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Electrochemical Oxidation of Methylene Blue Using Carbon Electrode from Battery Waste

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ABSTRACT

Methylene blue in the environment can disrupt the ecosystem because it does not decompose easily. Therefore, this research aims to oxidize methylene blue using an electrochemical oxidation method. The electrochemical oxidation of methylene blue was successfully carried out using carbon electrodes from battery waste. The influence of pH value and electrolysis time was successfully investigated using a UV-Vis spectrophotometer, and the decreased absorbance (DA(%)) was also analyzed. Based on the results, the optimum pH for electrochemical oxidation with a carbon electrode is at pH 1. It was possible to reduce the absorbance at this pH with a decreased absorbance of 56%. There was a decrease in absorption in the UV and visible regions. The optimum time for methylene blue electrochemical oxidation was 15 minutes, with a decreased absorbance percentage at 100%. The electrochemical oxidation method is simple and easy to use. This finding can be an excellent and effective wastewater treatment method.

Keywords: methylene blue, electrochemical, oxidation

1. INTRODUCTION

Environmental pollution is caused by synthetic dye waste from the textile industry. The pollution of water resources by wastewater containing artificial dyes, particularly from the textile sector, is a major ecological problem [1]. The substances employed for dyeing could pose serious health threats, such as skin irritations, allergic reactions, and even life-threatening situations. Dyes are hazardous, toxic, and can damage the environment [2]. Therefore, reducing the compound's concentration is crucial to reduce risk factors. These substances must be eliminated before the wastewater is released because they are detectable even at very low concentrations [3].

Methylene blue (MB) is a heterocyclic aromatic substance, its molecular structure represented as $C_{16}H_{18}N_3SCl$. Its application is in various industrial activities, especially as a textile dye [4]. The molecular weight of methylene blue, an aromatic heterocyclic basic dye, is 319.85 g mol^{-1} [5]. Methylene blue is a widely recognized primary thiazine dye with a maximum wavelength of 663 nm. Due to its high water solubility, it can be dissolved in water to form a stable solution at room temperature [6]. Methylene blue is a positively charged compound that belongs to the polymethine dye class and has an amino autochrome unit [7]. According to the International Union of Pure and Applied Chemistry (IUPAC), the chemical name is [3,7-bis(dimethylamino) phenothiazine chloride tetra methylthionine chloride], and its color index (CI) is 52015. Figure 2 shows the structure of the methylene blue molecule.

Generally, these dye-based compounds tend to be resistant to degradation [8]. Chemical coagulation [9], biological treatment [10], and activated carbon adsorption [11], [12] are the conventional methods for treating wastewater from textile industries. However, these methods are not sustainable because it is still difficult to eliminate the large amount of hazardous sludge. Furthermore, dye materials may harm the microorganisms found in treatment plants and gradually lose color when treated with conventional

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biological wastewater treatment. As a result, much research has been done on alternative oxidation techniques like electrochemical, photocatalytic, and ozonation oxidation. The advantages of electrochemical technologies, including their cost-effectiveness, environmental compatibility, and versatility, encourage their potential application in wastewater treatment. Another benefit of the electrochemical oxidation method is that it does not produce waste or sludge compared to conventional methods. Therefore, electrochemistry presents viable methods for anticipating pollution issues in the processing industry, and from early research to the present, there has been much interest in the viability of electrochemically converting or destroying organic substrates in wastewater. Electrochemical oxidation (EO) has recently drawn much interest as a highly successful technique for eliminating contaminants. The primary factors contributing to this technique's high dependability and widespread use are its efficiency and environmentally friendly results [13], [14].

Gunawan et al. [15] reported the degradation of methylene blue using Pb/PbO_2 electrode in seawater solution. The degradation efficiency was 92,68% with an electrolysis time of 60 minutes. Riyanto and Mawazi [16] fabricated C-PVC for the degradation of methylene blue with optimum conditions in 60 minutes and 1,5 A. Fadillah et al. [17] We developed an alginate-modified graphene adsorbent combined with an electrochemical method for treating methylene blue. The optimum condition was found at 30 minutes with a degradation percentage of> 90%. Several studies show that the pH of the methylene blue oxidation electrolyte solution has never been investigated, and the disadvantage of the results is the longer electrolysis time.

