A Bombastic Approach to Remove 2,4,6-T~~t~~richlorophenol (TCP) from Simulated Wastewater via Progressive Freeze Concentration (PFC): Effect of Operation Time & Optimization by using Response Surface Methodology (RSM)

Hariz Asyraf Hamizlan[a], Ikhmal Zariq Al Imran Jamal Ikhsan [a], Anwar Addini Mazzam [a], Muhamad Noor Faqeh Bakar [a], ~~Dr~~ Farah Hanim Ab Hamid[a]

[a]Faculty of Chemical Engineering, Universiti Teknologi MARA Shah Alam

Abstract

Nowadays, chemical industries have discharged the wastewater which contain a phenolic compound such as 2,4,6-trichlorophenol (TCP). This compound is toxic and hazardous as it belongs to a group of common environmental pollutant. It contributes to the shortages sources of clean water due to increment of population and rapid development of chemical industries. Therefore, the sources of water must be explored in order to get continuously supply of pure water. One of the ways to get pure water is by purifying the wastewater. This research is using progressive freeze concentration (PFC) to purify the wastewater. PFC is the process where the ice crystal is generated on the wall of the crystalliser which contain pure water through cooling process. The effect of operating time was then investigated on the performance of the PFC system through Effective Partition Constant (K) value and TCP reduction (%). TCP solution was used as ~~, as~~ simulated wastewater sample. The optimum condition was found at 40~~th~~ minutes, resulted in the lowest K and highest TCP reduction (%). Furthermore, Response Surface Methodology (RSM) was used for optimization of two parameters which are initial concentration and operating time. The K value and TCP reduction (%) were determined to investigate the efficiency of this system. STATISTICA s~~S~~oftware is then implemented to find the operating conditions. The best response for K and TCP reduction (%) were predicted by ANOVA were 0.13~~16~~ and 76.53~~28~~% respectively.

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1.0 Introduction

Water is a compound that is important in this world for all living things. The river has contributed 97% total usage of water main source for domestic [1]. Unfortunately, the clean and fresh water and its volume has decreased from time to time because of human's bad practices of habit. One of the main factors ~~and reasons~~ for this is because of the large volume production of wastewater discharged by domestic residences, commercial properties, industry and agriculture. Water shortage has become a~~the~~ serious issue and debatable particularly in developing countries. In 2016, half of billion people in the world are having water scarcity and this crisis has been identified as the biggest risk in the World Economic Forum[1].

In these days, wastewaters which contain phenolic compounds are a serious issue as it is water soluble and can be detected in ponds, soil and river [2]. Its chemical properties make it become toxic and hazardous and nowadays their amount in industrial wastewaters are increase [3]. Phenolic derivatives belong to a group of common environmental contaminants. The presence of the 2,4,6-trichlorophenol (TCP) even at low concentrations can be an obstacle to the use of waste water. It also contains a short term (acute) and long term (chronic) effects to the humans such as chronic bronchitis, chest wheezing, cough and pulmonary lesions [3, 4]. TCP also may recognize as toxic carcinogen in which it is produce through the process of producing by-product or chemical intermediates mainly in petrochemical [5, 6].

From literature, various technologies and techniques have been used to remove chlorophenols compounds from aqueous solutions such as biological treatment using anaerobic granular sludge [7] and dead fungus [8], catalytic wet oxidation [9], adsorption technology using activated clay [4] and activated carbon ~~and activated carbon~~ prepared from various precursors ~~[10]~~ [10]. However, the usage of activated carbon has been limited due to its high cost to the use of non-renewable starting material such as coal [10].

