Environ Res Tec, Vol. 5, Issue. 1, pp. 33–43, March 2022

Environmental Research and Technology
https://ert.yildiz.edu.tr - https://dergipark.org.tr/tr/pub/ert
DOI: https://doi.org/10.35208/ert.1014814

Research Article

Optimization of the effect of copper electrodes on the removal efficiency of 4-clorophenol from aqueous solution by electrocoagulation

Gülizar KURTOĞLU AKKAYA*[1], Muhammed Kamil ÖDEN[2]

[1]*Department Environmental Engineering, Necmettin Erbakan University, Konya, Türkiye*
[2]*Department of Environmental Protection Technology, Selcuk University Sarayönü Vocational High School, Konya, Türkiye*

ARTICLE INFO

Article history
Received: 26 October 2021
Revised: 14 December 2021
Accepted: 04 January 2022

Key words:
Copper; Electrocoagulation; MINITAB; 4-clorophenol

ABSTRACT

In this study, the investigation of 4-clorophenol (CP) removal from aqueous solutions using copper electrodes by electrocoagulation (EC) process was done. The effects of various experimental parameters such as pH, current density and exposure time, which affect the EC process, on 4-CP removal were investigated. To optimize the process, response surface methodology (RSM) Box Behnken Design was used by MINITAB program, a series of experimental sets were obtained and carried out. Afterward, 4-CP removal was analyzed and calculated. Results were entered into the MINITAB program as a response. At the end of the optimization, optimum operating conditions were determined as 74 mA/cm^2, 45 min, 4.24 for current density, exposure times and pH, respectively. When the results were evaluated, approximately 92% phenol removal efficiencies were obtained. Additionally, according to the model results, it was understood that the factors with the greatest effect on 4-CP removal were the exposure time and current density and these had a linear effect, but the pH value did not have a significant effect.

Cite this article as: Kurtoğlu Akkaya G, Öden MK. Optimization of the effect of copper electrodes on the removal efficiency of 4-clorophenol from aqueous solution by electrocoagulation. Environ Res Tec 2022;5:1:33–43.

INTRODUCTION

With the developing technology and increasing population, the reequipments of people have changed and increased. Uncontrollable increase in production and consumption has caused rapid depletion of resources and increased pollution. As a consequence, it increases the consumption of water, which is one of the most important natural resources and rapidly causes pollution of water resources.

Water is necessary for developing countries [1, 2]. Agricultural irrigation uses water resources the most with 70% of the total water consumption. This is followed by electricity generation, steam-based electricity generation and cooling waters [1].

The wastewaters are identified as waters, which are used in various processes in people activities and in some industries, are discharged to the receiving environments. They disrupt the ecological balance in the receiving environment where they are discharged or they cause great destruction. For this reason, they must be treated before been discharged into the receiving water environments and must obtain the legal discharge limit values [3].

***Corresponding author.**
*E-mail address: ka.gulizar@gmail.com

Published by Yıldız Technical University Press, İstanbul, Turkey

Wastewaters are treated using conventional processes such as biological processes [4], physico-chemical processes [5], as well as developing technologies, namely membrane filtration [6] and adsorption [7], advanced oxidation processes [8]. Advanced oxidation processes require strong oxidizers, which makes wastewater treatment safe and cost-effective. Biological processes, on the other hand, require tightly controlled conditions with long retention times. Chemical processes require extensive chemical addition, which not only increases the cost of the process but also complicates downstream processes with an increased risk of secondary contamination. Membrane filtration and adsorption methods alone cannot effectively treat wastewater unless integrated with extensive pretreatment processes, especially in the treatment of phenolic compounds. Therefore, wastewater treatment research using electrochemical processes is highly attractive [9, 10].

Recently, electrochemical treatment methods such as electrooxidation and electrocoagulation (EC) have drawn attention due to their environmental importance and economic efficiency [11, 12]. High removal efficiencies have been achieved for treating different wastewaters and drinking water using the EC process [3]. EC is a complex process in which sacrificial electrodes are used to form ions that act as coagulants in wastewater, including many removal mechanisms such as adsorption, co-precipitation, chemical oxidation-reduction and flotation [13]. Metal hydroxides are formed by the anodic dissolution and hydrolysis of metal anodes, such as aluminum and iron [14].

