [1]. Although our world consists of 71 % of water, not all of them are good for consumption. In fact, the composition of fresh water is only 2.53 % of the total amount of water [2]. Among 2.53 % of the fresh water, 68.7 % is located in the glaciers of Antartica, Greenland and Arctica, 30.7 % are groundwater and the remaining two percent are surface water, ground ice in permafrost zones and air humidity. While the world's population tripled in the 20th century, the use of renewable water resources has grown six-fold [3]. This statistic has led to the growth of water treatment plant all around the world so that water scarcity can be prevented and provide clean water supply for everyone.

Malaysia is blessed with abundance rainfall per year, 97 % are surface water and 3 % are groundwater. Even though this country is rich with water resources, Malaysia's water consumption is unsustainable. In 2014, the average water consumption per day of Malaysians was 212 litres which is 2 litres more than previous year 2013 [4]. This indicates that the consumption is still far beyond the recommended water usage by the World Health Organization (WHO). The WHO recommended 165 litres per day for Malaysians [4].

Since the use of water is incredibly in high demand, water has become a scarce resource [1]. Therefore, a sustainable and efficient water supply is a necessity. To prevent occurrence of water shortage in Malaysia, researchers need to find a new way to recover the water consumption such as water treatment plant. Stormwater runoff is non-point source (NPS) generated from rain and snowmelt occurrence that "runs off" across the land such as lawns, sidewalks, streets, roofs and farm land or impenetrable surfaces and conveys these to receiving water bodies [5]. Among stormwater components, heavy metal such as zinc is very hazardous to health.

There are many types of water treatment plant with different processes. Usually these water treatment plants use raw water from rivers, lakes, oceans and groundwater and physically and chemically purify the water. Many methods are introduced to purify water in industrial plants such as evaporation, membrane process and Ultraviolet (UV) disinfection. However, only certain technologies have been designed and applied to industries [6]. Major drawbacks with evaporation techniques are high investment costs, only feasible with very low capacities and corrosion whereas membrane process are expensive, has higher maintenance cost and produce waste more than water [7]. Moreover, disadvantages of membrane process are membrane fouling and operational life which leads to additional operating cost. UV disinfection is less efficient with suspended solids, color, turbidity or soluble organic compounds because they will react with UV radiation. Several different approaches have been studied in recent decades to purify water via freezing process [8]. The process has been acknowledged for industrial and municipal stormwaters because it is more economical than other processes.

Freezing process is one of crystallization technique in which has been applied in food and beverages process industry especially to produce fruit juice. Freeze concentration (FC) involves the partial crystallization of water in the aqueous solution, after which the crystals are separated from the concentrate [9].The process is used to remove water from the extract or solution by cooling the solution until ice crystal is formed and separated. This process can be implemented to purify contaminated water with same theory but in this case desired product is the water and the undesired product is the pollutants.

There are three types of freezing process which are suspension freeze concentration, progressive freeze concentration [10] and block freeze concentration [11]. Among these processes, suspension concentration process in used the most in industry [10]. The downside of this process is that it has complex separation method and requires many equipment which are costly [12]. PFC is a technique in which ice crystal is produced continuously layer by layer on a cooled surface until a single and large block of ice is formed [13].

In this study, progressive freeze concentration (PFC) was used as a water purification process and stormwater was used as an alternative to find a new sustainable water resource. PFC has been chosen for its benefit, low cost because it is much easier to separate the ice crystal from mother solution [14]. PFC is regarded as the option with the largest potential to treat water commercially. There are several conditions that could affect the PFC performance. Therefore, the objectives of this study are to investigate the effect of stirring speed and initial concentration in stormwater purification via progressive freezing concentration.

II. METHODOLOGY

A. Materials

A well-mix simulated stormwater solution was used in the experiments. Since stormwater sample varies with different locations, this experiment uses zinc chloride and distilled water to keep the stormwater sample constant. Ethylene glycol was used in the cooling bath as coolant to for the PFC process. To supply cooling energy to the system, 50% (v/v) of ethylene glycol-water solution was used. To accelerate the cooling process, dry ice was placed indirectly inside the ethylene glycol-water solution.

