Photolysis of methylene blue dye using an advanced oxidation process (UV/H$_2$O$_2$)

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Abstract: Photolysis of methylene blue was studied by using an advanced UV/H$_2$O$_2$ oxidation process. This study investigated different initial dye concentrations ($I_0$, 10, 20, 30 ppm) using different concentrations of H$_2$O$_2$ (10 %, 30 %, 50 %) in three additions (5 mL, 10 mL, 15 mL). The results showed that the degradation efficiencies of this dye at different concentrations were as follows: 99.86 % at 10 ppm using 15 mL of 10 % H$_2$O$_2$ after 60 min, 99.22 % at 20 ppm using 15 mL of 30 % H$_2$O$_2$ for 60 min, and 98.90 % at 30 ppm using 15 mL of 50 % H$_2$O$_2$ after 90 min. An increase in the optimum concentration of H$_2$O$_2$ was observed with an increase in the initial dye concentration. The de-coloration time also increased with increasing initial dye concentration.

Keywords: Advanced oxidation process; UV light; H$_2$O$_2$; UV/H$_2$O$_2$; Methylene blue dye.

I. Introduction

Dye production through the dyeing process is normally associated with the loss of approximately 15 % of the total global dye production to textile effluents. This colored effluent is often released into the ecosystem where it becomes a great source of disturbance to aquatic life and non-aesthetic pollution (Houas et al., 2001). Textile dyeing industries release dyes (a major form of complex organic compounds) to the environment which results in severe environmental pollution. Depending on the production process, textile dyeing is a water-intensive process, requiring about 25 to 250 m$^3$/ton of the fabric. There are about 20 to 30 groups of dyes based on their chromophores or chemical structures. Dyes as organic aromatic compounds absorb light at the wavelength range of 350-700 nm (visible spectrum) (Jafarnejad & Nemati, 2015). The quantity of dye released during a dyeing process has been estimated at 10 to 15% of the untreated dyestuff. Dye effluent or wastewater is normally treated via different chemical, biological, and physical methods like oxidation-ozonation, membrane filtration, coagulation, and adsorption processes. However, these traditional techniques are not efficient in the wastewater treatment since they simply work by shifting the phase of the compounds from the aqueous form to another phase, thereby eliciting complex pollution problems (Yao & Wang, 2010). The recent advancements in the chemical method of wastewater treatment improved the oxidative degradation process of suspended organic compounds in aqueous solvents (Lachheb et al., 2002).

A. Advanced oxidation process (AOP): Advanced oxidation processes comprises of different reaction systems which are all characterized by the same chemical advantage of hydroxyl roots production (selectivity of attack) which is a useful feature in wastewater treatment (Andreozzi et al., 1999). Figure 1. Shows the principal of AOP

![Figure 1. Principle of advanced oxidation processes (Krishnan et al., 2017)](image-url)
has considerable similarities because of the common hydroxyl roots in most of the mechanisms that exist during the reaction. The hydroxyl roots are very unstable and react due to their high level of instability (Esplugas et. al., 2002). AOP reactions mainly aim at free hydroxyl radicals (OH● generation; these radicals are characterized as non-selective highly reactive oxidizing agent (EH = 2.8 V) with the capability of destroying the most stubborn pollutants. Hydroxyl radicals’ generation is facilitated by the presence of ozone (O3), H2O2, titanium dioxide (TiO2), UV radiation, heterogeneous photocatalysis, or high electron beam radiation. The first step of AOPs is the production of hydroxide radicals (●OH, also indicated as OH● or OH'), not hydroxyl ion (OH¯). This ●OH is a strong oxidizing/ disrupting agent which can convert a complex organic compound into CO2 and H2O based on the condition (i.e. can cause the total disappearance or mineralization of the compound). In the second step of AOPs, the radicals produced in the first step react degradable compounds (both organic and inorganic) to cause their onward degradation. The formation of ●OH radicals is usually improved by the synergistic combination of several methods, such as UV, O3, H2O2, Fenton’s and TiO2. Such combination normally increases the rate of reactions by about 100 – 1000 times compared to the use of only O3, H2O2, or UV. For any oxidant, its ability to initiate chemical reactions is determined based on its oxidation potential, i.e., the ability of the oxidant to break, destroy, or disrupt molecules (Grote, 2012).

