Removal of Methylene Blue by Direct Electrochemical Oxidation Method Using a Graphite Anode

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Abstract. The present work is to degrade methylene blue dye from aqueous solution by direct electrochemical oxidation technique. For this purpose an electrochemical cell was used comprising of two electrodes made from graphite as anode and stainless steel 316 grade as cathode. Different operating parameters that affected the treatment process such as current density, electrolyte temperature and initial dye concentration had also been studied. The reaction mechanism of direct anodic oxidation of M.B. is undertaken and the kinetic follows a pseudo first order reaction. Results revealed that at 20ºC electrolyte temperature, 10 mA/cm² current density, 0.5 g/l Na₂SO₄ as supporting electrolyte and 60 min electrolysis time, the decolorization percents for initial concentrations of M.B. 50 and 400 mg/L were 72.51% and 77.94% respectively while at 60ºC the decolorization percent 99.75% and 99.60% respectively for the same others operating conditions. The power consumption increased from 2.055 to 11.714 Kw.h/m³ at applied voltage 14.6 V and 28.5 V respectively.

Keywords: Methylene Blue, Electrochemical Oxidation Treatment, Direct or Anodic Electrochemical Oxidation Process, Kinetics, Industrial Wastewater Treatment.

1. Introduction
Water is an important requirement for all living bodies. It has a significant role for industrial processes [1]. One of the greatest current and future challenges that face humankind is water deficiency as the world's population and water consumption rates continue to grow [2]; therefore the protecting of the fresh water resources has become a main worry for many countries in the world [3]. Large amount of manufacturing wastewater containing nondegradable and toxic organic compounds have recently been discharged into the environments [4]. Different types of dyes are formed worldwide and are used in several industries such as textile, paper, cosmetic, food and pharmaceutical industry [5].

Colored wastewater from textile industry affected the ecosystem in many ways, color reduce penetration of high into the water bodies thus affecting the photosynthetic activity of aquatic plants[6]; so that these pollutants should be destructed before the wastewater can be discharged [7].

2. Wastewater Treatment Methods
Various techniques are being used to carry out the elimination of toxic compounds from dye wastewater. These comprise physical, chemical and biological methods such as chemical oxidation, adsorption, and coagulation, flocculation combined with flotation and membrane filtration [8]. Biological treatment are generally unsuccessful for dye degradation because of the presence of aromatic rings and high biochemical stability [9], and it is obvious that chemical treatment happens just under conditions that electrostatic property of both pollutant and coagulant is compatible[10].
Physical methods although effective in decolorization have the disadvantage of sludge formation which requires the regular regeneration of the adsorbents [11]. These reasons pushed the scholar's efforts towards developing powerful and active treatment technologies [10].

In recent years, Electrochemical Advanced Oxidation Processes (EAOPs) have been proposed to be the alternative and effective ways for the treatment of wastewater. They are compatible for environment technologies which own advantages compared to other technics of high degradation efficiency, easy operation, no chemical reagents needed and preventing secondary pollution. Among EAOPs, one can name electro fenton oxidation $\text{H}_2\text{O}_2/\text{Fe}^{2+}$, electro photo fenton oxidation $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ with UV, and electrochemical oxidation (EO) [7, 11]. Electrocoagulation, electroflotation, electroreduction also consider usual methods of electrochemical treatments [12].

Electrochemical oxidation has attracted wide interesting as one of the environmental friendly technologies in wastewater treatment processes. It is an effective way to treat dye wastewater and considered to be a very powerful method for breaking up most of the resistance organic compounds [12, 18]. The study of E.O. was begun in 19th century when the dissociation of cyanide into its ions was tasted [1]. Mainly used for degradation aromatic compounds, dyes, pharmaceutical waste, pesticides, and other organics [13].

### 3. Theory

Electrochemical oxidation of pollutants can take place through two different oxidation mechanisms as shown below:

#### 3.1 Direct anodic oxidation:
Where the pollutants are destroyed at the anode surface as explained in figure (1)

![Figure 1. Direct oxidation mechanism.](image)

Direct oxidation of pollutants takes place in two steps:

- Diffusion of pollutants from the bulk solution to the anode surface
- Oxidation of pollutants at the anode surface [14]

The organic pollutants are oxidized on the anode surface by the adsorbed hydroxyl radicals electro generated by water [11]

$$2\text{H}_2\text{O} \rightarrow 2\text{OH}^+ + 2\text{H}^+ + 2\text{e}^- \quad (1)$$

