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Review **ETCE**

Electrooxidation of Methylene Blue Over Nanoparticle Coated DSA Synthesized by sol-gel Method

Akash Vaghela[1], Priya Saxena[2,*]

Abstract

The current study uses the sol-gel approach to synthesize a new Dimensionally Stable Anode (DSA) covered with nanoparticles. The objective is to enhance the electrocatalytic activity and overall performance of the anodes in treating synthetic industrial wastewater containing reactive dyes. CuO and TiO_2 nanoparticles are coated using a thermal decomposition technique on a titanium electrode. The DSA surface gains more surface area and better catalytic capabilities when nanoparticles are coated on it. By optimizing the electrochemical processes involved in effluent treatment, this novel approach seeks to improve the effectiveness and environmental friendliness of wastewater remediation in industrial settings. The nanomaterials coated DSA shows a notable improvement in the removal of reactive dye (methylene blue) from aqueous solutions. Absorbance was measured for untreated and treated samples withdrawn at periodic intervals of time at λ_{max} 665 nm for methylene blue dye using UV-spectrophotometer. These absorbances were further used to estimate percentage color reduction which is 94 % after 105 minutes of electro-treatment. This innovative approach offers enhanced catalytic activity and stability, making it well-suited for efficient electrochemical treatment of diverse industrial effluents. By using cutting-edge oxidation methods, the coating's incorporation of nanoparticles not only enhances the DSA's overall performance but also helps remove impurities. Through the provision of a sustainable and affordable wastewater remediation solution, the technology investigated in this work has the potential to completely transform industrial effluent treatment processes, encouraging environmental stewardship and guaranteeing regulatory compliance.

Keywords: DSA, Electrochemical oxidation, Methylene blue, Sol-gel, COD, Methylene blue

INTRODUCTION

The textile industry utilizes a staggering quantity of water and up to 8,000 chemicals, making it one of the main pollutants of surface and ground water resources. According to several sources, an average-sized textile sector uses over 1.6 million litres of water every day to produce 8,000 kg of fabric [1]. The textiles industry had remarkable growth in recent decades and is currently one of the largest sectors. Consequently, the use of dyes increased quickly. Textile industries require big amount of water. The usage of water in the textile industry results in wastewater that contains dyes intermediates and will be having colour, toxic pollutants which will have negative effect on environment and living species [2]. Effluents leaving from textile industry have higher COD and BOD concentration. Dyes and pollutants present in effluent can reduce photosynthesis and can cause various levels of mutagenesis, carcinogenesis, and toxicity in living things [3]. Components called reactive dyes are used to colour cellulose fibres. They are frequently employed when dying silk, wool, and cotton.

***Author for Correspondence**
Priya Saxena
E-mail: priyasaxena2080@gmail.com

[1]Research Scholar, Department of Chemical Engineering, Parul Institute of Technology, Parul University, Vadodara, Gujarat, India
[2]Associate Professor, Department of Chemical Engineering, Parul Institute of Technology, Parul University, Vadodara, Gujarat, India

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However, these components are having high water solubility, during manufacture, 10-15% of the effluent is left behind, and approximately 50% is wasted while colouring cellulosic Fibers [4]. One or more azo groups (R1-N=N-R2) and aromatic rings are typically substituted in reactive azo dyes by sulfonate groups. Their intricate structure gives them intense colour, great water solubility, and resistance to fading when exposed to light. water, soap, sweat, and light [5]. The ability of reactive dyes to make a covalent link with hydroxyl or amino groups found on the fibre is their most crucial characteristic [6]. Dye removal from wastewaters has been accomplished using a variety of approaches. The majority of the time, biological or enzymatic procedures are used to treat wastewaters in addition to processes that are either chemical or physical (such as ozonation, photocatalysis, incineration, chemical transformation, electrocoagulation, or adsorption). They are pricey but effective [7,8]. The electrochemical approaches have attracted particular attention for wastewater cleanup over the past 15-20 years. These processes include electrocoagulation, electrochemical reduction, electrochemical oxidation, light-assisted electrochemical procedures (photoelectron-Fenton, photo electrocatalysis), and indirect electro-oxidation with strong oxidants (electro-oxidation with active chlorine, electro-Fenton) and these are used individually or in combination for dye removal in wastewaters [9]. Generally speaking, mixed metal oxide electrodes, or DSAs, can be made in a number of ways, the most widely used method documented in the literature being the thermal decomposition approach. By using this process, DSA catalytic oxide coatings are created by dissolving the corresponding metal precursors in appropriate solvents and this coating solution is mostly by brush painting them onto titanium (Ti) metal substrates, then annealing them at a high temperature [10].

