

Anodic Oxidation of Methylene Blue Dye from Aqueous Solution Using SnO₂ Electrode

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ABSTRACT: This study was performed to investigate the electrochemical oxidation of a solution containing methylene blue dye by using a tin oxide (SnO₂) electrode. The effect of several operating factors such as electrolyte types, current density, initial dye concentration, and pH were investigated by following the discoloration and COD removal. The results show that the maximum color was removed by using chloride supporting electrolyte (i.e. KCl and NaCl) indicating that the indirect oxidation was promoted by the strong oxidant species (i.e. Cl₂ and ClO⁻) generated at the anode surface. The best experimental conditions were attained for $i = 60\text{mA/cm}^2$, 1% KCl and pH = 3, in which 100% of color was removed after 30 minutes and the COD removal reached 80.9% after 120 min. These results reveal that the anodic oxidation technique using SnO₂ electrode could be used to remove the methylene blue dye from textile wastewater.

KEYWORDS: Oxidation; Dyes; Discoloration; Methelyne bleu; SnO₂ electrode.

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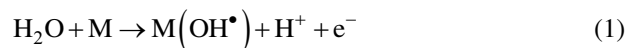
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INTRODUCTION

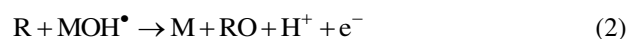
The textile industries effluents usually contain a high organic and inorganic load, which have carcinogenic and mutagenic effects. The dyes may cause skin irritation, eczema, de-coloration or even deaths as it comes in contact or due to absorption. The chemicals which are used for dyeing may cause severe health risks i.e. rashes, allergic condition, and even life hazards. Hence it is important to minimize the concentration of the compound to avoid risk factors. These compounds are noticeable even at very low concentrations and must be removed before the wastewater is discharged. Over 100,000 commercial dyes are available in the market and the productivity of these compounds has been projected between 750,000 and 800,000 tons per annum worldwide [1-3]. There are different technologies for the abatement of wastewaters containing dyes that have been extensively studied such as adsorption, coagulation-flocculation, and membrane filtration, etc. However, only some of these gained little success and some are non-cost effective[4]. In the last 10 years, the Advanced Oxidation Processes (AOP's) were believed to be the best alternative for removing organic pollutants from wastewaters, for example electro-oxidation [5-7], electro-coagulation [8], electro-Fenton and Photoelectron-Fenton processes[9-11], these techniques have received considerable attention to the environmental research community as cost-effective and eco-friendly processes. Among these methods, the electro-oxidation is considered a relatively proper technique and has certain significant advantages namely easy operation, environmental friendly and high efficiency [6, 12, 13]. The electrochemical technique has an optimum performance which is governed by some parameters, such as the material of the electrode, pH of wastewater, electrolyte and the applied current[14].

In the electrochemical oxidation process, the organic pollutants can be removed either by direct oxidation, where the pollutant exchanges electrons directly with the anode surface without the involvement of other substances or Indirect oxidation, where the organic pollutant does not exchange electrons directly with the anode surface, some oxidant species generated at the electrode surface and degrade the pollutant in the bulk of solution[5, 15]. The electrochemical process degrades and converts the toxic compounds into biodegradable products or mineralizes the organic matter into H₂O and CO₂ and some other less toxic mineral acids.

The electrochemical oxidation in wastewater can be divided into two steps[16], the first one consists of the formation of hydroxyl radicals (OH[•]), which is evolved at the anode (M) upon water discharge reaction (Equation 1).



In the second step, the (OH[•]) radical adsorbed on the electrode surface (M) as shown in (Equation 2) and hence the hydroxyl radical oxidized the organic compound in wastewater.



Some high oxygen over-potential material anodes as metal oxide were used effectively in the oxidation process for abatement of organic pollutants [10, 17-20]. The tin oxide electrode is a promising non-active anode material, which exhibits a high over-potential for the oxygen evolution reaction and a large accumulation of hydroxyl radicals on its surface, commercially available and comparatively low cost. It has been used extensively for electrochemical degradation of organic pollutants without production of hydroquinone and benzoquinone [21] such as the degradation of phenols [22], organic dyes[23, 24], organic acids[25], pesticides[26] and olive mill wastewaters [27, 28].

