Archives of Materials Science and Engineering

Volume 119
Issue 2
February 2023
Pages 56-61

International Scientific Journal
published monthly by the
World Academy of Materials
and Manufacturing Engineering

DOI: 10.5604/01.3001.0053.4741

Influence of process parameters in removing wastewater impurities via progressive freeze crystallization

A.A. Mazzam, H.A. Hamizlan, I.Z.A.I. Jamal Ikhsan, M.N.F. Bakar, F.H. Ab Hamid*

School of Chemical Engineering, College of Engineering, Universiti Teknologi MARA, 40450, Shah Alam, Selangor, Malaysia

* Corresponding e-mail address: farah88@uitm.edu.my

ORCID identifier: https://orcid.org/0000-0003-4307-1899 (F.H.A.H.)

ABSTRACT

Purpose: The research aims to investigate the effect of the process parameter of progressive freeze concentration to eliminate tricholorophenol in wastewater.

Design/methodology/approach: A stainless steel crystallizer was used throughout the experiment. Simulated wastewater containing trichlorophenol (TCP) was used as a sample solution, and ethylene glycol was utilized as a coolant to induce the heat transfer at a very low temperature. Progressive freeze crystallization (PFC) is an approach to purify water by implementing the fundamental concept of difference freezing point. In short, the PFC system produces ice-crystal layer by layer on a cooled surface until it forms a large and single-crystal block, leaving the impurities in the mother liquor.

Findings: It is established that operating time and initial concentration influence the PFC performance. The findings show that the intermediate operating time gave the highest removal of TCP in wastewater. Meanwhile, for the effect of initial concentration, it was discovered that the lowest initial concentration resulted in the best TCP reduction with high purity of the water was obtained.

Research limitations/implications: The results can be complemented by studies of the effect of coolant temperature and solution movement. These two parameters are believed to potentially improve the PFC performance.

Practical implications: The findings can be implemented to select the optimal operating condition to treat the wastewater, especially in the industrial area with hazardous TCP.

Originality/value: The obtained results testify to the predominant influence of operating time and initial concentration on the PFC performance in eliminating TCP in wastewater.

Keywords: Environmental management, Crystallization, Wastewater treatment, Tricholorophenol

Reference to this paper should be given in the following way:

A.A. Mazzam, H.A. Hamizlan, I.Z.A.I. Jamal Ikhsan, M.N.F. Bakar, F.H. Ab Hamid, Influence of process parameters in removing wastewater impurities via progressive freeze crystallization, Archives of Materials Science and Engineering 119/2 (2023) 56-61.

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MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

Chlorinated phenols or chlorophenol, widely used in industries, are of growing concern due to their high toxicity, carcinogenicity, and wide distribution in industrial waste [1]. 2,4,6- Trichlorophenol (TCP) has been classified as one of the primary pollutants, and it is compulsory to treat it to be less than 1 ppm as enacted by the Department of Environment (DOE), Malaysia in Environmental Quality Act 1979 (Sewage and Industrial Effluent) [2]. The removal of 2,4,6-TCP from the environment is extremely important because its toxicity, carcinogenic properties, structural stability, and persistence in the environment are all caused by the stable carbon-chlorine bond and the position of chlorine atoms in relation to the hydroxyl group, as shown in Figure 1 [3,4]. Thus, the process of removing TCP from water may be a bit tedious, and without proper removal, it will destroy the natural habitat and ecosystem of the river alongside any organism that lives in the river or near the river. Proper waste management is needed as it will be necessary for a sustainable environment [5,6].