In the present study, an assessment of the performance of DSA prepared via combine thermal decomposition and sol-gel method is conducted for treatment of methylene blue dye wastewater. DSA was assessed for its ability to remove methylene blue from the wastewater while keeping the color intensity and COD (chemical oxygen demand) within predefined process limits.

EXPERIMENTAL PART

Materials

For this study, a local dye business provided the methylene blue dye ($C_{16}H_{18}N_3OS.3H_2O$, molecular mass: 373.5 g/mol), which was selected as a typical pollutant with a maximum wavelength (λ_{max}) of 665 nm. Titanium (Ti) metal plate (area = 54 cm^2) is used as substrate to coat nanoparticles for catalytic coating(anode) and Stainless-steel metal plate (area=65 cm^2) is used as reference electrode (cathode). For TiO_2 nanoparticles preparation, TTIP (Titanium Tetra Isopropoxide [Ti $(OCH(CH_3)_2)]_4$) is used as precursor supplied by SRL, India. Isopropanol $(CH_3)_2CHOH$), is used as solvent for TiO_2 nanoparticles preparation. CuO nanoparticles are supplied by Ad nano technologies, India. Oxalic acid is used as etching agent for pretreatment of Titanium metal plate. NaCl is used as electrolyte to increase dye solution's conductivity. Table 1 depicts various properties of methylene blue dye used for experimentation purpose.

Synthesis of TiO_2 nanoparticles

Without any additional purification, Titanium Tetra Iso Propoxide [TTIP, Ti $(OCH(CH_3)_2)]_4$, SRL, India], and iso-propanol $(CH_3)_2CHOH$), were utilized as received. The 22 ml solution containing 10 ml of iso-propanol and 12 ml of distilled water was continuously stirred at 80ºC while a 20 ml solution of TTIP was added drop by drop into the beaker with a circular bottom. After one hour, the TTIP solution was supplemented with concentrated HNO_3 (0.8 ml) diluted with distilled water, and it was continuously stirred at 60ºC for six hours until a very viscous sol gel was produced. The prepared sol-gel was heated in a muffle furnace for one hour at 500ºC. The powder of TiO_2 nanocrystallines was formed after annealing. Further for coating of this nanoparticles onto substrate, nanoparticle powder was mixed with isopropanol [11,12].

Experimental workstation

The batch experiments were conducted using a 1 L electrochemical glass beaker with a working volume of 500 mL aqueous dye solution containing 100 ppm methylene blue dye and pH was measured to be 8.9. For experimental run, fabricated DSA as anode and stainless steel as cathode with 10 mm interelectrode distance were dipped inside the working volume of MB dye wastewater. To run the electrochemical cell at a controlled current density of 27 mA/cm^2, a direct current power supply system (Powertron, Mumbai, India) delivered constant potential. For experiment run, 4.0 g/L of sodium chloride (NaCl) was used as the electrolyte to increase dye solution conductivity, and 250 rpm magnetic stirring was used to ensure even mixing at room temperature. At regular intervals, number of samples were taken till complete visible colour removal was observed and the samples were further analysed for colour removal by UV–visible spectrophotometry. Figure 1 indicates the steps in synthesized DSA anode. Figure 2 indicates the experimental set-up for conducting electrooxidation of MB dye wastewater.