Methylene Blue (MB) is one of the most widely used water-soluble dye in pharmaceutical drugs and as a colorant in textile industries. The MB is a heterocyclic aromatic chemical compound with dimethylamino groups in its structure (Fig. 1) [29]. The use of MB has been restricted due to its toxicity and can cause anemia, bladder irritation and gastrointestinal problems [30, 31].

In this study, the electrochemical discoloration and degradation of MB dye was investigated using a tin oxide as a working electrode and the optimum conditions were determined for the electrochemical oxidation of a synthetic solution containing methylene blue. The effects of various parameters (current density, nature, and concentration of electrolyte support, pH_i, and initial dye concentration) on the MB removal efficiency were discussed.

EXPERIMENTAL SECTION

Materials and chemicals

The commercial dye methylene blue (C₁₆H₁₈ClN₃S, 98%) CI 52015 (Fig. 1) was used without further purification. The synthetic wastewater was prepared

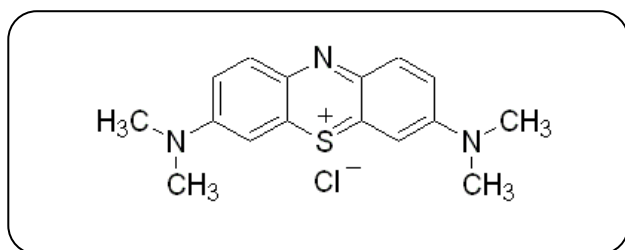


Fig. 1: The molecular structure of the methylene blue.

with 100 mg/dm³ of MB and the working solutions were prepared from the stock solution. The chemical products (i.e. Potassium chloride, sodium chloride, sodium sulfate, and sodium carbonate) were obtained from SOLVACHIMI and used as supporting electrolyte in the degradation process. Other chemicals were of analytical grade and purchased from Sigma Aldrich.

Degradation experiments

All the electrochemical experiments (galvanostatic electrolysis) were carried out using a computer-controlled Potentiostat/Galvanostat VItaLab Model (PGZ301) associated with "VoltaMaster 4" software, with a conventional three electrodes thermoregulated cell. The working electrode comprised commercial tin oxide grid (SnO₂) area of 1cm² exposed in solution, while the counter electrode consisted of platinum (Pt) wire with the same area, the Saturated Calomel Electrode (SCE) was used as the reference electrode. To stabilize the electrode surface and to obtain reproducible results, before each experiment, the tin oxide electrode was pretreated at ambient temperature by anodic polarization for 3 min in 0.5M H₂SO₄ solutions applying a current density of 30 mA cm⁻² to remove any kind of impurities from its surface. During experimentation, the dye solutions were collected at different time intervals and their UV-Visible spectra were recorded. The electrolysis was carried out at 25°C while stirring the solution for one hour. The influence of supporting electrolyte (KCl, NH₄Cl, Na₂SO₄, and NaCl), KCl concentration, initial dye concentration, current density (20–60 mA cm⁻²), and the pH_i were studied.

Analysis

UV-Visible

The color removal was determined using UV-Vis spectrophotometer (path length 1 cm, apparatus: UV 2300) by monitoring the band corresponding to the absorption

maximum of MB ($\lambda_{\max} = 664$ nm). The color removal was calculated according to the following equation:

$$\% \text{Color removal} = \frac{A_0 - A}{A_0} \times 100 \quad (3)$$

Where A and A_0 are absorbance values of dyes solutions before and after treatment concerning their λ_{\max} , respectively.

