

original article

Decolorization of methylene blue by the electro-Fenton process using stainless steel mesh electrodes

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ABSTRACT

Aim: In this study, the decolorization of methylene blue (MB) by the electro-Fenton process using stainless steel (SS) mesh electrodes was examined.

Materials and Methods: The effects of initial dye concentration, pH, and ratio of Fe: H₂O₂, current density, and type of electrode were studied. The kinetics of the reactions was also studied.

Results: The highest removal rate 99% was obtained at pH 3 within 20 min. Kinetics experiment studies showed that removal of dye was faster at lower initial dye concentrations. The results revealed that color removal was highest at a Fe²⁺:H₂O₂ ratio of 1:4. An increase in current density resulted in an increase in oxidation rate and faster removal of color. The results demonstrated that increasing the size of the mesh pores led to an increase in the percentage of dye removal. The highest removal percentage (94.5%) was observed in 25 min with a mesh 2 electrode. The constant rate of dye removal on steel mesh 2 was 6.6 times higher than a steel plate. Energy consumed in this state was = 1.6 kWh/m³, compared to 2.6 kWh/m³ under other conditions.

Conclusion: Using SS mesh electrodes was very effective in color removal for MB under optimal conditions. The present study showed that increasing the steel mesh size improved the conditions for color removal and reduced the energy consumption. Therefore, it is suggested that steel mesh be used as an electrode for electrochemical processes.

Key words: Advanced oxidation processes, electro-Fenton, methylene blue, stainless steel mesh, wastewater

INTRODUCTION

Synthetic dyes make our world beautiful and their application is increasing in multiple areas, such as various branches of the textile industry, leather tanning, paper production, food technology, agricultural research, photoelectrochemical cells, and hair dye.^[1] Releasing colored waste into the environment is an important esthetic source of pollution and disturbance to aquatic life.^[2,3] Synthetic dyes possess

special properties such as photolytic stability and resistance to bacterial and chemical degradation.^[4] Thus, there is a clear need to treat dyed wastewaters before they are discharged into the environment. However, dyes cannot be removed using conventional wastewater treatments.^[5] Traditional chemical and physical treatments separate dyes

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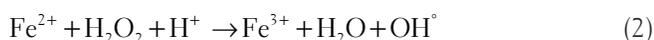
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from the aqueous environment without any changes in their chemical structure. These nondestructive methods include adsorption (generally with activated carbon), coagulation and sedimentation, flotation, distillation, extraction, volatility to air, membrane processes (micro-ultra-nano filtration, reverse osmosis, and ion exchange), and coagulation with lime, aluminum, or iron salts.^[6] These limitations of conventional wastewater treatment methods can be overcome by employing advanced oxidation processes (AOPs). AOPs are powerful and promising methods for the efficient removal of persistent organic pollutants from wastewater.^[7] AOPs are environmentally friendly chemical, photochemical, and electrochemical methods which have a common feature of *in situ* production and use hydroxyl radical ($\cdot\text{OH}$) as the main oxidizing agent.^[8] The electro-Fenton process is a powerful and effective technology for the destruction of a large number of hazardous and organic pollutants. In the electro-Fenton process and related methods, Fe^{3+} can be reduced to Fe^{2+} at the cathode, acting as an electrochemical catalyst.^[9] The general mechanism of the Fenton process was introduced by the formation of the hydroxyl radical according to the classic Fenton reaction.^[10]



Since this reaction is carried out in acidic medium, it can be written as follows:



Importantly, only a small quantity of catalyst Fe^{2+} is needed, because this ion is regenerated in reaction 3 between H_2O_2 and Fe^{3+} :



The effectiveness of electrochemical oxidation strongly depends on the nature of the electrode material. Studies have investigated electrodes such as graphite carbon, cast iron, active carbon fiber, Ti/Pt, Pt, TiO_2 , IrO_2 , PbO_2 , or boron doped diamond for the decolorization of colored wastes.^[11] It has been found that a porous electrode is capable of reducing the ferric species to ferrous species more efficiently, therefore increasing the rate of the reaction.^[12] The feasibility of utilizing stainless steel (SS) mesh in methanol fuel cells demonstrated more effectiveness in electrical performance than with nonporous graphite.^[13] SS mesh is less expensive and corrosion resistance so cathodes made of this material have high specific surface areas and can, therefore, achieve performance similar to carbon electrodes.^[14] No systematic investigation has been carried out on the decolorization of methylene blue (MB) dye using SS mesh electrodes. The aim of this research was to decolorize MB by the electro-Fenton process utilizing SS mesh electrodes and to determine the most effective parameters for removal, such as pH, initial color concentration, electrical current, and $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ ratio. In addition, the reaction kinetics and energy consumption of this system were studied.