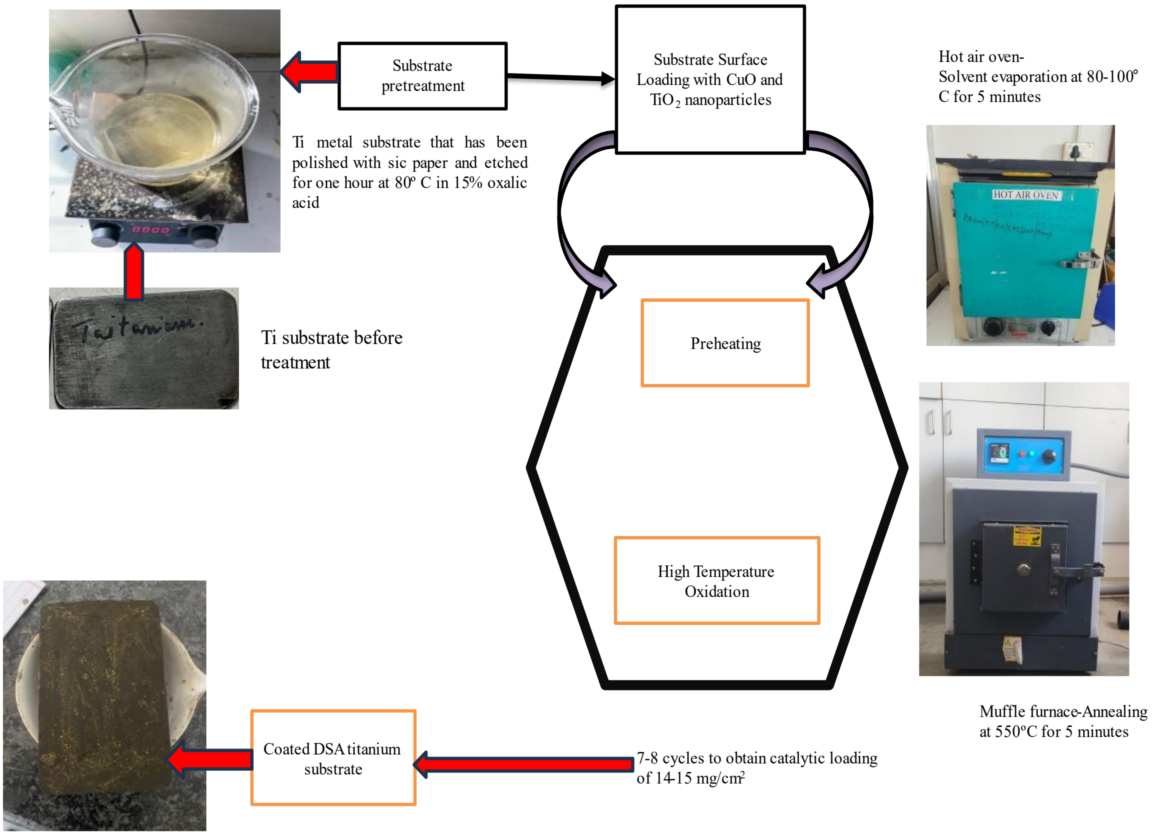


Figure 1. Laboratory scale DSA preparation via thermal decomposition method [3].

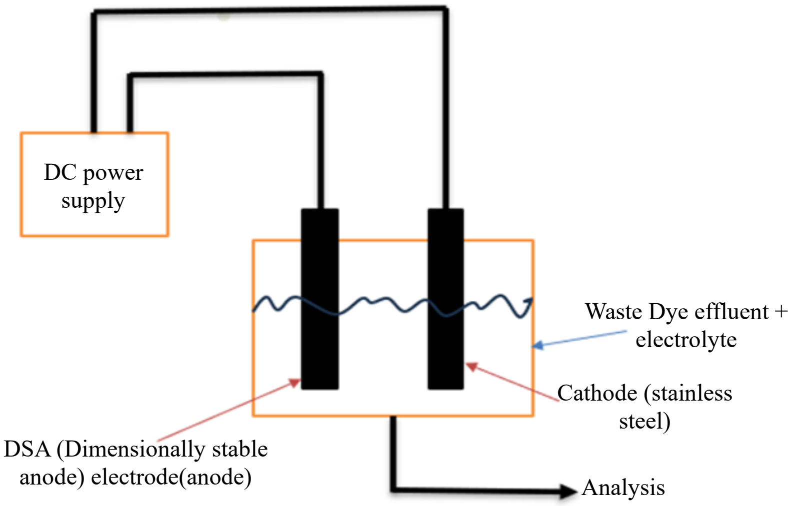
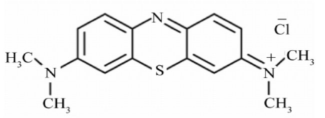


Figure 2. Experimental set-up for electrooxidation

Table 1. Properties of methylene blue dye.

