OPEN ACCESS

Saudi Journal of Engineering and Technology
Abbreviated Key Title: Saudi J Eng Technol
ISSN 2415-6272 (Print) | ISSN 2415-6264 (Online)
Scholars Middle East Publishers, Dubai, United Arab Emirates
Journal homepage: https://saudijournals.com

Original Research Article

Electrochemical Degradation of Methylene Blue using Aluminum Doped Copper Oxide Electrode: Modeling and Optimization

Emmanuel C. Nleonu[1, 2*], Chibuzor O. Okeke[1], Chiemeka Onyeulor[1], Ilham Ben Amor[3]

[1]Department of Chemistry, Federal Polytechnic Nekede, Owerri, Imo State-Nigeria
[2]Material and Electrochemical Research Unit, Federal Polytechnic Nekede, Owerri, Imo State-Nigeria
[3]Department of Process Engineering and Petrochemical, Faculty of Technology, University of El Oued, El Oued 39000, Algeria

DOI: https://doi.org/10.36348/sjet.2024.v09i11.002 | **Received:** 16.09.2024 | **Accepted:** 28.10.2024 | **Published:** 06.11.2024

***Corresponding author:** Emmanuel C. Nleonu
Department of Chemistry, Federal Polytechnic Nekede, Owerri, Imo State-Nigeria

Abstract

An electrochemical oxidation process with an aluminum-doped copper oxide (Al@CuO) anode was modeled and optimized for the degradation of methylene blue (MB). The Al@CuO anode material was prepared by the thermal decomposition method. X-ray fluorescence (XRF) analysis confirmed the successful deposition of CuO on the aluminum substrate. The influence of current density, electrolysis time, and MB concentration on the performance of the electrochemical degradation of MB was modeled using Box-Behnken design (BBD). The accuracy of the proposed quadratic model by BBD was confirmed with a p-value < 0.0001 and adj-R^2 > 0.9. The optimum MB degradation efficiency of 53.23 % was obtained at 80 mg MB concentration, 40 min electrolysis time, and 3.75 V applied current. The kinetics on the MB electrochemical degradation process using Al@CuO followed pseudo first-order kinetics model. These studies revealed that the Al@CuO anode electrode is not a promising anode for the electrochemical degradation of methylene blue.

Keywords: Anodic oxidation, electrochemical degradation, Al@CuO, methylene blue, Box-Behnken design.

INTRODUCTION

Globally, water portability is affected by pollution of water resources from industrial wastewater containing synthetic colour in a high percentage [1,2]. The protection of water resources has become a major concern and an important factor for future technological advancement, which has to meet sustainable development conditions. The textile and dyeing industry is one of the most generating large volumes of polluted wastewater [3]. The release of this dye effluent without treatment into the water stream is very dangerous as it contains strong colour, high chemical oxygen demand with varying pH values from 2 to 12, is carcinogenic, and poses a severe threat to the environment [4].

Methylene blue (MB) is classified as a thiazine cationic dye that has several applications in biology, chemistry, medical science, and the dyeing industry. Long-term exposure to methylene blue causes vomiting, nausea, hypertension, and anemia [5, 6]. The removal of methylene blue dye from effluent is difficult as it is recalcitrant to biodegradation. The strategies for water resources protection in industry involve wastewater treatment as well as the development of new processes or products that have less or no negative effects on the ecosystem [3]. Various conventional methods have been adopted in wastewater containing dye treatment, such as adsorption, biological oxidation, ozonation, and the ultransonic method [7-9]. However, some of these methods are non-destructive because they only transfer the pollutants from one phase to another, causing secondary pollutants that required further treatment [4].

Over the years, advanced oxidation processes (AOPs) have emerged as an alternative in the treatment of organic pollutants due to their ability to generate very reactive hydroxyl radicals, which oxidize a broad range of organic compounds in the waste water [10, 11]. Currently, the use of advanced oxidation processes is limited because they are energy-consuming and require the use of chemicals, which have an adverse effect on the cost-effectiveness of the treatment processes [12]. Currently, electrochemical methods have been largely

developed for the treatment of textile dye wastewater. Electrochemical techniques are classified based on electrode material, used chemicals, pollutant removal mechanisms, and degradation products [13]. The electrochemical treatment technique has been attracting attention from researchers due to its unique properties, like low cost, versatility, energy efficiency, and automation. The method is capable of completely oxidizing organic pollutants to water and carbon dioxide [14]. Electrochemical oxidation can be achieved either through active or inactive anodes. Active anodes (Pt, IrO_2, and RuO_2) have low oxygen evolution overpotential and possess chemisorbed $^{\bullet}OH$ radicals, allowing the partial oxidation of the organic compounds. On the other hand, inactive anodes (PbO_2, SnO_2, and BDD) present high oxygen evolution potential with $^{\bullet}OH$ radicals favoring complete mineralization of organic matter to H_2O and CO_2 [15].

The anode electrode selection is very vital in electrochemical techniques in order to obtain the desired result as the specific interaction between the anode surface and the pollutant to be oxidized in orientation of degradation pathways of the pollutant [1]. Boron-doped diamond (BDD) is one of the most widely used anodes for the electrochemical degradation of organic matter because of its high over potential for oxygen evolution and stability. However, its high cost and manufacturing process are complicated, owing to the difficulty of accessing cheaper materials for the deposition of the diamond layer [16]. In this regard, a metal oxide-doped electrode can be a suitable alternative anode material for wastewater treatment through the electrochemical method [17, 18]. Antimony-doped SnO_2 anodes are a good alternative to BDD due to their medium-to-high oxidation power and have been shown to be highly effective for the electro-oxidation of organics. The electrode material is easy to fabricate and cheap.

However, its major constraint is short service life and low stability when employed as anodes [15]. Also, PbO_2 electrode anode has shown good properties such as excellent electro-catalytic performance, long service lifetime, cheapness, good chemical stability, ease of preparation, high conductivity, and high oxygen evolution potential [19]. The possibility of releasing Pb ions, especially in basic solutions, has been identified as a main drawback of PbO_2 anodes [20].