There are many pollutants in wastewater that needs to be treated, depending on the variety of activities. Pollutants such as color, hardness, dissolved oxygen, detergent types, heavy metals, oil-grease, polycyclic aromatic hydrocarbons (PAH) and volatile organic compounds and similar toxic and/or carcinogenic pollutants, nitrogenous compounds, biological hazards and phenols are available in water and wastewater [15].

Phenolic compounds have significant effects on the environment and people health [16]. They are easily taken into the body by respiratory, oral and dermal routes. Phenol and phenol forms are contained in products such as nylon, epoxy resins, surfactants, synthetic detergents, plasticizers, antioxidants, phenolic resins, cyclohexanol, aspirin, dyes, wood preservatives, drugs, fungicides, gasoline additive, inhibitors, explosives and pesticides. Phenol causes excessive irritation and corrosion if it comes into contact with the skin and other tissues. Absorption of phenol can cause cyanosis, shock, weakness, liver and kidney damage, coma and death [17, 18].

The industry wastewaters are one of the sources of industrial phenolic pollutants. There are wastewaters containing high amounts of phenol in the world and in Turkey. These are mainly found in iron and steel factories, coke ovens, petrochemical facilities, pharmaceutical factories, socks factories, plastic factories, paper industry, photographic industry, explosive industry, paint, pharmaceutical and resin production facilities [19, 20].

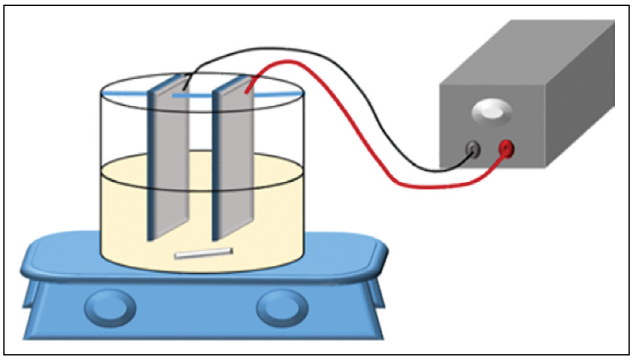

Figure 1. Schematic representation of EC in the laboratory.

Besides phenol which is a common research pollutant model, 4-chlorophenol (4-CP) is a highly toxic chemical compound which is difficult to degrade and is commonly found in industrial wastewater. Because of these properties, 4-CP was chosen as the target pollutant for this study. The treatment of it by EC was investigated. Here, the effects of operational parameters that significantly affect the EC process such as initial pH, current density and electrolysis time on 4-CP removal efficiency in a reactor using monopolar parallel connected copper electrodes were investigated.

EXPERIMENT

Material and Methods

Stock solutions of 4-CP were prepared by dissolving 1 g of analytical reagent grade (Merck, Germany) in 1 L of distilled water without pH adjustment. Experiments were conducted on 4-CP solutions with 50 mg/L concentration prepared during the experiment. 2 mg/L NaCl was added to increase the ionic strength of the solution. Each run volume was 250 ml. In Figure 1, a schematic representation of the laboratory scale system used in the EC process is given. The EC reactor, made of Plexiglas, has a diameter of 19 cm and a height of 15 cm. In the study, the copper plate electrodes were used on the anode and cathode (6 cm wide, 11 cm high and 0.2 cm wall thickness) and the distance between the electrodes was 2 cm. The total effective electrode areas were determined as 24 cm^2. The reactor was supplied with a direct current power supply. A homogeneous mixture of the solution was provided by means of a magnetic stirrer at 150 rpm. The electrodes were washed 2 times before each run. After run was completed, samples were waited for a 1-hour settling period. Supernatants of samples were collected and the remaining 4-CP concentration was determined according to the Direct photometric method (Standard Methods 5530-D) [21]. The method

Table 1. Experiment design input and factors

Factors	Factor	-1	0	1
Initial pH	X_1	4	7	10
Exposure time (min)	X_2	5	25	45
Current density (mA/cm^2)	X_3	10	42	74

based on the spectrophotometric analysis of the developed color resulting from the reaction of 4-CP with 4-aminoantipyrine. The absorbance of colored samples was measured at 500 nm by the Hach UV/Vis DR5000 spectrophotometer after 15 min of reaction. To find the 4-CP concentration, 11 standard solutions (0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 mg/L) were prepared and a calibration curve was drawn. After the analysis, the absorbances of 4-CP were read by spectrophotometer and put in the calibration equation. Afterwards, the 4-CP concentrations were calculated. 4-CP removal efficiency were obtained using equation 1.

$$R\% = \frac{100(C_0 - C_1)}{C_0} \quad (1)$$

where C_0 and C_1 are initial and final concentration, respectively.

