

Original Article

Electrochemical degradation of the acid orange 10 dye on a Ti/SnO₂-Sb anode assessed by response surface methodology

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ABSTRACT

Aims: The aim of this study was decolorization of the synthetic aqueous solution of the acid orange 10 (AO10) dye on Ti/SnO₂-Sb anode using the response surface methodology based on central composite design.

Materials and Methods: The Ti/SnO₂-Sb electrode was prepared using the standard thermal decomposition method and three variables: Current density (CD), pH, and supporting electrolyte concentration were assessed. The dye decoloration was monitored spectrophotometrically by measuring the absorbance of the remaining dye at the maximum absorption wavelength (λ_{max}) of 475 nm on a ultraviolet-visible spectrophotometer. To measure AO10 mineralization under optimum conditions, chemical oxygen demand (COD) and total organic carbon (TOC) removal also were evaluated.

Results: It was found by the model prediction, minimum dye decolorization was 39% (CD = 6 and pH = 7.5) and maximum dye decolorization was 101% (CD = 65 and pH = 2). Thus, the optimum conditions for AO10 decolorization in synthetic dye solution were electrolyte concentration of 75 mM/L, pH of 2, and CD of 65 mA/cm. Under optimum conditions, decolorization of 100 mg/L dye was complete, and 61.3% and 43.9% COD and TOC removal were recorded after 50 min of electrolysis, respectively.

Conclusion: High-efficiency electrochemical degradation of AO10 was achieved over Ti/SnO₂-Sb anode as a model electrode. It was concluded that the most effective factor for AO10 decolorization was CD. The electrochemical degradation using Ti/SnO₂-Sb electrode is a suitable and an environment-friendly method for the degradation of refractory dyes in aqueous solution.

Key words: Acid orange 10, central composite design, electrochemical degradation, response surface methodology, Ti/SnO₂-Sb

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DOI:
10.4103/2277-9183.163975

INTRODUCTION

Azo dyes are the largest group of synthetic dyes and are widely used in many cases due to their solubility, low cost,

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This article may be cited as:

Sarafraz M, Khosravi M, Bonyadinejad G, Ebrahimi A, Taghavi-Shahri SM. Electrochemical degradation of the acid orange 10 dye on a Ti/SnO₂-Sb anode assessed by response surface methodology. *Int J Env Health Eng* 2015;4:31.

durability, and color diversity.^[1] These dyes are persistent to biological degradation under aerobic conditions but can be effectively degraded under anaerobic conditions. However, anaerobic treatment of textile wastewater is not suitable because the breakdown of azo dyes causes for the formation of aromatic amines, which are more toxic than the parental dye molecules and should be eliminated before discharging the effluents into water resources.^[2,3] One of the members of the azo dyes, acid orange 10 (AO10), is a mono azo dye that is classified into the acidic dye group. This dye has showed the genotoxicity in some studied rodents^[4] and can also be hazardous to humans.^[5] The chemical structure of AO10 is shown in Figure 1.

Numerous wastewater treatment methods, including conventional physical, chemical, and biological technologies have been used, but they are not able to remove these compounds sufficiently. In recent years, advanced oxidation processes have been suggested as an effective and emerging alternative for the treatment of wastewater containing refractory organic pollutants.^[6,7] Among these methods, electro-oxidation, due to ease of operation, fast reaction rate, high energy efficiency, and being environmental-friendly, has significant attraction.^[8,9] In conventional processes, organic pollutants can be eliminated by direct and/or indirect oxidation process.^[9] The electrochemical oxidation of organic pollutants can be achieved with the participation of intermediates of the oxygen evolution reaction formed during water discharge at high anodic potentials, particularly the hydroxyl radical (OH[•]), which is one of the strongest oxidizing species in the indirect oxidation.^[10,11] This OH[•] species has a high reduction potential regardless of their amount and is able to react with various organic compounds and to oxidize them to CO₂ and H₂O, finally.^[12] Nonselectivity of OHs[•] helps to prevent the formation of unwanted by-products.^[13] Several types of electrodes including RuO₂,^[14] IrO₂,^[15] SnO₂,^[16] PbO₂,^[17] Pt-Ir,^[18] carbon nanotube,^[19] glassy carbon,^[20] Pt,^[21] and boron-doped diamond,^[22] have been investigated. Sb-doped SnO₂ electrodes and other metal oxide electrodes are believed to be superior for organic compounds oxidation. They can produce active (OH[•]) radicals to degradation of recalcitrant organic compound into carbon dioxide.^[23,24] SnO₂ without any dopant is an n-type semiconductor, which due to its high resistivity at room temperature is