Dye	C.I number	wavelength (λ_{max}) nm	Mw, g/mole	Structure
Methylene Blue (MB)	52030	665	373.5	

Mechanism of indirect oxidation at anode (DSA)

The particular chemical selectivity of electrode material has a significant impact on overall electrooxidation performance. DSA electrode used in the current study, sometimes referred to as active anodes, favor the partial oxidation of contaminants by indirect oxidation. A reaction mechanism for oxidizing organics at DSA type anodes is represented by equations (1), (2) and (3), with a propensity for oxygen to generate simultaneously through a secondary side reaction [13].

Water molecules get dissociated first to generate OH radicals (•OH) that adsorb strongly at electrode surface:

$$MO_X + H_2O \rightarrow MO_X\,(^{\bullet}OH) + H^+ + e^- \quad (1)$$

where M = Titanium At ‘‘active” DSA surface, these strongly adsorbed OH radicals through interaction with the anode, form MO_{x+1}:

$$MO_X\,(^{\bullet}OH) \rightarrow MO_{x+1} + H^+ + e^- \quad (2)$$

MO_{x+1} thus, representing the newly formed surface redox couple, further serve as a mediator causing partial electro-oxidation of organic species:

$$MO_{x+1} + R \rightarrow MO_x + RO \quad (3)$$

Additionally, this process leads to a competitive secondary/side reaction that evolves O_2, which lowers the anodic process efficiency.

RESULT AND DISCUSSION

UV Spectrometer Analysis

Presence of azo (N = N) bonds in reactive dye structure imparts severe color intensity to these dyes. These azo bonds get disintegrated during the electrooxidation of dye and results in color removal from the solution. Absorbance was measured for untreated and treated samples withdrawn at periodic intervals of time (15 min) at maximum wavelength (λ_{max}) of 665 nm for methylene blue dye using UV-V is spectrophotometer and the recorded data is represented in Table 2. It is observed that absorbance of methylene blue dye at initial stage was 3.638 and after 105 minutes of electrooxidation treatment absorbance was measured to be 0.193 which is substantially reduced showing almost complete dye removal from wastewater. Figure 3 depicts the peak reductions as the electrooxidation progresses.

Electrochemical Performance of Synthesized DSA Electrode

The following equations are used to assess COD reduction, color reduction and current efficiency of treated samples.

$$\mathit{COD\ removal\ efficiency} = \frac{COD\ i - COD\ f}{COD\ i} \times 100 \tag{4}$$

Table 2. UV-Visible Spectrophotometer data and colour removal efficiency.

Time (min)	Absorbance (A)	(%) Colour Reduction
0	3.638	0.0
15	2.737	24.8
30	1.739	52.2
45	1.434	60.6
60	1.412	61.2
75	0.73	79.9
90	0.577	84.1
105	0.193	94.7