B. Preparation of Standard Solutions of Simulated Stormwater

A simulated stormwater was prepared by dissolving 1 gram of zinc chloride in a beaker of 200 mL of distilled water. After the solution was well mixed, it was transferred into a 1 L volumetric flask by using a funnel. . Lastly, distilled water was added again in the flask until the total volume of solution is 1 L. The concentration of solution was measured in ppm by using Equation 1:

$$\text{Ppm} = \frac{(\text{weight or volume of solute})}{(\text{weight or volume of solution})} \times 10^6 \quad (1)$$

The original simulated stormwater concentration was 1000 ppm. Next, standard solutions for the simulated stormwater was set up by diluting the original simulated stormwater into five concentration, 2 ppm, 4 ppm, 6 ppm, 8 ppm and 10 ppm. To calculate the amount of original solution needed for each concentration, the dilution formula below was applied.

$$C_1V_1 = C_2V_2 \quad (2)$$

Where C_1 and V_1 are the original concentration and volume of simulated stormwater and C2 and V2 are the standard solution concentration and volume to be prepared.

C. Preparation of Calibration Curves by UV-Vis Spectroscopy

A blank was prepared by filling a clean cuvette with distilled water and the outside was wiped with lint-free paper to remove any fingerprints. The absorbance of the blank was measured at wavelength of 180μm to 400μm and the blank was adjusted to zero. The blank was replaced with all five samples in increasing order of concentration at same wavelength to construct a good calibration curve.

D. Progressive Freeze Concentration Procedure

The apparatus was set up as shown in Figure 1. Stormwater samples were prepared at desired concentration. Next, cooling bath was switched on to achieve the desired temperature of -8 ^{o}C. As the cooling bath reached the temperature, 500 ml of stormwater sample was fed directly into the crystallizer and immersed into the cooling bath. Stirrer attached with motor was placed inside the crystallizer and was turned on at designated stirring speed. For crystallization to occur, stormwater solution was left in circulation for 15 minutes. After the experiment, ice and liquid were separated. Final mass and volume of ice and concentrate were measured. Small portion of ice and concentrate sample were bottled and sent to UV-Vis to determine the concentration.

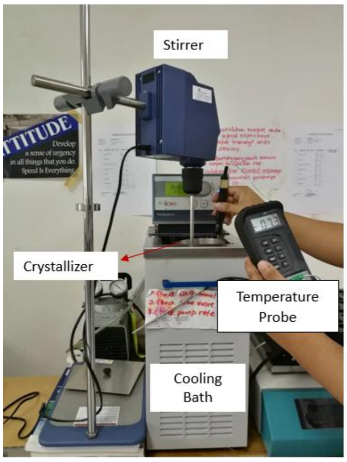

Figure 1. Equipment set up

E. Effect of Initial Concentration

The initial concentration of zinc chloride was varied at 2 mg/L, 4 mg/L, 6 mg/L, 8 mg/L and 10 mg/L respectively. In this experiment, initial concentration was designated as manipulated variable whereas temperature and stirring speed were kept constant at -8 ^{o}C and 350 rpm. This series of experiment were conducted at 15 minutes each. Data analysis of this variable was analyzed by using effective partition constant, solute recovery and efficiency of PFC system.

F. Effect of Stirring Speed

The effect of stirring speed was varied at 150 rpm. 200 rpm, 250 rpm, 300 rpm and 350 rpm respectively. In this experiment, stirring speed was designated as manipulated variable whereas initial concentration and temperature were kept constant at 4 ppm and -8 ^{o}C. this series of experiment is conducted 15 minutes each. The recommended level for zinc in irrigation water is 2 ppm [15].The concentration value was increased to 4 ppm because stormwater accumulates zinc when run-off. Data analysis of this variable was analyzed by using effective partition constant, solute recovery and efficiency of PFC system.

G. Determinant Parameters

There were three determinant parameters applied to evaluate the efficiency of PFC. First was effective partition constant (K), second solute recovery (Y) and lastly efficiency of PFC system. Samples of ice and concentrate were analyzed at wavelength 180μm to 400μm to determine final concentration.

K is a normal measurement for calculating the efficiency of a PFC process in which acts as separation effectiveness index. The value of K is determined by using Equation 3:

$$K = 1 - \left(\frac{\log\left[\frac{C_0}{C_L}\right]}{\log\left[\frac{V_L}{V_0}\right]} \right) \quad (3)$$

Where C_o and C_L are initial and final solute concentration of solution. Meanwhile, V_o and V_L are initial and final volume of solution.

