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EXTENDED ABSTRACT

Treatment of Wastewater Containing Persistent Organic Pollutants Through the Advanced Oxidation Process (Ozonation)

Amir Masoud Yaseri [a], Farhad Qaderi [a,*], Behnoosh Khataei [b]

[a] *Faculty of Civil Engineering, Babol Noshirvani University of Technology, Babol, Iran*
[b] *Faculty of Earth Sciences Engineering, Arak University of Technology, Arak, Iran*

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1. Introduction

By cities development, population increase and industries expansion, the importance of controlling organic and phenolic pollutants is increasing. Chlorophenols have a high absorption by river sediments and remain stable due to their long life. Different methods such as absorption by adsorbents, absorption in a solvent, ion exchange, membrane process, reverse osmosis and electrochemical process have been presented to remove phenolic compounds. Today, instead of the traditional and costly methods, advanced oxidation processes (AOPs) are used to treat toxic organic compounds (Sheikholeslami et al., 2020). Ozonation has a good effect on the oxidation of resistant pollutants due to its higher oxidation potential and formation of secondary oxidizers (Yang et al., 2020; Liang et al., 2021). Nowadays, the environmental effects of various industrial factors have been investigated many times through modeling (Babanezhad et al., 2017; Ebrahimi Ghadi et al., 2019; Ebrahimi and Qaderi, 2021).

Response surface methodology (RSM) is a set of mathematical and statistical techniques used for regression model and evaluation of parameters interactions, development and optimization of processes (Ashrafi et al., 2015; Miranzadeh et al., 2020). RSM is a powerful method to determine the influence of variables on the pollutant removal process and can reveal the factors by greater impact on the process (Fard et al., 2012). One of its main objectives is to determine the optimum conditions of the process (Mourabet et al., 2012). According to the review of other studies, in this research, the removal of 4-chlorophenol was investigated by the ozonation method and under laboratory conditions. For this purpose, after designing the experiment with the response surface methodology, the interactions of the determined independent variables, the optimum conditions and the proposed model were evaluated.

2. Methodology

The pollutant 4-chlorophenol (C_6H_5ClO) by molecular weight of 128.56 g/mol was purchased from Merck, Germany. RSM is used to design the experiments, extract the model and find the optimum conditions. Based on the pretests and the review of other research, the range of independent variables was selected (Table 1).

The pollutant absorption was measured by spectrophotometer at a wavelength of 225 nm. Response surface methodology (Quadratic model) and Design expert-13 software were used to present a model in this research. The P-value index is used to check the accuracy of the resulting model. An increase in P-value indicates a

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* Corresponding Author
E-mail addresses: amirmasoud.yaseri@stu.nit.ac.ir (Amir Masoud Yaseri), f.qaderi@nit.ac.ir (Farhad Qaderi), b.khataei@arakut.ac.ir (Behnoosh Khataei).

decrease in the accuracy of the model; therefore, when this index is less, it can be concluded that the model is highly accurate.

Table 1. Levels of the investigated parameters

Independent parameters	Unit	desired range		Independent parameters	Unit	desired range	
		-1	+1			-1	+1
Pollutant concentration	mg/L	35	100	pH	-	4.5	11
Ozone	g/h	2.5	5	Time	min	10	30

3. Results and discussion

The modified Quadratic model based on effective independent parameters was proposed and analysis of variance of the new model was investigated. According to previous research, a P-value exceeding 0.05 means the significance of the parameter effect (Wang et al., 2022; Dabbaghi et al., 2021). Based on this, all variables are significant. Only the P-value of the effect of time and ozone gas shows a number of 84%, which is the result of the high effect of the ozone on the process. The parameters pH, ozone, and pollutant concentration have P-values less than 0.0001. In addition, time is valid at 95% probability level. Pollutant concentration and pH interaction have a 0.025 P-value, so there is a possibility of an effect on the model and its removal is omitted. Also, the simultaneous effect of ozone gas and time due to its high P-value shows the lack of significant interaction.

3.1. The interactions of parameters

Fig. 1 shows the simultaneous effect and interaction of parameters. In Fig. 1a, by increasing the pollutant concentration, the reaction rate and the removal efficiency decrease slightly; As a result, pollutant concentration has had a reverse effect on time. This procedure has also been reported in other research for POPs (Tavakoli Moghadam and Qaderi, 2019). Fig. 1b shows the reverse effect of pollutant concentration and ozone. Other studies have reported this behavior related to the oxidizing agent using AOP (Khalegh and Qaderi, 2019). Based on Fig. 1c, by increasing the pollutant concentration, the reaction rate decreased slightly; so, these parameters have a reducing effect on each other. Fig. 1d displays the increasing effect of pH and ozone gas (similar to the study of Tamadoni and Qaderi (2019)). Finally, by passing time and increase of pH, the pollutant concentration decreases, and so, the two have an additive effect on each other (Fig. 1.e).