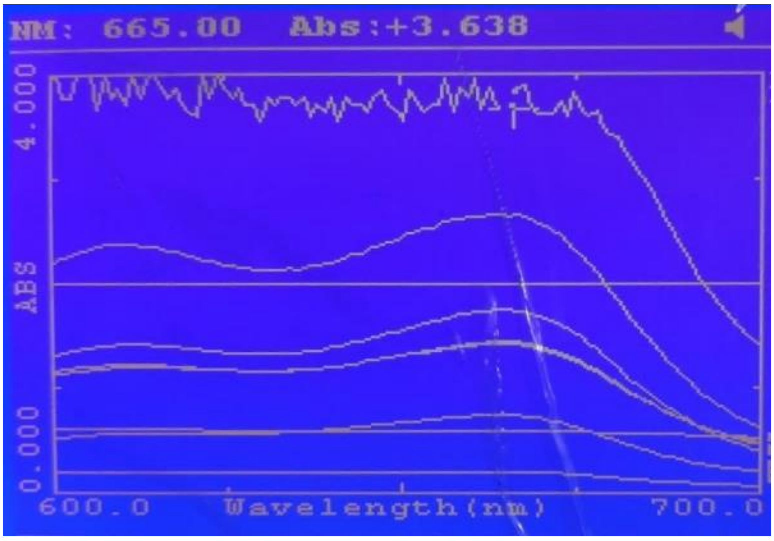


Figure 3. Peak reductions observed in UV-VIS Spectrophotometer for dye samples collected at regular intervals.

where, COD I and COD f are the absorbances before electrolysis and after an electrolysis

$$\mathit{Colour\ removal\ efficiency} = \frac{ABS\ i - ABS\ f}{ABS\ i} \times 100 \tag{5}$$

where, ABS i and ABS f are the absorbances before electrolysis and after an electrolysis

$$\mathit{Current\ efficiency} = \frac{(\Delta COD)\ F\ V_s}{8\ I\ t} \times 100 \tag{6}$$

where, F is the Faraday constant (96,487 C /mol), V_s is the solution volume (m^3), I is the applied current (A), 8 is the oxygen equivalent mass (g /eq) and t is the electrolysis time (s).

The equations (4), (5), and (6) bear traditional meanings and are discussed in various other works [14,15].

Figure 4 illustrates visual colour disappearance from initial to final time of electrolysis.

Color Removal

Calibration of UV-spectrometer was done using different dye concentration solutions to determine Beer-Lambert relationship which is further used for calculating colour removal efficiency. Figure 5 shows calibration plot of MB dye for known concentrations of the dye which resulted in related absorbance (A) with dye concentration (C) as A = 0.0526 C. Figure 6 depicts color reduction as a function of electrolysis time and Figure 7 shows appreciable drop in dye concentration from initial value to 3.67 ppm as electrooxidation treatment progresses. Colour removal efficiency was measured using eqn (5) using absorbance data of UV-vis spectroscopy. Colour removal efficiency was found to be 94.7% after 105 minutes of treatment.

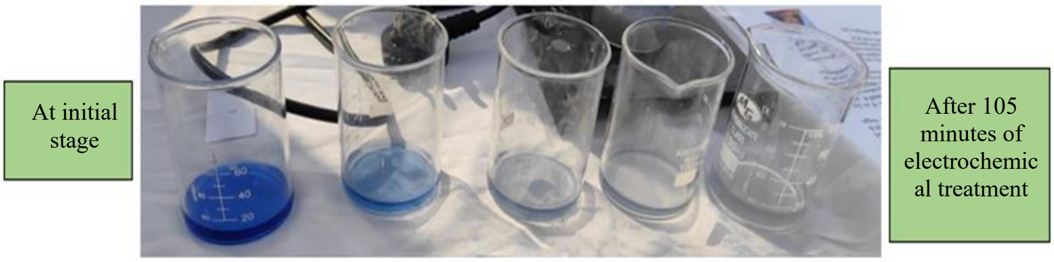


Figure 4. Visible colour change of treated samples during experiment

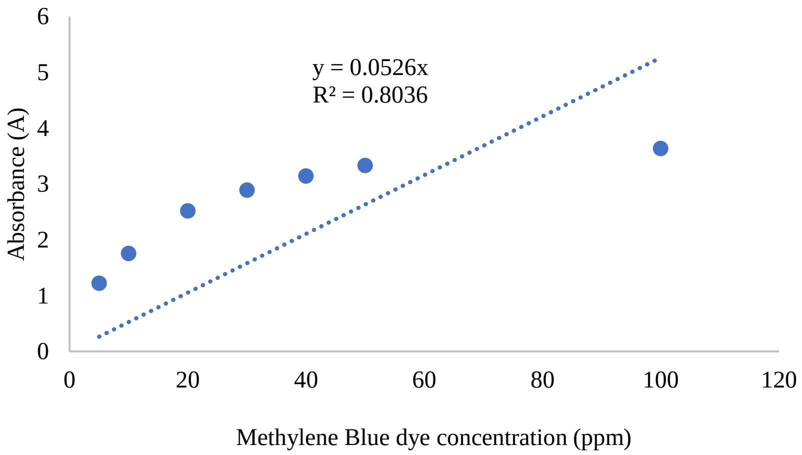


Figure 5. Calibration plot for Methylene Blue dye at maximum wavelength of 665 nm.