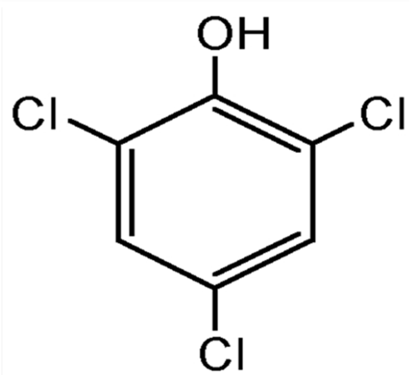

Fig. 1. Trichlorophenol structure

Several methods can be used to properly separate the pure water and the contaminant inside the affluent. Reverse osmosis, freeze concentration and evaporation is the most common method used in the separation process [7,8]. Although evaporation and reverse osmosis are very well-developed methods, both methods have major drawbacks. The major drawback of evaporation is that it involves a high processing temperature, leading to high energy consumption [9]. Meanwhile, the major drawback of RO is that the membrane is easily clogged by the content of the effluent, which affects the cost highly due to constant replacement [10]. In addition, the membrane characteristic itself plays the main role in determining the separation performance, such as hydrophobic properties [11].

Therefore, progressive freeze concentration or crystallization (PFC) is introduced as an alternative separation method. Compared to other crystallization processes, such as suspension freeze concentration and block freeze concentration, PFC is chosen because of its energy saving and also less complicated equipment is needed [12]. The PFC process is versatile and can be used to separate contaminants in water by implementing the fundamental concept of different freezing points. In short, the PFC system produces ice-crystal layer by layer on a cooled surface until it forms a large and single-crystal block [13]. Few applications have been successfully developed using the PFC system. PFC is an effective separation technique, especially in the desalination of seawater [14], and concentrates liquid foods such as dairy products and fruit juice in the food industry [12,15]. Thus, these good reputations of the PFC system need to be developed further to be applied to other water-solute removal processes, such as TCP removal from wastewater.

This study applied PFC to purify the wastewater by separating the water and TCP. Initial concentration is one of the most crucial factors in developing a superior PFC process. Initial concentration influences the efficiency of the PFC process as it affects the number of solutes that need to be separated. Another important parameter that needs to be focused on in this study is operating time, where the time consumed to form the ice crystal layer will determine the purity of the output. This study aims to ascertain how both characteristics affect PFC performance.

2. Research methodology and materials

2.1. Material

Samples of simulated wastewater with TCP were used throughout the experiment. The simulated wastewater consisted of 100 ppm of TCP at 500 mL in volume. Moreover, ethylene glycol mixed with water in a ratio of 1:1 was employed as a coolant to provide the system with cooling energy. [16]. To transfer heat at a very low temperature, ethylene glycol was used as it is a good cooling medium.

2.2. Equipment

The equipment used for the PFC process consists of four main parts, which are a cooling bath (Brand: PolyScience, model: Programmable Temperature Controller 9112A12E), a motor with a stirrer (Brand: Tuff), and a 1000 mL stainless-steel container act as a crystallizer where the crystallization process occurred as illustrated in Figure 2.

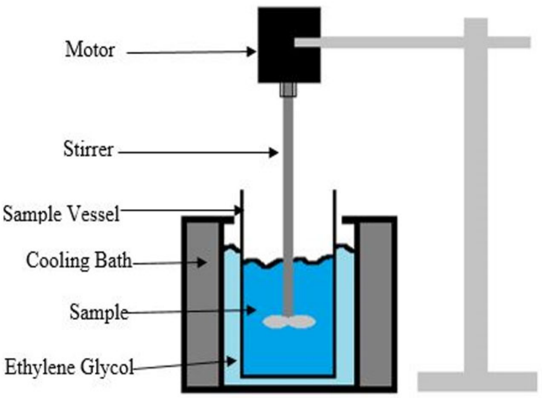

Fig. 2. Experimental setup

2.3. 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 containing 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. 500 mL sample solution was then poured inside the crystallizer. The crystallizer was then immersed into the cooling bath at the constant coolant temperature, stirring speed, and initial concentration at -5°C, 700 rpm, and 100 ppm, respectively for about 10 minutes.

Table 1.
Range of operating conditions

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

After desired operating time was reached, the circulation of the stirrer was stopped, and the liquid solution was drained out completely into a beaker to collect the layer of ice which remained in the crystallizer. The volumes of concentrated solution and ice were measured, and the concentrations were determined using UV-Vis. Using STATISTICA Software Version 12, the design of the experiment (DOE) was determined to run the experiment properly. Table 1 shows the experimental range implemented. The operating parameters involved are named X_1 for initial concentration and X_2 for operating time. 10 sets of experiments were done based on the DOE generated, and each run was tabulated in Table 2. All range was decided based on the preliminary experiments and depended on the ability of the equipment. To get a reliable outcome, the tests were run three times.