Recently, focus has been given ~~of this~~to the wastewater treatment which is freeze concentration (FC). It is an effective method to remove various impurities from industrial wastewater and liquid waste [11]. The freeze concentration consists of two (2) types which are suspension and progressive freeze concentration [12]. Suspension freeze concentration (SFC) is a system in which the tiny sizes of the ice were generated in the mother solution while progressive freeze concentration (PFC) is a process in which a big single ice crystal is generated in the process and formed on the crystalliser surface [13]. The main difference between these~~is~~ two technologies are size of ice crystal generated. ~~which is I~~If the limited size of ice crystal is formed it can make the separation from the mother solution become harder and need a complex procedure to produce large of ice crystal [14]. The SFC is commonly used because of its efficiencies although with high investment cost and operating cost [15, 16]. In this experiment, PFC has been used even it has a lower productivity and efficiency as compared to SFC but to decrease the operation cost, the PFC has a much simpler system and lower cost [14].

The objectives of this study were to evaluate the effect of operating time in separation of TCP from simulated wastewater using PFC on effective partition constant (K) and TCP reduction (%) and to study the relationship between operating time and optimum condition in separation of TCP by using Response Surface Methodology (RSM). ~~[17] [18] [17] [18] [17] [18] [17] [17] [18] [17] [18] [17] [18] [17] [18] [17] [18] [17] [18] [17] [18] [17] [18] [17] [18] [17] [17] [18] [17] [18] [17] [17] [16] [17] [16] [16] [15] [14] [13]~~

2.0 Methodology

2.1 Material and Equipment

A simulated wastewater containing TCP and acetone which act as solvent were used throughout the experimental work to represent simulated wastewater discharged from chemical industries. The sample used contain 100 ppm of TCP with the volume at 500mL. A 50% of ethylene glycol (EG) and 50% of water were used for the coolant in the cooling bath to ensure the freezing point of mixture is depressed. It also used to supply cooling energy to the system [13]. The crystalliser used is made up of stainless steel structured in cylindrical shape and the purpose is to provide a surface area where ice crystal will form and attach to. The cooling bath (PolyS~~s~~cience) is act as a cooling chamber for the cooling process. The purpose of cooling bath is to maintain the process at the desired temperature. Ultraviolet-visible Lambda 750 (UV-Vis) (Perkin Elmer) was used to determine the absorbance value and concentration of the mother solution and ice produced.

2.2 Apparatus Setup

The system consisted of cooling bath, crystalliser and a stirrer (Tuff). The stainless steel structured with cylindrical shape with volume of 1000 mL was used as crystalliser.~~ The volume of 500 mL simulated wastewater which contain TCP was placed inside the crystalliser. The coolant which contain 50% ethylene glycol (EG) and 50% water were poured inside the cooling bath. Next, the crystalliser contained the simulated wastewater was fully immersed inside the cooling bath. Then the motor stirrer was placed inside the crystalliser. The stirrer was put near the ice front. The purpose of stirrer is to equalize the entire liquid phase concentration solution and lowered the concentration at the ice front~~ [19]. The Figure 1 shows the apparatus set up for PFC process.

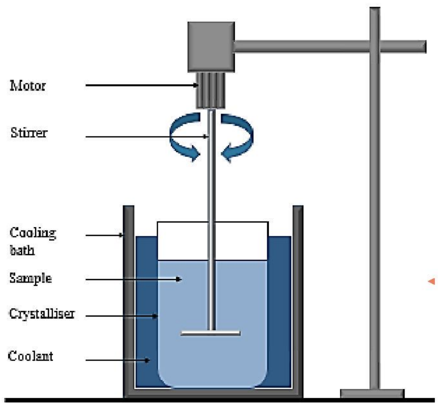

Figure 1: Apparatus set up for PFC process

2.3 TCP Calibration Curve Procedure

In order to prepare the calibration curve of TCP, it was~~is~~ required to prepare the stock solution. Thus, 1000 mg of TCP in powder form was dissolved in 100 mL of acetone which act as solvent due to its solubility characteristic. Then the distilled water was filled until the level of solution rises on datum line of 1000 mL volumetric flask. The concentration (ppm) of TCP were prepared from 0, 50, 100, 150, 200, 250 and 300 ppm. The calibration curve of TCP was based on the absorbance value taken from UV-Vis.

