REMOVAL OF 2, 4, 6 TRICHLROPHENOL FROM SIMULATED WASTEWATER VIA PROGRESSIVE FREEZE CONCENTRATION: EFFECT OF INITIAL CONCENTRATION WITH THE USAGE OF RESPONSE SURFACE METHODOLOGY AS THE MEANS OF OPTIMIZATION

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Abstract

2, 4, 6-Trichlorophenol (TCP) has been used primarily in various pesticide formulations and as a wood preservative. Only the slightest amount of TCP in wastewater is harmful and it can be the cause of many diseases, thus the importance to remove the TCP from wastewater is imminent. In this study, Progressive Freeze Concentration (PFC) was used to remove TCP from a simulated wastewater. The aim for this study is to determine the effect of initial concentration on effective partition constant (K) and TCP reduction (T_R). The second objective of the study is to determine the optimum condition for initial concentration and operation time of PFC system via Response Surface Methodology. The experiment was done by varying the initial concentration of the PFC system by 50, 100, 150, 200, 250 ppm. From the results of the experiment, initial concentration of 50 ppm brings out the highest efficiency of the PFC system as the K-value is 0.3048 and the T_R value of 0.9046. The regression model generated by RSM was a good fit since the R^2 obtained were 0.81767 for K and 0.87622 for T_R. From ANOVA analysis, the optimum initial concentration and operation time to obtain the lowest K value at 0.1316 can be achieved at the value 93.2 ppm and 83min respectively. As for T_R value, it can be summed up that the optimum T_R of 76.53 could be achieved at initial concentration of 51.4 ppm and operation time of 60.5 min.

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1.0 Introduction

Chlorinated phenols or chlorophenol, widely used in industries, are of growing concern owing to their high toxicity, carcinogenicity and wide distribution in industrial wastes [1]. 2,4,6-Trichlorophenol (TCP) has been classified as one of the primary pollutants as enacted by the Department of Environment (DOE), Malaysia in Environmental Quality Act 1979 (Sewage and Industrial Effluent) which should be treated to be less than 1 ppm for inland water discharge [2]. The stable carbon chlorine bond and the position of chlorine atoms relative to the hydroxyl group are responsible for their toxicity, carcinogenic properties, structural stabilization and persistence in the environment, making the removal of 2,4,6-TCP from the environment very crucial[3]. Thus, the process of removing TCP from water may in fact be a bit tedious and without proper removal, it will destroy the natural habitat and ecosystem of the river alongside any organism that live in the river or near the river. A proper waste management is needed as it will a necessity for a sustainable environment [4].

To properly separate the pure water and the contaminant inside the effluent, several methods can be used. Reverse osmosis, freeze concentration and evaporation is the most common method used in separation process [5]. Although evaporation and reverse osmosis is a very well-developed method, both methods have major drawbacks. The major drawback of evaporation is that it require a lot of energy to achieve the boiling point of solvent (water) [6], meanwhile the major drawbacks of RO is that the membrane is easily clogged by the content of the effluent which effect the cost highly due to constant replacement [5].

Progressive freeze concentration (PFC) was used in this study. Four main factor which affect the efficiency of the system was used in this study which is initial concentration, circulation flow rate, operational time and coolant temperature. PFC process is a versatile process that can be used to separate contaminant in water by using the difference in freezing point. In the application where PFC is used in wastewater treatment system, PFC system produced an almost pure water from the thawed ice crystals while in application to liquid food, PFC system is preferred when concentrating liquid with aromatic quality that should be detained after concentration process [7].

In this study, PFC was applied to purify the wastewater by separating the water and TCP. One of the most important parameters in obtaining an excellent PFC process is initial concentration [8]. Initial concentration influences the efficiency of the PFC process as it affects the freezing point of the solution. Another important parameter that needs to be focused on the study is the operation time.