In this work, an aluminum electrode doped with copper oxide was fabricated as a low-cost and environmentally friendly metallic electrode for the degradation of methylene blue dye (Figure 1) by direct electrochemical oxidation. The effect of different experimental parameters such as electrolysis time, initial concentration of MB dye, and current density were all evaluated. The kinetics of methylene blue degradation were evaluated. Also, the effect of operational variables on the process optimization using the Box-Behnken Design (BBD) method from Response Surface Methodology (RSM) was investigated.

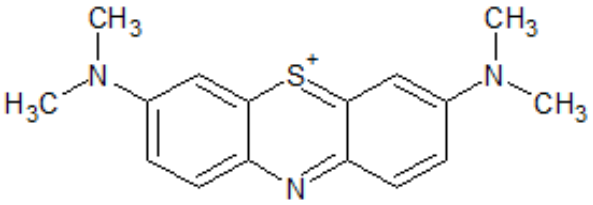


Figure 1: Methylene blue structure

MATERIALS AND METHODS

Chemical

The methylene blue solution was prepared by dissolving 1000 mg/l in double-distilled water containing 1% NaCl as a supporting electrolyte. Analytical-grade reagents supplied by Chemie Ltd. were used in the electrolytic experiments without further purification.

Electrode Material Preparation

A rectangular aluminum plate of 9.5 cm by 2 cm was used in this study. Mechanical polishing of the aluminum plate was carried out using 1000-grit silicon carbide abrasive paper. The aluminum surface was chemically etched for 10 minutes in 30 % oxalic acid at 80 °C to remove the aluminum oxide layer. Then, the aluminum plate surface was washed with distilled water and rinsed with acetone. The aluminum-doped copper oxide anode electrode was prepared by the thermal decomposition method in an ethanolic solution of 1 *M* $CuSO_4$ on a rectangular aluminum plate. Elemental composition of the aluminum plate and aluminum dropped copper oxide plate was analyzed using x-ray fluorescence (XRF) (Model: Empyrean).

Electrochemical Degradation Studies

The experimental setup for the electrolysis is shown in figure 1. A polished aluminum plate electrode of 9.5 cm by 2 cm by 0.2 cm was used as the cathode, and aluminum-doped copper oxide with equal dimensions was used as the anode. The effective electrode area was 42.5 cm^3. The distance of the anode and cathode was 2 cm. Supporting electrolytes, such as 1% NaCl, were added to the electrolytic MB dye solution to increase the conductivity of the dye solution and reduce the electrolysis time. The electrolytic solution was kept under agitation using a magnetic stirrer. The electrolytic experiments were conducted

galvanostatically with a DC power supply (Nan Ling). The study of the effect of the experimental parameters on the methylene blue degradation using aluminum-doped copper oxide as an anode was focused on electrolysis time, applied current density, and the initial dye concentration.

UV-Visible Studies

The absorbance values of the dye solution before and after electrolysis were measured by a UV-Vis spectrophotometer (Drawell-8) at a maximum wavelength of 660 nm [8]. The degradation efficiency was calculated using the relation:

$$\%D = \frac{A_i - A_f}{A_i} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where A_i and A_f are the initial and final absorbance readings of MB dye solution, respectively. The kinetics degradation percentage was monitored to estimate the reaction rate constants for the first and second order kinetics models using equations 2 and 3, respectively.

$$ln\frac{A_0}{A_1} = K_1 t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$\frac{1}{A_1} - \frac{1}{A_0} = k_2 t \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Fourier Transform Infrared (FTIR) Studies

The spectra of the MB dye solution were recorded using a Fourier transform infrared (FTIR) spectrophotometer (FTIR-8400S) to identify the functional groups present in the MB solution before and after degradation, respectively.

Experimental Design and Optimization Process

Response Surface Methodology (RSM) is the most extensively used method in experimental design for water and wastewater treatment processes. Box-Behnken Design (BBD) is one of the most widely used RSM techniques for modeling the effect of independent variables on system response [21]. In this study, the influence of three independent variables was investigated at three levels (-1, 0, + 1). The number of experimental runs was calculated by the following relation of Box-Behnken experimental design [22].

$$N = 2 \times K\,(K-1) + \theta \quad \ldots\ldots\ldots\ldots\ldots (4)$$

Where K is the number of independent factors, N is the number of experimental runs, and is the number of points in the center. The experimental design and data analysis were performed using Design-Expert 13.0 software. The methylene blue concentration (A), electrolysis time (B), and applied current density (C) were chosen as the influential factors on the electrochemical degradation of MB dye. The number of experimental runs (N) required to construct the three factors Box-Behnken Matric was 15 (K = 3 and 3). The experimental BBD levels selected for each independent factor in this study are tabulated in Table 1. All other experimental variables of the electrolysis process, such as ambient temperature (298 K), stirring speed (200 rpm), and volume of the solution (0.1 L), were fixed during the experiments. The percentage degradation (%D) calculated by Eq. (1) was chosen as the response in this experimental design.

Table 1: Independent variables and their levels of operating parameters

Independent Variables	Symbols	Coded Level			Unit
		-1	0	+1	
MB concentration	A	10	45	80	PPM
Electrolysis Time	B	10	30	50	Mins
Current Density	C	1.50	3.75	6.00	Volts

The analysis of variance (ANOVA) yielded the P-value and F-value, which indicated the effectiveness of the BBD model in predicting system responses and the significance level of the proposed equation of the linear, interactive, and quadratic model to investigate input variable influence on the degradation response. The model quality and accuracy were examined based on R^2 and adjusted R^2 coefficients.