#### 3.2 Indirect anodic oxidation:
Anodically generated strong oxidizing agent such as chlorine and/or hypochlorite can be used to destroy oxidizable pollutants. In most cases, both inorganic and organic pollutants can be eliminated in the presence of a suitable amount of chloride as explained in figure (2) [14, 15].
In indirect electro oxidation, chloride salts of sodium or potassium are added to the wastewater for better conductivity and generation of hypochlorite ions. The reaction of anodic oxidation of chloride ions to form chlorine is given as [16, 17]:

\[
2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \quad \text{Anode reaction (2)}
\]

At bulk solution reactions, the liberated chlorine form hypochlorous acid:

\[
\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^- \quad \text{(3)}
\]

\[
\text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{H}^+ + 2\text{e}^- \quad \text{(4)}
\]

And further dissociates to give hypochlorite ion.

\[
\text{HOCl} \rightarrow \text{H}^+ + \text{OCl}^- \quad \text{(5)}
\]

\[
\text{M.B.} + \text{OCl}^- \rightarrow \text{dye intermediate} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Cl}^- \quad \text{(6)}
\]

\[
\text{M.B.} + \text{HOCl} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{HCl} \quad \text{(7)}
\]

4. Experimental

4.1 Chemical materials and method

Stock solution was prepared by dissolving 1 g/L of M.B. dye (C_{16}H_{18}ClIN_{3}S, Merk, Germany, M.wt:319.85 g/mole) in deionized water. Amount of Na_{2}SO_{4} salt is added for supporting electrolyte to increase conductivity. MB is a basic dye therefore pH of electrolyte solution approximately 7 and it is the same after experiment's time end. Working M.B. solution containing solutions of desired concentrations was obtained by diluting the stock solution with deionized water. 0.5g/l of Na_{2}SO_{4} added for each concentration. The molecular structure of the methylene blue is illustrated in figure (3).

![Methylene Blue Structure](image)

Figure 3. The molecular structure of the methylene blue.
The electrochemical oxidation of methylene blue was conducted in an electrochemical cell as shown in figure (4). The cell comprised of two compartments naming anodic and cathodic.

![Experimental set-ups](image)

**Figure 4.** Experimental set-ups.

1. Water bath  2. Power supply  3. Resistance box  4. Ammeter  5. Voltmeter  
6. Graphite  7. Stainless steel  8. Thermometer  9. Electrolytic cell  10. Stand  
11. Electrical wires

Parallel rectangular shape (semi-cube) electrode used as the working electrode (Anode) made of special type of graphite having the dimensions, length 1.1 cm, width 0.6 cm, and height 4 cm. The total surface area of electrode submerged in the electrolyte was 14.26 cm$^2$. Rectangular plate used as counter electrode (Cathode) made of stainless steel (316) grade having the dimensions, length 4 cm, width 5.5 cm. The side which not facing the anode was totally isolated by using self-adhesive paper to control the deposit area. The total surface area submerged was 22 cm$^2$. Two electrodes immersed in 0.5 L solution and the distance between them 2 cm. Total electrolysis 1 hr. Samples of M.B. solution were collected at constant interval 5 min for analysis the remaining concentration.

### 5. Analytical method

A UV-vis spectrophotometer (JENWAY 6800UV/VIS, Britain) was used to measure the concentration of M.B. at 661nm. The removal percent was calculated by equation (8): 

$$\text{Removal \%} = \frac{C_0 - C_t}{C_0} \times 100\%$$ \hspace{1cm} (8) 

Where $C_0$ and $C_t$ are concentration of the M.B. initially and at time t (mg/l) respectively.

The specific energy consumption ($E_c$ in kWhm$^{-3}$) is determined using equation (9):

$$E_c = \frac{U.I.t}{3600V} \times 10^{-3}$$ \hspace{1cm} (9) 

Where $U$ is the average cell voltage (V), $I$ is the current (A), $t$ is the electrolysis treatment time (s), and $V$ is the volume of electrolyte solution (m$^3$).

### 6. Kinetics Study of M.B. Degradation
The governing kinetic equation for color removal can be written as considering both OH radical and M.B. concentration taking part in the reaction, removal rate equation can be expressed as:

\[
d \frac{dc}{dt} = -K \cdot [C_{M.B.}]^n \cdot [OH]^m
\]  

(10)

Working under galvanostatic condition (constant current), the concentration of OH\(^+\) can be approximated is constant (in steady state), thus \(K \cdot [OH]^m\) can be written as \(K^* \cdot C_{o}^q\).

\[
K \cdot [OH]^m = K^* \cdot C_{o}^q = K^*
\]

(11)

Thus equation (3) can be written as:

\[
- \frac{dc}{dt} = K^* \cdot [C_{M.B.}]^n
\]

(12)

In order to determine order of the reaction a plot between ln(C/C\(_0\)) Vs.t was constructed.