COD analysis

Chemical Oxygen Demand (COD) monitored the degradation, which was measured according to the technique published in Standard Methods for Examination of Water and Wastewater[32]. The COD values were determined by the opened reflux (Classic Method), a dichromate titration method. The analyzed samples were taken during electrolysis at various time intervals. The following relation expressed the rate of mineralization as a percentage of COD:

$$\% \text{COD} = \frac{\text{COD}_i - \text{COD}_t}{\text{COD}_i} \times 100 \quad (4)$$

Where COD_i and COD_t are the values of COD (mg/L of O₂) at an initial time and at time t respectively.

RESULTS AND DISCUSSION

Effect of supporting electrolytes

Initially, some experiments were performed to ascertain the effectiveness of different supporting electrolytes such as NaCl, KCl, Na₂SO₄, and NH₄Cl while applying a current density of 60 mA/cm² for 60 min of electrolysis to 100 mg/L of BM dye. Fig. 2 (a) shows a color removal of 99.03%, 96.2%, 55.3% and 6.4% for KCl, NaCl, Na₂SO₄ and NH₄Cl, respectively after 60 min of electrolysis. The maximum color was removed using KCl and NaCl by indirect oxidation, this is explained by the strong oxidant species generated at the anode surface[33, 34]. It is well known that the electrolysis of KCl generates some strong oxidants, such as free chlorine (Cl₂) and hypochlorite anions (ClO⁻) [35, 36] by chemical reactions (6-7)[37]. In this study, the formation of hypochlorite anions by the degradation of chloride supporting electrolytes (without dye) during electrolysis was confirmed by UV-Visible spectrophotometry as shown in Fig. 2. As can be seen, there is a maximum peak (at 292 nm) that corresponds to ClO⁻ anions [38].

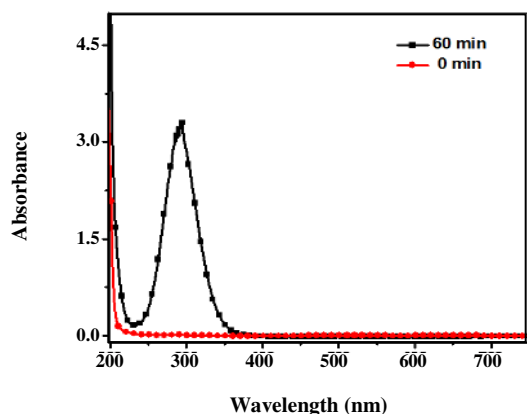
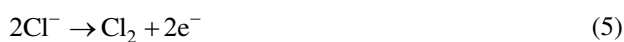


Fig. 2: UV-visible spectra of a 1% KCl solution submitted to a current density of 60 mA/cm² at t=0 and t= 60 min.

Anode reaction:



Cathode reaction:



Bulk solution reaction:



Similarly, the spectra of dye concentration at time zero have two broad absorption peaks, one in the UV region ($\lambda_{\text{max}} = 292$ nm) and another one in the visible region ($\lambda_{\text{max}} = 664$ nm) as shown in Fig. 3 (b). The signal in the UV region is related to $\pi \rightarrow \pi^*$ transition in the aromatic group and the visible region is associated with the color removal indicated by the linkage chromophore group of the dye MB[32].

Chloride ions Concentration

The effect of chloride concentration on the removal of MB was studied by varying KCl from 0.5 to 3% while keeping the other conditions constant. Fig. 4 shows the effect of different chloride concentration on the de-colorization of MB solution carried out at 60 mA/cm. It is observed that the BM can be removed completely, even at low KCl concentrations.

For instance, when the concentration of KCl is 1%, the de-colorization efficiency has attained 100% after the first 20 min, a further increase in the chloride concentration (>1%) results in a slight improvement in decolorization efficiency of MB causing

a “potentiostat buffering” by the chlorine redox system and consequently a decrease of the anode potential, so the optimal concentration of chloride ions used in the successive experiment was 1%. The concentration allows inhibiting the water discharge into oxygen and promotes hydroxyl and chloride radicals formation. The electro-oxidation process of MB on the tin oxide electrode is determined not only by the charge transfer step but also by the mass transfer step of chloride ions to the anode surface. Fig. 4 (b) shows the concentration of MB after 60 min of degradation at different concentrations of KCl. The band at 664 nm disappeared completely after 60 min of electrolysis using 1% KCl as supporting electrolyte with SnO₂ electrode signifying total color removal of MB. Fig. S1 of supplementary information shows the development of the absorbance over time when using different KCl concentrations during electrolysis. At 1% KCl only 15 min of electrolysis were sufficient to eliminate the highest absorption peak at 664 nm.