As far as we are aware, there is a research gap in the literature about the application of aluminum doped with CuO for the BBD model's electrochemical degradation of MB and RSM optimization processes. Therefore, this study investigated electrochemical degradation of MB in an aqueous medium by aluminum-doped CuO and optimization processes using the RSM-BDD model. Furthermore, the kinetic degradability of the process was also studied.

RESULTS AND DISCUSSION

Characterization of Aluminum and Aluminum Doped Zinc Oxide

X-ray fluorescence (XRF) was utilized to study the elemental composition of the uncoated and aluminum coated with CuO. Based on the XRF study tabulated in Table 2, the coated aluminum electrode showed deposition of CuO on the surface, as shown in the percentage composition of the copper and oxygen compared to the uncoated aluminum plate. The XRF result revealed that the chemical decomposition method was effective in the fabrication of aluminum-doped CuO electrodes.

Table 2: Elemental Composition of Undoped and Aluminum Doped Copper Oxide

Element	Si	Fe	Cu	Mg	O	Al
Undoped aluminum (%)	0.65	0.60	0.31	0.24	2.90	97.1
Aluminum doped CuO (%)	56	1.02	17.76	0.35	6.59	72.80

Effect of Independent Variables on MB Degradation

The effects of different operating variables, such as current density, dye concentration, and electrolysis time, were studied.

Effect of Current Density

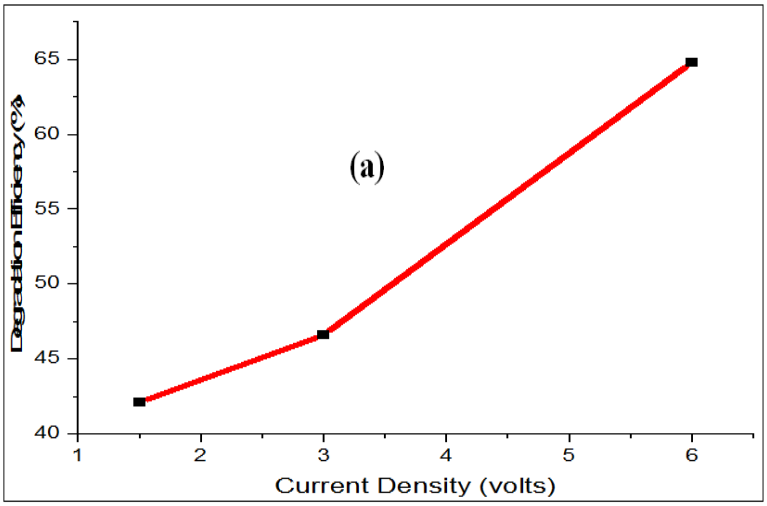
Current density is a vital operating condition in electrochemical engineering [23]. The effects of current density (1.5, 3.0, and 6.0 volts) were applied to examine the electrocatalytic degradation of MB dye in a 1% NaCl solution of 40 mg dye concentration at 30 °C. The results illustrated in Figure 2a showed the variation of MB dye degradation at different current densities. The data reveal that there is a gradual increase in the percentage degradation with an increase in current density. The increase in the electrochemical degradation of MB by increasing the current density at a constant electrolysis time observed in this study may be attributed to the increase in the rate of water oxidation at the Al-doped CuO surface and leads to the high production of hydroxyl radicals [24, 25]. However, in the present study, MB dye degradation increased from 42% to 65% by increasing the current density in the range of 1.5–6.0V. Consequently, the desirable current density applied for the continuous electrochemical degradation of MB dye was 3V, indicating a higher current density will consume more energy.

Effect of Electrolysis Time

To ascertain the effect of electrolysis time on the oxidation ability of an Al-doped CuO anode electrode on MB dye, different electrolysis times in the range of 10–50 mins were used in 40 mg of MB dye containing 1% NaCl. The percentage degradation plot determined for this experiment is shown in Figure 2b. A gradual increase in percentage degradation from 39% to 74 % with corresponding electrolysis time from 10 min to 40 min was observed in this study. A maximum percentage degradation of 74 % was achieved at 40 min of electrolysis with the Al-doped CuO electrode. The increase in degradation efficiency up to 40 min shows the longer stability of the electrode, whereas a decrease at 50 min may be attributed to the fouling of the electrode by the intermediate of the MB dye formed during the process. Previous studies have shown that longer electrolysis time decreases degradation efficiency due to the production of hardly oxidizable intermediates and involvement of the wasting reactions [12].

Effect of MB Dye Concentration

To study the effect of the methylene blue initial concentration on the electrochemical oxidation ability of the Al-doped CuO anode electrode, a series of five electrolyses were performed by treating 10, 20, 40, 60, and 80 mg/l of MB dye solutions. The result displayed in Figure 2c indicated that the optimum electrochemical degradation of the methylene blue was achieved at 40 mg in 1 % NaCl, an electrolysis time of 40 mins, and a 3 V current density. Inspection of the plot in Figure 4 shows that at a given electrolysis time, the MB percentage degradation decreased from 50 to 37 % with increasing initial concentration from 10 to 80 mg, respectively. However, the decrease in the electrochemical degradation rate observed with an increase in MB dye concentration might be because of a decrease in the ratio of hydroxyl radicals produced with the increase in dye concentration [3]. The trend revealed in this work might also be attributed to the generation of chloride (Cl^-) ions, which is a strong oxidizing agent on the electrode surface, and did not increase in applied current density [20]. The poor electrochemical degradation values show the weak oxidation rate of MB at high concentrations and result in a large presence of oxidation intermediates in the solution [12].



