
Progressive Freeze Concentration: Effect of Circulation Flowrate on 2, 4, 6-Trichlorophenol Removal and Optimization via Response Surface Methodology.

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Abstract

2,4,6- Trichlorophenol (TCP) is a toxic and mutagenic yet carcinogenic compound which is found in the emissions from combustion of fossil fuel, incineration of municipal waste and process of chlorination of water containing phenol or some aromatic acids with hypochlorite and disinfection process of water for domestic used or others. This study attempted to prove that TCP in wastewater can be separated through PFC method; which is simple yet cost effective. The wastewater then can be dumped into water-channels after removing TCP from simulated wastewater due to lower concentration of TCP in wastewater thus lowering water pollution aftermath. The objectives of this study are to study the relationship between the circulation flowrate of specimen in separating TCP from simulated wastewater using progressive freeze concentration (PFC) and its effectiveness through effective partition constant, K and TCP reduction efficiency (Eff) and to determine the optimum circulation flowrate of specimen in PFC for optimization of separation process. In this research, a method of experiment was designed to study PFC which was circulation flowrate. This method focused on the effect of solution on the crystallization by freeze concentration of simulated wastewater. The best circulation flowrate found was at 900 rpm which resulted in lowest K value and highest Eff. The model of experiment made by RSM was found to be a great model as the calculated F value of 17.6662 and 10.1723 for K value and Eff are larger than tabulated which was 6.26. The best responses for K and Eff forecasted by ANOVA were 0.1528 and 84.8% respectively.

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1.0 Introduction

Chlorophenols are a group of chemicals resulting from addition of chlorines to phenols group. They are regarded as one of many common organic pollutants widely used in industry, agriculture and public health [1]. Some of industrial wastewaters rich in chlorophenols are from pesticide, paint, wood, pharmaceuticals, paper and pulp industries as well as water disinfecting process [2]. Chlorophenols with at least two chlorines are used in pesticides whereas four

chlorines are benefited in antiseptics [3]. Chlorophenols are hazardous towards living organisms as they can permeate into skin in vitro and promptly absorbed by gastro-intestinal tract [2].

2,4,6- Trichlorophenol (TCP) is a toxic and mutagenic yet carcinogenic compound which is found in the emissions from combustion of fossil fuel, incineration of municipal waste and process of chlorination of water containing phenol or some aromatic acids with hypochlorite and disinfection process of water for domestic used or others [4]. Aside

from that, researches confirmed that TCP also can cause adverse effects on human nervous system as well as respiratory problems, for instance, cough, modified pulmonary function and chronic bronchitis [5]. Such traits of hazards and toxicity to biological environment are due to the stable C-Cl bond in addition due to the position of chlorine atoms relative to the hydroxyl group [6], hence its removal from the environment is essential.

Suspension Freeze Concentration (SFC) is a crystallization process which uses freezing point as datum to separate a component from the mother liquor. Components' molecules with higher freezing point would crystallize firsthand and form suspension in the mother liquor, leaving more concentrated solution behind [7]. The freezing separation method requires filters and washers to acquire zenith segregation of crystals from the solution, thus adding to capital and operational cost [7].

To compensate such flaw, progressive freeze concentration (PFC) is geared as alternative method. PFC uses the same datum to separate between components in a solution where higher melting/freezing points solution will be crystallized earlier, layer by layer forming a single block of ice at the end of the process. Components with lower freezing/melting points remain as liquid form, thus easing separation process between the two phases; simply by draining the concentrated liquid from the system [8].

Past researches have been using PFC to treat wastewater from few industries for instance, pharmaceutical [9], fluoride removal [10], chromium (VI) removal [11], and chemical (Grignard reagent)[12]. Seemingly, PFC is keen to be applied in removing TCP in wastewater from various industries. On the same subject, this study was conducted to investigate the performance of PFC towards simulated wastewater containing TCP. The optimum operating conditions were determined while varying circulation flowrate to acknowledge the performance of PFC in which changes in effective partition constant (K) and TCP reduction efficiency (Eff) were analysed to clarify the effect of circulation flowrate. Last but not least, optimization process was conducted at varied coolant temperature and circulation flowrate by using response surface methodology (RSM).