2.4 Experimental Procedure

A simulated TCP wastewater was prepared at 100 ppm of concentration by diluting a 1000 ppm of stock solution of TCP. The simulated wastewater contains 100 ppm of TCP was pre-cooled in the chiller at 4°C as the initial temperature of the sample should be not far from the water freezing point temperature. ~~The~~ 500 mL sample solution was~~is~~ then poured inside the crystalliser. The crystalliser~~sample~~ then was immersed into the cooling bath at constant coolant temperature, circulation flowrate and initial concentration at 5°C, 700 rpm and 100 ppm respectively for about 10 minutes. After desired operating time was reached, ~~Next,~~ the circulation of the stirrer ~~at~~ was stopped, and the liquid solution~~crystalliser~~ was drained out completely into a beaker to collect the layer of ice which remain in the crystalliser. The volume of concentrated solution and ice were measured~~calculated,~~ and the concentrations were determined by using UV-Vis. After that, same procedures were repeated with different operating ~~of~~ time at 20, 30, 40 and 50 minutes. ~~The experiment was repeated for each value of operating time~~ as shown in Table 1 below.

Table 1: Value of varied and constant variable

Variables	Range	Constant		
		Flowrate (rpm)	Coolant Temp. (°C)	Initial Conc. (ppm)
Operating time (min)	10	700	-5	100
	20			
	30			
	40			
	50			

2.5 Analytical Procedure

The concentration of concentrated solution and ice were measured analytically by using UV-Vis and glass cuvettes were used during analysis. This analytical method gave the absorbance value at a wavelength 295 nm and it is used to determine the concentration from the calibration curve.

2.6 Calibration Curve

A calibration curve graph of TCP solutions was plotted, and it was constructed in Figure 2. The calibration curve of TCP was determined by prepared a series of TCP solution in the range of 0 ppm to 300 ppm.

The calibration curve was used to determine the changes of concentration of TCP at both concentrated solution and ice crystal. The value of concentration of both were evaluated to determine the PFC system efficiency by calculation effective partition constant (K) and TCP reduction (%) value.

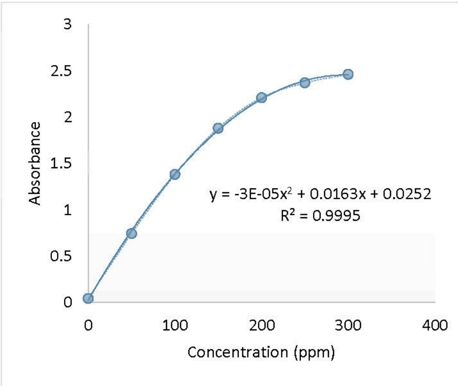

Figure 2: Calibration curve of TCP solutions

2.7~~6~~ Effective Partition Constant (K)

The effective partition constant (K) can be obtained by dividing the solute concentration in ice, C_s with solution phase, C_L as shown by using Equation (1) [18, 19]. K value can be determined the efficiency of~~for~~ the PFC system. The lower the value of K indicates the best efficiency for the process. The K value is range from 0 to 1. When K=0 it means ice is fully separate from the TCP and when K=1 means the separation process of TCP is not take place.

$$K = \frac{C_S}{C_L} \tag{1}$$

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2.8~~7~~ TCP Reduction (%)

TCP reduction (%) is~~is~~ also an essential parameters~~s~~ in this experiment to determine the PFC system efficiency. The reduction of TCP in this research was calculated in percentage by using Equation (2).

$$\text{TCP Reduction (\%)} = \frac{C_i - C_f}{C_f} \times 100\% \qquad (2)$$

Where C_i and C_f are the concentration of initial solution and concentration of TCP in ice layer. Higher value of TCP reduction (%) is better as it indicates a better efficiency of PFC process.

2.9~~8~~ Experimental Design for RSM

In preparing the experimental design of PFC process, initial concentration and operating time were chosen as the parameters that can give an effects the efficiency of the system. The range for all the independent variables were based on the limitation of equipment and by according the literatures, as listed in Table 2~~4~~. It needs a total of 10 runs to optimize the PFC system designed. The runs were performed in duplicate [11]. The chosen parameters were substituted into the resulting model in order to calculate the predicted response as shown in Equation 3.