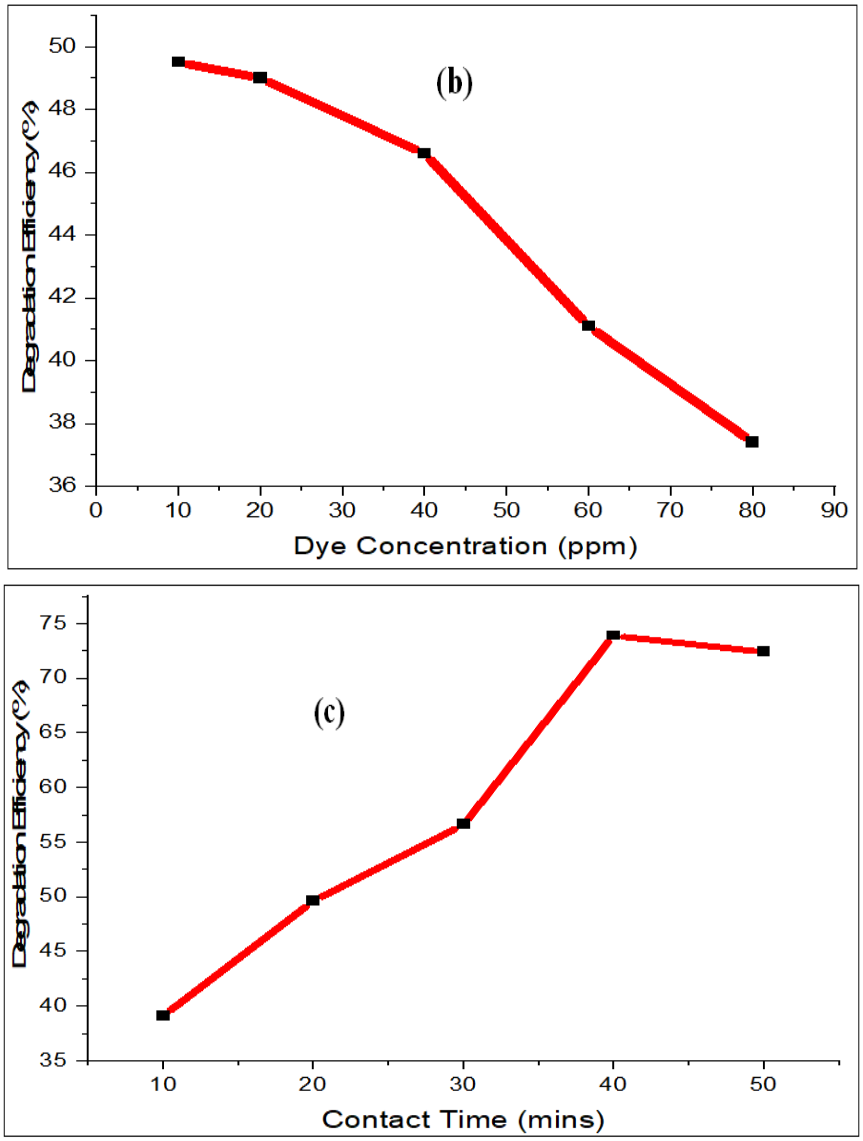


Figure 2 (a-c): The relation between degradation efficiency (%) and (a) current density, (b) dye concentration, and (c) contact time

Modeling of MB Degradation and Process Optimization

Model Validation

To study the methylene blue degradation through the electrochemical oxidation method using an aluminum-doped copper oxide anode electrode, 15 experimental runs were designed by the RSM via the BBD experimental design. The BBD matrix obtained from the key operating parameters such as applied current density, electrolysis time, and initial dye concentration, along with experimental and predicted values of MB percentage degradation obtained, is presented in Table 3. The optimum degradation of the MB dye obtained was within the range of 41-61% for the actual results with a deviation of less than 5 % from the predicted values. The experimental data in this study fitted to a quadratic model. Accordingly, three linear effects (A, B, and C) and three quadratic effects (A^2, B^2, and C^2) were significant, while the three interactive effects (AB, AC, and BC) were non-significant in this study.

The model-coded equation value of the input parameters (A: initial dye concentration, B: electrolysis time, and C: applied current density), their interaction (AB, AC, and BC), and quadratic (A^2, B^2, and C^2) as a function of the response/percentage degradation is stated in Equation 5. The positive sign indicates the synergistic effect of the term on the response, whereas the negative sign shows an antagonistic effect. Therefore, the increasing order of the effect of the terms for the degradation of MB in the coded model follows: B > C > C^2 > (AB = AC) > BC > B^2 > A^2 > A. The equations of the quadratic model in term-coded factors are stated in equations 3 and 4, respectively.

$$MB\%D = +50.33 - 2A + 5.5B + 3.75C + 0.25AB + 0.25AC - 0.25BC - 1.29A^2 - 0.797B^2 + 2.21C^2 \quad \ldots\ldots\ldots\ldots\ldots (5)$$

Table 3: Experimental and predicted values of methylene blue degradation

Run	A: Concentration (ppm)	B: Electrolysis time (min)	C: Current Density (V)	Degradation percentage Experimental (%)	Degradation percentage Predicted (%)
1	45	30	3.75	50.00	50.33
2	80	30	6	53.00	53.25
3	45	10	1.5	42.00	42.25
4	80	50	3.75	52.00	52.00
5	80	10	3.75	41.00	40.50
6	45	10	6	50.00	50.25
7	45	50	1.5	54.00	53.75
8	10	30	6	57.00	56.75
9	10	10	3.75	45.00	45.00
10	45	50	6	61.00	60.75
11	80	30	1.5	45.00	45.25
12	10	30	1.5	50.00	49.75
13	45	30	3.75	50.00	50.33
14	10	50	3.75	55.00	55.50
15	45	30	3.75	51.00	50.33

Analysis of Variance (ANOVA)

The statistical significance and validity of the experimental data and model were tested via the analysis of variance (ANOVA). The fit statistics, as tabulated in Table 4, show that the F-value and P-value of the model were 138.64 and <0.0001, respectively, which reveals that the quadratic model is significant and adequate to predict the system response [26]. The lack of fit F-value of 1.00 and P-value of fit is not significant. The model analysis predicted that there is 53.52 % chance that a lack of fit F-value could occur due to noise. Therefore, the non-significant value of lack of fit indicated that the model was well fitted with the available data [27]. The model robustness in the present study was examined by interpreting the regression coefficient (R^2) and adjusted R^2 with an estimated difference of less than 0.2 (Table 5). The validity of the proposed model shows that predicted R^2 and adjusted R^2 were 0.9960 and 0.9888, respectively, and their difference was less than 0.2, suggesting good predictability of the quadratic model. The adequate precision parameter is 42.96, which statistically represents the signal-to-noise ratio, which shows that the BBD model was a favorable design space. The model variance coefficient (C.V %) value of 1.15 % in this study was less than 10 % indicating high reproducibility of the model.