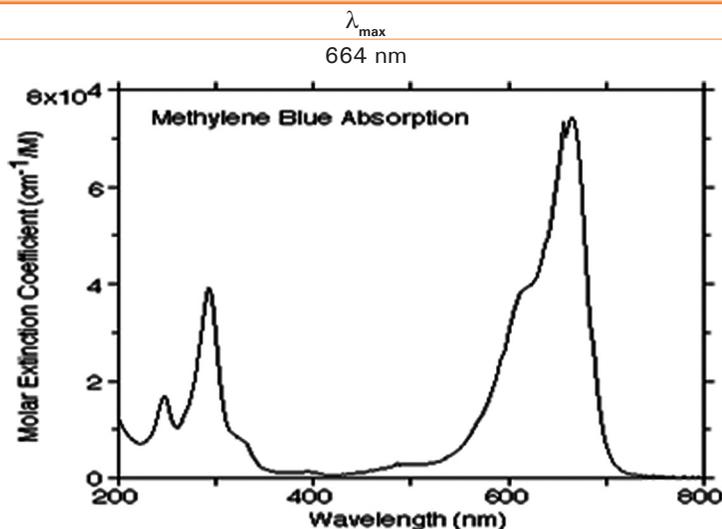
MATERIALS AND METHODS

MB was purchased from Dystar (Munich, Germany) and used without further purification. The chemical structure of the dye is illustrated in Table 1. For the experiments, dye solutions were prepared utilizing distilled deionized water. Analytic grade ferrous sulfate 7 hydrate, hydrogen peroxide (30% w/v), sulfuric acid, sodium hydroxide, and sodium chloride were purchased from Merck, and all solutions were prepared in distilled water. Fenton oxidation of the MB occurred in a single chamber reactor with a volume

Table 1: Characteristics of methylene blue

Structure

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of 500 ml. The SS mesh electrodes with size of 2 cm were connected to a DC power supply (Atten APS3005-3D). pH was adjusted to the desired value by 1 M sulfuric acid and 1 M sodium hydroxide. The experiments were carried out at laboratory temperature. A specific volume of MB solution of determined concentration was inoculated into the reactor until the volume reached 500 ml. After adjusting the pH, a specific amount of ferrous sulfate and the necessary amount of hydrogen peroxide were added to the solution. Thereafter, at different time periods, samples of the solution were taken and filtered. The samples were immediately analyzed for color intensity at a wavelength of 664 nm using a UV-VIS 9200 spectrophotometer (RAYLEIGH). The experiments were carried out under various conditions, testing different values for pH (2, 4, and 6), electrical current (100, 200, 400, and 600 mA), ratios of $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ (1:2, 1:4, 1:6, and 1:8), concentrations of MB (0.05, 0.1, 0.2, and 0.4 mM), and mesh size (2, 4, and 10). The optimal conditions were determined and the results of the different electrodes were compared. The percentage of color removal was calculated using equation 4:

$$\text{Color removal (\%)} = \frac{A_0 - A_t}{A_0} \times 100 \quad (4)$$

Reaction kinetics was studied by plotting variations $\ln A/A_0$ against oxidation time. The direct relationship between these two parameters demonstrated that the reaction is a pseudo first-order reaction. The following kinetic equation was utilized:

$$\frac{\ln A_0}{A} = K_{\text{obs}} \times t \quad (5)$$

Where A is absorption in time t , A_0 is the absorption of untreated sample, and K_{obs} is the constant rate of pseudo first order degradation. The energy consumption was calculated by the equation 6:

$$E = \frac{U \times I \times t}{V} \quad (6)$$

Where E is the energy consumed (kWh/m^3), U is the applied voltage (V), I is the current intensity (ampere), t is time (h), and V is volume of the treated solution (L).

RESULTS

Effect of initial pH

The pH of the solution is an important control parameter in all Fenton processes. The experiments were performed at a pH within the range of 2–6. Figure 1 illustrates the effect of pH on the rate of degradation of MB. The highest removal percentage and the highest rate constant were obtained at pH 3 and were respectively 99% and 0.002 s^{-1} at a time of 35 min. The optimum pH was found to be 3. At pH 2, the percentage of color removal was 98.5%.