i) UV light

the early 20th century ushered in the use of UV light for disinfection of drinking water. Despite the failure of the early efforts at using this technology, it has emerged again as a common treatment technique (Monge, 2011). Several factors can affect the effectiveness of any UV disinfection system; such factors include the wastewater characteristics, the UV intensity, the exposure time of the microbes to UV, as well as the architecture of the reactor. The disinfection efficiency of any treatment process is a direct function of the concentration of particles (colloidal and particulate) suspended in the wastewater (EPA, 1999).

ii) Hydrogen peroxide (H2O2)

H2O2 is a colorless liquid which has a bitter taste at room temperature. It is unstable and can be rapidly decomposed into water and oxygen with the release of energy. It is non-flammable and a strong oxidant which when in contact with organic materials can cause spontaneous combustion. Hydrogen peroxide is used in the industries at higher concentrations to bleach textiles and paper; it is also one of the constituents of rocket fuels. Another use of H2O2 is in foam and rubber production. Hydrogen peroxide is used at 3-9 % concentration in households for medical purposes, as well as to bleach clothes and hair (ATSDR, 2002).

iii) UV/H2O2

The UV light can be combined with several materials and used for advanced drinking water oxidation. The reason for the combination of UV with H2O2 for water treatment is to produce hydroxyl radicals which can facilitate the oxidation of pollutants. The UV/H2O2 combination facilitates the splitting of H2O2 by UV to produce hydroxyl radicals per unit of absorbed radiation (Monge, 2011) as in the following reaction (1):

\[ H_2O_2 + hv \rightarrow 2.OH \]

(1)

This process involves the injection and mixing of H2O2 in a reactor with a light wavelength range of 200 to 280 nm. During the mixing process, the UV generated by the reactor attacks the O-O bond in H2O2 facilitating the generation of hydroxyl radicals as described in the following reactions:
Here, Eq 1 is the rate-limiting reaction since it has a lower reaction rate compared to the other equations. Theoretically, it is believed that a higher initial H₂O₂ concentration in a UV/H₂O₂ process will generate more hydroxyl radicals (Eq. 1) owing to the degradation of more target compounds. However, there is an optimal required concentration of H₂O₂ since over-concentration will favor the generation of HO₂⁻ (Eq 2) instead of hydroxyl radicals. The UV absorption capacity of H₂O₂ is low and if much UV is absorbed by the water matrix, most of the input UV light to the system will be lost. Therefore, specially-designed reactors are needed for such processes whilst the residual H₂O₂ must be treated before discharge. This process is affected by factors such as the volume of H₂O₂ used, the pH of the wastewater, the presence of bicarbonate, as well as the reaction time (Stasinakis, 2008).

The method provides an inexpensive and reliable source of hydroxyl radical and its efficiency is comparable when UV radiation is applied together with ozone. It is an effective oxidation process for aromatic compounds removal. However, the major issue with this process is that the presence of compounds which may compete with hydrogen peroxide for UV absorption can present reduce the efficiency of the process. The UV/H₂O₂ process can be used for the treatment of wastewater from tannery treatment or even for degradation of effluent from cork manufacturing (Pieczykolan et al., 2012).