not able to use as electrode material directly.^[25] Dopant ions can significantly increase the electrode's conductivity, stability, and electrocatalytic oxidation. The most frequent dopant used in SnO₂ electrode is antimony (Sb) which plays an important role in conductivity improvement and electrocatalytic activity.^[26] Cost effectiveness, high oxygen evolution over-potential ease of preparation, and long lifetime are the main advantages of Ti/SnO₂-Sb electrode.^[27] Optimization of the operating conditions of an experimental system and recognition of the way in which the experimental parameters affect the final output of the system are realized using modeling techniques.^[28] Besides, it is possible to determine the relationships and interactions between the variables through these techniques. In this regard, statistical methodologies, like the response surface methodology (RSM), are suitable for studying and modeling a particular system. As electrochemical degradation of the AO10 azo dye using Ti/SnO₂-Sb anode has not yet been reported the aim of the present study was to investigate the electrochemical oxidation of a synthetic dye solution containing AO10, using Ti/SnO₂-Sb anode and determine optimum conditions by RSM. The effects of current density (CD), pH and Na₂SO₄ concentration (electrolyte [EL]) were been evaluated in terms of color, chemical oxygen demand (COD), and total organic carbon (TOC) removal.

MATERIALS AND METHODS

Preparation and characterization of Ti/SnO₂-Sb electrode

The Ti substrates with 2 mm thickness were cut into strips (4.8 cm × 4 cm, 99.7% Aldrich), and pretreated according to the following procedures: The substrate was polished on 320-grit paper strips,^[29] to eliminate the superficial layer of TiO₂ (an electrical semiconductor) and increase surface roughness (for efficient adherence of SnO₂-Sb). Then, the substrate was degreased in an ultrasonic bath of acetone for 10 min and then in distilled water for 10 min. Afterward, the substrate was etched for 1 h in a boiling solution of oxalic acid (10%) and rinsed with ultrapure water.^[30] The technique of electrode preparation was dip-coating and standard thermal decomposition using a solution containing 10% SnCl₄·5H₂O (provided by Aldrich Co., Germany) + 1% SbCl₃ (purchased from Merck) dissolved in an absolute ethanol, where after concentrated HCl was added dropwise until the solution was clear and then the solution was put in ultrasonic for 1 h. The electrode was dipped into the solution and then it was dried in an oven at 95°C for 10 min and then placed into a preheated furnace at 500°C for 20 min. After each coating, the prepared electrode was weighted. This procedure was repeated 25 times until the electrode weight addition reached to 2 mg/cm. Finally, the electrode was annealed at 500°C for 1 h in a furnace. The X-ray diffraction (XRD) tests were performed using a diffractometer (Bruker, D8 Advance, Germany). The electrode sample was scanned under Co K α radiation (wavelength: 1.7890 Å) at 40 kV and 40 mA. Scanning electron microscope (SEM) (SEM; Philips

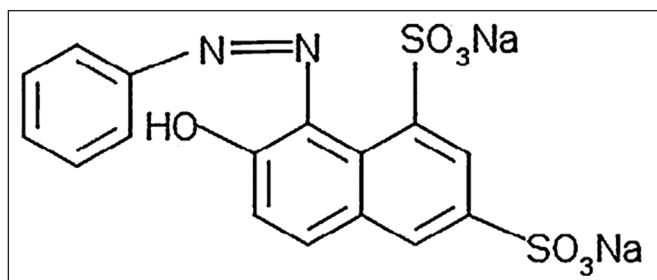


Figure 1: Chemical structure of the azo dye acid orange 10

XI30, Netherlands) was employed to observe the surface morphology of the electrodes.

The electrochemical process set up

Synthetic wastewater was prepared by dissolving AO10 dye in distilled water at a concentration of 100 mg/L. The electrochemical degradation of AO10 was performed in a batch reactor (0.45 L) equipped with 41.12 cm² Ti/SnO₂-Sb as the anode and a 80.32 cm² stainless steel plate as the cathode in conjunction with an adjustable power supply unit (HANI, Iran) [Figure 2]. The gap between the anode and cathode was 1 cm. The duration of all the electrolysis experiments was 50 min. The reactor was placed on a magnetic stirrer for mixing its content during the experiment to maximize mass transport.