Current density

Applied current density is an important operating variable of the electrochemical degradation process, which is the current input divided by the surface area of the electrode. Different current densities (20, 30, 40, 50 and 60 mAcm⁻²) were applied to investigate the influence of current density on the electrochemical degradation of MB using 1% KCl concentration and 100 mg/L of MB. Fig. 5 presents the obtained results. The results clearly showed that increasing the current density, a decrease in the charge loading for the degradation of dye is observed, this is due to the increased rate of generation of oxidants such as chlorine/hypochlorite and hydroxyls radicals at higher current densities. The rate of color removal was almost proportional to the current density. The increase in current density signifies also an increase in the value of the operating potential of the system, thus, increasing current density led to increasing the overpotential and hydroxyl radicals (OH[•]) that are associated with the degradation of MB, which also results in increased energy consumption[39].

This behavior indicates that applying these experimental conditions, the oxidation of MB is completely under mass transport control and an increase of the applied current favors only the secondary reaction of oxygen evolution:



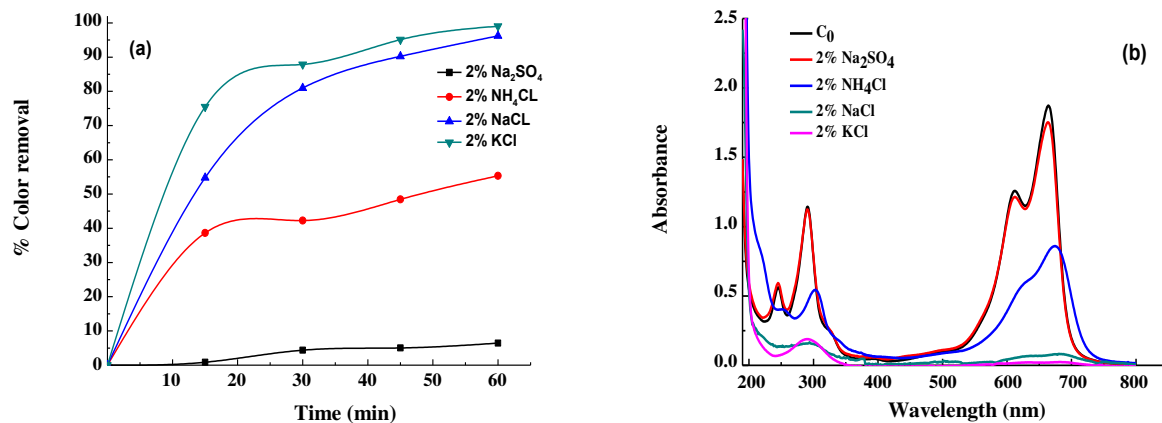


Fig. 3: (a) Variation of color removal efficiency with electrolysis time and (b) UV-Visible spectra of dye solution during electrolysis at different supporting electrolytes ($i = 60 \text{ mA/cm}^2$, MB 100 mg/L temperature ambient) during 60 min.

