2, 4-dichlorophenol removal from aqueous solution using advanced oxidation process

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Abstract

Herein, an electrochemical treatment process has been developed for efficient removal of 2, 4-dichlorophenol (2, 4-DCP) from industrial wastewater using electro-Fenton (EF) process. To optimize the operating parameters, response surface methodology (RSM) has been applied. The significance of the predicted model and the independent variables effects on response has been confirmed by analysis of variance (ANOVA). The best removal efficiency of 98.5 percentage has been achieved under optimal experimental condition including H_2O_2 dosage 90 µL, 2, 4-DCP concentration 6.0 mg L^{-1}, current density 8.0 $mA.cm^{-2}$, during reaction time of 10 min. The polynomial equation of the model revealed that, H_2O_2 dosage had the most significant effect on 2, 4-DCP removal efficiency among other variables. According to the obtained experimental data, the kinetics of the degradation process was in satisfactory agreement with the first order model with correlation coefficient.

Keywords: advanced oxidation process; Electro Fenton; 2, 4-dichlorophenol; aqueous solution; Response surface methodology.

1.Introduction

Releasing the industrial wastewater contain organic pollutants into the aquatic environments results in serious contamination of ground and surface water around the world during the last decades. Most of the generated intermediates in petrochemical, plastic and pesticide industries contain phenolic compounds which represent high risk to the environment (1). Moreover, extensive usage of chlorine as a common water treatment agent leads to producing various chlorophenol compounds throughout the process which provide serious ecological problems. 2,4 –dichlorophenol (2, 4-DCP) as a member of chlorophenol compounds with high toxicity and persistence in the environment has been introduced as a priority pollutant by the US EPA in the Clean Water Act (2). Literature survey revealed that, due to carcinogenic and mutagenic effects of chlorophenol compounds on human, its consumption is limited to 0.1 $\mu g.L^{-1}$ and 0.5 $\mu g.L^{-1}$ for individual phenol and total phenols, respectively. Chlorophenol compounds may damage the kidney, liver and pancreas and moreover, cause paralysis of the central nervous system, denaturing of protein, and tissue erosion. Therefore, great attempt with different techniques have been applied by several research groups to remove 2, 4-DCP from industrial wastewater including coagulation, flocculation, membrane filtration, adsorption and biological treatment before its releasing into aquatic environments. However, the mention methods suffer from several problems and limitations such as producing large amounts of sludge, high energy consumption and low efficiency for high concentration of pollutants etc (3, 4).

It is noteworthy to mention that, in addition to all techniques mentioned above; advanced oxidation processes (AOPs) as an effective and efficient technique received high attention due to its satisfactory performance in removal of persistent organic contaminants from aquatic and soil environments. The highly reactive hydroxyl radicals (•OH) as the key component of AOPs play an important role in degradation of resistant organic molecules by various interactions such as dehydrogenation, redox or hydroxylation. Among the several methods for producing hydroxyl radicals, electro-Fenton (EF) as an electrochemical method with high-efficiency has been considered for generation of hydroxyl radicals (5, 6):

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + {}^{\bullet}OH \qquad (1)$$

EF process as an environmentally friendly technique considered to have non-toxic effect because there are no harmful chemical reagents involving through the process. Moreover, EF process is benefitted from some other advantages including easy set up and simple reactor, no sludge and consequently no disposal problem.

Current work deals with investigation the effect of main parameters including initial 2, 4-DCP concentration, current density, and H_2O_2 dosage on 2, 4-DCP removal efficiency and optimization of experimental condition using a central composite design by RSM. Moreover, several kinetics models were applied to figure out the exact mechanism of 2, 4-DCP degradation through EF process.

2.Materials and methods

2.1 Chemical and reagent

Analytical grade 2, 4-dichlorophenol, titanium (III) sulfate solution, tert-butanol, sodium phosphate, sodium sulphate, acetonitrile and phosphoric acid (were purchased from Sigma-Aldrich and was used in the electrolytic experiments without further purification. Hydrochloric acid, sulfuric acid, H_2O_2, sodium hydroxide, formic acid, sodium chloride, sodium bicarbonate was purchased from Merck company. All solutions were prepared using deionized water.

2.2 Experimental procedure & Apparatus

The experiments were conducted in the batch mode using cylindrical Pyrex cell with working volume of 500 mL as the electrochemical reactor. The EF unit equipped with two iron electrodes with dimensions of 0.2 mm thickness, 5.0 cm length and 1.5 cm width placed parallel to each other and supporting electrolyte of 50 mM Na2SO4 was used throughout all the experiments. DC power supply was used to adjust the desired current density.

2.4 Design of Experiments

Experimental design through response surface methodology was applied to enhance the removal efficiency of EF process by optimizing the effects of main variables and their interactions and minimizing the imprecision of experiments. In addition, regression analysis were developed to fit the equations and the significance of main variables including 2, 4-DCP initial concentration (X_1), H_2O_2 dosage (X_2), and current density (X_3) were investigated (see Table 1).