In this work, the electrochemical oxidation of methylene blue (MB) has been successfully investigated using carbon electrodes from battery waste. The effect of pH and electrolysis time was determined using a UV-Vis spectrophotometer.

2. METHODS

2.1. Instrument and Materials

All chemicals used were prepared using deionized distilled water. Sodium hydroxide (NaOH) and sodium chloride (NaCl) were used for pH adjustment. Methylene blue (MB) was obtained from Merck (Germany). A carbon rod was used as a cathode, and an anode was obtained from battery waste. The carbon rod was manually removed from the used battery, then washed with detergent and rinsed with distilled water. A spectrophotometer UV-Vis (Safas Monaco SP2000) was used to measure the absorbance of the solutions. The decreased absorbance (DA(%)) was determined by following Equation (1) [18].

$$DA(\%) = \frac{A_0 - A_t}{A_0} \; x \; 100\% \qquad (1)$$

A_o and A_t represent the initial and final absorbance, respectively. The electrolysis condition was set at 10 volts, and the schematic reactor is shown in Figure 1.

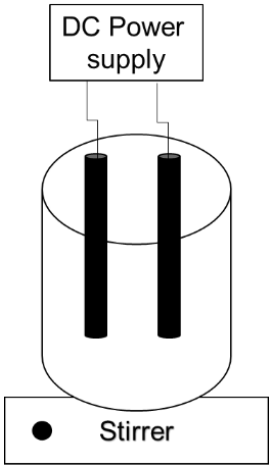

Figure 1. Electrolysis reactor

2.2 Effect of pH

The effectiveness of electrooxidation was investigated at pH levels 1–12 by varying the pH of a dye solution containing 50 mg/L in 100 mL. The desired pH was achieved by titrating the samples with NaOH or HCl. The samples were subjected to voltage using a carbon electrode, and the dye absorption was measured using a UV-Vis spectrophotometer.

2.3 Effect of electrolysis time

100 mL of dye solution was placed in the reactor. The samples were then electrolyzed at various times (5, 10, 15, and 20 minutes). The voltage was kept at 10 volts, and the pH was set in optimum condition. A Spectrophotometer UV-Vis was used to monitor the color changes in the dye solutions to examine electrolysis time's impact on the percentage of decreased absorbance.

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3. RESULTS AND DISCUSSION

Figure 2 illustrates the redox reaction of methylene blue. Most research on methylene blue redox reactions concentrated on converting kinetics into leucomethylene blue. Methylene blue's reduction-oxidation characteristics make it a valuable indicator in analytical chemistry. When exposed to a reducing agent, methylene blue becomes less color and becomes leucomethylene blue (LMB) [19].

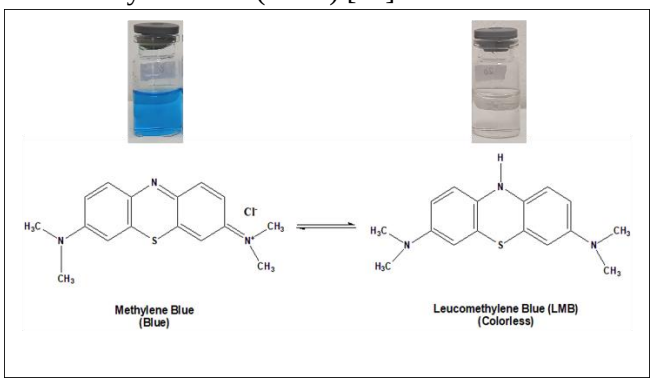

Figure 2. An oxidation-reduction reaction of methylene blue

3.1 The effect of pH

Figure 3 shows the influence of pH on the absorption of methylene blue at 10 volts. There are peaks in the ultraviolet and visible regions at wavelengths 292 nm and 662 nm, respectively. This is similar to previous reports by Yu et al. [20] and Dinh et al. [21]. The absorption peak at the wavelength of 292 nm shows the properties of phenothiazine species and benzene rings. While at 662 nm, it shows the chromophore group of methylene blue [20].