**Hydroxyl radical**

The reaction between H₂O₂ and UV light produces hydroxyl radicals (powerful oxidant). The first discovery of hydroxyl radicals was made by H.J.H. Fenton in 1894 when he oxidized malic acid with H₂O₂. Since then, more studies have been dedicated to the understanding of the capabilities of hydroxyl radicals. The oxidation potential is normally used to describe the capability of an oxidant to bring about the oxidation of water contaminants. Molecules with higher oxidation potential normally present a higher rate of contaminants’ degradation compared to those with weaker oxidation potential (Monge, 2011). The rate of •OH generation is determined by the ability of H₂O₂ to absorb UV light; it is also dependent on the physicochemical properties of the solvent that will be used during the oxidation process (Mierzwia et al, 2018). Other factors which can affect the rate of •OH generation include the type of UV light source used (low pressure or medium pressure), the optical path length in the reactor medium, as well as the optical properties of the effluent, such as the absorption of the UV light by certain particles or chemicals (Mierzwia et al., 2018). Hydroxyl radical is one of the strongest oxidizing agents employed in the treatment of water and wastewater owing to its capability of facilitating the rate of contaminants’ oxidation (Zhou and Smith, 2002).

**IV. Methylene blue dye**

One of the most used materials in the textile industry is Methylene blue (MB); hence, it has been selected as an organic contaminant in this study. This study focused on the degradation of MB in the presence of magnetite under both solar and UV radiations. As a cationic thiazine dye, MB has essential characteristics as it contains
tetramethyl thionine chloride. MB is commonly used as a model in environmental sciences to evaluate the suitability of various materials for wastewater discoloration (Reza et al., 2016). For a better understanding of this photochemical reaction, several major factors have been investigated, such as the concentration of dye, the oxidation factor concentration (H₂O₂), light sources, pH, and inorganic salts (Reza et al., 2016). In the textile industry, MB is commonly used as a dye for dyeing wool, linen, and land silk. Among the side effects of wastewater contamination with MB among humans are vomiting, eye scratches, diarrhea, and nausea. Being that textile industries are heavily dependent on water, they normally release huge volumes of contaminated wastewater. Hence, AOPs have been considered as the achievable way of effluents decontamination (Jafarnejad & Nemati, 2015).

II. EXPERIMENTAL

The photolysis of methylene blue dye using hydrogen peroxide and ultraviolet light at room temperature was studied.

1. Materials used

*Methylene blue dye*

Methylene blue dye was used in this study. A 1000 mg/L stock solution of the dye was prepared by dissolving 1 g in 1 L of distilled water. The stock solution was diluted to a concentration of 10 mg/L (by adding 18.93 mL of the stock solution to 1892.5 mL of distil water), 20 mg/L (by adding 37.85 mL of stock solution to 1892.5 mL of distil water), and 30 mg/L (by adding 56.78 mL of stock solution to 1892.5 mL of distil water). Table 1 showed the chemical characteristics of the MB dye while Figure 2 showed the chemical structure of MB dye.

| Item                  | Methylene blue (MB) |
|-----------------------|---------------------|
| Trade name            | Desmoid pillar, desmoidpillen, panatone, urolene blue, vitableu |
| Molecular formula     | C₁₆H₁₈N₃SCl |
| Density               | 1.0g/mL at 20 °C |
| Wavelength (nm)       | The maximum absorption of light is near 670 nm. |
| Molecular weight      | 319.86 g/mol |
| pH                    | 3 in water (10 g/L) at 25°C (77°F) (acid dye). |
| Solubility            | 43.6 g/L in water at 25°C; also soluble in ethanol |

Figure 2. Methylene blue Structure (http://cameo.mfa.org/wiki/File:Methylene_blue)
Hydrogen peroxide ($\text{H}_2\text{O}_2$)

The hydrogen peroxide was used in this study at the concentration was 50 % but further diluted to 10 % and 30 % concentrations. Table 2 showed the chemical characteristics of the hydrogen peroxide used in this study.