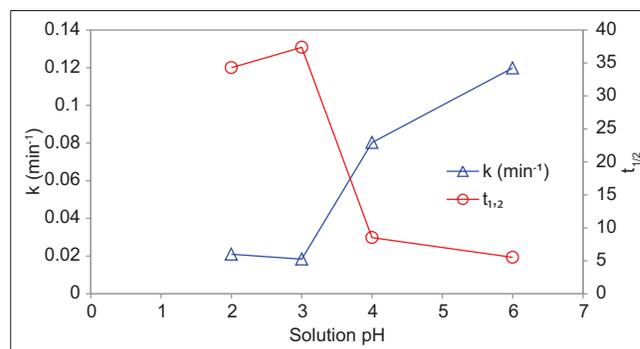


Figure 1: The effect of initial pH on the apparent rate constant (k_{app}) and half-life ($t_{1/2}$) in the decolorization of methylene blue (Fe^{2+} : 1 mM, H_2O_2 : 0.5 mM, dye concentration: 0.05 mM)

Effect of initial dye concentration

To study the effect of initial dye concentration on decolorization rate, solutions of MB with concentrations of 0.05, 0.1, 0.2, and 0.4 mM in acid medium were treated in the presence of catalyst Fe^{2+} (1 mM), H_2O_2 (0.5 M), and at a current of 100 mA. The results revealed that the highest removal occurred with initial lower concentrations of dye. In this study, the highest removal was 99%, which occurred at an initial dye concentration of 0.05 mM and time of 80 min [Figure 2].

Studying reaction kinetics in this step demonstrated that increasing the dye concentration resulted in a decreased rate constant of the reaction. As illustrated in Figure 3, at lower concentrations, the rate constant is higher. At the beginning of the reaction, in all states, the reaction rate was fast and slowed as time progressed. The degradation reaction of dye in the present study follows a pseudo first order equation. It was observed that the highest degradation rate was obtained at the lowest concentration of dye (0.05 mM), which was $= 9.79 \times 10^{-4} \text{ s}^{-1}$ and nearly four times higher than the rate at the highest concentration of dye (0.4 mM).

Determination of optimum ratio of $\text{Fe}^{2+}:\text{H}_2\text{O}_2$

The other effective factor on reaction rate is the ratio of Fe^{2+} to H_2O_2 . To determine the optimum ratio of $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ on the decolorization of MB, the experiments were carried out by changing the concentration of H_2O_2 and stabilizing the concentration of Fe^{2+} at 1 mM at a dye concentration of 0.2 mM and a current of 100 mA. Table 2 shows the dye decolorization as a function of the $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ ratio. The results revealed that at a time point of 20 min, the highest dye removal (99%) was observed at a $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ ratio of 1:4.

Effect of current density on color removal

Current density is an important parameter for controlling the reaction rate inside the reactor. The effect of current density on color removal efficiency was studied utilizing various current densities. Figure 4 illustrates the percentage of color removal against applied current density. Increasing

the current density led to an increase in oxidation and color degradation rate. The highest decolorization was 96% in 60 min, at a pH of 3 and current density = 150 A/m².

Effect of mesh size on the percentage of color removal and reaction rate

In this study, the effect of SS mesh size (2, 4, and 10) on color removal and reaction rate was investigated. Mesh characteristics are summarized in Table 3. Figure 5 shows that increasing the size of the mesh pores led to a reduction in the percentage of color removal. The highest percentage of color removal (95%) was observed with mesh 2 at a time point of 25 min. The consumed energy was calculated using equation 6. The results revealed that the lowest energy for mesh 2 was = 1.6 kWh/m³ for dye treatment with a concentration of 64 mg/L, compared with 2.1 and 2.6 kWh/m³ for the 4 and 10 mesh steel electrodes, respectively. Studying the reaction kinetics revealed that the rate constant of color removal at mesh 2 was higher than the other mesh sizes. It was also 6.6 times more efficient at color removal than the steel plate [Table 4]. In addition, there was less loss of anode mass with mesh 2 (mesh 2 = 0.5, mesh 4 = 0.52, mesh 10 = 0.54 kg/m³).