Table 4: Analysis of variance (ANOVA) results of quadratic model for methylene blue degradation

Source	Sum of Squares	Degree of Freedom	Mean Square	F-Value	p-Value	
Model	415.93	9	46.21	138.64	< 0.0001	significant
A: MB Concentration	32.00	1	32.00	96.00	0.0002	Significant
B: Electrolysis Time	242.00	1	242.00	726.00	< 0.0001	Significant
C: Current Density	112.50	1	112.50	337.50	< 0.0001	Significant
AB	0.2500	1	0.2500	0.7500	0.4261	Not significant
AC	0.2500	1	0.2500	0.7500	0.4261	Not significant
BC	0.2500	1	0.2500	0.7500	0.4261	Not significant
A^2	6.16	1	6.16	18.48	0.0077	Significant
B^2	2.31	1	2.31	6.94	0.0463	Significant
C^2	18.01	1	18.01	54.02	0.0007	Significant
Residual	1.67	5	0.3333			
Lack of Fit	1.00	3	0.3333	1.00	0.5352	Not significant
Pure error	0.6667	2	0.3333			
Cor Total	417.60	14				

Table 5: Analysis of variance (ANOVA) results for the response linear models of methylene blue degradation

Parameter	MB Degradation
Standard deviation	0.5774
Mean	50.40
Coefficient of variance (CV,%)	1.15
Coefficient of determination (R^2)	0.9960

Parameter	MB Degradation
Adjusted R^2	0.9888
Predicted R^2	0.9581
Adequate precision	42.9567
PRESS	17.50

Numerical optimization

Numerical optimization was carried out to predict the maximum percentage degradation in the electrochemical degradation of MB with an Al-doped CuO anode electrode. In the BBD method, three independent variables were set within their respective ranges, such as MB concentration (10–50 mg/l), electrolysis time (10–80 min), and applied current density (1.5–6 V), whereas the response (%D) was set at maximum with a 95% confidence level. The desirability function approach was evaluated, and the optimized conditions obtained are presented in Figure 3(a-c). Based on the model prediction, the maximum MB %D obtained is 50 % at optimum dye concentration of 80 mg, electrolysis time of 40 min, and applied current density of 3.75 V, respectively.