Experimental Study and System Design

4-CP removal by EC process was optimized using the Response-Surface Method (RSM). The current density, exposure time and pH affecting the EC process were optimized using RSM. The Box-Behnken design model included in Minitab 17 (Trial version) software is used to determine the individual and combined effects of operating parameters on pollutant removal efficiency. In this study, experiments for 4-CP removal were designed by the Box-Behnken design. As shown in Table 1, the three-factor Box-Behnken response surface was used in the optimization and investigation of the process variables, namely initial pH (4–10), exposure time (5–45 mins), current density (10–74 mA/cm^2). With the runs created in the program, 15 batch EC processes were conducted and the effects of initial pH (X_1), current density (X_2) and exposure time (X_3) changes on 4-CP removal efficiency were determined. Depending on the responses, the relationships between the criteria affecting the removal efficiency were determined.

The effects of the selected independent variables and their interactions on responses according to BBD were described using the second order polynomial equation 2.

$$Y_i = \beta_0 + \sum_{i}^{k} \beta_i x_i + \sum_{i=1}^{k} \sum_{j \geq i}^{k} \beta_{ij} x_i x_j + c \quad (2)$$

where β_0 , β_i , β_{ii}, and β_{ij} are constant, linear, quadratic, and cross-factor interaction coefficients, respectively; X_i and X_j represent the independent variables; Y_i is the predicted response; and k and C are the number of factors and the residual terms, respectively [22].

Table 2. Experimental results

Run order	pH	Current density (mA/cm^2)	Exposure time (min)	Efficiency (%)
1	4	10	25	1
2	10	10	25	7
3	4	74	25	44
4	10	74	25	73
5	4	42	5	1
6	10	42	5	4
7	4	42	45	83
8	10	42	45	41
9	7	10	5	1
10	7	74	5	1
11	7	10	45	11
12	7	74	45	81
13	7	42	25	44
14	7	42	25	50
15	7	42	25	48

RESULTS AND DISCUSSION

Response Analysis and Interpretation using BBD Three factors in the three-level Box-Behnken response surface design (BBD) is used to optimize and examine the effect of process variables. Table 1 shows the BBD matrix of the independent variables and the response values. Then, the experimental results for 4-CP removal efficiency (Table 2) were entered to software Minitab 17 (trial version). The calculated response functions correspond to the experimental data for Y (Efficiency) R^2=92.51.

Regression Equation in Uncoded Units

$$Y=-58{,}7+7{,}2\ X_1+0{,}624\ X_2+2{,}94\ X_3-0{,}366\ X_1{*}X_1-0{,}01215\ X_2{*}X_2-0{,}0290\ X_3{*}X_3+0{,}0591\ X_1{*}X_2-0{,}189\ X_1{*}X_3+0{,}0273\ X_2{*}X_3 \quad (3)$$

The adequacy of the quadratic model and the quality of the correlation between parameters and responses were examined by analysis of variance (ANOVA) at 95% confidence interval (CI). For a term to be meaningful in ANOVA, its p-value must be less than 0.05. The p-value is used as a tool to check the significance of each factor [23]. The ANOVA table of the factors is given in Table 3. When the Table 3a, b is examined, it is seen that the factors that have the greatest effect on 4-CP removal, exposure time and current density factors have a linear effect, and the p-values are 0.007 and 0.003. However, the p-value of the pH is 0.935 and it does not have a significant effect.