To further investigate the relationship between initial concentration and operation time, Response Surface Methodology was used as the means of optimization. RSM can be viewed as the procedure for performing a sequential search or finding the path towards the optimum value or best condition for the best result of the experimentation [9]. In this case, RSM is used to search for the best combination of initial concentration and operation time of PFC process in order to obtain the best separation condition of the water and TCP. RSM can help in investigating the interactive effect of process variables and in building a mathematical model that accurately describes the overall process [10].

2.0 Methodology

2.1 Material

A wastewater containing 2, 4, 6 Trichlorophenol was simulated using acetone and distilled water. Moreover, ethylene glycol mixed with water was used as coolant to supply cooling energy to the system [11]. To transfer heat in a very low temperature, ethylene glycol was used as ethylene glycol is a good cooling medium.

2.2 Equipment

The basic equipment setup used in the experiment to determine the effect of initial concentration on PFC process composed of a sample vessel (crystallizer), a cooling bath (PolyScience), and a stirrer (Tuff) as shown in Figure 1.

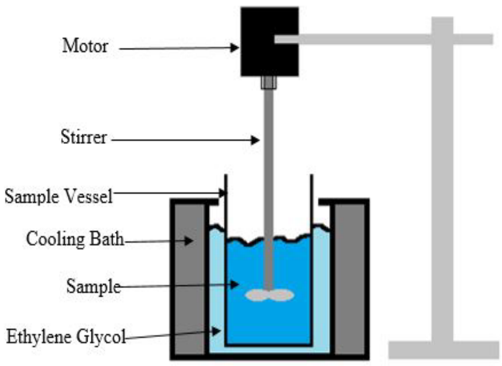

Figure 1*: Experimental Set-up*

2.3 Methods

A stock solution with the concentration of 1000ppm was prepared. The solution was then diluted to the desired initial concentration before being precooled inside a refrigerator with the temperature of 4°. The precooling solution is needed to ensure that the fluctuation of cooling bath temperature is minimised [12]. Next, ethylene glycol was filled into cooling bath. 500 ml of the effluent was fed into the crystallizer The level of the effluent must be below the coolant level in order to ensure the effluent was fully immersed. After that, the stirrer was then put properly in the middle of the crystallizer and the stirring speed was set at 700 rpm.

The process was ran for 30 minutes after the water bath reached -5°C as there will be some fluctuation on the temperature of the water bath due to the different in temperature of water bath and the sample. The experiments were repeated with initial concentration of 50, 100, 150, 200 and 250 ppm.

After 30 minutes of operation time, the process was stopped and the sample was collected in the form of ice and liquid. The volume of ice and liquid produced were collected and measured for the purpose of analysis. The sample collected was then analysed using UV-Vis Spectrometer with the wavelength of 295nm [13] to identify the concentration of the ice and liquid produced from the PFC process.

2.4 Performance analysis

2.4.1 Effective Partition Constant (K)

Several determinant parameters were chosen to evaluate the effectiveness of PFC process. Effective partition constant (K) was used to determine the effectiveness of the PFC process in separating the TCP and water. To measure the PFC process, the main index for separation effectiveness to be considered is the K-value [14].The zero value of K indicates that the PFC is 100% efficient and the value of 1 indicates that the PFC is at 0% performance [15]. The equation (1) shows the ratio between the ice phase and the solution:

$$K = C_S/C_L \qquad (1)$$

Where,
C_s = solute concentration in ice phase
C_L = solute concentration in solution phase.

2.4.2 TCP Reduction (T_R)

Other than effective partition constant (K), TCP reduction (T_R) is also one of the important determinant parameters to be determined in this study in order to know the system efficiency. Thus, the amount of TCP reduced from the initial solution was determined in percentage and calculated using equation (2).

$$T_R = M_I - M_S/M_I \times 100\% \qquad (2)$$

Where,
M_I = initial mass of TCP in initial solution
M_S = mass of TCP in ice phase