**Figure 5.** The kinetic fitting curve of M.B. direct removal (Na\(_2\)SO\(_4\) 0.5 g/l, current density 20 mA/cm\(^2\), at 40°C).

**Table 1.** The first order reactions kinetic parameters of different concentrations of M.B. removal process.

| \(C_{o}\) (mg/l) | \(K^*\) (min\(^{-1}\)) | \(R^2\) |
|-----------------|---------------------|-------|
| 50              | 0.036               | 0.964 |
| 100             | 0.040               | 0.960 |
| 200             | 0.015               | 0.981 |
| 400             | 0.012               | 0.948 |
Figure (5) between $\ln(C/C^0)$ and time shows that $\ln(C/C^0)$ increase in almost linear relationship with time, so that the electrochemical reaction of methylene blue removal follows a pseudo first-order reaction, $n=1$, and that in a good agreement with findings by (Huimin Yang) [7].

Integrate equation (12) with following boundary conditions:

$$
\int_{C_0}^{C_t} \frac{dc}{c} = K^* \int_0^t \, dt
$$

$$
-\ln(C) = K^* t
$$

By taken ln to equation (11) equation (15) can be obtained:

$$
\ln K^{**} = \ln K^* + q \ln C_0
$$

By fitting $\ln K^{**}$ and $\ln C$ in figure (6) to get intercept $\ln K^*$ and the slope $q$ of equation (15).

![Figure 6. fitting between $\ln C$ and $\ln K^{**}$](image)

Slop ($q$) = -0.5283

Intercept ($\ln K^*$) = -0.7, taken exponentional to get value of $K^*$

$$
K^* = 0.4965 \, \text{mg/L.min} = 8.2764 \times 10^{-3} \, \text{mg/L.s}
$$

The values of the correlation coefficient ($R^2$) implies that equation (15) is acceptable and the relation between OH$^-$ conc. and M.B conc. is credible. M.B. removal rate equation can be expressed as:

$$
- \frac{dc}{dt} = 8.2764 \times 10^{-3} \, C_0^{-0.5283} \, \cdot M.B.
$$

7. Results and Discussion

7.1. Effect of current density

The effect of current density was tested for initial dye concentration of 50-400 mg/l in the range 10-30 mA/cm$^2$. Figure (7) shows the effect of current on removal percent. it has been noticed that the decolorization rate or the oxidation rate of Methylene Blue increase linearly with increase in current density, due to the fact that by increasing the current density, it means a large amount of charge entering the electrochemical cell and electro-generating more of hydroxyl radicals from electrolysis of water at anode surface according to the following equation (1):
Which is in turn will increase the oxidation rate of M.B.

\[ 2\text{H}_2\text{O} \rightarrow 2\text{OH}^- + 2\text{H}^+ + 2e^- \quad E^\circ = -2.8V \]  
(17)

7.2. Effect of electrolyte temperature

The electrochemical reaction of M.B. is highly electrolyte temperature dependent and shows an increase of it will strongly expedite the removal of M.B. Thus the effect of electrolyte temperature considers one of the most important parameters that are effect on the anodic oxidation process. It can be seen from figure (8) that an increase of electrolyte temperature leads to an increase the decolorization rate. A sharp increase was happened especially when electrolyte temperature increase from 20°C to 40°C. On the other hand a slight increase can be noticed at 60°C, removal of methylene blue is nearly completely. The main influence of the electrolysis temperature on the decolorization rate is the production of hydroxyl radicals so that it may be obvious to operate at higher temperatures for complete removal of M.B.

7.3. Effect of initial dye concentration
Figure (9) shows that as the initial M.B. concentration varied from 50 to 400 mg/l and there is no very evident effect of increasing concentration on the removal and that was in a good agreement with findings by (Yao Xing Liu) [9] for example at 20°C when the initial concentrations were 50 and 400 mg/l, the decolorization rates were 76.590% and 77.709% respectively after 60 min of electrochemical treatment for the same others operating conditions i= 20 mA/cm² while at 60°C high M.B removal rates were obtained for all four dye concentrations studied almost complete removal at all current densities 10, 20 and 30 mA/cm².

![Figure 9. Effect of initial dye concentration on removal percent at 40°C and 30 mA/cm²](image)

8. Conclusion

Direct electrochemical oxidation of methylene blue with sodium sulphate as supporting electrolyte is used to treat the textile industrial effluents. The process was carried out using graphite as anode and stainless steel 316 grade as cathode. The optimal conditions were 0.5 g/l from Na₂SO₄ salt and 60 min for electrolysis time. Under these experimental conditions, the removal percent in creased with increasing current density and electrolyte temperature while initial dye concentration had no evident effect on the decolorization percent.

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