2.0 Methodology

2.1 Material

The main materials applied in this experiment as test subject was simulated wastewater containing TCP. TCP powder; weighted 1 gram, is dissolved in 100 ml of acetone and then water was poured in until the solution achieved 1000 ml. 50 ml of TCP from stock solution were retrieved and diluted with 450 ml of distilled water to simulate wastewater with 100 ppm of TCP which were made constant for each experiment. Whilst, ethylene glycol mixed with water to achieve 50% v/v was used as coolant for progressive freeze concentration process.

2.2 Calibration Procedure

1 gram of TCP powder was dissolved in 100 ml of acetone due to its solubility in organic solvent and distilled water was added until 1000 ml of solution was formed as stock solution. Calibration curve of TCP concentration based on absorbance value received from UV-Vis Spectrophotometer was constructed based on respective volume of stock TCP solution as per tabulated in Table 1.

Table 1 Absorbance value obtained from UV-Vis Reading

Concentration (ppm)	Absorbance value
50	0.7429
100	1.3794
150	1.8804
200	2.2088
250	2.369
300	2.4602

2.3 Experimental Procedure

In this experiment, a 1L stainless-steel container brand Zirafah was used to carry out the separation process. These parameters; temperature of coolant, concentration of TCP and operation time, were constant at -5°C, 100 ppm and 30 minutes accordingly. Figure 1 portrays the experimental set-up to run the experiment.

To start the operation, the simulated wastewater was put into the crystallizer with the volume of 500 ml and then, were fully immersed into an open water bath model from Polyscience contained of mixture between water and ethylene glycol in the same ratio which was

set to a constant coolant temperature of -5°C , which was pre-cooled beforehand. The sample solution was then stirred with a digital overhead stirrer model from Tuff- which has been equipped to the crystallizer, ranging from 500, 600, 700, 800 and 900 rpm to control the flowrate of the solution.

The ice layer formed and the liquid solution remained in the container were segregated simply by pouring out the liquid at the end of each experiment. After the ice molecules were melted, both samples were tested in UV-Vis spectrophotometer for their respective concentration with regard to calibration curve drawn beforehand.

In this study, the efficiency of segregation between TCP and water in simulated wastewater was determined by effective partition constant, K and TCP reduction efficiency (Eff).

Partition coefficient, K of solute between liquid and ice phase is the most vital component in progressive freeze concentration process. According to Fujioka [13], the K value is between 0 to 1 with $K=0$ means TCP is completely removed, whilst $K=1$ means the separation process was a failure. The K value can be calculated by using equation (1).

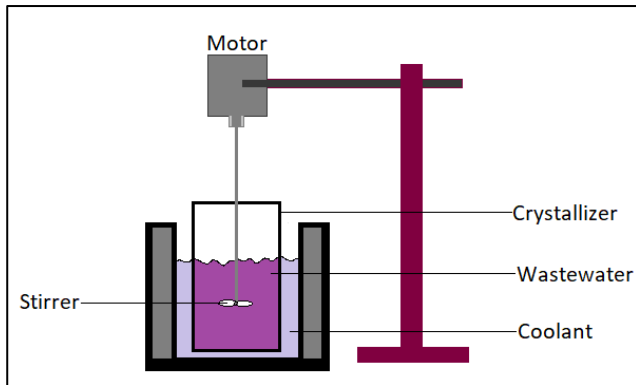


Figure 1 Set-up of Experiment

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

Where, C_S = Concentration of solute in ice phase (wt%) and C_L = Concentration of solute in solution phase (wt%).

TCP reduction efficiency, Eff was calculated using equation in which higher percentage of TCP reduction efficiency indicates better separation using the following equation (2),

$$\text{Eff} = \frac{C_0 - C_i}{C_0} \times 100 \quad (2)$$

Which, C_0 = Initial concentration of TCP in simulated wastewater solution (mg/l) and C_i = Final concentration of TCP in ice counterpart (mg/l).

2.4 Experimental Design for RSM

First and foremost, the design of experiment (DOE) was planned with appropriate variables selection, clarifying DOE spreadsheet and completing the experiment with adequate results. Central Composite Design (CCD) was the cliché design in RSM study to clarify the connection of the process variables and to forecast the optimum condition for the highest separation percentage. Table 1 shows the parameters used; circulation flowrate and temperature of coolant, and Table 2 shows the ranges used for the experiment.