Experiment

To model and determine the optimum conditions for electro-oxidation of AO10, the experimental conditions were designed using central composite design (CCD) coupled with RSM, with CD, EL, and pH as the main variables. All experiments were designed using StatSoft, Inc., (2011). STATISTICA [(data analysis software system), version 10. www.statsoft.com, StatSoft, Inc. (2011)]. The rotatable experimental plan was performed with the three variables at five levels (-1.68, -1, 0, 1, 1.68). Table 1 shows the values and levels of the variables. Five replications were established at the center point of the design to evaluate the pure error and consequently the lack of fit. Table 2 shows the CCD matrix of the degradation experiments.

The relationship between response Y and the three independent variables X₁, X₂, and X₃ could be approximated by the quadratic polynomial equation as follows:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \quad (1)$$

Where Y is the predicted response; b₀ is a constant; b₁, b₂, and b₃ are the linear coefficients, b₁₂, b₁₃, and b₂₃ are the cross-product coefficients; and b₁₁, b₂₂, and b₃₃ are the quadratic coefficients. In the present study, linear and quadratic form of variables and two-way interaction of variables in the pool of variables were provided, and backward variable selection for multiple regression modeling was used. The Anderson-Darling test was used for check normality of regression residuals. Lack of fit test performed for assess fit of the final model. Validation of the final model assessed using predicted R² that estimate the power of the model in prediction with new observations based on leave-one-out technique.

Optimum values of the final model calculated using numerical methods. Experimental range predictors divided into a grid and then final model calculated for all possible combinations of predictors in the grid. If the predicted response of the final model in the grid was outside of the

possible range of response, it replaced with the nearest possible value (>100% replaced with 100) and frequency of this problem was reported.

Chemicals and instrumentation

Analytical-grade azo dye AO10 was purchased from Sigma-Aldrich Co., (USA) and used without further purification.

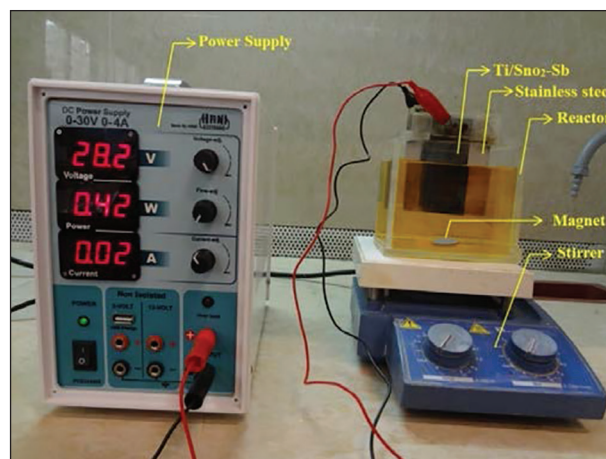


Figure 2: Experimental setup for electrochemical degradation of acid orange 10

Table 1: The range and codification of the independent variables (X_i) used in the experimental design

Variables	Actual values for the coded values				
	-2	-1	0	1	2
pH (X ₁)	1.95	4	7	10	12.05
Na ₂ SO ₄ concentration (mM) (X ₂)	32.96	50	75	100	117.04
CD (mA cm ⁻²) (X ₃)	6.36	20	40	60	73.64

CD: Current density

Table 2: CCD matrix of electrochemical degradation of AO10

Experimental number	pH	EL	CD	Color removal (%), Y	
				Predicted	Observed
1	4.00	50.00	20.00	64.77	70.72
2	4.00	50.00	60.00	95.01	94.61
3	4.00	100.00	20.00	64.77	56.85
4	4.00	100.00	60.00	95.01	97.99
5	10.00	50.00	20.00	63.07	63.56
6	10.00	50.00	60.00	93.31	95.16
7	10.00	100.00	20.00	63.07	59.15
8	10.00	100.00	60.00	93.31	91.77
9	1.95	75.00	40.00	91.67	91.34
10	12.05	75.00	40.00	88.80	90.62
11	7.00	32.96	40.00	82.39	82.61
12	7.00	117.04	40.00	82.39	84.83
13	7.00	75.00	6.36	39.65	42.60
14	7.00	75.00	73.64	90.51	88.99
15	7.00	75.00	40.00	82.39	83.25
16	7.00	75.00	40.00	82.39	81.87
17	7.00	75.00	40.00	82.39	82.91
18	7.00	75.00	40.00	82.39	82.24
19	7.00	75.00	40.00	82.39	80.92