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_{11} + \beta_{22} X_{22} + \beta_{12} X_1 X_2 \qquad (3)$$

where Y is the predicted response value, β is the regression coefficient, a weighting factor which is a number calculated by the statistical program to fit the experimental data, X is an experimental factor influencing the process.

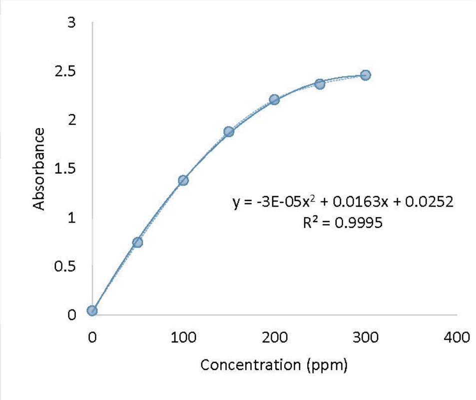
3.0 Results and discussion

In this PFC process, the ice crystal will be generated on the wall of the crystalliser made up from stainless steel. The Figure 3~~2~~ below shows the solid of ice generated on the wall of crystalliser at PFC experiments. During the experiment, the thickness of the ice solid formed on the wall of crystalliser were~~are~~ varied with the different operating of time.

Figure 3~~2~~: A close-up of the ice layer formed

~~*3.1 Calibration Curve*~~

~~A calibration curve graph of TCP solutions was plotted, and it is constructed in Figure 3. The calibration curve of TCP was determined by prepared a series of TCP solution in the range of 0 ppm to 300 ppm. The absorbance value obtained are summarized in Table 2.~~



~~Figure 3: Calibration curve of TCP solutions~~

~~Table 2: Absorbance value obtained at each concentration~~

~~Concentration (ppm)~~	~~Absorbance Value~~
~~0~~	~~0.0424~~
~~50~~	~~0.7429~~
~~100~~	~~1.3794~~
~~150~~	~~1.8804~~
~~200~~	~~2.2088~~
~~250~~	~~2.3690~~
~~300~~	~~2.4602~~

~~The calibration curve was used to determine the changes of concentration of TCP at both concentrated solution and ice crystal. The value of concentration of both were evaluated to determine the PFC system efficiency by calculation effective partition constant (K) and TCP reduction (%) value.~~

3.1~~2~~ Effect of Operating Time

The studied range of operating time in this study were~~is~~ 10 minutes until 50 minutes. This range was chosen based on the size of the crystalliser and stirrer impeller. ~~During this experiment, for each operating time in this range, an experiment was carried out. The operating time. The other operating condition such as circulation flowrate, coolant temperature and initial concentration were kept constant as listed in Table 1. Next, graph of K value vs operating time was plotted to indicate the effect of this parameter through PFC system.~~

The K value correlated with operating time was~~was~~ illustrated~~summarize~~ in Figure 4~~Table 3. and its effect can be indicated in Figure 5.~~ As shown in Figure 4~~5~~, the graph shows that the value of K decreases with increases of time until it reaches fortieth minutes. From 10 minutes to 40 minutes, the values of K remain decrease which is highly desired. However, as the operating time was further increased~~d further~~ until 50 minutes, the values started to increase. This result for TCP reduction (%) is inversely proportional to K value where the value increases with increases of operating time until it reached fortieth minutes and started to decrease until 50 minutes.

Generally, when the cooling process started, the degree of crystallinity of the ice layer generated on the wall is still low with the presence of dendrite structures [13]. From Figure 4~~5~~, it can be seen that the K value decrease and TCP reduction (%) increase as the operating time increase from 10 minutes to 40 minutes. The ice layer grows thicker leaving the unfrozen solution in a state approaching saturation level [13].