For analyzing the solute recovery, solute yield (Y) is calculated to investigate the relationship between the mass of solute present in the separated liquid and the mass of solute present initially in the original solution. The equation of Y is as below:

$$Y = m_{s\ liq} / m_{s\ o} \quad (4)$$

Where Y is solute yield, $m_{s\ liq}$ is solute mass in the liquid fraction and $m_{s\ o}$ is the initial solute mass.

Lastly, efficiency (E) of PFC system can be calculated by using Equation 5:

$$E(\%) = \frac{(C_L - C_i)}{C_i} \text{ x } 100\% \quad (5)$$

Where C_L and C_0 are the concentration of solute in the concentrated solution and ice layer.

III. RESULTS AND DISCUSSION

A. Formation of ice crystal

Ice crystal layer has been efficaciously formed on the wall of the crystallizer for the period of 15 minutes freezing process. Figure 2 shows the ice crystal layer formation. There are three analysis used which are K, Y and efficiency of PFC system. Calibration curve was constructed as shown in Figure 3 to determine the concentration of ice and liquid sample.

Figure 2. Formation of ice crystal.

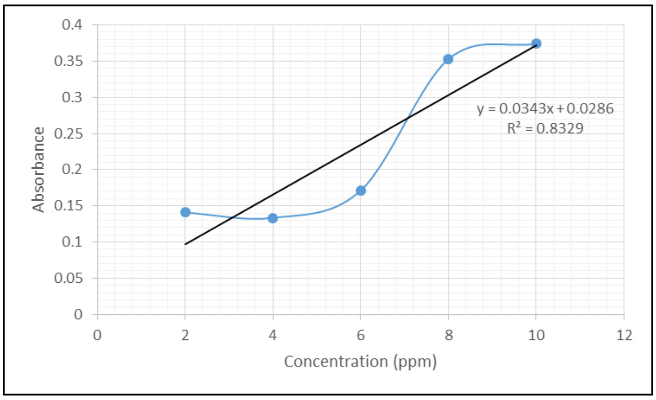

Figure 3. Calibration curve

B. The effects of initial concentration and stirring speed

Initial concentration is one of the most important parameters in PFC because it symbolizes the amount of solute exists in sample solution.

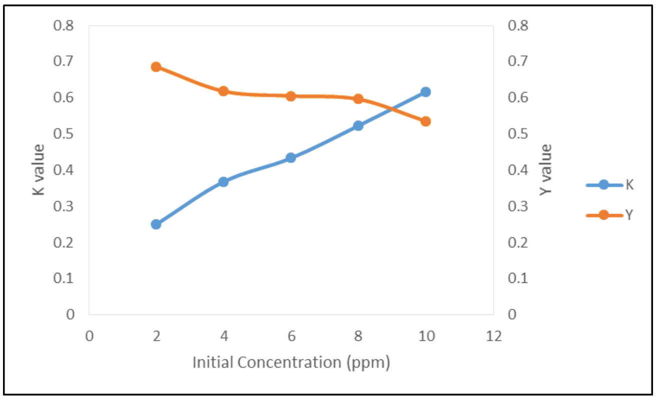

Figure 4 Effect of initial concentration on K and Y value.

From the graph in Figure 3, it can be observed that the K value increases steadily as initial concentration increases. The lowest K value, 0.25 is obtained at the lowest value of initial concentration, 2 ppm. Lower initial concentration indicates that small amount of solute presents in the sample solution. It is highly possible that contamination of ice is lower at lower initial concentration because lesser amount of solute was trapped in the ice. Solute content in the solution was observed to be only small amount at lower initial concentration, resulting in less solutes stuck at ice-liquid interface [16]. This is in line with a study by Ab. Hamid et al. [17] for the greater accumulation of solutes will be resulted at the ice-liquid interface if higher initial concentrations present in sample solutions.

Solute recovery was discovered to decrease as initial concentration decrease. It was expected as in PFC system, the solute concentration in the liquid will be increased and concentration in ice will be decreased from its initial concentration. From Figure 3, the highest Y value, 0.686 was obtained at 2 ppm which means not only highest purity of ice but also highest efficiency of PFC correlates with efficiency calculated in Table 1. Highest efficiency was determined at lowest initial concentration, 75%. It shows that if there is low solute at initial concentration, then the chances for the solute trapped in ice during solid-liquid interface will be low. The data shows similar result with Liu et al. [18] that the low-concentration solution contains a small amount of solute resulting in less contaminant being trapped in the ice compared to the high concentration where there is more chance for contaminants to be entrained in the ice.