CCD: Central composite design, AO10: Acid orange 10, CD: Current density, EL: electrolyte

SnCl₄·5H₂O Sigma-Aldrich Co., (Germany), SbCl₃, ethanol and HCl was used for electrode preparation. Other chemicals, purchased from Merck Co., (Germany), were of analytical grade. Initial pH of the solution was adjusted using sodium hydroxide and sulfuric acid. Sodium sulfate was used as the supporting electrolyte. All the solutions were prepared using deionized water.

The performance of electrochemical degradation was evaluated on the basis of three main factors, namely, removal of color, COD, and TOC. The dye decoloration was monitored spectrophotometrically by measuring the absorbance of the remaining dye at the maximum absorption wavelength (λ_{max}) of 475 nm on a ultraviolet-visible spectrophotometer (DR-5000, HACH LANGE, USA). The amount of color removal was calculated using the following formula:

$$\text{Color removal (\%)} = \frac{ABS_0^{475} - ABS_t^{475}}{ABS_0^{475}} \times 100 \quad (2)$$

Where, ABS_0^{475} and ABS_t^{475} are the absorbances at 475 nm before and after treatment, respectively.

The COD and TOC removal were analyzed to measure the mineralization of AO10 under the optimum condition of color removal. The COD was determined colorimetrically by the dichromate method using a COD reactor (Model 45600, HACH Company, USA) and a (DR-5000, HACH LANGE, USA). A SHIMADZU TOC-V_{CSH} analyzer (Japan) was used to measure the TOC of the samples. The COD and TOC removal efficiencies were calculated as follows:

$$\text{COD and TOC removal (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (3)$$

Where, C_0 and C_t are the COD or TOC of the dye solution before and after electrolysis for t minutes, respectively.

RESULTS

Central composite design analysis and modeling

In order to study the combined effect of all variables, experiments were performed in different combinations which statistically designed by CCD.

The first model that was built with all linear, quadratic, and two-way interaction of predictors is shown by Eq. 4.

$$Y = 65.85 - 4.93X_1 - 0.32X_2 + 1.65X_3 + 0.31X_1^2 + 0.0004X_2^2 - 0.015X_3^2 + 0.004X_1X_2 - 0.002X_1X_3 + 0.005X_2X_3 \quad (4)$$

Then, backward method with several steps used for variable selection. At the first step, interaction of pH*CD removed from the regression model ($P = 0.931$). In the next steps, the quadratic form of EL and interaction of pH*EL were removed, respectively (P values of EL^2 and $pH*EL$ were 0.774 and 0.751, respectively). Hence, the Eq. 5 was obtained with an adjusted R^2 of 96.5% and predicted R^2 of 92.5%.

$$Y = 61.66 - 4.60X_1 - 0.23X_2 + 1.64X_3 + 0.3083X_1^2 - 0.0153X_3^2 + 0.0046X_2X_3 \quad (5)$$

Although all predictors in this model were being significant at $\alpha = 0.05$ (Wald method) but lack of fit test was rejected ($P = 0.012$). Hence, the bootstrap nonparametric method with 10,000 resamples used to examine this model. Bootstrap method revealed that the interaction of $EL*CD$ and linear form of EL was insignificant ($P = 0.234$ and 0.212 , respectively). Therefore, stricter conditions used in the backward method ($\alpha = 0.01$). In the following steps, interaction of $EL*CD$ and linear form of EL were removed from the regression model. The final regression model with an adjusted R^2 of 95.1% and predicted R^2 of 92.4% is given in Eq. 6.

$$Y = 44.76 - 4.60X_1 + 1.98X_3 + 0.3083X_1^2 - 0.0153X_3^2 \quad (6)$$

Lack of fit test for the final model was insignificant ($P = 0.730$) that confirms fit of this model. Furthermore, Anderson-Darling test for normality was insignificant that confirm this assumption of the model. Bootstrap nonparametric method with 10,000 resamples also confirm that all predictors in the final model were significant ($P < 0.05$). Hence, the final model parameters are given in Table 3. It should be noticed that adjusted R^2 shows interval validity and predicted R^2 , which calculated by leave-one-out (Jackknife) technique, shows the external validity of the model [Figure 3]. Thus, the final model has high external validity, and a small number of predictors in the model that's means good prediction with minimum information.