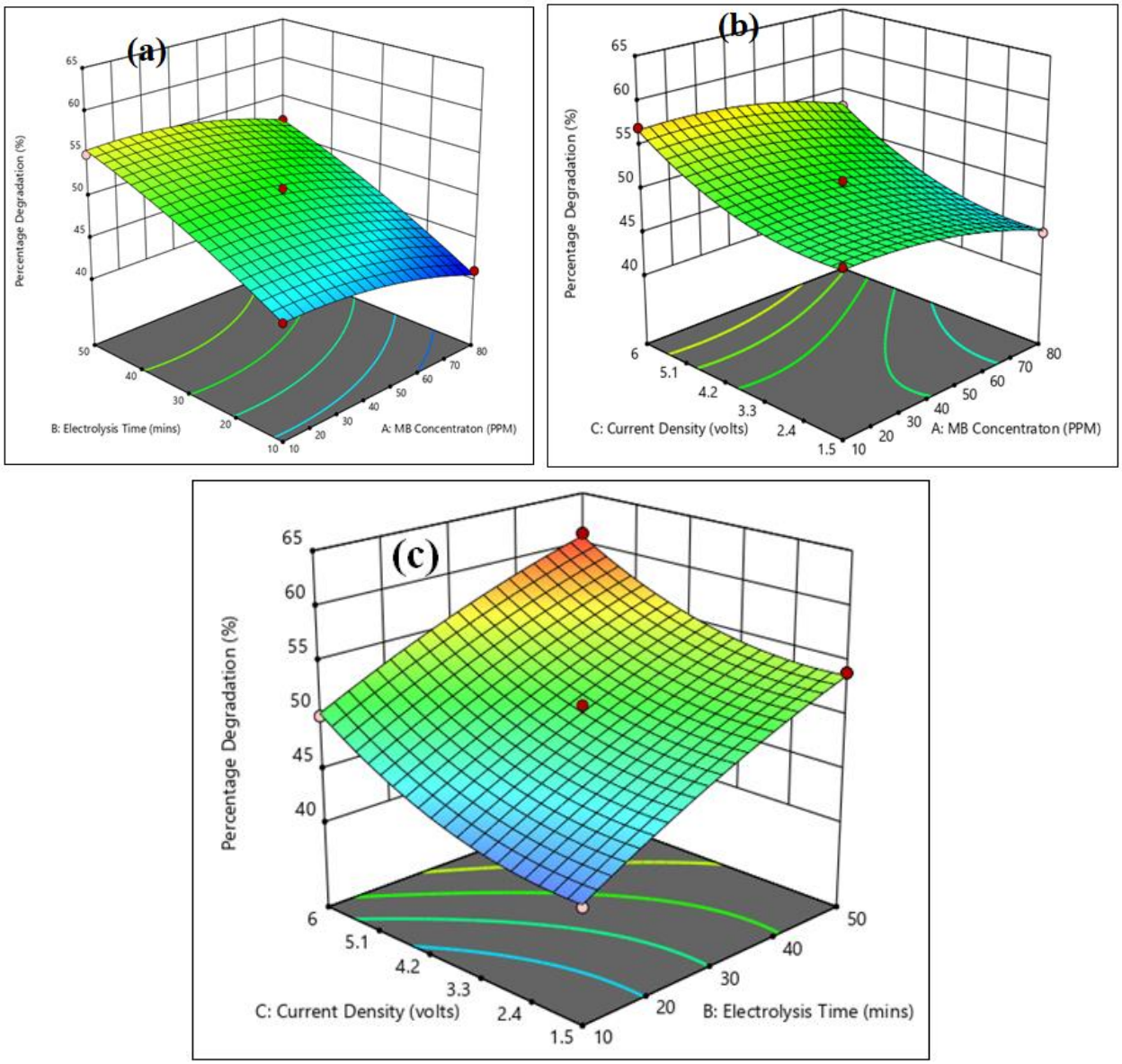


Figure 3: Response plots showing interaction of (a) effect of MB concentration and electrolysis time, (b) effect of MB concentration and current density, (c) effect of electrolysis time and current density

Degradation Kinetics for Methylene Blue Dye

The electrochemical degradation kinetics of methylene blue dye on an Al-doped CuO electrode were monitored by measuring the absorbance reading of the dye at different electrolysis times. The degradation rate constants were estimated as 0.0121 min^{-1} and 0.0276 min^{-1} for pseudo-first-order and pseudo-second-order, respectively, at regression coefficient (R^2) values of

0.9671 and 0.9362, respectively. However, the results revealed that the degradability of MB dye was a function of the electrolysis time, thus confirming the reaction between MB and the Al-doped CuO is related to pseudo-first-order kinetics.

FTIR Analysis of MB Dye

A FTIR spectrophotometer was used to compare the functional groups in MB dye before and after degradation. The most crucial and usual groups affecting the absorption and chemical characteristics of MB are the amine groups in the structure. The degradation of MB is expected to occur through the amine groups aromatic rings and thiazine, as it is ring vulnerable to radical attack. The FTIR spectra of MB dye before and after degradation are shown in Figures 4a and b. The change in the peaks of the MB after electrolysis indicated mineralization of the methylene blue dye.

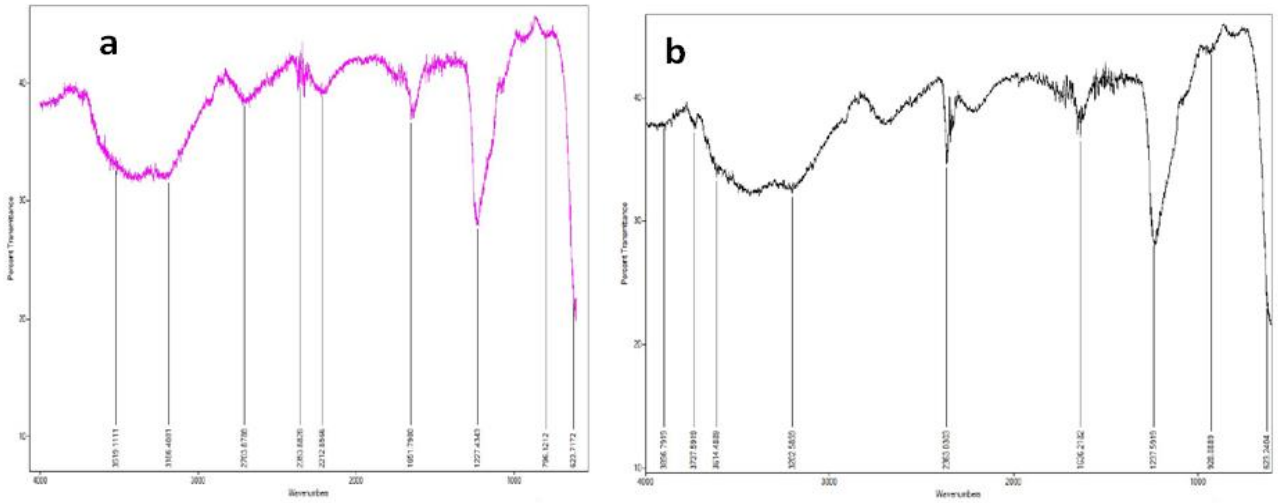


Figure 4: FTIR spectra of methylene blue, a) before degradation b) after degradation

Mechanism of Methylene Blue Degradation

The degradation of methylene blue solutions was investigated by anodic oxidation using an Al-doped CuO electrode as the anodic electrode and an Al plate as the cathodic electrode. In the electrochemical technique, the oxidation of methylene blue dye in an Al-doped CuO electrode proceeds according to the following reaction [15, 28].

$$Al@CuO + H_2O \longrightarrow Al@CuO(^{\bullet}OH) + H^+ + e^- \quad \ldots\ldots\ldots\ldots (6)$$

Al@CuO(˙OH) can react with MB dye to produce CO_2, H_2O and other degradation products through reaction (7).

$$Al@CuO(^{\bullet}OH) + MB \longrightarrow Al@CuO + mCO_2 + nH_2O + H^+ + e^- \quad \ldots\ldots\ldots\ldots (7)$$

The Al@CuO(˙OH) can further oxidized to generate O_2 gas through reaction (8); the oxygen radical can also interact with MB, leading to the production of CO_2, H_2O, and inorganic ions until total mineralization is achieved (9) [28].

$$Al@CuO(^{\bullet}OH) \longrightarrow Al@CuO + \tfrac{1}{2}O_2 + H^+ + e^- \quad \ldots\ldots\ldots\ldots (8)$$

$$O_2^- + MB \longrightarrow CO_2, H_2O \text{ and other degradation products} \quad \ldots\ldots\ldots\ldots (9)$$

The hydroxyl oxygen radicals produced help in the degradation of MB in electrochemical processes. The reaction of ˙OH and radicals with the thiazine and aromatic rings was observed in the dye colour change. The break of the thiazine bond by the radicals causes the decolorization in MB due to a change in absorption properties. The results of percentage degradation efficiency reveal colour intensity decreases with an increase in electrolysis time. A low colour intensity observed in this study after degradation indicates non-formation of insoluble metal oxides. This suggests that the formed oxidizing intermediates facilitated the destruction of the dye. The reaction between hydroxyl radicals with thiazine and aromatic rings causes oxidative degradation through the formation of hydroxylated products or complete degradation of the MB dye into smaller molecules such as CO_2, H_2O, benzene derivatives, phenols, and carboxylic acids [29, 30].