Generally, the coefficient of determination (R-square-adj) explains the total variability taken into account by the independent variables in the regression model. In

Table 3a. ANOVA table for 4-CP removal (analysis of variance)

	Analysis of variance				
Source	**DF**	**Adj SS**	**Adj MS**	**F-value**	**P-value**
Model	9	12443.7	1382.63	6.87	0.024
Linear	3	9575.7	3191.91	15.85	0.005
X1	1	1.5	1.46	0.01	0.935
X2	1	4027.4	4027.42	20	0.007
X3	1	5546.8	5546.85	27.55	0.003
Square	3	999.8	333.27	1.66	0.29
X1*X1	1	40	40	0.2	0.674
X2*X2	1	571.1	571.14	2.84	0.153
X3*X3	1	495.4	495.37	2.46	0.178
2-way interaction	3	1868.1	622.71	3.09	0.128
X1*X2	1	129	128.98	0.64	0.46
X1*X3	1	515.9	515.91	2.56	0.17
X2*X3	1	1223.2	1223.24	6.07	0.057
Error	5	1006.8	201.36		
Lack-of-fit	3	986.9	328.95	32.96	0.03
Pure error	2	20	9.98		
Total	14	13450.5			

Table 3b. ANOVA table for 4-CP removal (continued-coded coefficients)

	Coded coefficients					
Term	**Effect**	**Coef**	**SE coef**	**T-value**	**P-value**	**VIF**
Constant		47.14	8.19	5.75	0.002	
X1	-0.85	-0.43	5.02	-0.09	0.935	1
X2	44.87	22.44	5.02	4.47	0.007	1
X3	52.66	26.33	5.02	5.25	0.003	1
X1*X1	-6.58	-3.29	7.38	-0.45	0.674	1,01
X2*X2	-24.87	-12.44	7.38	-1.68	0.153	1,01
X3*X3	-23.17	-11.58	7.38	-1.57	0.178	1,01
X1*X2	11.36	5.68	7.1	0.8	0.46	1
X1*X3	-22.71	-11.36	7.1	-1.6	0.17	1

Table 3c. ANOVA table for 4-CP removal (continued-model summary)

	Model summary		
S	**R-sq**	**R-sq(adj)**	**R-sq(pred)**
14,1902	92.51%	79.04%	0.00%

this model, the Adj. R^2 sufficient to explain the variability were found to be 79.04% (Tablo 3c).

The residuals are the differences between the observed and the predicted values of the data. It is a diagnostic measure used when evaluating the quality of a model, is known as errors. Residues are important when determining the quality of a model. The residuals are normally distributed. Figure 2 is shown residual plots. The normal probability plot shows