Thus, it can be said that K value is highly dependent on initial concentrations. Efficiency of PFC system decreases as initial concentration increases.

In this study, a shaker was used to properly mix the sample solutions and to allow even circulation flow. This will further contribute to the reduction of solute accumulates near the ice-liquid interface [19].

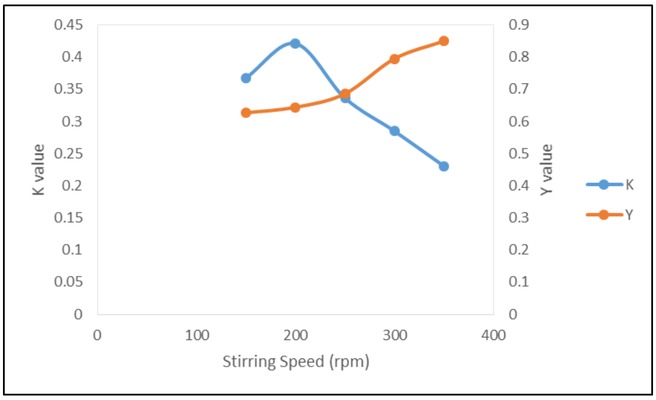

Figure 5. Effect of stirring speed on K and Y value.

Figure 5 shows the high K value, 0.4211 at 200 rpm then decreases as the stirring speed increases afterwards recording the lowest K value, 0.2305 and representing the highest efficiency of the system in this particular analysis. At 200 rpm, high K value was detected probably when particles are more concentrated in one region than in another, there will be a net movement away from the region of high concentration [20]. This net movement occurs because there are more particles available to move out of the region of high concentration than there are to move back in. At 200 rpm, there is a possibility of diffusion occur resulting increase concentration of ice layer. Thus, high K value was observed.

Theoretically, higher stirring speed will tend to give higher separation efficiency [21]. More pure ice was obtained when using higher circumferential velocity of the stirrer. Same result was obtained by Miyawaki et al. [22] that support higher rate of mixing can decrease the accumulation of solute at the ice-liquid interface. This explains clearly about the decrease in K value as well as the increase in Y value from 200 to 350 rpm because it shows at higher stirring speed that not only small amount of solute trapped in ice but also displays high solute recovery in the concentrate.

On the other hand, the observed trend of Y value is in decline as stirring speed increases which is in contrast to the trend observed for K value. The highest Y value, 0.85 was obtained at 350 rpm. Increase in stirring speed will increase the shear force of the fluid. When high shear force occurs, the solute that was attached between ice layer dendritic structure will be taken away and remain in the liquid [16]. Similar result was observed by Samsuri et al. [23] that claims the solutes were brought away and not easily caught from the surface of the static ice layer, causing the concentrated solution having higher amount of solutes.

From Table 1, it can be concluded that the efficiency of PFC system increases when stirring speed increases. The highest Y value from Figure 4 points to the highest efficiency of PFC system, 76.95%. From the finding, the best condition, 76.95% efficiency is at 350 rpm producing low value of K, 0.2305 and highest Y value of 0.85.

Table 1. Efficiency of PFC

Initial Concentration (ppm)	Efficiency (%)	Stirring Speed (rpm)	Efficiency (%)
2	75	150	63.24
4	63.24	200	57.89
6	56.69	250	66.36
8	47.74	300	71.5
10	38.38	350	76.95

IV. Conclusion

This study has successfully proven that PFC system is highly possible to be used for stormwater treatment. At low initial concentrations and high stirring speed, the system has reached its finest performance. The optimum condition for effect of initial concentration was at 2 ppm, resulted K and Y value of 0.25 and 0.686 with highest efficiency of 75%. Meanwhile, the ideal condition for effect of stirring speed was at 350 rpm, K and Y value of 0.2305 and 0.85 with best efficiency of 76.95%. Relationship between K and Y value was found to be opposite with each other. PFC system is perfectly complete when K value approaching to zero and Y value approaching to one.

Acknowledgment

Thank you to my supervisor, Dr. Farah Hanim Bt Abdul Hamid for her endless support and guidance and Universiti Teknologi Mara.

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