Degradation of Methylene Blue Dye Using Dimethyl Dioxirane as oxidizing agent

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Abstract: Dyes produced by the textile, printing and paper industries can end up in waste waters and are therefore a potential source of pollution of rivers and waterways. To overcome this problem many techniques are followed to degrade the dye contaminates in waterways among them AOP (Advance Oxidation Process) is the advanced process. This study reports on the advanced oxidation of methylene blue by means of the combined action of dimethyl dioxirane. The influence of different parameters, such as oxidizing agent concentration, initial dye concentration and pH in the oxidative process has been studied. The degradation of methylene blue dye was evaluated under dark condition at room temperature by using dimethyl dioxirane as oxidizing agent. The effect of pH, effect of oxidizing agent and initial dye concentration on the degradation efficiency of methylene blue was investigated. The results reveal that the optimum oxidation conditions of methylene blue are as follows: pH = 7; oxidizing agent= 500μL and 10 mg/L methylene blue dye concentration. Under these conditions, the removal efficiency of methylene blue was 99.2%.

Keywords: Advance Oxidation Process; Methylene blue; pH; Initial Dye concentration; Dimethyl Dioxirane.

1 INTRODUCTION

One of the most important environmental problems of the textile industry is the generation of large volumes of highly coloured wastewater (Balanosky et al., 2000), the release of which into the ecosystems causes esthetic pollution, eutrophication, and perturbation in aquatic life (Vautier et al., 2001). Despite the fact that the release of colour wastewater into the earth comprises just a little extent of water contamination, the way that colours are obvious at low fixations—combined with ever stricter governments guidelines—is constraining material enterprises to get their waste effluents an undeniably elevated expectation preceding releasing them into the nearby sewage framework or to the rivers (Robinson et al., 2001; Venkata et al., 2003). Consequently, colour removal from wastewater is frequently viewed as considerably more significant than the evacuation of solvent lacklustre natural substances, a noteworthy reason to the synthetic oxygen request (COD) of the accepting waters (Pal Toor et al., 2006). Conventional treatments have been used to decolorize industrial textile wastewaters, such as adsorption (Faria et al., 2005) chemical coagulation (Sanghi and Bhattacharya, 2005), chemical oxidation processes—some of which utilize Fenton reagent (Perez et al., 2002), ozone (Alaton et al., 2004), and the combined action of these oxidants or any of them with H₂O₂ (Hassan et al., 2002, Uner et al., 2004), and electrochemical oxidation (Lorimer et al., 2000). Biological processes have been also used to decolorize effluents from the textile industry, and in particular on azo dyes (Shaw et al., 2002).

But they are not always effective in removing colour because of the low biodegradability of textile dyes and so tertiary treatments are needed to decolorize dye effluents before discharge (Van der zee and Villaverde, 2005). Therefore, most biological and physical-chemical treatments have limited applicability, and thus present significant disadvantages for colour removal and so, recently, the application of so-called advanced oxidation processes (AOPs) has been increasingly observed (Ledakowicz et al., 2001; Robinson et al., 2001) mainly applied to decolorize effluents containing azo dyes. These technologies are based on the initial formation of hydroxyl radicals, usually generated by the combined action of UV radiation and diverse oxidants, such as Fenton reagent, O₃, H₂O₂, or a mixture of some of them (Legrini et al., 1993). These radicals further oxidize organic matter, compounds that are recalcitrant to conventional biological and physical-chemical treatments, such as most dyes used in the textile industry. The present paper is focused on the advanced oxidation of methylene blue dye, in order to enhance the efficiency of this AOP by means of addition of low dimethyl dioxirane concentration, aimed at producing a nontoxic colourless effluent in a short period of time. The substrate was a highly coloured aqueous solution of methylene blue whose optical absorbance at 663 nm. The influence of different parameters, such as oxidizing agent concentration, and pH had been studied.

2 EXPERIMENTAL METHODS

2.1 Materials

All the chemicals used for preparation of dimethyl dioxirane are analytical grade reagents with 99% purity. Potassium peroxy monosulfate is obtained from TCI chemicals. Acetone from Pure chems and sodium bicarbonate from Merck. All chemicals are used as such without further purification.

2.2. Preparation of oxidizing agent

Acetone and water were taken in (1:2) ratio and cooled in an ice at 20°C. Sodium bicarbonate and potassium peroxy monosulfate were added in (2:1) ratio with constant stirring. The colour of acetone turned pale yellow, which indicates the formation of dimethyl dioxirane.
3 RESULTS AND DISCUSSION

3.1 Visual observation of oxidizing agent formation
The formation of DMDO was initially confirmed by visual observation. The change in colour of the reaction mixture confirms the formation of dimethyl dioxirane. Addition of sodium bicarbonate and potassium peroxy monosulfate to the aqueous solution of acetone and water, there will be colour change from colourless to pale yellow (Robert murray and Ramasubbu jeyaraman 1985). It is due to the formation of dimethyl dioxirane as shown in fig 1.