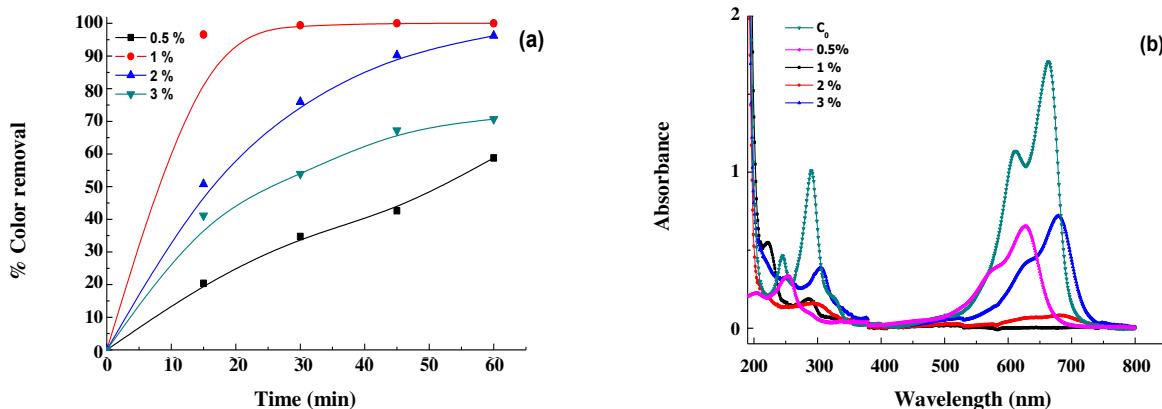


Fig. 4: (a) Variation of color removal efficiency with electrolysis time and (b) UV-Visible spectra of 100 mg/L dye solution during electrolysis at different KCl concentrations ($i = 60 \text{ mA/cm}^2$, $T = 25^\circ\text{C}$).

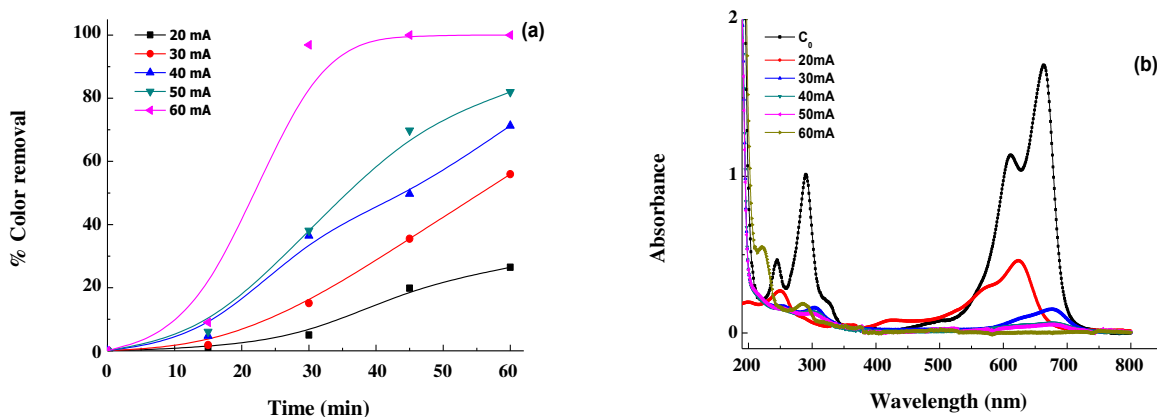


Fig. 5: (a) The influence of the applied current density on the color removal (b) UV spectra changes during electrolysis of the methylene blue on the SnO₂ anode (Electrolyte: 1% KCl, $T = 25^\circ\text{C}$).

At higher current densities (60 mA/cm²), the degradation efficiency was almost constant. Therefore, the optimal current density for the successive electrochemical degradation was fixed at 60 mA/cm². Fig. S2 of Supplementary Information shows the variation of MB spectra during anodic electrolysis while applying different current densities after 60 min. The curves show that the absorption of the major peak at 664 nm decrease and the color removal achieved was 26.5%, 55.9%, 71.3%, 81.9% and 100% at a current density of 20, 30, 40, 50 and 60 mA/cm², respectively after 60 min of electrolysis. At 60 mA/cm², the band at 664 nm disappeared completely after 60 min of electrolysis signifying total color removal of MB.

Kinetics of electro-degradation processes

The kinetic data derived from the plots shown in Fig. 6 were best fitted to the pseudo-zero-order model represented by:

$$\frac{C}{C_0} = -k_{app}t \quad (9)$$

Where C and C_0 are the concentrations of MB at time t (min) and at the initial time, respectively, and k_{app} (min⁻¹) is the apparent rate constant.