The lowest K and highest TCP reduction (%) value obtained during this PFC experiment were~~is~~ on the fortieth minute which is 0.49~~72~~ and 64.85% respectively. By looking at the trend on the graph, it can be said that 40 minutes is a suitable operating time in order to achieve high efficiency of PFC process. As the operating time became much higher than 40 minutes, it started to produce ice solid with higher impurities because the ice formed almost filled nearly half of crystalliser which resulted in narrow space for unwanted concentrate to circulate around the wall of crystalliser [20]. This makes the impurities easily trapped in the ice crystal layer. This condition reduced the path diameter of the fluid flow and produce a narrow space for concentrate to circulate. Thus, ice growth become easier to trap the solute in the concentrated solution resulted an increase value of K [20].

The range of first 10 minutes was chosen to be the lowest operating time because according to the study made by previous researcher [20], below 10 minutes the ice layer generated on the wall of crystalliser is in dendrites structure and not solid which shows the PFC process is not complete. This happen when operating time was carried out until 50 minutes according to Figure 5~~5~~. The ice solid formed almost filled half volume of the crystalliser that could interrupt the impeller of the stirrer.

~~Table 3: Value obtained at each operating time~~

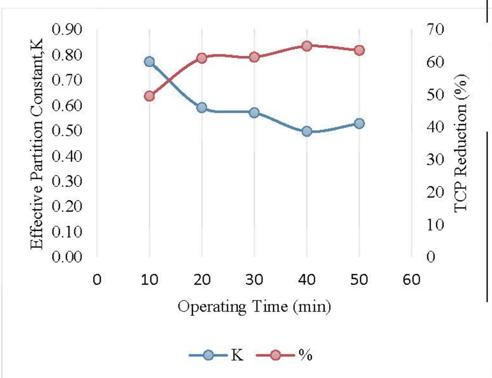


Figure 4: Changes in K and TCP reduction (%) value at different operating time

Figure 5: A close-up of the half-filled crystalliser

3.2~~3~~ RSM Models

To start the experiment, the STATISTICA software was used to determine the design of experiment (DOE). Regression analysis was carried out using this software. The range of process parameters for the PFC process in this study was tabulated in Table 2~~4~~. The chosen parameter are names as $\boldsymbol{X_1}$ for initial concentration and $\boldsymbol{X_2}$ for operating time. The results of K value for each run were~~are~~ tabulated in Table 3~~5~~.

Table 2~~4~~: Range of process parameters for the PFC process

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

Equation 4 and Equation 5 represent a regression equation for K (Y_1) and TCP reduction (Y_2) as a function of initial concentration (X_1) and operating time (X_2) and their interaction using linear and quadratic regression coefficient.

$$Y_1 = 0.645193 - 0.001965X_1 - 0.010177X_2 + 0.000011X_1^2 + 0.000062X_2^2 \quad (4)$$

$$Y_2 = 81.3942 + 0.15473X_1 - 0.29221X_2 - 0.0005X_1^2 + 0.00314X_2^2 - 0.00171X_1X_2 \quad (5)$$

The adequacy of the generated regression model was also evaluated using ANOVA method which is to determine significant effects of process variables to the response and to fit the models to the experiment data.

Table 3~~5~~: DOE and the responses

Run	X_1	X_2	**K**	**TCP (%)**
1	50.00	10.00	0.3~~79~~8~~3~~	88.78~~754~~
2	50.00	50.00	0.14~~14~~	82.08~~42~~
3	250.00	10.00	0.62~~193~~	83.76~~572~~
4	250.00	50.00	0.38~~776~~	63.41~~17~~
5	8.60	30.00	0.46~~44~~	71.00~~0.9967~~
6	291.42	30.00	0.83~~29~~	61.21~~42~~
7	150.00	1.72	0.68~~39~~	89.44~~34~~
8	150.00	58.28	0.28~~19~~	67.85~~484~~
9	150.00	30.00	0.34~~04~~	79.70~~00~~
10	150.00	30.00	0.34~~04~~	79.68~~11~~

3.3~~.4~~ Analysis of Variance (ANOVA)

ANOVA was used to determine the adequacy of the generated regression model. It also may ~~use~~use to evaluate the significant effects of process variables. Table 4~~6~~ and Table 5~~7~~ show~~ws~~ the outcome of such an analysis for both response K and TCP reduction (%) respectively. To determine the accuracy of the model using ANOVA, F-value need to be observed. The F-value calculated by ANOVA should be higher to the tabulated value for the model to be considered appropriate. From Table 4~~6~~ and Table 5~~7~~, the F-value obtained were~~is~~ 3.5877 and 5.6633 and both values are~~is~~ lower than tabulated $F_{(0.05,5,4)}$ which is 6.26. Thus, the empirical model is considered not appropriate.