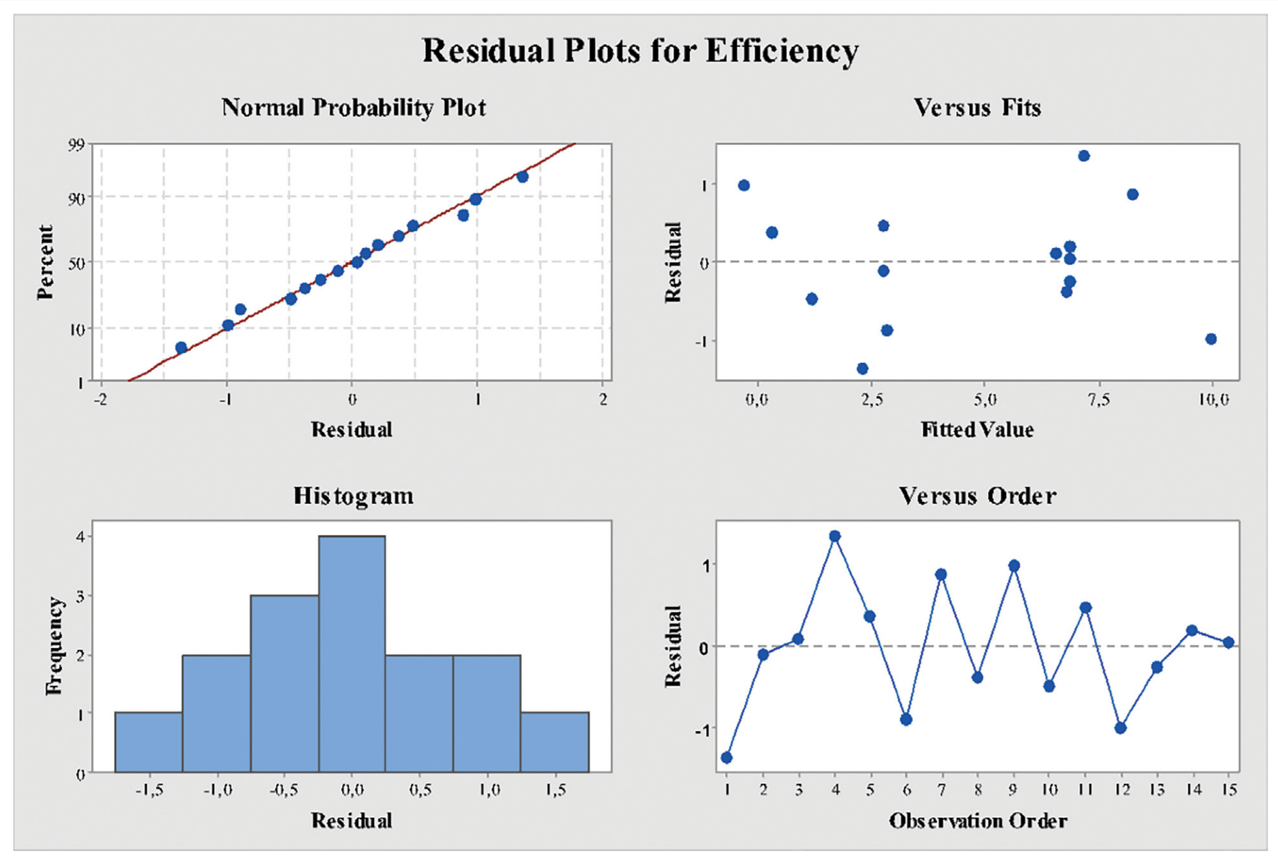

Figure 2. Residual plots for efficiency.

that the data are normally distributed and that variables affect the response. In this model, outliers were not found in the data. The fitted values against the residual values show that the variance is constant and there is a non-linear relationship. The histogram proves that the data is not skewed and that there are no outliers. Residuals by order of data indicate systematic effects on data due to time or order of data collection.

Effects of Operating Parameters

4-CP was removed from the water by floc formation due to oxidation of the anode. This was a three-step process with oxidation of the anode, adsorption/replacement of contaminants, and precipitation of aggregated mass of coagulant with 4-CP. During the initial processing, the anode material changed from coagulant to its hydroxides (insoluble in water). In the second step, 4-CP was adsorbed on the coagulant surface. In the third step, the flocs are precipitated and then removed from the water by filtration. Experiments were conducted at pH 4.0–10.0, under both acidic and alkaline conditions. 4-CP removal was observed in both acidic and basic environments, confirming the hydroxide formation in both cases. The electrochemical reactions of hydroxide formation for copper electrodes are shown below.

Reactions occurring on copper electrodes [24].

Anodic electrochemical dissolution:

$$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^- \quad (4)$$

Oxidation of copper ions:

$$Cu^{2+}_{(aq)} + 2H^+_{(aq)} + \frac{1}{4}O_{2(g)} \rightarrow Cu^{2+}_{(aq)} + \frac{1}{2}H_2O(I) \quad (5)$$

The hydrolysis reaction:

$$Cu^{2+}_{(aq)} + 2H_2O(I) \rightarrow Cu(OH)_{2(s)} + 2H^+_{(aq)} \quad (6)$$

The cathodic electrochemical reaction:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \quad (7)$$

Overall reaction:

$$2Cu_{(s)} + 3H_2O(I) + \frac{1}{2}O_{2(g)} \rightarrow 2Cu(OH)_{2(s)} + H_{2(g)} \quad (8)$$

The Cu^{2+} and Cu^{3+} ions hydrate and hydrolyses to form monomeric and polymeric species: $Cu(OH)_2^+$, $CuOH^{2+}$, $Cu_2(OH)_2^{4+}$, $Cu(OH)_4^-$, $Cu(H_2O)_2^+$, $Cu(H_2O)_5OH^{2+}$, $Cu(H_2O)_4(OH)_2^+$ etc. [25].

Electrical conductivity in metals is a result of the movement of electrically charged particles. Atoms of metal elements are characterized by the presence of valence electrons. It is 'free electrons' that allow metals to conduct an electric current. Copper has high conductivity (6.30×10^7 S/m at 20°C) and less resistivity (1.59×10^{-8} Ω m at 20°C). °C). Energy transfer is strong when there is little resistance. For this reason, it was effective in the removal of 4-CP.