Fig. 6 shows the normalized concentration decrease versus time and the insight graph shows the degradation kinetics for various current densities and KCl concentration values, with slopes of the straight lines being associated with the values of the apparent velocity constant k_{app} (min⁻¹). The analysis of k_{app} values indicates that the constant velocity increases with increased current density, KCl concentration, and the degradation reactions follow pseudo-first-order kinetics. The Fig. 6 shows an exponential relationship between the normalized concentration and the time of electrolysis, and their inserts show that there is a linear correlation between the $(\ln C_t/C_0)$ of normalized concentration and the time of electrolysis. This suggests that the electrochemical degradation reaction of MB followed a pseudo-first-order reaction kinetic in all the cases. Therefore, the velocity of MB electrochemical degradation reaction depends on the concentration of the dye and it is controlled by mass transport. The apparent rate constants reported in Table 1 show that a fast MB removal was achieved by anodic oxidation using SnO₂ within 30 min at 60 mA/cm² current density and 1% KCl. At this condition the highest apparent rate constant,

0.132 min⁻¹ and 0.146 min⁻¹ was found. Therefore, the most appropriate condition to degrade the MB dye is applying 60 mA/cm² and 1% KCl as supporting electrolyte.

Effect of initial Concentrations of Methylene Blue

The initial concentration of pollutant is always an important parameter in wastewater treatment. The influence of the initial dye concentration was studied, for concentrations ranging from 50 to 200 mg/L by keeping the other conditions constant. Fig. 7 (a) shows the effect of the initial concentration of MB on color removal and Fig. 7(b) shows the corresponding spectra. Complete degradation of MB blue was obtained for concentrations of 50 and 100 mg/L. However, increasing the dye concentration up to 100 mg/L results in a decrease in the electrocatalytic rate of degradation, this may be explained by the fact that dye molecules tend to associate with increasing dye concentration to form clusters of low diffusivity, this lowers the rate of dye diffusion to the anode surface. Moreover, the rate of hydroxyl radicals formation is decreased, consequently, a decrease in the rate of dye oxidation is observed. Although the color removal percentage decreased with initial concentration, the absolute removal amount decreased.

Effect of initial pH

Fig. 8 shows the de-colorization performance of MB via the electro-degradation process at different initial pH values. The color of MB solution depends upon the concentration of H⁺ and OH⁻ ions. Fig. S4 of supplementary information reveals the variations of MB absorption spectra with time at initial pH 3, which has shown the best de-colorization performance, with the MB absorption peaks plummeting most rapidly. In only 20 min, the peaks at 610 and 664 nm disappeared, indicating the breakdown of the MB dimmer and the destruction of chromophore groups. The decolorization efficiency of MB increases with the decrease of the initial pH solution, the color removal efficiency of 100% was reached in 20 min for pH values of 3.0 and 6.0, but only about 60% was achieved for initial pH of 9.0, indicating that the degradation process was more favorable in acidic solution, H⁺ in acid solution would inhibit the decomposition of the reaction of oxygen evolution and hydroxyl radical, which improved the ability to remove the MB[40]. Furthermore, the higher efficiency of MB oxidation at low

Table 1: Removal percentage of color and apparent rate constants (K_{app}), following 60 min of electrochemical degradation using SnO_2 electrode at different applied current densities and different KCl concentrations. ($i = 60 \text{ mA/cm}^2$, 25°C).