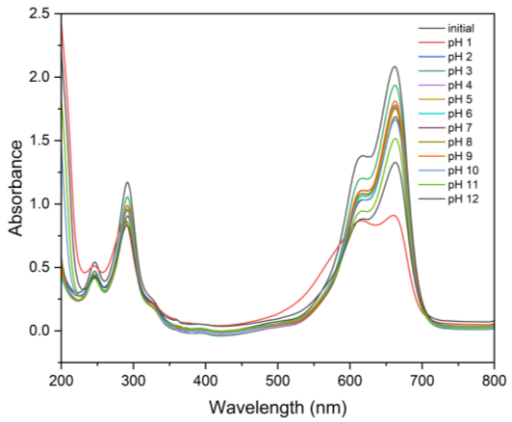

Figure 3. UV-visible spectra of methylene blue with different pH values.

Figure 4 illustrates the percentage of decreased absorbance (DA) of methylene blue through the electrochemical oxidation process at various pH values. The color intensity of the methylene blue solution is influenced by the concentrations of OH^- and H^+ ions. At pH 1, the absorption spectra of methylene blue showed the most effective decolorization, with the absorption peaks declining rapidly. The absorption at the peak of 662 nm decreased, indicating the breakdown of the methylene blue dimer and the destruction of chromophore groups. A decreased absorbance (DA(%) was achieved at this pH of about 56%, while only about 36% was achieved at pH 12. This suggests that the electrooxidation process is more effective in acidic conditions. The increased production of oxidants (OH•) from water under acidic conditions explains the higher efficiency of methylene blue oxidation at low pH [22]. The active chlorine in the solution electrogenerated the hypochlorous acid and hypochlorite ions in situ until an equilibrium was reached (Eq. 2).

$$HClO \rightleftharpoons H^+ + ClO^- \quad (2)$$

Meanwhile, compared with the electrocoagulation methods, the pH of the solution can influence the reactions that occur during the electrocoagulation process. In the alkaline condition, it accelerates the coagulation process. At neutral (pH 7), the reaction between H_2O ions and Al leads to $Al(OH)_2$, $Al(OH)_3$, and H_2. Under acidic pH conditions, $Al(OH)_2$, H_2, and O_2 are produced, while alkaline pH conditions produce $Al(OH)_3$ and H_2O [23]. According to research by Guna et al. [23], $Al(OH)_3$ can affect the speed of the deposition process because $Al(OH)_3$ has a larger weight fraction and density compared to $Al(OH)_2$.

It can be concluded that pH 1 is the optimum pH for the electrooxidation of methylene blue. Previous studies have also demonstrated that a decrease in COD values and degradation of methylene blue were achieved at acidic conditions with pH levels of 1.7 to 2.7 [24].

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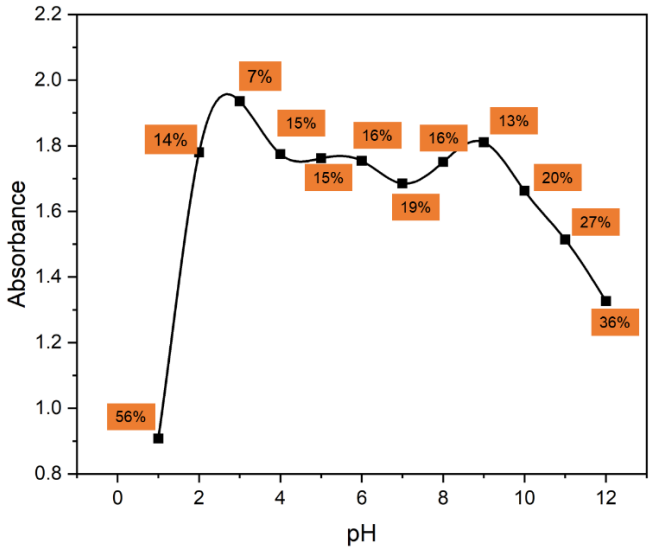

Figure 4. Effect of pH value on the DA(%) of methylene blue

3.2 The effect of electrolysis time

In this study, the variations of electrolysis time were 5, 10, 15, and 20 minutes. The effect of varying electrolysis time on the electrooxidation of methylene blue has been studied. The electrooxidation process was monitored using a UV-Vis spectrophotometer. Figure 5 shows a dominant peak in the ultraviolet and visible region at 292 nm and 662 nm, respectively. For both peaks, the absorbance decreased during the electrolysis time from 5 minutes to 20 minutes. After 5 minutes, there was a sharp drop in the peak, and after 10 to 20 minutes, there was no more absorbance. This shows that the peak absorption decreased with the increasing electrolysis time.