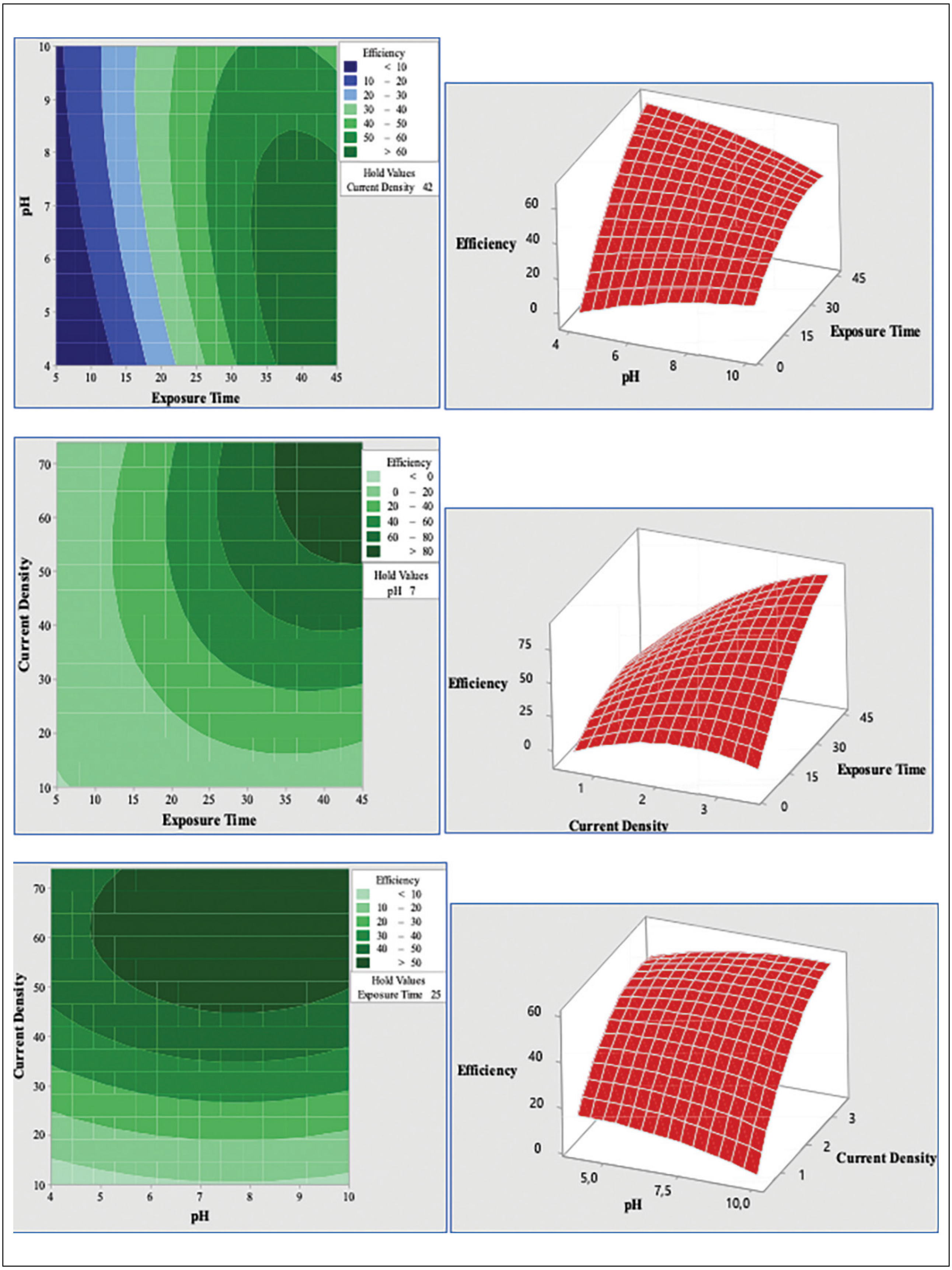

Figure 3. Contour plots and 3D plots.