DISCUSSION

The optimal pH for dye removal was found to be 3. The pH of the solution is an important control parameter in all Fenton processes and affects the oxidation of organic substances as well as the generation of hydroxyl radicals; thus, it can affect the efficiency of oxidation.^[15,16]

Table 2: The effect of Fe²⁺/H₂O₂ ratio on color removal (pH=3, [Fe²⁺]=1 mM, I=100 mA, [dye]=0.2 mM)

Fe ²⁺ /H ₂ O ₂ ratio	Decolorization of methylene blue percentage
1/2	68
1/4	99
1/6	43
1/8	42

Table 3: Characteristics of stainless steel meshes used in the study

Mesh size	Wire diameter	Aperture	Open area
2	0.063	0.437	76.4
4	0.047	0.203	57.6
10	0.02	0.08	26.1

Table 4: Comparing the kinetics of the different steel electrodes

Type of electrode	Rate constant (min ⁻¹)	Ratio
Steel plate	2.44 × 10 ⁻²	1
Mesh 10	6.50 × 10 ⁻²	2.7
Mesh 4	7.30 × 10 ⁻²	3
Mesh 2	16.00 × 10 ⁻²	6.6

Numerous studies have reported a high efficiency of this system at pH 2–3.^[17] The efficiency decreases at higher pH due to the formation of ferric hydroxide precipitate.^[18] In addition, dissociation and decomposition of H₂O₂ can cause inefficient degradation at pH >3. This lower degradation observed at lower pH is due to the hydroxyl radical scavenging of H⁺ ions (equation 7).



In this study, the highest removal was 99%, which occurred

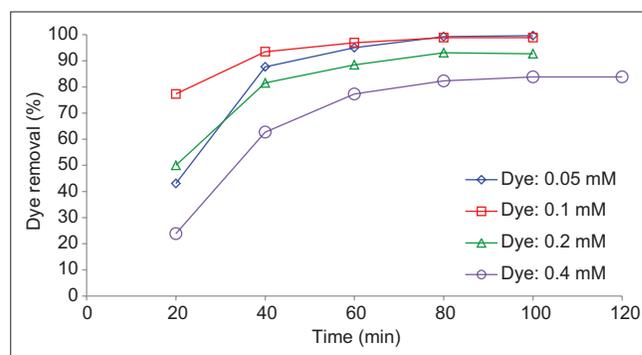


Figure 2: The effect of initial concentration of methylene blue on color removal efficiency (Solution pH: 3, Fe²⁺: 1 mM, H₂O₂: 0.5 mM, I: 100 mA)

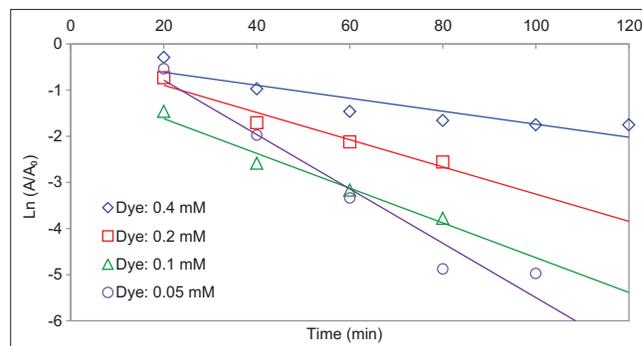


Figure 3: Kinetics of decolorization at different concentrations of methylene blue (Solution pH: 3, Fe²⁺: 1 mM, H₂O₂: 0.5 mM, I: 100 mA)

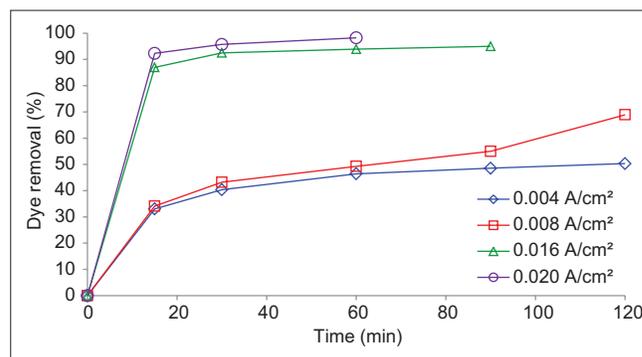


Figure 4: The effect of current density on color removal (Solution pH: 3, dye concentration: 0.5 mM, Fe²⁺: 1 mM, H₂O₂: 4 mM)