The values of R^2 for the regression model for K and TCP reduction (%) are 0.81767 and 0.87622 respectively. It has been recommended that the R^2 value would be at least 0.75 in order to be considered as a good fit model [21]. According to the R^2 values of K and TCP reduction (%), 81.77% and 87.62% of the sample variation could be attributed to the variable and only 18.23% and 12.38% of the total variance could not be explained by the model, respectively. The data shows that there is a good correlation between the experimental data and the predicted K value obtained.

Table 4~~6~~: ANOVA results for the model relating K to the operating parameters

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 5~~7~~: ANOVA results for the model relating TCP reduction (%) to the operating parameters

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			

After the adequacy and validity of the model has been achieved, the factors that would give the most significant affect to the PFC process can be identified. Generally, p~~-~~-value must be lower than 5% in which it will bring significant effects to the responses. The data w~~ereas~~ constructed in Table 6~~8~~ and Table 7~~9~~ show the regression analysis for K and TCP reduction (%), which can be used to determine the significance of each factor in the regression model. Basically, the highest F-value and lowest p-value will give the most significance affect to the process. From Table 6~~8~~, it shows that the linear term of X_2(operating time) is the most significance parameter as it has the highest F value and lowest p~~-~~-value which are 0.010835 and 0.049446 respectively. From Table 7~~9~~, regression analysis also shows that the linear term of X_2(operating time) is the most significant parameter where the highest F value is 14.36438 and lowest ~~p value~~p-value is 0.019268.

Table 6~~8~~: Regression analysis for K

Factor	Coefficient Estimation	Standard Error	F	p~~P~~
X_1	-0.001965	0.002167	0.002167	0.056857
X_1^2	0.000011	0.000006	0.000006	0.158830
X_2	-0.010177	0.010835	0.010835	0.049446
X_2^1	0.000062	0.000155	0.000155	0.712001
X_1X_2	-0.000000	0.000033	0.000033	0.98918

Table 7~~9~~: Regression analysis for TCP reduction (%)

Factor	Coefficient Estimation	Standard Error	F	p~~P~~
X_1	0.15473	0.087537	6.10152	0.06893
X_1^2	-0.00050	0.000251	3.98453	0.11663
X_2	-0.29221	0.437686	14.36438	0.01926
X_2^1	0.00314	0.006280	0.24991	0.64339
X_1X_2	-0.00171	0.001343	1.61569	0.27258

3.4~~5~~ Response Surface Contour Plots Analysis

The three-dimensional response surface curves called contour plots were plotted to determine the optimum level of each variable and the effect of their interactions on responses as a function of two variables. Additionally, the contour plots were used to aid visualization of the interaction between two effects. Figure 6 and Figure 7 show~~s~~ the contour plots value of K and TCP reduction (%) respectively as a function of independent variables which are initial concentration and operating time.

According to ~~the 3D plot of~~ Figure 6, it shows that lowest value of K can be achieved at the range of 25 ppm to 175~~200~~ ppm for initial concentration and 50~~47~~ minutes to 70 minutes for operating time. The K value increases as the value of initial concentration increases. This is due to the high concentration of TCP in the solution may result in ~~—~~high amount of TCP contamination on the ice formed [20]. According to the result, low value of initial concentration will give high K value at certain point because of low operating time in which an ice layer formed is not satisfactory to separate the concentrate solution.

As the operating time increases, the value of K seems to be at low value. The 3D contour plots show that as operating time is increasing up to 50 minutes with intermediate initial concentration applied, the value of K decreases. It means that the purification of simulated wastewater from TCP has effectively occurred. This is due to when the low operating time will result in incompletely crystallization process, thus the separation process was inefficient.