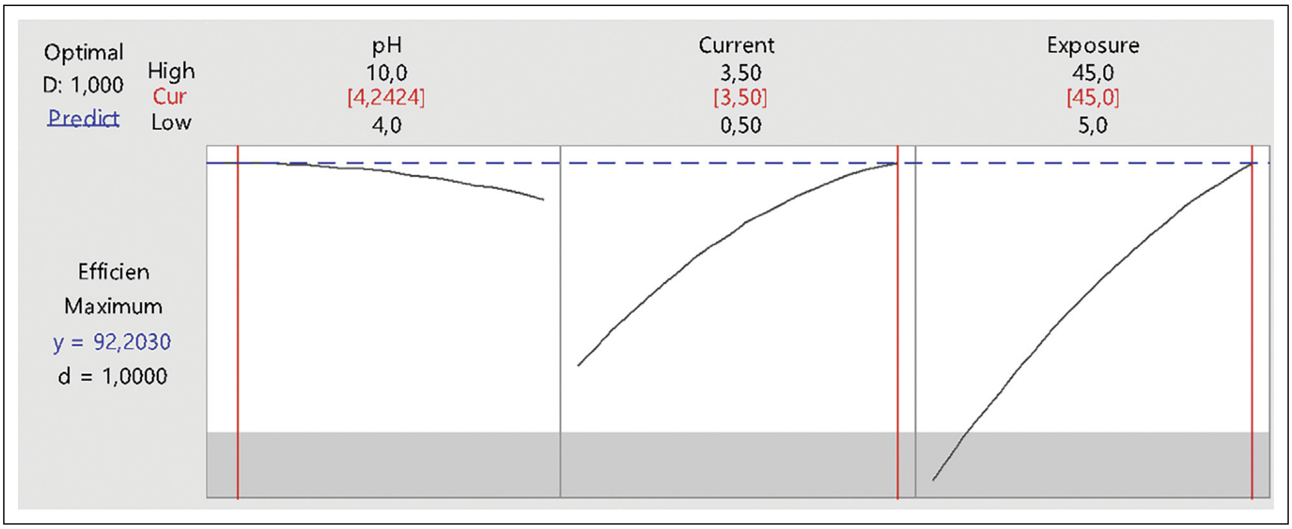

Figure 4. Process optimization for 4-CP removal.

The pH of the EC process is one of the most fundamental factors for controlling the removal of contaminants [26, 27]. To examine the pH effect in the EC, experiments were conducted at various pH values covering acidic, neutral and basic conditions (range 4–10 pH). Maximum 4-CP removal occurred at pH 4–7. The applied current density, on the other hand, directly affects the coagulant dosage rate and bubble generation rate, the current density, which determines the size and growth of the flocs, and affects the removal efficiency of any electrochemical process [28]. Considering the results in Table 2, the increase in the applied current density increased the 4-CP removal, too. The current density produced divalent ion Cu^{2+} and removed it by reacting with 4-CP. Applying the current density for a long time provided ion increase and increased the removal efficiency. 4-CP removal efficiency was 44% in Run 12, while it was 83% in Run 13. After the 25th minute of the exposure time, there was an increase in the removal efficiency.

The combined effects of these 3 factors affecting the EC process were evaluated. For this, the Contour Graph in RSM was used to examine the relationship between a response variable and two predictive variables. In a contour plot, the values of the two predictive variables are represented on the x and y axes, and the values of the response variable are represented by darksome regions called contours. In this study, two-dimensional (2D) contour graphs were drawn representing the interaction effects of pH-Current density, pH-Exposure Time and Current Density-Exposure time on 4-CP removal efficiencies.

In the graphs (Fig. 3), the darker regions show the high removal efficiency achieved by the interaction of the two factors pH and current density. When the contour graph is examined, it is seen that the current density partially interacts with pH and affects the removal efficiency. However, exposure time and current density significantly interact with each other. With the increase of theirs, it was increased to release of copper ions. Thus, easier precipitation of pollutants is ensured and 4-CP removal efficiency is increased. It is indisputable that current density and exposure time greatly affect 4-CP removal with copper electrodes.

Exposure time is one of the most important parameters in the EC. In the EC process, the sufficient time is required for the copper electrodes to dissolve, produce hydroxide, and complete the coagulation. It is seen that the removal efficiency increases with the increase in the study time. This trend can be explained by the greater current supplied to the electrodes, resulting in a greater dosage of coagulant into the water [29].