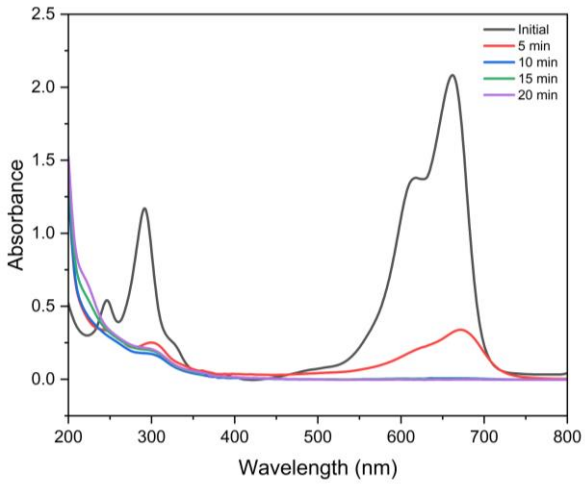

Figure 5. UV-visible spectra of methylene blue with different electrolysis times.

As illustrated in Figure 6, the electrooxidation of methylene blue increased rapidly with electrolysis time, reaching its maximum at 15 minutes. Methylene blue's decreased absorbance (DA(%)) also progressively improved as electrolysis time was extended. This suggests that the oxidation rate of methylene blue is enhanced with longer electrolysis durations. The degradation process of methylene blue is closely linked to the concentration of hypochlorite ions generated electrochemically in the solution. As the electrolysis time increases, the production of hypochlorite ions rises at a constant current density. Based on the results, the optimum electrolysis time was 15 minutes. In the future, this technique can be applied to treat real dye wastewater with the advantage of this method as a low-cost material with a high-efficiency level. Table 1 summarizes various methods for methylene blue degradation.

Table 1. Comparison of various reports on the degradation of methylene blue.

No	Method	Electrode/material	Efficiency (%)	Time (minutes)	Ref.
1	Electrochemical	Pb/PbO_2	92,68	60	[15]
2	Electrochemical	C-PVC	-	60	[16]
3	Electrochemical	Alginate-modified graphene	>90	30	[17]
4	Adsorption	Activated carbon	80	30	[25]
5	Electrocoagulation	Iron rod (anode)-graphite (cathode)	>50	60	[26]
6	Electrochemical	Carbon electrodes from battery waste	100%	15	This work

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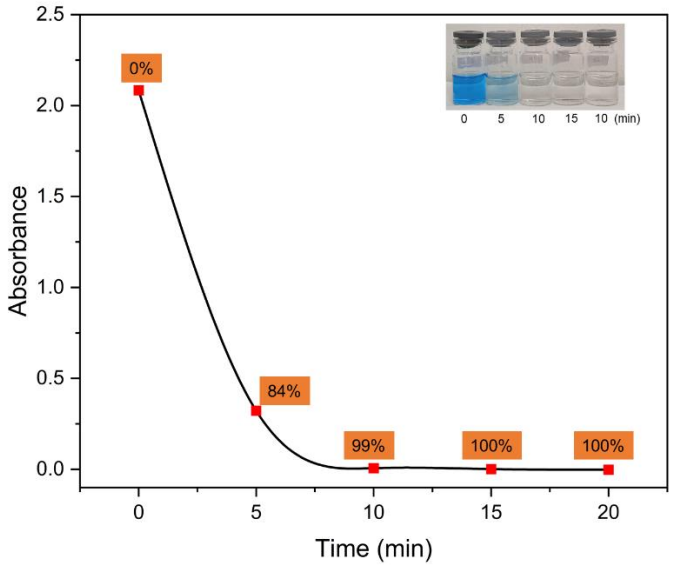

Figure 6. Effect of electrolysis time on DA(%) of methylene blue

4. CONCLUSION

It can be concluded that the electrochemical oxidation of the methylene blue compound was successfully carried out. Carbon electrodes from battery waste can be used in this process. The optimal pH value for the electrooxidation process was achieved at pH 1 with a decreased absorbance of 56%. The optimal time for 100% methylene blue electrooxidation was 15 minutes.

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