3.0 Results and discussion

3.1 Effect of Initial Concentration on PFC process (K-value)

The initial concentration of the sample was varied from 50 to 250 ppm to investigate the effect of initial concentration to the PFC process. From Figure 2, it can be observed that the lowest K-value and the highest T_R was achieved at the lowest initial concentration and the graph continued to increase in a parallel manner for the K-value and vice versa for the T_R as the initial concentration increases. Due to the low amount of TCP in the solution, low amount of ice contamination occurs on the ice formed by the PFC process thus results in purer ice crystal formation. In theory, purer ice crystal formation was obtained due to smaller probability of the TCP being trapped by the ice growth during PFC process with low initial concentration of solution compared to higher initial concentration [16]. Thus, it can be concluded that the higher the initial concentration, the higher the K-Value and the lower the T_R which translated to a lower efficiency of the PFC process to separate the TCP from the water body.

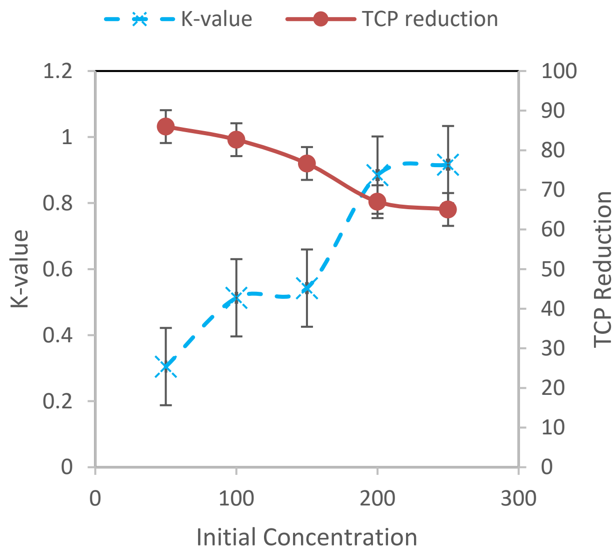

Figure 2: *Effect of initial concentration on K-value and T_R.*

3.2 Response Surface Methodology Models

By using STATISTICA Software Version 12, the design of experiment (DOE) was determined to properly run the experiment. Table 1 shows the experimental range implemented for the purpose of optimising the PFC process. The operating parameter involved are named as X_1 for initial concentration and X_2 for operation time. 10 sets of experiment were done based on the DOE generated. The initial concentration and operating time for each runs were tabulated in Table 2 as well as the results of K and T_R.

Table 1: Range of Experiment

Parameter	$-\alpha$	-1	0	+1	$+\alpha$
Initial Concentration, X_1(ppm)	50	100	150	200	250
Operating Time, X_2(Min)	10	20	30	40	50

Equation 3 and equation 4 represent the multiple regression equation for K (Y_1) and T_R (Y_2) assessed as a function of the two variables of initial concentration (X_1) and operation time (X_2) and its association using quadratic and linear regression coefficient.

$$Y_1 = 0.645193 - 0.001965\, X_1 - 0.010177\, X_2 + 0.000011 X_1^2 + 0.000062\, X_2^2 \quad (3)$$

$$Y_2 = 81.3942 + 0.15473\, X_1 - 0.29221\, X_2 - 0.00050\, X_1^2 + 0.00314\, X_2^2 - 0.00171 X_1\, X_2 \quad (4)$$

Analysis of Variance and coefficient of determination (R^2) were utilised to examine the goodness of fit of the model between the experimental and predicted values.

Table 2: DOE & Experimental Results

Run	X_1	X_2	K	T_R
1	50	10	0.3793	88.7754
2	50	50	0.1414	82.0842
3	250	10	0.6193	83.7572
4	250	50	0.3776	63.4117
5	8.6	30	0.4644	70.9967
6	291.42	30	0.8329	61.2142
7	150	1.72	0.6839	89.4434
8	150	58.28	0.2819	67.8484
9	150	30	0.3404	79.7000
10	150	30	0.3404	79.6811

3.3 *Analysis of Variance (ANOVA)*

To verify the adequacy of the regression model, ANOVA was used. The results of ANOVA for the responses of K and T_R are summarized in Table 3 and Table 4 respectively. For the model of regression to be considered appropriate, the F-value calculated by ANOVA should be greater than the tabulated F-value [17]. From the tabulated results in Table 3 and Table 4, the F-value for both responses are lower than the tabulated $F_{(0..05,5,4)}$ which is 6.26.

