Degradation of Methyl Blue by Fenton process

Research article

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Abstract

In this study, the oxidative degradation of Methyl Blue (MB) triphenylmethane dye, in aqueous solution by Fenton oxidation process was investigated. The UV-Vis spectral changes of Methyl Blue dye during discoloration process were studied. Kinetic study was done to find out the effect of pH on discoloration rate of dye solution.

Keywords: triphenylmethane dye, Methyl Blue, Fenton oxidation, kinetic study

1. INTRODUCTION

Industrial wastewaters contain a wide variety of organic substances like dyes, pesticides, phenols [1, 2]. These pollutants are posing severe threats to the living organisms due to their harmful and toxic effects. Dyes are highly toxic and pose the strong tendency toward eutrophication [2]. Only 47 % of synthetic dyes are biodegradable.

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Conventional techniques for wastewater treatment (like precipitation, adsorption and coagulation/flocculation) produce secondary sludge and require a long operation time. Advanced oxidation processes (AOPs) are effective technologies for organic compounds degradation [3]. Among AOPs, Fenton process is very promising because it offers a cost-effective source of hydroxyl radicals, achieves high reaction yields and it is easy to operate [4, 5]. The Fenton reagent is effective for treating industrial wastewater components such as pesticides [6], aromatic amines [7], surfactants [8] and a wide variety of dyes [9, 10].

The main objective of this study was to analyze the influence of pH on Methyl Blue degradation with Fenton reagent.

2. MATERIALS AND METHODS

2.1. Materials

The triphenylmethane dye Methyl Blue, ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), hydrogen peroxide (30 % w/w) and sulfuric acid were all purchased from Fluka or Aldrich. All reagents were used without further purification. Distilled water was used to prepare the colored solutions. The molecular structure of Methyl Blue is presented in Figure 1.

Figure 1. Chemical structure of Methyl Blue

2.2. Analysis methods

Batch experiments of Fenton oxidation process were performed in an Erlenmeyer glass equipped with refrigerator bottom with Fenton concentration of 4×10^{-5} mol L⁻¹ of Fe²⁺ and 2×10^{-3} mol L⁻¹ of H₂O₂. All experimental determinations were performed for aqueous solutions of dye, with an initial concentration of 6.5×10^{-5} mol L⁻¹ at temperature of 25 °C and different pH values: 3, 4, 5 and 6, respectively.

For each experiment, 100 mL of dye solution were introduced into the Erlenmeyer flask. Predetermined quantities of ferrous sulphate and hydrogen peroxide were added to the Erlenmeyer flask. pH was adjusted to the above mentioned values by using 0.05 M H₂SO₄ and was measured with a model Consort C533 pH-meter. The Erlenmeyer flask containing dye solution was placed in a thermostat water bath with constant temperature. The solution was stirred by a magnetic stirrer.

The kinetics of dye oxidation was followed by taking samples at 1-minut intervals. The UV-Vis spectra of Methyl Blue samples were recorded from 200-800 nm by using an UV-Vis Varian Cary 50 Bio spectrophotometer at the maximum absorption wavelength. In visible range, the maximum absorption wavelength ($\lambda_{\max}$) MB is 600 nm. This peak corresponded to the absorption of the n- π^* transition related to the quinone structure and was used in order to monitor the compound discoloration. In the UV region, a shoulder around 213 nm and a band at 312 nm were observed. These wavelengths were ascribed to π - π^* transitions corresponding to the conjugated aromatic system (Figure 2). Therefore, concentration of dye in water was measured at $\lambda_{\max}$.

Figure 2. UV-Vis absorbance spectrum of Methyl Blue

3. RESULTS AND DISCUSSION

3.1. Chemical degradation

Experimental determinations were performed for aqueous solutions of MB at 25 °C and different pH values: 3, 4, 5 and 6, respectively.

The color removal was determined using Eq. 1.

$$\text{Color removal (\%)} = (1 - A / A_0) \cdot 100 \quad (1)$$

where A_0 and A are the absorbances at initial time and after time t , respectively.

UV-Vis spectrum obtained during the degradation of MB at $t = 25$ °C and $\text{pH} = 4$ is presented in Figure 3. It can be observed that the absorbance decreases in time which demonstrates the discoloration and degradation of Methyl Blue. For the other pH values, similar spectra were obtained.

Figure 3. UV-Vis spectral changes during the degradation of Methyl Blue in the presence of Fenton reagent at $t = 25$ °C and $\text{pH} = 4$

Figure 4 illustrates the effect of pH on the Fenton oxidation of Methyl Blue triphenylmethane dye. With increasing pH, the color removal values at the same reaction time present a significant decrease hence a smaller rate of discoloration. Thus, the color removal after 1 min decreases from 46.68 % calculated at $\text{pH}=3$ to the value of 32.67 % at $\text{pH}=6$.

Figure 4. Effect of pH on Methyl Blue Fenton oxidation

3.2. Kinetic approach

The kinetics of Methyl Blue degradation by Fenton oxidation process under various temperature values has been investigated. For discoloration of triphenylmethane dyes by Fenton reagent, first order kinetic model has been suggested. The expression of concentration variation in time for first order reaction kinetics is the following:

$$\ln \frac{[\text{dye}]_0}{[\text{dye}]} = k t \quad (2)$$

where $[\text{dye}]_0$ is the initial concentration of dye (mol/L); $[\text{dye}]$ is the dye concentration at a certain moment "t" (mol/L); k represents the rate constant (min^{-1}).

Because the absorbance is directly proportional with the concentration of dye subjected to degradation, Eq. 2 can be written as follows:

$$\ln \frac{A_0}{A} = k t \quad (3)$$

where:

A_0 and A – absorbances of the dye at initial time and at time "t", respectively;

Verification of integrated rate law

The curves $\ln(A_0/A) = f(t)$ obtained from experimental data during the Fenton oxidation of MB are shown in Figure 5.

Figure 5. Plot of $\ln(A_0/A) = f(t)$ in case of MB degradation at different pH values

The equations and deviations from linearity (R^2) are inserted in the graph. Rate constant (k) decreases with the increasing of pH and have values ranging from 0.3134 min^{-1} for pH = 5 to 0.4166 min^{-1} for pH = 3. The R^2 values are close to unity at pH = 3-5 which indicates the pseudo-first-order kinetic model is applicable to the MB degradation.

4. CONCLUSION

The present study demonstrated that triphenylmethane dye Methyl Blue can be degraded effectively by Fenton process.

The increase of pH from 3 to 6 leads to a decrease of color removal from 46.68 % to 32.67 %, after 1 min of reaction.

The Fenton oxidation process of Methyl Blue in aqueous medium at pH = 3-5 follows the first order reaction kinetics.

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