3.0 Results and discussion

Ice crystals were formed on the inner wall of stainless-steel container used. Figure 2 shows the layer of ice formed at the end of the experiment. The thickness of ice layer formed was due to different operating conditions applied throughout the experiment- circulation flowrate. In this experiment, distilled water used to simulate the wastewater containing TCP was forecasted to form ice layer earlier compare to TCP mixed with acetone solution due to higher freezing point of water. Consequently, the component in the mother liquor with higher freezing point is frozen first on the cooling surface leaving the other component with lower freezing point remain in liquid form, which describes on how the separation of water and TCP work.

Such indicators could be influenced by circulation flowrates, temperature of coolant, operating time and initial concentration of TCP [14].

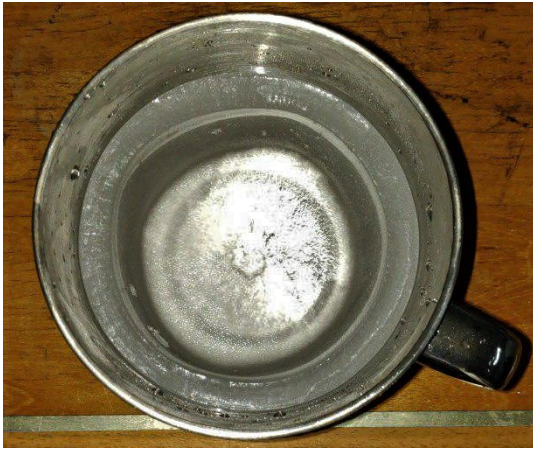


Figure 2 Ice formed on inner wall of container.

3.1 Calibration Curve Trendline

From Figure 3, polynomial trendline was used to represent concentration of TCP based on the amount of absorbance value obtained from UV-Vis spectrophotometer with polynomial equation,

$$y = -3 \times 10^{-5}x^2 + 0.0163x + 0.0252 \quad (3)$$

And with correlation coefficient, $R^2 = 0.9995$ which is an acceptable value as agreed by previous researches for UV-Vis spectrophotometer [15]. Construction of calibration curve was mainly to reduce bias in instrument reading at the same time reducing random errors that could affect the precision of an instrument.

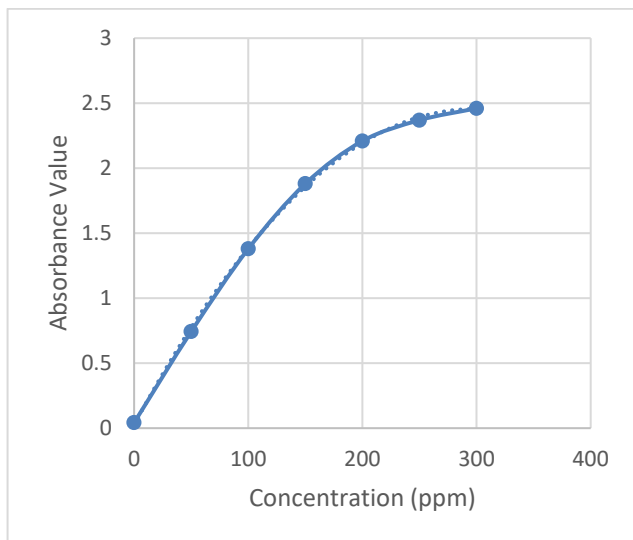


Figure 3 Graph of Absorbance Value vs Concentration (ppm)

3.2 Effect of Circulation Flowrate on Value of K and TCP reduction efficiency.

Circulation flowrate is one of the most crucial operating condition in performing PFC since solution

movement has a connection with mass transfer of a freezing system [16]. The efficiency of a PFC system also facilitated by the advancement rate of the ice front together with mass transfer depending on circulation flowrate [17]. Introduction of circulation flowrate would create movement in the solution thus providing uniform distribution of flow, consequently accumulation of solute near the ice-liquid interface will be decreased [17].