Electric Energy Consumption

Energy consumption is a major consideration in the fabrication of cheap electrodes during the electrochemical process. The electrical energy consumption (E) required in degrading 40 mg/l MB at various applied current densities was calculated using equation 10:

$$E = \frac{Vlt_E}{V_s} \times 10^{-3} \quad \ldots\ldots\ldots\ldots (10)$$

Where E is the electrical energy consumption ($KWhM^{-3}$), V is the applied voltage (V), 1 is the applied current (A), t_e is the electrolysis time (0.5 h), and Vs is the volume of MB 0.0001 M3. The results obtained indicate a connection between applied current and energy consumption (Table 6). The minimum electrical energy consumption was 3750 $KWhM^{-3}$ for MB dye at 0.5 A applied current. The operating cost of utilizing the electrochemical process in the treatment of MB dye solution was calculated using the dollar exchange rate in Nigeria within the present study. The high electrical consumption at higher applied current may be due to the increase in hydrogen and oxygen evolution during the process [31].

Table 6: The electric energy consumption during degradation of MB dye

Applied Voltage (V)	Current (A)	Energy Consumption ($KWhM^{-3}$)	Operating Cost ($)
1.5	0.5	3750	550
3.0	1.0	15000	2200
6.0	1.6	48000	7040

CONCLUSION

In the present study, an aluminum-doped copper oxide electrode was prepared by thermal decomposition and used as anode material for electro-degradation of methylene blue in an aqueous solution at different parameters such as current density, electrolysis time, and MB concentration. Results obtained from Box-Behnken design (BBD) matrix employed for modeling and optimization of the earlier mentioned operating conditions developed a quadratic model with a high correlation between the experimental values and model predicted values. The optimal condition was found at a current density of 3.75 A, electrolysis time of 80 min, and MB concentration of 40 mg/l, respectively, for 52.23% of degradation through numerical optimization. The mineralization of MB achieved implies poor anodic properties of Al@CuO electrode material.

ACKNOWLEDGEMENT

The authors acknowledge Tertiary Education Trust Fund (TETFund) for their financial support. We also appreciate the assistance of Miss Mbachu Millicent Chinaza of the Materials and Electrochemical Research Unit (MERU) of the Chemistry/Biochemistry Department, Federal Polytechnic Nekede, Owerri, Nigeria, for her laboratory assistance.

Funding: This research was funded by grant from the Tertiary Education Trust Fund (TETF/DR&D/CE/POLY/NEKEDE/IBR/2024/VOL.1).

Conflict of Interest: The authors declare no conflict of interest.

REFERENCES

1. Gomathi, E., Balraj, B., & Kumaraguru, K. (2018). Electrochemical degradation of scarlet red dye from aqueous environment by titanium-based dimensionally stable anodes with SS electrodes. *Appl Biol Chem*, *61*(3), 289-293.
2. Shokoohi, R., Moradnia, M., Shabanloo, A., Shabanloo, N., & Marofi, S. (2020). Catalytic activation of persulphate with Mn_3O_4 nanoparticles for degradation of acid blue 113: process optimization and degradation pathway. *International Journal of Environmental Analytical Chemistry*, 1-20.
3. El Hajji, M, Baddouh, A., Rghuiti, M., Jbara, O., Tara, A., Bazzi, L., Benlhachemi, A., & Hilali, M. (2015). Electrochemical degradation or organic dye by electrochemical oxidation on a Ti/CU_2O electrode. *Appl J Envir En Sci*, *1*(1), 1-8.
4. Charan, K. H. C., Shilpa, R., Ravishankar, R. V., & Ananda, S. (2017). Electrochemical degradation of acridine orange dye at Pd/graphite modified electrode in aqueous solution. *International Journal of Applied Chemistry*, *15*(2), 219-234.
5. Pathania, M., Sharma, S., & Singh, P. (2017). Removal of methylene blue by adsorption onto activated carbon developed from *Ficus carica bast Arab J Chem*, 1-10.
6. Alver, F., Metin, A. U., & Brouers, F. (2020). Methylene blue adsorption on magnetic alginatelrice husk biocomposite. *International Journal of Biological Macromolecules*, 154, 104-113.
7. Uhiara, F. E., Unegbu, C. C., Iheagwam, U., & Nleonu, E. C. **(**2011). Biosorption of Indigo Dye using *Enteromorpha sp*., A Seaweed Algea. *Journal of Research in Physical Science*, *7*(2), 60-65.
8. Nleonu, E. C., Okeke, P. I., Onyemenonu, C. C., Gaya, U. I., Nazir, M. A., Shoaib, S., & Shah, A. (2023). Fabrication of Zinc Incorporated Magnetic Iron Oxide Nanoparticles for Photocatalytic Degradation of Methylene Blue. *Iranian Journal of Chemistry and Chemical Engineering*, *42*(11), 3590-3600.
9. Chima, G. C., Nleonu, E. C., & Amor, I. B. (2023). Comparative Optimization of Photocatalysis and Adsorption of Methylene Blue Using Aluminum Doped Magnetic Iron Oxide by Central Composite Design. *International Journal of Research Publication and Reviews*, *4*(8), 3091-3097.
10. Ezeibe, A. U., Nleonu, E. C., Onyemenonu, C. C., Arrousse, N., & Nzebunachi, C. C. (2022). Photocatalytic Activity of Aluminium Oxide Nanoparticles on Degradation of Ciprofloxacin. *Saudi Journal of Engineering and Technology*, *7*(3), 132-136.