The final model was assessed in the experimental range of predictors. Model prediction was calculated for 6999 different combination of predictors. The mentioned grid of predictors was from 2 to 12 by 0.1 increments for pH and was from 6 to 74 by 1 increments for the CD. By the model prediction, minimum dye decolorization was 39% ($CD = 6$, and $pH = 7.5$) and maximum dye decolorization was 101%

Table 3: Final regression model parameters for color removal

Variable	Coefficients	SE	T statistic	P (Wald)	P (Bootstrap)
Constant value	44.76	6.08	7.36	<0.001	0.013
pH	-4.60	1.41	-3.28	0.006	0.041
CD	1.98	0.18	10.90	<0.001	0.001
pH ²	0.3083	0.0981	3.14	0.007	0.040
CD ²	-0.0153	0.0022	-6.94	<0.001	0.007

Adjusted $R^2 = 95.1$, Predicted $R^2 = 92.4$ and RSD = 3.30. SE: Standard error, RSD: Residual standard deviation, CD: Current density

(CD = 65, and pH = 2). In 49 cases (0.006%), the predicted values were >100. Therefore, they were replaced with 100 because this is the upper bound.

The XRD pattern and the SEM surface images of the Ti/SnO₂-Sb electrode are shown in Figures 4 and 5, respectively. Figure 6 displays three-dimensional surface plot for the color removal of AO10 as a function of CD and pH. In addition, the final model parameters are given in Table 3. Figure 3 shows the leave-one-out prediction of the final model versus that observed for color removal. Figure 7 illustrates the model prediction for color removal versus pH at different CD (mA/cm²) values and Figure 8 also reveals the model prediction for color removal versus CD (mA/cm²) at different pH values.

DISCUSSION

Characterization of Ti/SnO₂-Sb electrode

Figure 4 shows the XRD pattern of the prepared electrode. The SnO₂ peak exists on the electrode confirmed that the

used coating method was appropriate. In addition, the SEM was used to characterize the morphology and surface structure of the Ti/SnO₂-Sb [Figure 5]. The Ti/SnO₂-Sb electrode that was prepared using the thermal decomposition method shows a “cracked-mud” structure which is typical for oxide electrodes. This prepared electrode has a coating with deep and wide cracks which surround “islands.”

Effect of initial pH

The effect of initial pH on AO10 dye degradation was examined by adjusting the pH of the dye solutions to the following values: 1.95, 3, 7, 10, and 12.05. Despite the fact that the initial pH is an important factor in the oxidation process, the results and mechanism of influence are controversial owing to the diversity of the degraded dyes and electrode materials.^[31] As shown in Figures 6 and 7 and by the Eq. 6, the color removal efficiency was minimum at neutral pH (7.5) and increased when the pH was acidic or basic. From this final equation (Eq. 6), it can be noted that maximum color removal efficiency was obtained at an acidic pH condition (pH = 2). However, the rate of increase in the AO10 dye degradation, when the pH was altered toward basic or acidic values, was approximately the same. An increase in the AO10 dye degradation efficiency in acidic pH conditions

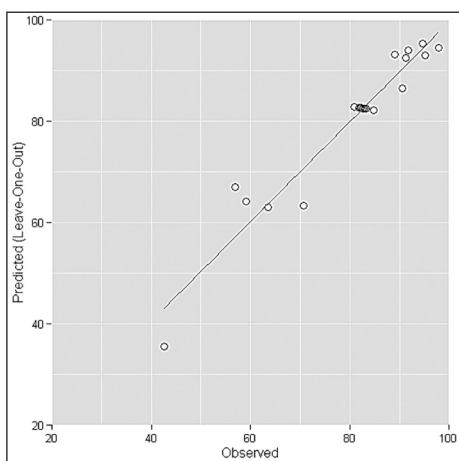


Figure 3: Leave-one-out prediction of the final model versus that observed for color removal