Table 2.
Design of the experiment

Run	X_1	X_2
1	50	10
2	50	50
3	250	10
4	250	50
5	8.6	30
6	291.42	30
7	150	1.72
8	150	58.28
9	150	30
10	150	30

2.4. Analytical procedure

A UV-VIS spectrophotometer (Brand: Perkin Elmer Lambda 750) was used to measure the absorbance value of the solution to determine the concentration of TCP after undergoing the PFC process. To prepare a TCP calibration curve for this purpose, 1 g of 2,4,6-TCP powder was dissolved in 100 mL of acetone in a 1000 mL volumetric flask. The volumetric flask was topped with distilled water up to the datum line. Samples at concentrations of 0 ppm, 50 ppm, 100 ppm, 150 ppm, 200 ppm, 250 ppm, and 300 ppm were prepared by diluting the stock solution. Finally, the absorbances of the seven samples were measured using a UV-Vis spectrophotometer at 296 µm wavelength to obtain the calibration curve [17].

2.5. Performance analysis

Two determinant parameters were chosen to evaluate the effectiveness of the PFC process, which are effective partition constant (K) and TCP reduction (T_R). Effective partition constant (K) was used to determine the effectiveness of the PFC process in separating the TCP and water, as the K value is the main index for separation effectiveness to be considered in the PFC [18]. 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. Equation (1) shows the ice phase and solution ratio:

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

where,
C_S= solute concentration in the ice phase,
C_L= solute concentration in the solution phase.

Other than effective partition constant (K), TCP reduction (T_R) is also one of the important determinant parameters to be determined in this study to perform the system efficiency. Thus, the amount of TCP reduced from the initial solution was determined in percentage and calculated using equation (2) [19]:

$$T_R=(C_i-C_L)/C_i \times 100 \quad (2)$$

where:
C_i = the initial concentration of TCP in simulated wastewater,
C_L = the final concentration of TCP in the ice fraction.

3. Research result and analysis

3.1. Overview

In this PFC process, the ice crystal will be generated on the wall of the crystallizer made up of stainless steel. Figure 3 shows the solid ice generated on the wall of the crystallizer during the PFC process. During the experiment, the thickness of the ice solid formed on the wall of the crystallizer varied with the different operating times.

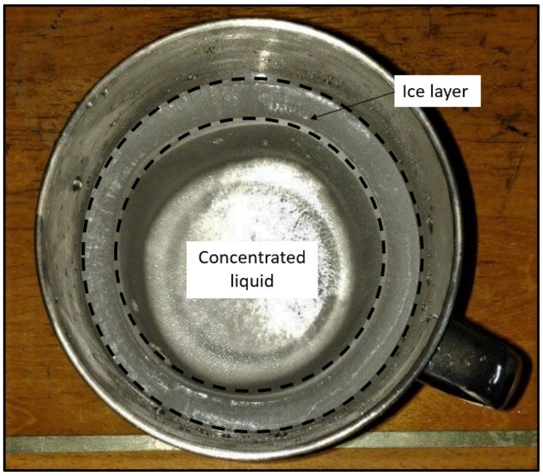

Fig. 3. Close-up of ice formed

3.2. Effect of operating time and initial concentration

Figure 4 illustrates the value of K as a function of independent variables, which are initial concentration and operating time. It shows that the lowest value of K (less than 0.2) can be obtained at the intermediate range of 45 ppm to 150 ppm for initial concentration and 50 to 70 minutes for operating time. The K value increase when the initial concentration increases, demonstrating that a high initial concentration produces a high solute concentration on the ice formed from the PFC system [20].

Subsequently, the K-value decreases when a longer operation time is applied, as a longer operation time is needed to allow the complete crystallization process to occur [21], resulting in the complete separation of TCP and water. Thus, it shows that the combination of lower initial concentration and higher operation time brings higher efficiency to the process resulting in a lower K-value.