Table 2: Characteristics of the hydrogen peroxide

| Item                  | Hydrogen peroxide |
|-----------------------|-------------------|
| Molecular formula     | $\text{H}_2\text{O}_2$ |
| CAS number            | 7722-87           |
| Molecular weight (g/mol) | 34.01          |
| Assay                 | 50 %              |
| Boiling point         | 150.2°C           |
| Freezing/Melting point| -0.43°C           |
| Specific gravity/Density | 1.35 at 20°C   |
| Acidity (pKa)         | 11.75             |
| Viscosity             | 1.245 CP at 20°C  |
| Origin                | UK                |

2. Devices

Ultraviolet Water Sterilization System

A UV light source (Model = 6W, input =230 V, AC 50/60 Hz, UV lamp = 6W) was installed inside a tight metal casing on a wooden board designed on the basis of the entry of water contaminated dye from the input pipe and output pipe from the other hole in a tank the size (6 L). This was done by pumping dye-contaminated water using the pump [Min flow = 0.5 GPM (110 L/h, 1892.5 mL/min), max flow = 1 GPM (226 L/h / 3785 mL/min)] as shown in Figure 3.
III. Results and discussion

The effect of $\text{H}_2\text{O}_2$ concentration was examined based on the dye removing efficiency at different concentrations of MB dye. The results showed that UV alone or $\text{H}_2\text{O}_2$ alone could not significantly remove the color; hence, the combination of UV and $\text{H}_2\text{O}_2$ was necessary. An increase in the concentration of $\text{H}_2\text{O}_2$ from 10 to 50 % and the increase in volume from 5 to 15 mL brought about a significant reduction in the required time to completely decolorize the MB solution. The same result was observed after increasing the initial concentration of MB dye from 10 ppm to 20 and 30 ppm (Figure 4.) However, higher volumes of $\text{H}_2\text{O}_2$ were needed to decolorize high initial MB concentrations; thus, the optimum volume of required $\text{H}_2\text{O}_2$ could be said to increase with the initial MB blue concentration as illustrated in Figures 5 to 10.

![UV treatment device used in research](image)

![Figure 3. UV treatment device used in research](image)
c-10 ppm MB15ml 10% H₂O₂

Figure 4: De-coloration of 10 ppm MB and 10% H₂O₂ (5 mL, 10 mL, 15 mL).

Figure 5. Relationship between removal efficiency with time (10 ppm from MB and 10% H₂O₂)
Figure 6. Relationship between removal efficiency with time (10 ppm from MB & 30 % H2O2)

Figure 7. Relationship between removal efficiency with time (10 ppm from MB and 50 % H2O2)
Figure 8. Relationship between removal efficiency with time (20 ppm from MB and 10 % H₂O₂)

Figure 9. Relationship between removal efficiency with time (20 ppm from MB and 30 % H₂O₂)
Figure 10. Relationship between removal efficiency with time (20 ppm from MB and 50\% H\textsubscript{2}O\textsubscript{2})

However, with increasing MB dye concentration, larger volumes of H\textsubscript{2}O\textsubscript{2} were required to completely decolorize the dye. A longer duration of UV exposure was also required to obtain noticeable dye removal. Thus, it can be said that the optimum value of H\textsubscript{2}O\textsubscript{2} concentration and the duration of UV exposure increases with the increase in MB concentration as shown in Figures 11-13 (Banat et. al, 2005):

Figure 11. Relationship between removal efficiency with time (30 ppm from MB and 10\% H\textsubscript{2}O\textsubscript{2})
IV. Conclusion

From the achieved results in this study, it can be concluded thus:
1. The UV/H₂O₂ process is an efficient method for the remediation of solutions with low MB concentration.
2. The de-colorization time reduces with increasing H₂O₂ concentration until the optimum concentration of H₂O₂ is reached and beyond this point, the rate of de-coloration becomes indirectly related to the H₂O₂ concentration as it begins to scavenge the generated hydroxyl radicals.
3. Increases in the MB and H₂O₂ concentrations increases the efficiency of decolorization as the appropriate addition of H₂O₂ and a suitable duration of exposure to UV radiation will facilitate the oxidation process.

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