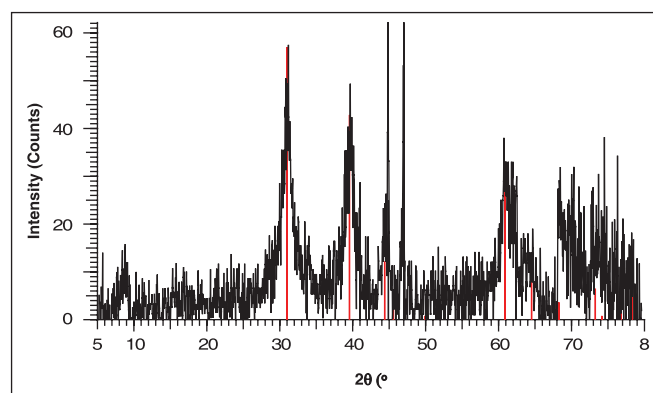


Figure 4: X-ray diffraction pattern of prepared Ti/SnO₂-Sb electrode

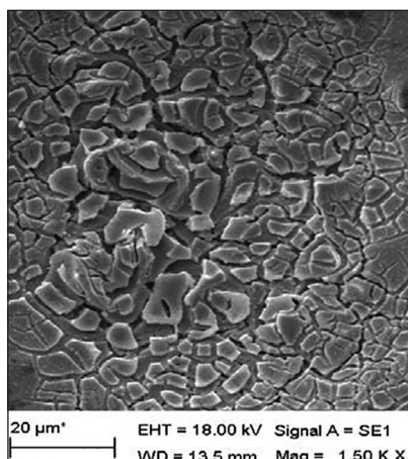


Figure 5: Scanning electron microscope surface images of the Ti/SnO₂-Sb electrode

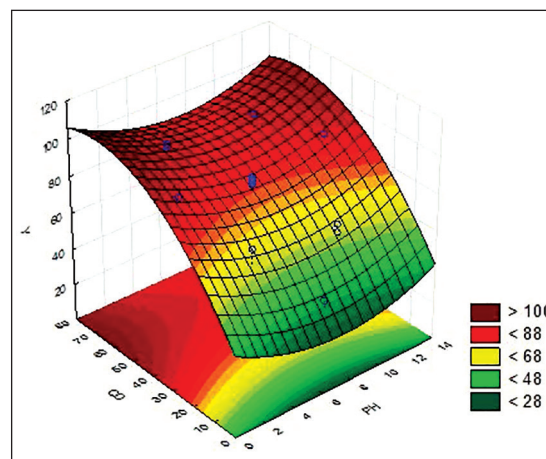


Figure 6: Three-dimensional surface plot for the color removal of acid orange 10 as a function of current density and pH

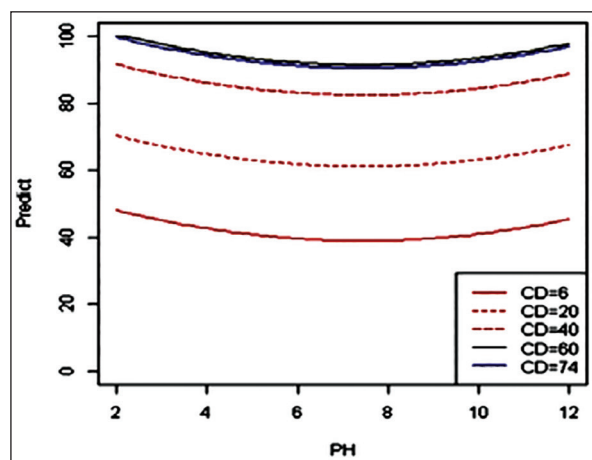


Figure 7: Model prediction for color removal versus pH at different current density (mA/cm²) values

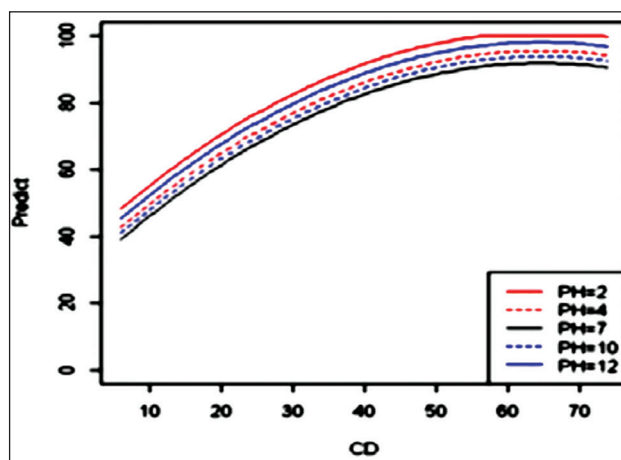


Figure 8: Model prediction for color removal versus current density (mA/cm²) at different pH values