BBD Optimization

The model was finalized with the multi-response numerical optimization technique. According to the BBD results in Figure 4, the maximum 4-CP removal efficiency was obtained under the following operating conditions at a pH of 4.24, an exposure time of 45 min, and a current density of 74 mA/cm^2. Under these optimal conditions, the 4-CP removal efficiency was 92.20%. It can easily be deduced from this graph that while current density and exposure time have a positive effect, pH removal has not much effect.

As can be seen in Table 4, phenol types removal from real and synthetic wastewater were investigated. The phenol removal efficiencies vary between 100% and 59%. The electrodes used such as aluminum, iron, zinc, steel and metals enriched with different substances. In this study, 4-CP removal was demonstrated using monopolar parallel connected copper electrodes. With the study, approximately 92% phenol removal was achieved. In this study, better efficiency was obtained than many studies in the literature. However, it will be more important to work with real wastewater and achieve the same efficiency in the field.

Table 4. Some studies in literature about removal of phenol types from wastewaters

Wastewater type	Treatment technology	% Phenol removal efficiency	Initial [phenol] (mg L^{-1})	Reference
Phenol wastewater	Persulfate enhanced electrochemical oxidation [EC/PS oxidation ($CuFe_2O_4$/ACF cathode and RuO_2/Ti anode, adding PS)]	97	500	[30]
High salinity waters	Electrochemical advanced oxidation	>70	50	[31]
Synthetic phenol solution	Ti/Pt and MMO (Mixed Metal Oxide) electrodes	84	0.5	[32]
Pistachio processing wastewater (PPW)	The combined electrochemical-assisted fungal treatment process	88.7	3205	[33]
Synthetic phenol solution	Electrochemical filtration carbon membrane (ECM)	91.65	50	[34]
Synthetic phenol solution	Bioelectrochemical Technologies [oxygen-diffused microbial electrochemical systems (MESs)]	59	200	[35]
The simulated and the real wastewater (olive mill)	EC (Zn anode/stainless steel cathode)	84.2–72.3	327–740	[36]
Real refinery wastewater	EC (Al electrode)	100	3	[18]
Synthetic phenol solution	EC (Al and Fe electrode)	94.72–98	5	[37]
Petroleum refinery wastewater	electrochemical oxidation by using boron doped diamond anode (BDD)	98.74	192.9	[29]
Paper mill effluents	EC (Al and Fe electrode)	98–93	0.535	[38]
Synthetic phenol solution	Electrochemical oxidation (ruthenium mixed metal oxide electrode)	99.7	200	[39]
Olive mill wastewater (OMW)	EC (Al electrode)	91	2420	[40]
Synthetic 4-chlorophenol solution	Biochar-load particle electrodes	99.93	500	[41]
Synthetic 4-chlorophenol solution	Two Pd/graphene gas-diffusion cathodes and one Ti/IrO2/RuO2 anode	94.9%	–	[42]
Paper industry wastewater (4-chlorophenol)	Al electrode	100%	0.28	[43]
Paper mill waste water (4-chlorophenol)	Stainless steel (316 L) electrode	99.4%	0.56	[44]
Synthetic phenol solution	EC	92	50	This study

Besides EC, other treatment methods are used efficiently in 4-CP removal [45, 46]. For example, 4-CP removal performances were investigated by synthesizing different carbon adsorbents and 4-CP absorbability was observed as 90% [47]. In a different study, it was proven that 4-CP can be removed 40% from the solution by using composite TiO2 material [48]. Also, over 80% 4-CP removal was achieved with magnetic activated carbon [49]. It is observed from this study that the removal of 4-CP is effective with 92%.

CONCLUSION

In this study, the effect of initial pH, current density and electrolysis time on 4-CP removal efficiency in a reactor using parallel connected copper electrodes was investigated. In the optimization study using the RSM, the maximum phenol removal was found as a function of the current density, reaction time and initial pH value affecting the EC process. The ANOVA results showed the fit of the second-order regression with the experimental data. As a result of this study, it has been determined and optimized that 4-CP is effectively removed from the wastewater with the copper electrodes.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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