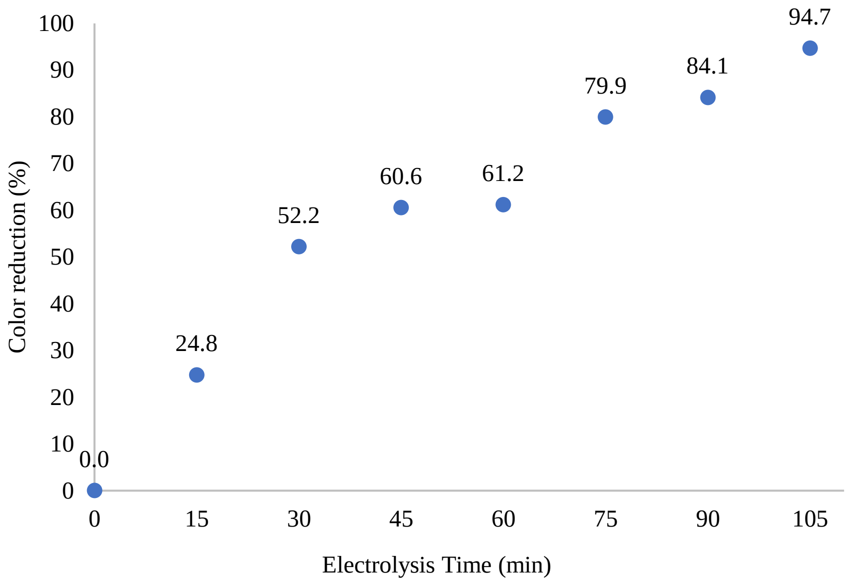


Figure 6. Color reduction (%) vs. Electrolysis time (min).

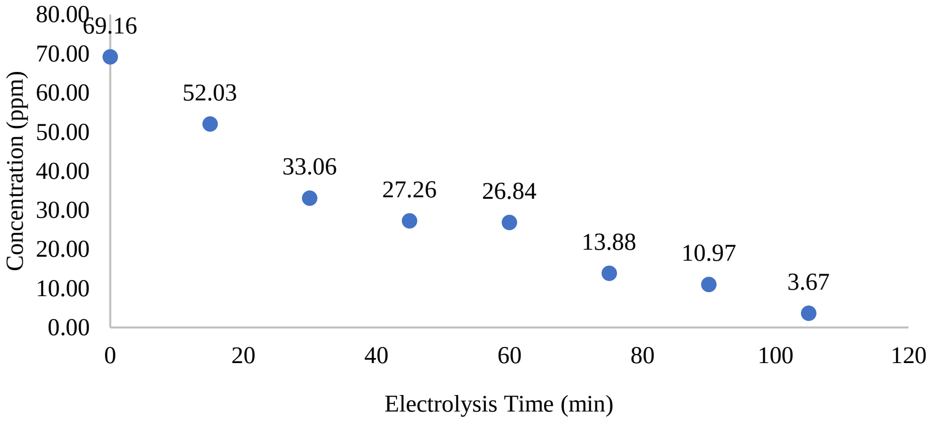


Figure 7. MB Concentration (ppm) vs. Electrolysis time (min).