However, the R^2 for K value is 81.767% while for T_R is 87.622%. This value proves that both experimental and the predicted K value and T_R obtained from the models are in appropriate condition. For the model to be considered appropriate and suitable for further study, the minimum number of R^2 should be 0.75 [18]. Thus, both value of R^2 for the K-value and TR is considered a good fit for this study.

Table 3 *: ANOVA for model of K-value*

Source	Sum Of Squares	Degree of Freedom	Mean Squares	F-value
Regression	0.3171	5	0.06342	3.5877
Residual	0.0707	4	0.017677	
Total	0.3878	9		
R^2	0.81767			

Table 4*: ANOVA for model of T_R*

Source	Sum Of Squares	Degree of Freedom	Mean Squares	F-value
Regression	816.8768	5	163.3754	5.6633
Residual	115.3921	4	28.8480	
Total	932.2689	9		
R^2	0.87622			

In ANOVA analysis, p-value must be lower than 5% for all factor so that it will bring a better effect to K and T_R [19]. In general, the variable that has lower p-value and higher F will bring the most significant effect to the process. From Table 5 and Table 6, X_2 (linear term of operation time) was identified as the most significant parameter for both K-value and T_R as it has the lowest p-value and highest F in both Table 5 and Table 6.

***Table 5**: Regression analysis for K-value*

Factor	Coefficient Estimation	Standard Error	F	P
X_1	-0.001965	0.002167	7.0337	0.0569
X_1^2	0.000011	0.000006	2.9902	0.1588
X_2	-0.010177	0.010835	**7.7693**	**0.0495**
X_2^1	0.000062	0.000155	0.1572	0.7120
X_1X_2	-0.0000	0.000033	0.0003	0.9892

***Table 6**: Regression analysis for T_R*

Factor	Coefficient Estimation	Standard Error	F	P
X_1	0.15473	0.087537	6.1015	0.0689
X_1^2	-0.00050	0.000251	3.9845	0.1166
X_2	-0.29221	0.437686	14.364	0.0192
X_2^1	0.00314	0.006280	0.2499	0.6433
X_1X_2	-0.00171	0.001343	1.6157	0.2726

3.4 Analysis of Response Surface Contour plot

By plotting a three-dimensional response curves known as contour plots, the optimum level of each variable and the effect of their interaction on response as function of two variables were studied [20]. Figure 3(a) and Figure 3(b) illustrate the value of K and T_R, respectively, as a function of independent variable which are initial concentration and operation time.

3D plot of Figure 3(a) shows that lowest value of K can be obtained at the intermediate range of 45ppm to 150ppm for initial concentration and 50 to 70 minutes for operation time. The K value increase when the initial concentration increases, this shows that high initial concentration produces high solute concentration on the ice formed from the PFC system[19]. Subsequently, the K-value decreases the longer the operation time as a longer operation time is needed in order to completely crystallize the water completely [21] which will result in complete separation of TCP and water. Thus, it shows that the lower initial concentration and higher operation time brings a higher efficiency of the process results in lower K-value.