Table 1. Coded and actual values of experimental parameters used for the CCD

Coded Variables (X_i)	Factors (U_i)	Experimental Field				
		-1 level	0	+1 level	-α	+α
X_1	A: 2,4-DCP initial concentration ($mg.L^{-1}$)	4	6	8	2	10
X_2	B: H_2O_2 dosage (μL in 250 mL)	50	70	90	30	110
X_3	C: current density ($mA.cm^{-2}$)	7	8	9	6	10

3.Results and Discussion

The obtained removal efficiency of 2, 4-DCP according to the designed experiments using CCD was done. The effect of independent variables on the removal efficiency presented through a quadratic model expressed as below:

$$removal\ (\%) = 53.8 - 3.5X_1 + 2.3X_2 + 1.9X_3 + 2.56X_2^2 \quad (7)$$

according to the analysis done by ANOVA, independent variables including 2, 4-DCP initial concentration (X_1), H_2O_2 dosage (X_2), current density (X_3) significantly affected the removal efficiency. Moreover, the quadratic effect of X_2 revealed significant effect on the response (P-values<0.05; F-values≥12.9). According to the obtained parameters of P-value< 0.0001 and a R^2 equal to 0.9834, it can be concluded that the predicted model is well developed and is suitable to describe the experimental data.

The normal plot of residuals was presented in Fig.1, which demonstrated a normal distribution of the obtained results for removal efficiency of 2, 4-DCP. Since a normal distribution of data was observed for response in the current work, therefore, no transformation function needs to be applied. Moreover, Fig. 2 as an alternative conformation for supporting the normality of the data presented the predicted values versus actual values of removal efficiency (7). On the other hand, since the obtained values for R^2 and Adj.R^2 which are 0.9765 and 0.9675, respectively, are close to each other supported the mentioned state above for normality of the obtained results.

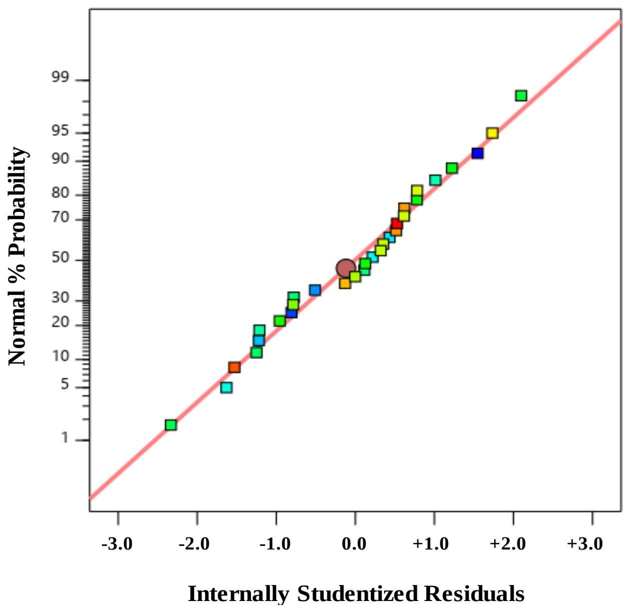

Figure 1. Removal of the 2, 4-DCP model showing normal plot of residuals.

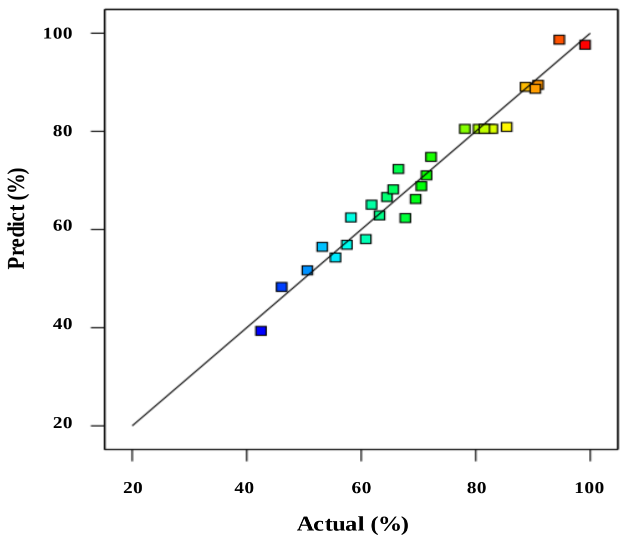

Figure 2. Goodness-of-fit plot between the actual value and the predicted value by the obtained model.

It can be concluded that the initial concentration revealed inverse relationship with removal efficiency, so that, by increasing the initial concentration from 2.0 to 10.0 mg.L^{-1}, the removal efficiency decreases from 95.3% to 53.6%. while the other parameters were their central points. It is noteworthy to mention that, the negative effect of increasing the initial concentration on removal efficiency can be attributed to the amount of available hydroxyl radical (•OH) which is not sufficient to attack and degrade the 2, 4-DCP molecules (8-10).