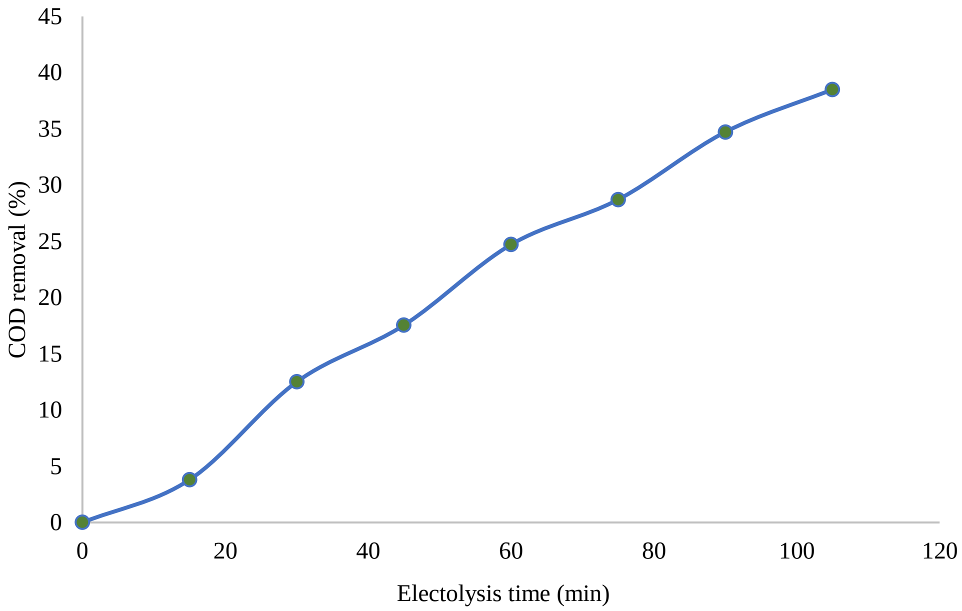


Figure 8. COD removal (%) vs. Electrolysis time (min).

COD Removal

Figure 8 depicts reduction in COD as a function of electrolysis time. At initial concentration of dye (100 ppm), COD value was 535 ppm which under constant operating condition of electrooxidation, reduced to 329 ppm leading to an overall COD reduction of 38.50%.

Kinetic Analysis Based on COD Reduction and Dye Concentration

Kinetic analysis based on COD removal and dye concentration was conducted to examine the relative rates of colour removal and COD deterioration using eqns (7) and (8). A pre-calibrated plot was used to determine the concentrations of the MB dye samples based on their relationship to absorbance.

$$\ln \frac{\mathrm{CODo}}{\mathrm{CODt}} = \mathrm{k1t} \tag{7}$$

$$\ln \frac{\mathrm{Co}}{\mathrm{Ct}} = \mathrm{k2t} \tag{8}$$

The rates of COD and color elimination were investigated by graphing, respectively, ln COD_o/COD_t and ln C_o/C_t vs. time, where COD_o and C_o represent the initial COD concentration and initial dye concentration, and COD_t and C_t represent the COD concentration and dye concentration at a certain treatment time. When both COD and colour were reduced, the straight-line plots in Figure 9 and 10 demonstrated appropriate fits of the kinetic model that obeyed pseudo first order kinetics [16,17]. Table 3 displays apparent kinetic rate constants (k_1 for COD reduction and k_2 for colour reduction) for tested anode that were calculated from the slopes of the corresponding linear fits.

Table 3. Kinetic rate constants based on COD and colour reduction.

Rate constant based on COD reduction (k_1)	*Rate constant based on color reduction (k_2)*
0.0048 min^{-1}	0.0287 min^{-1}