The relationship between initial concentration and operating time for TCP reduction (%) was~~is~~ constructed in Figure 7. ~~Figure 7~~It shows that the higher value of TCP reduction (%) can be achieved between 50~~8.579~~ ppm to 150~~291.421~~ ppm and 40~~1.716~~ minutes to 65~~20~~ minutes for initial concentration and operating time respectively. This indicates that longer operating time can generate purer ice crystal. The result~~s show that when initial concentration and operating time is applied together~~ shows that intermediate operating time and initial concentration will give~~ will bring~~ a better efficiency in which reflected in lower K value and higher TCP reduction (%).

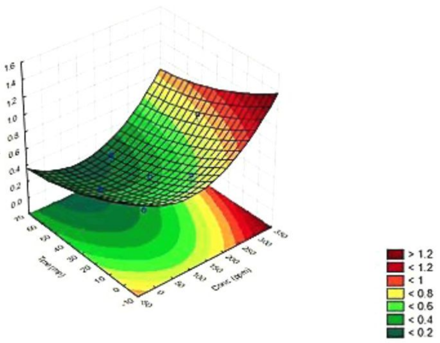


Figure 6: 3D contour plot for interaction between factors affecting response K

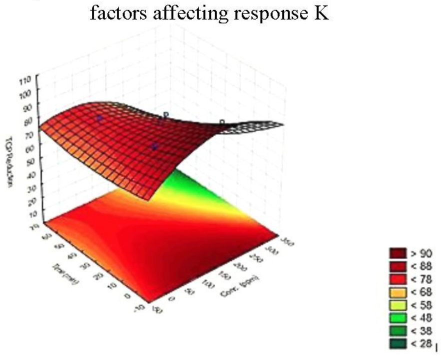


Figure 7: 3D contour plot for interaction between factors affecting response, TCP reduction (%)

3.5~~6~~ Optimum Condition

From the model, the predicted optimum conditions for K value and TCP reduction (%) were obtained.~~as generated from this RSM.~~ Table 8~~7:~~ shows the optimum value for each investigating operating parameter. The optimum conditions for response K generated from RSM were~~as~~ at 93.21~~1~~ ppm of initial concentration and 82.92~~2.924~~ minutes for operating time. For TCP reduction (%), the optimum conditions were~~as~~ at 51.3~~436~~ ppm for initial concentration and 60.49~~0.492~~ minutes for operating time. An optimum response of K and TCP reduction (%) with 0.13~~16~~ and 76.53%~~28~~ were predicted.

Table 8~~7~~: Optimum condition for K and TCP reduction (%)

Responses	Initial Conc. (p~~P~~pm)	Operating Time (m~~M~~ins~~s~~)	Predicted
K	93.21~~1~~	82.92~~4~~	0.13~~16~~
TCP Reduction (%)	51.3~~436~~	60.49~~2~~	76.53~~28~~

Conclusions

This research has proven that the simulated wastewater of TCP can be ~~concentrating~~ concentrated efficiently by using PFC system and it ~~-~~has a potential towards removal of TCP. Effect of operating time has been studied where at 40 minutes. ~~From the result,~~ the lowest K value ~~is at 40 minutes~~ and highest TCP reduction (%) are~~is~~ at 0.49~~72~~ and 64.85~~33~~% respectively. ~~It also proves that high operating time with intermediate other parameters such initial concentration, circulation flowrate and coolant temperature resulted in lower K value and high TCP reduction (%) which indicates better efficiency for the PFC system.~~

The optimization by using RSM also was successfully applied to obtain the optimum condition of operating time and initial concentration for concentrating the simulated wastewater of TCP. According to STATISTICA software, the best K value could achieve is 0.13~~16~~ when operating time is 82.92~~2.924~~ minutes and initial concentration at 93.21~~1~~ ppm. For TCP reduction (%), the highest value could obtain is 76.53~~28~~% when operating time is 60.49~~0.492~~ minutes and 51.3~~436~~ ppm for initial concentration.

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