Variable	Studied range	Color removal %	K_{app} (min^{-1})
Current Density (mA/cm^2)	20	26.25	0.022
	30	55.91	0.034
	40	71.29	0.045
	50	81.98	0.069
	60	100	0.132
KCl Concentration (%)	0.5	58.75	0.016
	1	100	0.146
	2	96.22	0.053
	3	70.68	0.025

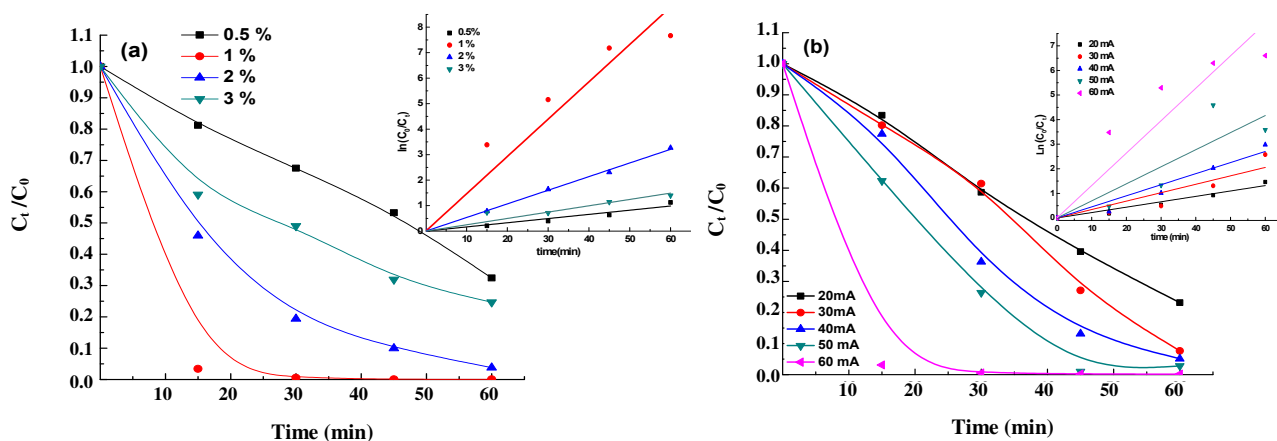


Fig. 6: Normalized concentration decay of MB in the presence of SnO_2 anode (a), different concentration electrolyte KCl and (b), different current density. The initial concentration of MB dye was 100 mg/L , $T = 25^\circ\text{C}$.

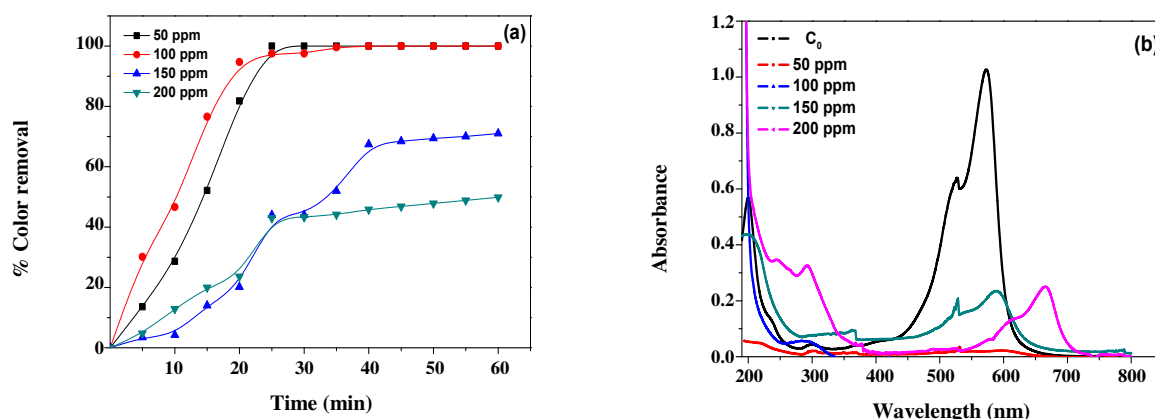


Fig. 7: (a) The influence of the dye initial concentration on the color removal (b) UV spectra changes during electrolysis of the methylene blue on the SnO_2 anode. Electrolyte: $1\% \text{ KCl}$, $i = 60 \text{ mA/cm}^2$, $T = 25^\circ\text{C}$.