is owing to the increase in oxygen over-potential that inhibits the oxygen evolution reaction and favors the production of more potent oxidizers that are suitable for the oxidation of organic compounds.^[27,32] As a result, in the present study, a pH of 2 was chosen as the optimum pH value for maximum AO10 dye degradation. From the Eq. 6, the difference between minimum and maximum color removal efficiency related to pH is 9.2%, indicating that anodic oxidation of AO10 using Ti/SnO₂-Sb anode is not very sensitive to the initial pH and that AO10 could be degraded under a wide pH range. A similar outcome was reported by other studies.^[31,33]

Effect of current density

The CD is a key experimental factor that affects the electrochemical degradation process because it adjusts the ability of electron transfer and OH[•] generation on the electrode surface. In the present study, the effect of the CD was investigated at five levels (6.36, 20, 40, 60, and 73.64 mA/cm²). To find the optimum CD for AO10 dye degradation, Eq. 6 was independently differentiated with respect to CD (X_3) and then equated to zero, which produced a value of 65 mA/cm². As shown in Figures 6 and 8, the color removal efficiency significantly increased with the increasing CD until 65 mA/cm². It is mainly due to the fact that the formation rate of OH[•] increased with the increasing CD. Similar results have also been reported by many researchers.^[27,33,34] The results indicated that the most effective factor for AO10 decolorization was CD. Furthermore, the color removal significantly increased with increasing CD until 65 mA/cm² which removal efficiency reached highest amount. However, it should be noted that the rate of color removal was retarded when the CD was above 65 mA/cm² which is probably due to undesirable side reactions, such as electrolysis of water and oxygen evolution from OH[•], that compete with the electro-oxidation of the contaminant, and decrease the rate of AO10 oxidation.^[35]

Effect of electrolyte

The electroconductivity of solution is another important factor in the electrochemical degradation. Good electroconductivity

leads to faster electrons transport and better degradation rate, so the effect of electrolyte (Na₂SO₄) on the degradation of AO10 in range of 32.96, 50, 75, 100 and 117.04 mM/L was investigated. As described earlier, color removal was not affected by EL within the investigated range. In the present study, the concentration electrolyte 75 mM/L was chosen as the optimum because excessive high electrolyte concentration was the cause of a supersaturated solution, which led to the decrease in conductivity and degradation rate and excessive low electrolyte concentration could not supply enough ions for the generation of reactive oxidative species (OH[•]), and thus caused a poor degradation efficiency of pollutant.^[32,33,36,37]

Color, total organic carbon, and chemical oxygen demand removal under optimum conditions

Maximum color removal efficiency was obtained under the following optimum conditions: pH = 2, EL = 75 mM/L and CD = 65 mA/cm². Under these conditions, decolorization of 100 mg/L AO10 dye was complete after 50 min of electrolysis. The obtained COD and TOC removal efficiencies were 61.3% and 43.9%, respectively.

CONCLUSION

The complete mineralization of the AO10 dye is not reached in SnO₂ based electrodes but, in practice, the indirect oxidation of AO10 dye has shown promise degradation at a significant rate. The color removal was successfully studied and modeled using experimental design coupled with RSM to predict and also maximize the removal of the AO10 dye. The use of RSM based on CCD permitted determination of the behavior of the electrode on dye degradation, without requiring a large number of experiments, and delivered sufficient information. Besides, the CCD facilitated in detect optimum conditions for decolorization. Validation of the final model was evaluated using leave-one-out technique. Predicted R² was 92% that confirmed the external validity of the final model. In addition, lack of fit test was

nonsignificant with ($P = 0.73$) that confirmed fit of the final model. The results of the present study demonstrated that electrochemical degradation using Ti/SnO₂-Sb electrode is a suitable and an environment-friendly method for the degradation of refractory dyes in aqueous solution.

ACKNOWLEDGMENTS

This study is an MSc approved research thesis of Eng. Mansour Sarafraz (No. 392284) performed in Isfahan University of Medical Sciences (IUMS), Iran. The authors are thankful for the funding provided by the Department of Environmental Health Engineering and Environment Research Center, IUMS.

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Source of Support: Isfahan University of Medical Sciences, **Conflicts of Interest:** None declared.