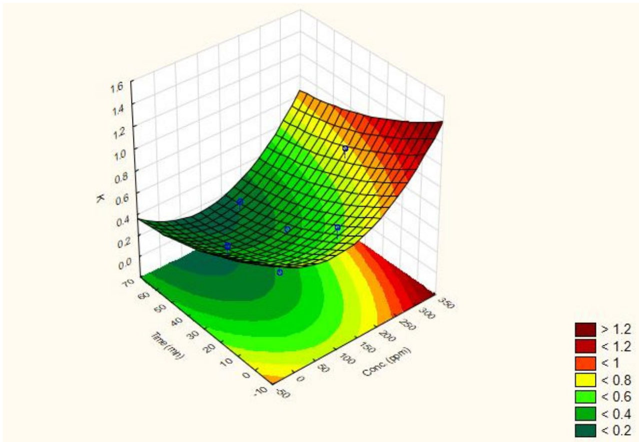

Fig. 4. Interaction between initial concentration and operating time on K value

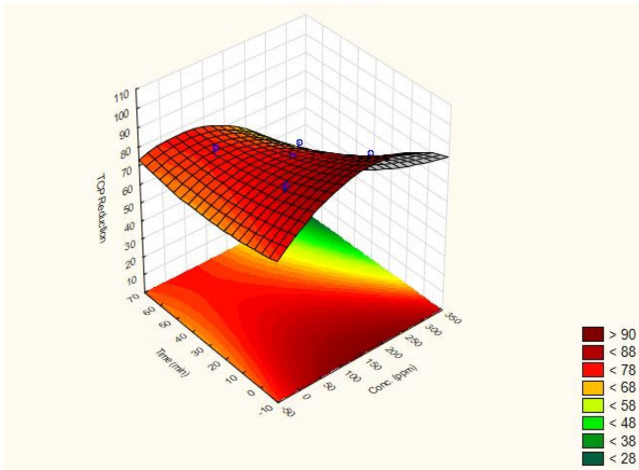

Fig. 5. Interaction between initial concentration and operating time on T_R

Figure 5 shows the relationship between initial concentration and operating time for responses of T_R. It reveals that the higher T_R (more than 90%) can be obtained between 10 ppm to 150 ppm for initial concentration and 1 to

20 minutes for operating time. This removal rate is improved compared to the previous study, which recorded a removal rate of 85.7% [17]. The range determined shows that the low initial concentration and intermediate operating time bring a higher efficiency of the process resulting in higher T_R.

A low initial concentration produces a low solute concentration at the interface or ice formed [20], which means that the lower the initial concentration, the lower the mass of TCP on the ice formed and the high purity of ice crystal obtained. As for the operating time, the longer the operation time, the higher the probability of TCP being trapped inside the solid interface, which increases the concentration of TCP on the ice formed. As the process further continues, the amount of ice formed increases in volume, and the volume of liquid decreases, thus leaving the contaminant to be trapped in the ice crystal formed on the wall of the crystallizer.

4. Conclusions

This research has proven that the TCP in the simulated wastewater can be removed efficiently using the PFC process, and it has the potential to be explored. The effect of two important parameters in PFC, which are operating time and initial concentration, has been investigated in this study. Based on the findings, the best condition to obtain the lowest K value was found at the intermediate initial concentration range (45 to 150 ppm) and operating time of 50 to 70 minutes. Meanwhile, for the T_R value, the combination of a low concentration of 10 to 150 ppm and an intermediate range of operating time (1 to 20 minutes) resulting the highest removal of TCP, which is more than 90%. The promising finding shows the light on the PFC system to be further explored in the future. In order to identify the ideal operating condition for the PFC process, the impact of additional parameters, such as coolant temperature and sample solution flow rate, can also be considered.

Acknowledgements

The authors would like to send our gratitude to the School of Chemical Engineering, College of Engineering, Universiti Teknologi MARA Shah Alam for its support.

Additional information

The article was presented at the 5th ICET 2021: 5th International Conference on Engineering Technology Virtual Conference KEMAMAN, Malaysia, October 25-26, 2021.

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