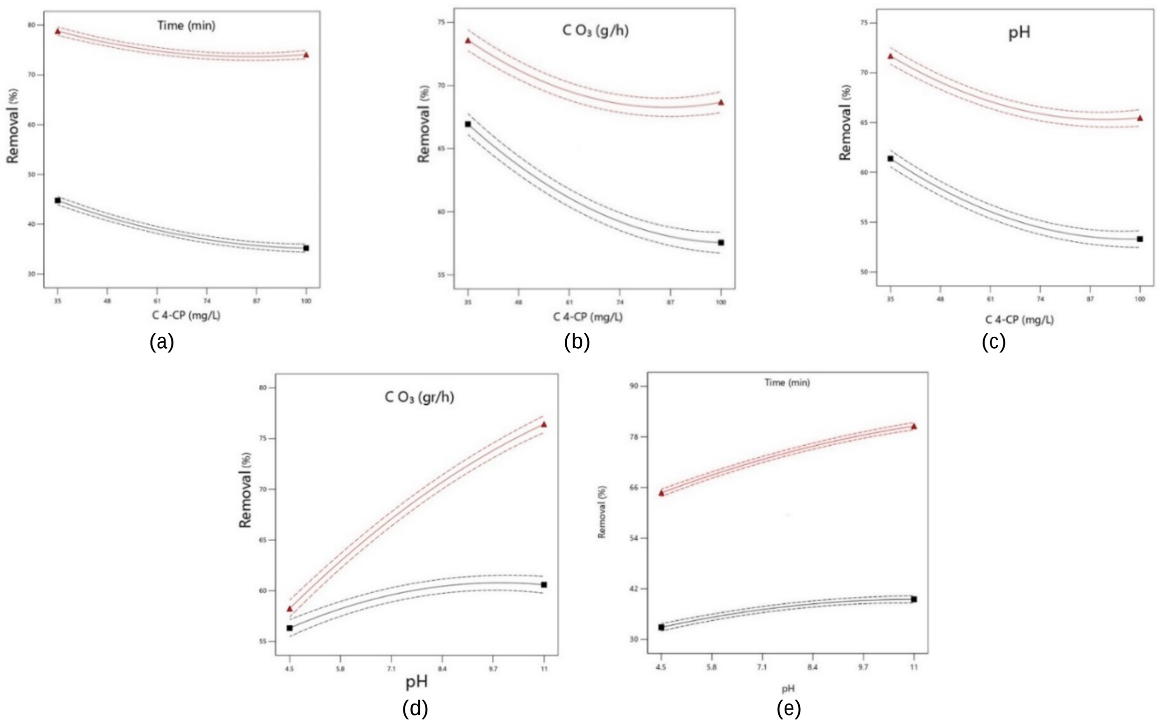

Fig. 1. Interaction of parameters: a) pollutant concentration and time, b) pollutant concentration and ozone, c) pollutant concentration and pH, d) pH and ozone, e) pH and time

3.2. Provided model by RSM

In this research, based on the variance analysis of the results, the independent variables affecting the treatment were identified. By RSM, the modified Quadratic model is proposed to predict the removal in the form of coded and actual in equations 1-2 (A: the pollutant concentration, B: pH; C: ozone, and D: time). In Fig. 2, the accumulation of the points to the inclined line represents the closeness of predicted and actual values.

$$Removal = 62.43 - 3.57(A) + 5.62(B) + 4.44(C) + 18.24(D) + 0.4648(AB) + 1.12(AC) + 1.21(AD) + 3.48(BC) + 2.29(BD) + 2.17(A)^2 - 1.63(B)^2 + 2.09(C)^2 + 6.38(D)^2 \quad (1)$$

$$Removal = 50.18188 - .599002(A) - 0.797454(B) - 14.99679(C) + 3.57867(D) + 0.0044(A)(B) + 0.027563(A)(C) + 0.003178(A)(D) + 0.856123(B)(C) + 0.7053(B)(D) + 0.002054(A)^2 - 0.154383(B)^2 + 1.34053(C)^2 - 0.06813(D)^2 \quad (2)$$

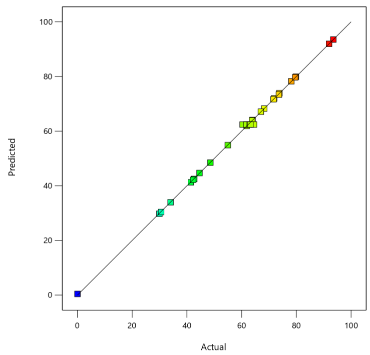

Fig. 2. Predicted values versus the actual values of the response

4. Conclusions

In this research, during the zonation process, 4-chlorophenol was investigated as a POP. Considering its dangerous level and long life, it is necessary to remove it effectively. Therefore, while achieving this goal, the optimization of the conditions governing the treatment process, the modeling to predict the process behavior and the removal efficiency of different conditions were discussed. For this purpose, using the RSM, pH, 4-chlorophenol pollutant concentration, ozone gas amount, and time were considered as independent variables, and pollutant removal efficiency was considered as response. In continue, the interactions of the parameters as well as the effects of each were evaluated. According to the optimum conditions resulting from the experiments, the removal efficiency reached more than 90%; which shows that the investigated process can successfully treat the wastewater containing 4-chlorophenol.

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