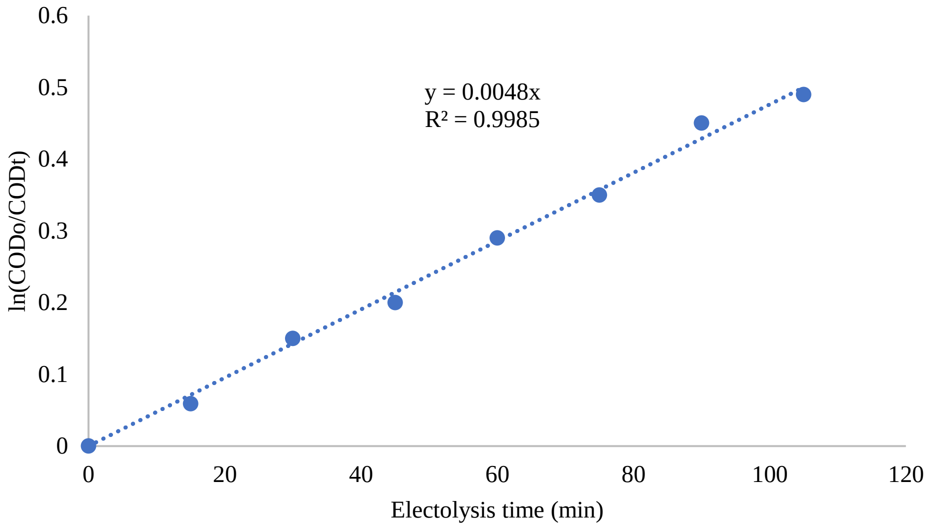


Figure 9. ln (CODo/COD t) vs. Electrolysis time (min).

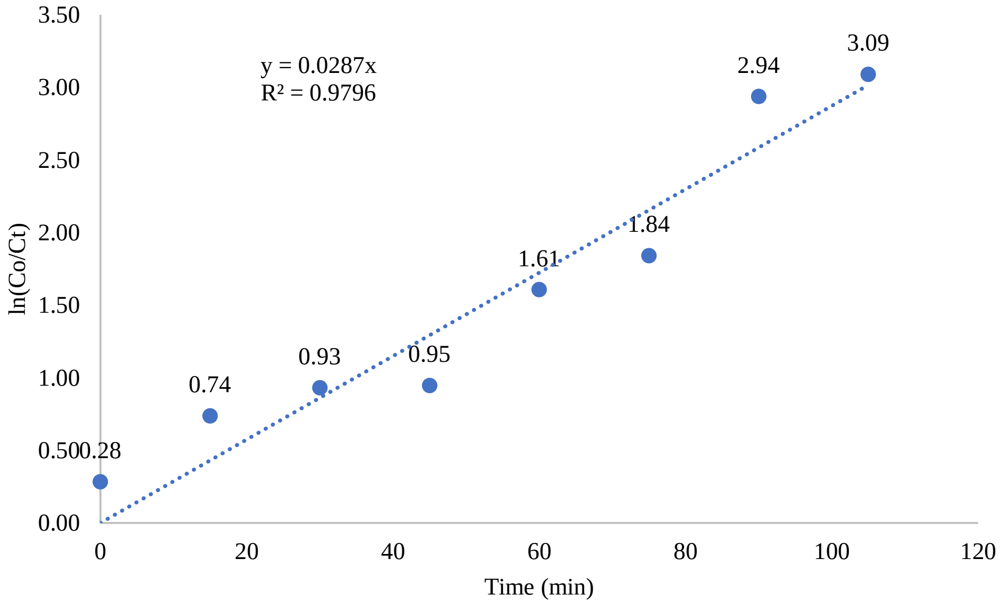


Figure 10. ln (C_o/C_t) vs. Electrolysis time.

From the values of k1 and k2, it is clearly evident that color reduction is much rapid compared to reduction in COD which emphasis easy breaking of azo bonds in dye structure.

CONCLUSION

In the current study, laboratory synthesized nanoparticle coated DSA electrode (Ti/TiO_2-CuO) was employed to study the electrooxidation of synthetic methylene blue dye effluent (100 ppm) in the presence of supporting electrolyte. According to the results of the experimental and analytical research, colour nearly vanished (~94%) and COD removal of 38.50% was attained in 105 minutes of electrolysis. The sol-gel synthesis method presented in this study offers a simple and effective route for the fabrication of TiO_2 nanoparticles using Titanium Tetra Isopropoxide (TTIP) as a precursor. The resultant nanoparticles show promising characteristics for sensing, energy conversion, and photocatalysis, among other uses. The rate and extent of decolorization were significantly larger and faster than those of COD removal, according to kinetic studies and rate constants for COD and colour removal were based on pseudo first order kinetic model. From experiments, it is observed that prepared DSA favoured almost complete colour removal but with partial dye degradation resulting in lower COD reduction.

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