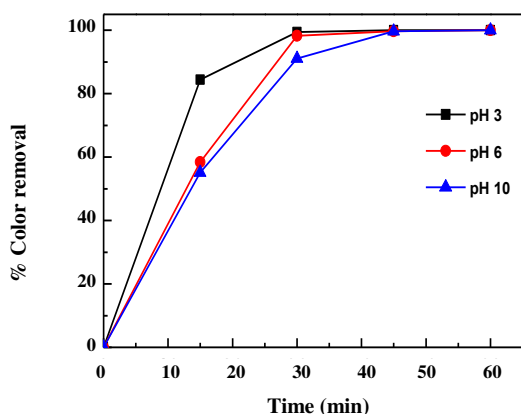


Fig. 8: Effect of pH on color removal on SnO₂ electrode of the MB dye 100 mg L⁻¹ solution during the different pH values ($i = 60 \text{ mA/cm}^2$, $T = 25^\circ\text{C}$, electrolyte: 1g/L KCl after 60 min of electrolysis).

pH can be explained by the production of higher amounts of oxidants (OH[•]) from water at acidic conditions[41]. In the solution, the hypochlorous acid and hypochlorite ions are in-situ electrogenerated from the active chlorine (Equations (5-7)), which reach an equilibrium (Equation (10)).



The increase in color removal at low pH can be ascribed to the higher standard potentiality of Cl₂ and HClO than ClO⁻. Therefore, the oxidative ability of Cl₂ and HClO species is stronger than ClO⁻. In addition, the formation of these species at various pH ranges is as follows: Cl₂ (pH ≈ 3), HClO (8 > pH > 3) and ClO⁻ (pH > 8) [24, 42].

Chemical oxygen demand

Fig. 9 presents the COD, and color removal during the degradation of 100 mg/L MB. The complete removal of color was achieved within 30 min of electrolysis. At the same time, the COD removal has reached 47.6%. However, 80.1% of COD was removed after 120 min of electrolysis. The complete color removal does not mean the whole degradation of organics but more destruction of the chromophores, indicating that MB was oxidized firstly to colorless intermediates. It is well known that the removal of color is due to the cleavage of the chromophores bond in the dye molecule. Nevertheless, the oxidation of the aromatic ring, compounds take a long time and hence the removal of COD is limited because of the formation of lower molecular weight aliphatic compounds, which are resistant to chlorine/hypochlorite attack[43].

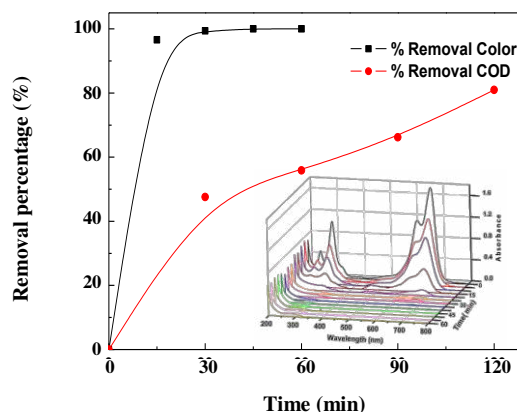


Fig. 9: Color and COD removal during electrochemical degradation of Methylene blue in optimal conditions (initial pH 3, current density 60 mA/cm², KCl 1%, Methylene Blue concentration 100 mg/L, reaction temperature 25°C, reactor volume 100mL).

CONCLUSIONS

This work is considered as the first attempt to investigate the degradation of MB in electrochemical treatment using SnO₂ electrode. The effects of various operating parameters were studied. Operating at acidic pH_i, and higher chloride concentration, increasing current density and decreasing initial dye concentration favored the decolorization efficiency. The electro-oxidation process could efficiently remove the MB in solution. The MB was completely decolorized at a current density of 60 mA/cm² and 1% KCl within 60 min of electrolysis. However, 80.1% of COD was removed after 120 min of electrolysis under the optimum conditions. The degradation followed a pseudo-first-order kinetic reaction, the indirect electro-oxidation has controlled the electrochemical degradation of the MB dye since in the presence of KCl some strong oxidants have generated. Besides, this study has illustrated revealed that tin oxide can act as an efficient material anode to perform better degradation of MB dye from the wastewaters of textile industries.

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