As it illustrated in Fig. 3, through the 3-D surface plot of congruent effect of H_2O_2 dosage and current density on removal efficiency it can be concluded that increasing the H_2O_2 dosage has a positive effect on the 2, 4-DCP removal efficiency. The obtained results revealed that, the best removal efficiency was achieved at the current density of 9.0 mA.cm^{-2} with H_2O_2 dosage of 90 µL. Through further increasing of H_2O_2 dosage a significant reduction on removal efficiency of 4-DCP has been observed which can be attributed to the excess amount of H_2O_2 molecules and •OH species which compete with the contaminant molecules as strong electron scavenger. However, extra concentrations of H_2O_2 may results in exceeding the ratio of H_2O_2/Fe^{2+} to upper limit in compare to optimum level and therefore some competing side reactions take placed as below (11-13):

$$^{\bullet}OH + H_2O_2 \longrightarrow {}^{\bullet}OOH + H_2O \qquad (2)$$
$$^{\bullet}OH + Fe^{2+} \longrightarrow Fe^{3+} + OH^- \qquad (3)$$
$$^{\bullet}OH + {}^{\bullet}OH \longrightarrow H_2O_2 \qquad (4)$$

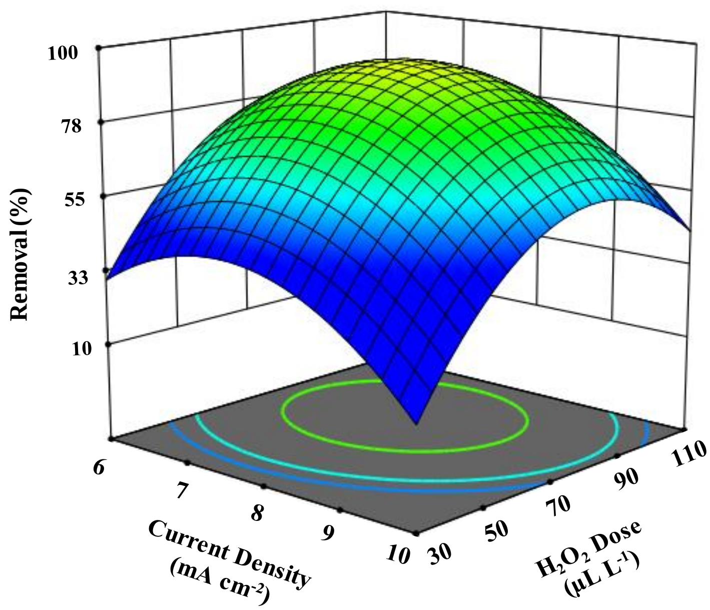

Figure 3. 3-D surface plot for the combined effect of H_2O_2 dosage and current density.

As it can be seen from Fig. 3, increasing the current density from 6.0 to 8.0 mA.cm^{-2} resulted in increasing the removal efficiency of 2, 4-DCP which can be attributed to accelerating the anodic scarification process that increase the generated Fe^{2+} ions concentration. Consequently, according to the Fenton reaction, generation of Fe^{2+} ions resulted in increasing the •OH generation (14-17).

However, owing to the anode superfluous scarification because of increasing the current density from 8.0 mA.cm-2 to 10.0 mA.cm^{-2}, a slight decreasing in 2, 4-DCP removal efficiency has been observed. The optimum mole ratio of H_2O_2 to Fe^{2+} was found to be 2.1.

Kinetics of 2, 4-DCP

The prediction of batch kinetics gives the most important information for designing batch systems. Numerous kinetic models have been used to describe the reaction order of the system and to express the mechanism of removal. In order to investigate mechanism, characteristic constants of removal were determined using two kinetic models, first order and second order equation (18, 19). Results and details of linear form of first and second order model demonstrated in table 2.

Table 2. Mathematical models and result of the used kinetic models.

Kinetics model	**Equation**	**k**	**R^2**
First order	$\ln\left(\frac{C_0}{C_t}\right) = +k_1 t$	0.325	0.9943
Second order	$\frac{1}{C_t} = k_2 t + (\frac{1}{C_0})$	1.36	0.6351

4.Conclusions

In this investigation, the Response surface methodology (RSM) method was used to determine the optimum conditions for the 2, 4-DCP using EF process in aqueous solution. The significance of independent variables, quadratic and their interactions and were tested by analysis of variance (ANOVA). The design results indicated that polynomial equations and response plots soundly justified the interrelationship between the dependent response and the independent variables. Under optimized condition more than 98.5% removal was achieved within 10 min. EF process follows first order kinetics for removal of 2, 4-DCP. Based on the result of this study, EF process as an effective method can be used for removal of 2, 4-DCPfrom Aqueous solution.

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6.References

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