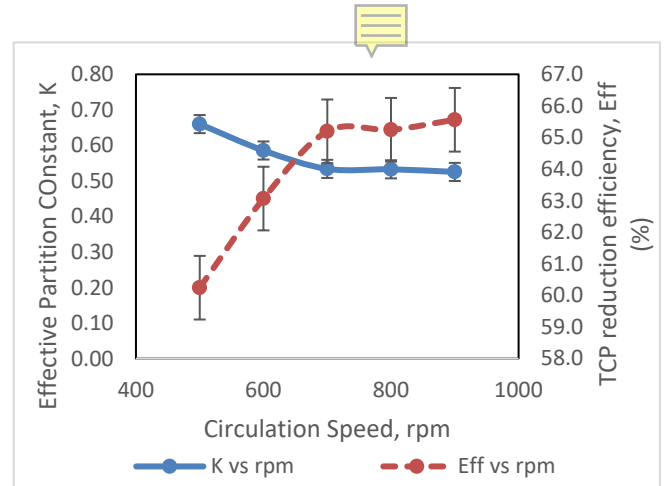


Figure 4 Graph of K Value and Eff vs Circulation flowrate (rpm)

From Figure 4, it shows that lower circulation flowrate would result in higher K value, simultaneously higher TCP reduction efficiency. The content ratio of solute in ice phase over liquid phase is high thus producing a higher value of K due to high tainted of ice layer formed.

Other than that, lower circulation flowrate would result in having slurry of ice in the solution thus turning the system into SFC instead of PFC which rather difficult to separate between ice molecules and its liquid counterpart. Such circumstance is due to failure to stir away the solutes from the ice-solution interface onto the wall surface of the container.

On the other hand, higher circulation flowrate does prove to be effective in producing low value of K. Higher circulation flowrate promotes slower rate of solidification which causes less solutes captured in ice, thus encouraging more solutes to remain in the liquid phase and higher purity of ice crystals will be obtained. Higher circulation flowrate ensures prevention of high solutes or contaminants concentration in the solid ice phase as the phenomena of solutes being stirred away from the solution-ice interface occurs continuously resulting in high purity of water ice crystal. This result is in favour as the findings from Miyawaki [16] and Samsuri [18].

3.3 Response Surface Methodology (RSM)

To evaluate and solve multivariant equations, RSM was used as a statistical method that uses quantitative data from appropriate experiments. RSM techniques consist of designing of experiments to provide adequate and reliable measurement of the response, developing a mathematical model for best fit between data and acquiring optimal value of the variables of the experiment [19]. The experimental range of operating conditions involved in this experiment was tabulated in Table 2. Table 3 shows the result of K and Eff for each experiment ran. The operating parameters inclusive in this experiment are named as X_1 for coolant temperature and X_2 for circulation flowrate.

Table 2 Experimental Range

Type of Parameter	Range				
	$-\alpha$	-1	0	1	$+\alpha$
Coolant Temperature ($^{\circ}\text{C}$) (X_1)	-2.2	-3	-5	-7	-7.8
Circulation Flowrate (rpm) (X_2)	417	500	700	900	982

Generally, to acknowledge whether the model is appropriate or otherwise, the F value calculated by ANOVA should be more than the tabulated value [20]. From the Table 4 and Table 5, the calculated F value of 17.6662 and 10.1723 both responses are larger than tabulated $F_{(0.05,5,4)}$ which is 6.26. Therefore, the empirical model is considered to have a goodness of fit to the experimental data.

In general, factor with lowest p-value and the highest F-value is regarded the most essential effect to the process [20]. To ascertain whether the model is to be considered appropriate or otherwise, the F-value calculated from ANOVA which is referred to as Fisher's test (F-test) ought to be several times greater than the tabulated value [21].

Whilst, as for R^2 value, according to Keshani et al [19], the model is considered describing the real situation at best as the value of R^2 is larger than 0.90. The R^2 for K value is 95% while for Eff is 92%

Table 3 K value and Eff at respective model of experiments

Run	Circulation flowrate (rpm)	Temperature of Coolant ($^{\circ}\text{C}$)	K	Eff (%)
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The interaction using linear and quadratic regression coefficient and the assessed multiple regression equations for K (Y_1) and Eff (Y_2) as a function between two operating conditions of coolant temperature (X_1) and circulation flowrate (X_2) were presented in Equation 3 and Equation 4.

The determination coefficient (R^2) and ANOVA were carried out to determine the best fit of the model between forecasted values and the experimental data.