![Image](2(a))  ![Image](2(b))

**Fig.1.** (a) Acetone and water mixture solution, (b) After addition of potassium peroxy monosulfate and sodium bicarbonate, formation of dimethyl dioxirane.

3.2 Ultra Violet-Visible spectroscopic characterization
Fig.2. displayed maximum UV-vis absorption at wavelength of 663 nm (Jun yao and Chaoxia wang 2010). The maximum absorption almost kept the same during the degradation progress. This indicated that it was a sign of MB concentration level after degradation. So it was possible to measure the absorbance at 663nm each time, and the resulting data of degradation ratio were valid. The absorption peak of the spectra rapidly decreased with increased time and almost disappeared for 25 min as seen from Fig.2.

![Image](Fig.2. UV-visible spectrum of methylene blue and the chemical structure of Methylene blue dye.)

3.3 Effect of pH
It is well known that the pH value influences the rate of degradation of some organic compounds and so it was of interest to study its influence on the degradation of methylene blue. It was also an important operational variable in practical wastewater treatment. The role of the effect of pH on the degradation of methylene blue over dimethyl dioxirane is reported in the pH range of 5–9 using 20mg of catalyst, 0.5mL of oxidant and 10mg of 50mL dye solution under room temperature at 15mins. The degradation efficiency of methylene blue was calculated by using the following equation:

$$\text{% degradation efficiency} = \frac{C_0 - C}{C} \times 100 \quad \text{(2)}$$

Fig.3. demonstrates the results of degradation efficiency of methylene blue with different pH values. The results revealed that the degradation efficiency decreases with the increase in pH. At neutral pH value (pH = 7) the degradation efficiency reached to 86.30%, when the pH value of methylene blue dye solution increases from 5&6, the degradation efficiency of methylene blue is 83.3% & 76.5% respectively and then the degradation efficiency increased to 86.30% at pH 7. Further increases in pH value of methylene blue dye solution to 9 lead to further decreasing in degradation efficiency from 86.30% to 66.5%. Further experiments were performed at neutral pH 7.

![Image](Fig.3. Effect of pH of dye solution on the degradation efficiency of methylene blue.)
3.4 Effect of dimethyl dioxirane

Effect of dimethyl dioxirane on the degradation of methylene blue (10mg/L) with neutral pH 7 was investigated with varying dimethyl dioxirane. The range of dimethyl dioxirane ranges from 100µl to 800µl. The degradation efficiency was increased as the concentration of dioxirane increased. The percentage of degradation increases 48.2% to 94.3% from 100µl to 500µl. The degradation efficiency was decreased after 500µl to 800µl. It is due to 500µl was enough to decolourize the dye solution efficiently as shown in fig.4. The percentage of degradation decreases from 94.3% to 90.2%. Further experiment was carried out at pH 7 and dimethyl dioxirane 500µl.

![Fig.4]  
**Fig.4.** Effect of dimethyl dioxirane on the degradation of methylene blue dye and the chemical structure of dimethyl dioxirane.

3.5 Effect of initial dye concentration

The effect of initial dye concentration was investigated by varying the initial concentration from 10 to 60 mg/L using 500µl of oxidizing agent with pH 7 under room temperature at dark condition for 25 min. The results obtained are showed in fig.5. It can be seen that the degradation efficiency of methylene blue is inversely proportional to its concentration, which means, the lower of the dye concentration, the higher efficiency of the dye degradation. As seen, increasing the initial dye concentration from 10 to 60 mg/L decreases the degradation efficiency of methylene blue from 99.2 to 61.3%. The degradation efficiency relates to the formation of hydroxyl radicals, which is the critical species in the degradation process. Hence an explanation to this behaviour is that the higher the initial concentration, the higher the adsorbed organic substances on the surface of the oxidizing agent and the solution became more intensely coloured. Therefore, there are only fewer active sites for adsorption of HO• so the generation of HO• will be reduced. (El-bahy., et al., 2009; Byrappa., et al., 2006). So, the optimal initial dye concentration is 10 mg/L, the degradation efficiency is 99.2%.

4 CONCLUSIONS

- In the present study, the Dimethyl Dioxirane was successfully prepared by using acetone, Deionized water; potassium peroxy monosulfate and sodium bicarbonate as base. High production yield was obtained by this method: The method used is a simple and cheap method.
- The organic dye was characterized using UV-Visible spectroscopy. The optical absorption peak intensity is found to be at 663nm.
- Dimethyl dioxirane was used as an oxidizing agent for the decolourization of methylene blue dye.
- Removal efficiency was decreased by increasing pH, initial dye concentration.
- The decolourization efficiency was increased as an oxidant increased, 500µl is sufficient for the decolourization of methylene blue dye.
- The decolourization efficiency decreases as the concentration of dye solution increases.

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5 REFERENCES