11. Ezeibe, A. U., Achilike, J. B., Nleonu, E. C., & Atuegbu, O. M. (2019). Photocatalytic Degradation of Ciprofloxacin using magnetic Iron Oxide. *International Journal of Scientific & Engineering Research*, *10*(6), 1445-1448.
12. Ammar, S., Asma, M., Oturan, N., Abdelhedi, R., & Oturan, M. A. (2012). Electrochemical degradation of anthraquinone dye alizarin red: role of the electrode material. *Current Organic Chemistry*, 16, 1978-1985.
13. Palanisamy, S., Nachimuthu, P., Awasthi, M. K., Ravindron, B., Chang, S. W., Palanichamy, M., & Nguyen, D. D. (2020). Application of electrochemical treatment for the removal of triazine dye using aluminium electrodes. *Journal of Water Supply*; *Research and Technology*, *69*(4), 345-354.
14. Zakaria, Z., Othman, M. R., Hasan, S. Z., & Ahmad, W. Y. W. (2019). Electrochemical degradation of reactive orange 16 by using charcoal-based metallic composite electrodes. *Sains Malaysiana*, *48*(4), 791-801.
15. Droguett, T., Mora-Gomez, J., Garcia-Gabaldon, M., Ortega, E., Mestre, S., Cifuentes, G., & Perez-Herranz, V. (2020). Electrochemical degradation of reactive black 5 using two-different reactor configuration. *Scientific Reports*, 1-11.
16. Aquino, J. M., Rocha-Filo, R. C., Ruotolo, L. A. M., Bocchi, N., & Biaggio, S. R. (2014). Electrochemical degradation of a real textile wastewater using β-PbO_2 and DSA anodes. *Chem Eng J*, 251, 138-145.
17. Rao, A. N. S., & Venkatarangaiah, V. T. (2014). Metal oxide-coated anodes in wastewater treatment. *Environ Sci Polut Res*, 21, 3197-3217.
18. Wu, W., Huang, Z. H., & Lim, T. T. (2014). Recent development of mixed metal oxide anodes for electrochemical oxidation of organic pollutants in water. *Appl Catal A Gen*, 480, 58-78.
19. Yao, Y., Ren, B., Yang, Y., Huang, C., & Li, M. (2019b). Preparation and electrochemical treatment application of Ce-PbO_2/ZrO_2 composite electrode in the degradation of acridine orange by electrochemical advanced oxidation process. *J. Hazard Mater*, 361, 141-151.
20. Gaber, M., Ghalwa, N. A., Khedr, A. M., & Salem, M. F. (2013). Electrochemical degradation of reactive yellow 160 dye in real wastewater using C/PbO_2, Pb + Sn/PbO_2 + SnO_2, and Pb/PbO_2 modified electrodes journal of chemistry, 1-9.
21. Onyemenonu, C. C., Osuji, L. C., & Ngobiri, N. C. (2023). Investigation and optimization of cadmium ion adsorption from wastewater using raw and activated carbon of *Pterocarpus santalinoides* fruit. *International Journal of Science and Research Archive*, *10*(01), 951–965.
22. Szpisják-Gulyás, N., Al-Tayawi, A. N., Horváth, Z. H., László, Z., Kertész, S., & Hodúr C. (2023). Methods for experimental design, central composite design and the Box–Behnken design, to optimise operational parameters: A review. *Acta Alimentaria*, 1-17.
23. Nakamura, K. C., Guimaraes, L. S., Magdalena, A. G., Angelo, A. C. D., De Andrade A. R., Garcia-segura, S., & Pipi, A. R. F. (2019). Electrochemical driven mineralization of reactive blue 4 cotton dye: on the role of in situ generated oxidants. *J Electroanal Chem*, 840, 415-422.
24. Dai, Q., Zhou, J., Weng, M., Luo, X., Feng, D., & Chen, J. (2016). Electrochemical oxidation of metronidazole with Co modified PbO_2 electrode: Degradation and mechanism. *Sep Purif Technol*, 166, 109-116.
25. Wang, C., Wang, F., Xu, M., Zhu, C., Fang, W., & Wei, Y. (2015). Electrocatalytic degradation of methylene blue on Co doped Ti / TiO_2 nanotube / PbO_2 anodes prepared by pluse electodeposition. *J Electro and Chem*, 759, 158-166.
26. Salari, M., Dehghani, M. H., Azari, A., Motevalli, M. D., Shabanloo, A., & Ali I. (2019). High performance removal of phenol from aqueous solution by magnetic chitosan based on response surface methodology and genetic algorithm. *Journal of Molecular Liquids*, 285, 146-157.
27. Rahmani, A. R., Shabanloo, A., Fazizadeh, M., Poureshgh, Y., & Vanaeitabar, M. (2019). Optimization of sonochemical decomposition of ciprofloxacin antibiotic in US/PS /nZVI Process by CCD-RSM methods. *Desalination Water Treat*, 145, 300-308.
28. Kumar, A., Omar, R. A., & Verma, N. (2020). Efficient electro-oxidation of diclofenac persistent organic pollutant in wastewater using carbon film-supported Cu-rGO electrode. *Chemosphere*, 248, 1-12.
29. Pignatello, J. J., Olivpros, E., & Mackay, A. (2006). Advanced oxidation processes for organic contaminant destruction based on feton reaction and related chemistry. *Critical Reviews in Environmental Science and Technology*, *36*(1), 1-84.
30. Xu, Y., & Wang, D. (2012). Degradation of azo dye methyl orange in aqueous solutions of Fenton's Reagent. *Chemosphere*, *79*(4), 326-331.
31. Kariyajjanavar P., Narayana J., & Nayaka Y. A. (2011). Degradation of textile wastewater by electrochemical method. *Hydrol Current Res*, *2*(1), 1-7.