3.4 Model Adequacy

By using analysis of variance (ANOVA), verification of the adequacy of the regression model can be done.

indicated that both models imputed to the independent factors and only 5% and 8% for both responses respectively are not clarified by the model. This circumstance proves that both experimental and the predicted K value and Eff obtained from the models are in good accordance.

In ANOVA analysis, the significance of effect to K and Eff dependent on p-value which ought to be lower than 5% for all factors [22]. Table 6 and Table 7 tabulate the regression analysis for responses of K and Eff. While F value determines the significance of the regression coefficients of the parameters, p-value act as tool to verify the significance of each factor and interaction between factors [21]. Therefore, from Table 6 and Table 7, X_1^2 (quadratic term of coolant temperature) was determined as the most crucial parameter as it has highest F and lowest p-value which are 50.87884 and 0.002043 for K and 35.37610 and 0.004009 for Eff respectively.

1	417	-5	0.515	65.992
2	500	-3	0.444	69.268
3	500	-7	0.685	59.361
4	700	-2.2	0.627	61.47
5	700	-5	0.736	57.995
6	700	-5	0.284	82.631
7	700	-7.8	0.282	82.766
8	900	-3	0.431	69.865
9	900	-7	0.464	68.285
10	982	-5	0.125	88.446

$$Y1 = 2.7117 + 0.6192X_1 + 0.0501X_1^2 - 0.0018X_2 - 0.0001 X_1X_2 \quad (4)$$

$$Y2 = -72.6075 - 34.7116X_1 - 3.0008X_1^2 + 0.1624X_2 - 0.0001X_2^2 + 0.0052X_1X_2 \quad (5)$$

Table 4 ANOVA for model K

Sources	Sum of squares (SS)	Degree of Freedom (d.f)	Mean Squares (MS)	F-Value	R ²
Regression (SSR)	0.319251	5	0.0638502	17.66623781	0.95668
Residual	0.014457	4	0.00361425		
Total (SST)	0.333708	9			

Table 5 ANOVA for model Eff

Sources	Sum of squares (SS)	Degree of Freedom (d.f)	Mean Squares (MS)	F-Value	R ²
Regression (SSR)	935.156	5	187.0312	10.17234074	0.92709
Residual	73.545	4	18.38625		
Total (SST)	1008.701	9			

Table 6 Regression analysis for K

Factor	Coefficient Estimation	Standard Error	F	P
X₁	0.619166	0.088439	6.33996	0.065501
X₁²	0.050141	0.007029	50.87884	0.002043
X₂	-0.001834	0.001059	21.34205	0.009883
X₂²	0.000000	0.000001	0.49650	0.519906
X₁X₂	-0.000130	0.000075	2.99263	0.158697

Table 7 Regression analysis for Eff.

Factor	Coefficient Estimation	Standard Error	F	P
X₁	-34.4888	6.30787	1.82884	0.247663
X₁²	-2.9821	0.50137	35.37610	0.004009
X₂	0.1633	0.07552	11.58256	0.027194

X_2^2	-0.0001	0.00005	2.52218	0.187451
X_1X_2	0.0052	0.00536	0.94280	0.386541

3.5 Analysis of response surface contour plot

By plotting three-dimensional response surface curves also known as contour plots, the ideal level of

each variable and the effectiveness of their interactions were studied at ease. Additionally, this contour plots were used to facilitate in visualization as a whole the interaction between two effects while at the same time keeping constant other variables at its middle range. Figure 5 and Figure 6 shows the value of K and Eff respectively, as a function of independent variable which are circulation flowrate and coolant temperature.

The plot in Figure 5 illustrate that the lowest value of K can be retrieved at the highest range between 920 rpm to 1100 rpm for circulation flowrate while middle range of -3.9 °C to -5.5°C for coolant temperature. Formation of ice progressed efficiently as the coolant temperature decreases thus resulting in lower value of K. Nevertheless, the trend is proved to be otherwise as the coolant temperature kept on decreasing. Such circumstance is due to higher tendency of ice crystal to form, inclusive of higher amount of solute to be frozen at ice surface thus increasing the K value [17]. Higher circulation flowrate contributes to increased heat transfer rate for crystallization, resulted in development of ice crystals in a planar form, thus discarding the impurities away from the ice-liquid interface yielding pure ice crystals.