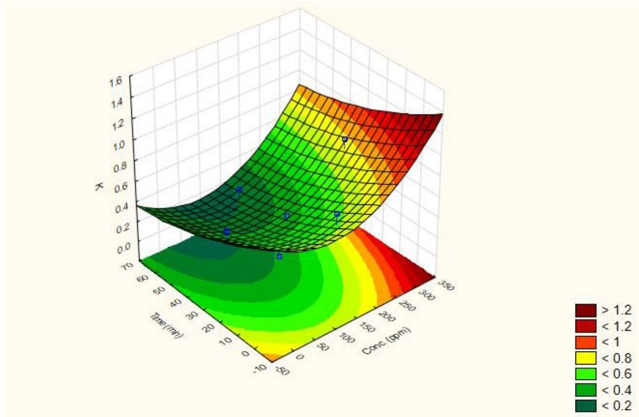

***Figure 3(a)** 3D contour plot for interactions between factors affecting response K*

Figure 3(b) shows the relationship between initial concentration and operation time for responses of T_R. From Figure 3(b) it shows that the higher T_R can be obtained is between 8.57 ppm to 150 ppm for initial concentration and 1.72 to 40 minutes for operation time. From the range obtained, it shows that the intermediate initial concentration and operation time brings a higher efficiency of the process results in higher T_R. Low initial concentration produces low solute concentration at the interface or ice formed [19], which means that the lower the initial concentration the lower the mass of TCP on the ice formed. As for the operation time, the longer the operation time the higher the probability of TCP being trapped inside the solid interface which in terms increase the concentration of TCP on the ice formed. As the process continues, the amount of ice formed increases in volume and the volume of liquid of liquid decreases thus leaving the contaminant to be trapped in the ice crystal formed on the wall of the crystallizer.

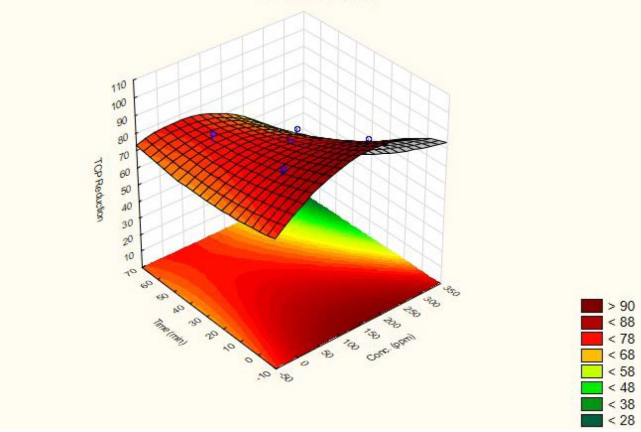

Figure 3(b) *3D contour plot for interactions between factors affecting response T_R*

3.5 Optimum Condition

From the model, optimum condition for initial concentration and operation time were obtained as presented in Table 7. The optimum response of K-value with the value of 0.1316 were predicted under the optimum conditions of initial concentration of 93.2 and operation time of 83 minutes. Under the optimum condition of initial concentration of 51.4 ppm and operation time of 60.5 minutes, an optimum response of T_R was predicted with the value of 76.53%.

Table 7: Optimum Condition for K and TR

Responses	Initial Concentration (Ppm)	Operation Time (Min)	Predicted
K	93.2	83	0.1316
T_R	51.4	60.5	76.53

4.0 Conclusions

In conclusion, for the study of effect it shows that the lower the initial concentration, the lower the K-Value and the higher the T_R which translated to a higher efficiency of the PFC process to separate the TCP from the water body. From the results of the experiment, initial concentration of 50 ppm brings out the highest efficiency of the PFC system as the K-value is 0.3048 and the T_R value of 0.9046. The results obtained from the experimental sequence backs up the statement that that low initial concentration is the optimum condition for the PFC process. Next, for the optimization sequence, RSM was thoroughly applied to determine the optimum condition of initial concentration and operation time for removing the TCP from the simulated wastewater via PFC. The regression model generated by RSM was a good fit since the R^2 obtained were 0.81767 for K and 0.87622 for T_R. From ANOVA analysis, the optimum initial concentration and operation time to obtain the lowest K value at 0.1316 can be achieved at the value 93.2 ppm and 83min respectively. As for T_R value, it can be summed up that the optimum T_R of 76.53 could be achieved at initial concentration of 51.4 ppm and operation time of 60.5 min.

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