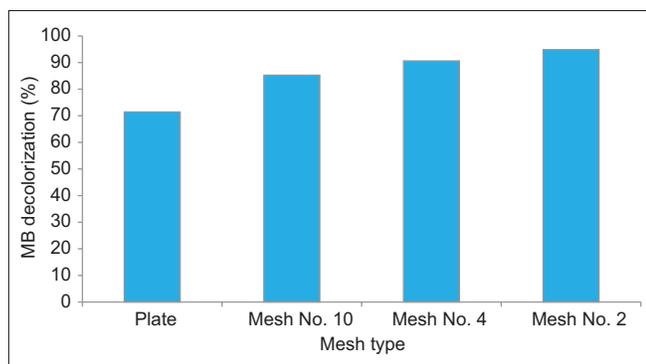


Figure 5: Effect of mesh size on decolorization (Solution pH: 3, dye concentration: 0.5 mM, Fe^{2+} : =1 mM and H_2O_2 : 4 mM)

at an initial dye concentration of 0.05 mM and time point of 80 min. Removal loss in high concentrations may be due to the formation of dimer molecules during sequential reactions of the dye molecule. It is difficult to break down dimers and this leads to reduced removal efficiency.^[19] These results are completely consistent with other studies.^[20] Studying reaction kinetics in this study demonstrated that the degradation reaction of dye in the present study, like similar studies, follows a pseudo first order equation.^[21,22]

Other studies have shown that the controlled addition of H_2O_2 leads to reduction in $\cdot\text{OH}$ waste; therefore, the other effective factor on reaction rate is the ratio of $\text{Fe}^{2+}:\text{H}_2\text{O}_2$. The study demonstrated that dye decolorization is a function of the $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ ratio.^[23] Other studies have reported that the optimal ratio of $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ is 1:5.^[24] Hydrogen peroxide at high concentrations acts as a receiver of peroxide radicals, and the efficiency of the $\text{Fe}-\text{H}_2\text{O}_2$ compound is reduced according to reaction 8. The highest decolorization was 96% in 60 min at a pH of 3 and current density = 150 A/m^2 . In all electrochemical processes, current density is an important parameter for controlling the reaction rate inside the reactor.^[8]

The results also revealed that increasing the size of mesh pores leads to a reduction in the percentage of color removal. During the electro-Fenton process, molecular oxygen, and ferric ions are simultaneously reduced at the cathode to generate hydrogen peroxide and ferrous ions according to reactions (9) and (10). The classical Fenton reaction then occurs in solution to generate $\cdot\text{OH}$ radicals. The ferric ions produced by reaction (3) are regenerated in reaction (10). The Fenton's reagent (H_2O_2 , Fe^{2+}) used in this reaction was generated *in situ* through electrochemistry. Cathodes made of SS with high specific surface areas can achieve performance similar to carbon cathodes containing a platinum catalyst in microbial electrolysis cells.^[25,26] Studying the reaction kinetics demonstrated that the rate constant of color removal with mesh 2 was higher than with other mesh sizes, and was 6.6 times higher than the steel plate, indicating that the pore size of the electrode is effective in increasing the total interface in solution and thus the reaction rate.^[13] Electrochemical impedance spectroscopy revealed that charge

transfer and diffusion resistances decreased on increasing the mesh opening size. Oxygen permeability increased with mesh opening size, accounting for the reduced diffusion resistance.^[27] In other studies, energy consumptions were 15.10 kWh/m^3 for the Fe–Fe pair, 14.02 kWh/m^3 for the Al–Al pair, 15.42 kWh/m^3 for the Fe–Al pair, and 11.99 kWh/m^3 for the Al–Fe pair. The electrode consumptions were 1.62 kg/m^3 for the Fe–Fe electrode pair, 0.52 kg/m^3 for the Al–Al electrode pair, 1.62 kg/m^3 for the Fe–Al electrode pair, and 0.52 kg/m^3 for the Al–Fe electrode pair.^[28]

CONCLUSION

Removal of MB dye from aqueous solution by the electro-Fenton process was investigated using different meshes of SS and various parameters. The results revealed that color removal efficiency was highest at pH 3. The percentage of color removal was reduced with increasing initial color concentration. The highest color removal of MB was observed at a ratio of Fe^{2+} to hydrogen peroxide of 1:4. In all states, higher percentages of removal and kinetics were obtained for the SS mesh than for the steel plate. Studying the reaction kinetics revealed that the rate constant of color removal at mesh 2 was highest, reading 6.6 times higher than the steel plate. The results showed that the lowest energy for mesh 2 was 1.6 kWh/m^3 for removing an initial dye concentration of 64 mg/L , compared with 2.1 and 2.6 kWh/m^3 for the 4 and 10 mesh steel electrodes, respectively. In addition, the loss of anode mass was smallest with mesh 2 (0.5 kg/m^3 vs. mesh 4 = 0.52 kg/m^3 and mesh 10 = 0.54 kg/m^3). The results revealed that steel mesh can be an efficient and economic electrode in the removal of dye from wastewaters.

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Conflicts of interest

There are no conflicts of interest.

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