The plot in Figure 6 portrayed the highest value of Eff can be achieved at coolant temperature between -5.5°C to -6.5°C and circulation flowrate between 850 rpm and 950 rpm. Such circumstance was to prove that purer ice can be obtained when the circulation flowrate is higher, but higher than the said range, would cause breakage of ice formed thus compromising the efficiency of TCP reduction. Simultaneously, any coolant temperature lower than the said range would cause tendency for solute to form ice at the ice phase counterpart thus increasing impurity at the same time lowering its efficiency to remove TCP.

3.6 Optimum Condition

Table 8 Optimum Condition for K and Eff.

Responses	Coolant Temperature (°C)	Circulation Flowrate (rpm)	Predicted
K	-4.54	1255	0.1528
Eff	-5.0	862	84.8

From the model, Table 8 tabulated the optimum conditions for coolant temperature and circulation flowrate. The lowest K value of 0.1528 was predicted at condition of -4.54°C and 1255 rpm. While under condition of -5.0°C coolant temperature and 862 rpm of circulation flowrate, Eff yielded was 84.8%.

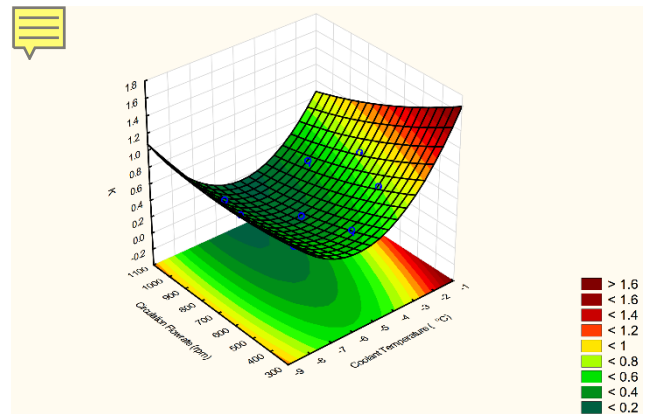


Figure 5 3D contour plot for interactions between coolant temperature and circulation flowrate affecting response K.

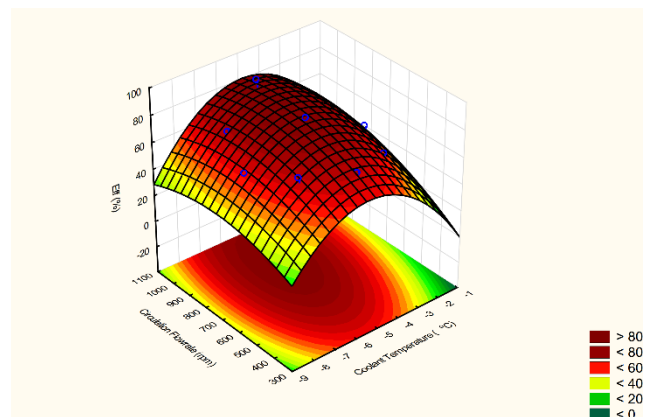


Figure 6 3D contour plot for interactions between coolant temperature and circulation flowrate affecting response, Eff.

4.0 Conclusion

This study proved the effectiveness technique to purify wastewater through PFC. This process has a great opportunity to be implemented for industries that require separation process with cost-friendly yet easy to handle upper hand among any other separation techniques. In this study, determination of effective partition constant (K) and TCP reduction efficiency (Eff) were crucial to clarify the effectiveness of circulation flowrate (rpm) on the efficiency of PFC process. As a result, the lowest K value obtained was 0.5253 and the highest Eff was 65.56% with the best operating circulation flowrate at 900 rpm. Aside from that, to determine the optimum condition of coolant temperature and circulation flowrate to remove TCP via PFC, RSM was majestically applied. From the result, R^2 obtained were 0.95668 for K value and 0.92709 for Eff indicated that the regression models generated by RSM has a good accuracy. From ANOVA analysis, it can be summed up that the optimum K and Eff for this system could be achieved at coolant temperature of -4.54°C and circulation flowrate of 1255 rpm yielded lowest K value which is 0.1528. As for Eff counterpart, the highest value that can be achieved was 84.8% with coolant temperature -5.0°C and circulation flowrate of 862 rpm. The former and latter value for both K and Eff predicted, indicate purer ice crystal was obtained. This study would be extremely useful to uncover the ability of PFC as an alternative approach to remove TCP from wastewater.

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