

Effects of some Advanced Oxidation Processes and Chlorine on disappearance of Methylene Blue

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ABSTRACT: Disappearance of Methylene Blue (MB) in distilled water has been investigated when it was treated by sunlight and /or chlorine and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system at different pH values. It is found that the above elements and systems have actions on MB disappearance with different efficiency. The disappearance efficiency by using each system was compared in terms of percentage and kinetics disappearance. By exposing Methylene Blue (MB) aqueous solutions to solar rays, kinetic disappearance increased slowly with increased pH. This fact, which became faster, is inverted by regarding pH when free chlorine is added to the same aqueous solutions of MB. However, when free chlorine is coupled with sunlight, a remarkable enhancement, at higher pH, of the disappearance activity compared to obtained results with isolated elements. On the other hand, the system $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ was also tested to remove MB in terms of kinetic curves at different pH. Important and faster removal levels were obtained at acidic pH.

KEYWORDS: Methylene blue, disappearance, chlorination, sunlight, Fenton's reagent, Advanced Oxidation Process.

1 INTRODUCTION

Methylene blue (MB) which is a heterocyclic aromatic chemical compound is widely used in different fields such as chemical and biology. Generally, this product may be release to the environment through various waste streams. If released into water, Methylene blue may be expected to adsorb to suspended solids and sediment.

To treat water, oxidizing systems were commonly used such as chlorination, and in the last time, advanced oxidation processes (AOPs) that showed significant importance in environmental restoration by generating highly reactive oxidizing species able to attack and degrade organic substances.

Using free chlorine (HClO or ClO^-) as a disinfectant is its potential to react via HClO or ClO^- species with organic charge present water to form a number of disinfection by-products (DBPs) which have been linked to cancer, mutagenicity and teratogenicity [1], [2], [3]. It must recall that content of each species (HClO or ClO^-) depend on pH of medium.

On the other hand, among the different approaches for pollutants removal from water and/or minimizing the formation of DBPs, advanced oxidation processes (AOPs): UV/HClO or ClO^- , UV/ClO_2 , $\text{O}_3/\text{H}_2\text{O}_2$, UV/O_3 , TiO_2/UV , Fenton and Fenton-like processes are recognized as mainly efficient for organic molecules degradation [4], [5], [6], [7], [8].

In this work, actions of chlorination and some Advanced Oxidation Processes on Methylene blue aqueous solutions have been tested by being interested in its disappearance under sunlight and/or free chlorine, and Fenton's reagent. The kinetics of its disappearance was established but the detailed description of the main steps of the process was not treated. Initial rate of each experience were summarized in tables.

2 MATERIALS AND METHODS

Methylene blue (MB), sodium hydroxide (98% of purity), sulphuric acid (98% of purity) and ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were purchased from Loba Chemie. H_2O_2 (30%) was from Aldrich. Source of free chlorine was from concentrated bleach (12 degrees). Concentration of free chlorine in this stock solution was measured out by iodometry titration. pH of medium was adjusted with sodium hydroxide for basic and by sulphuric acid for acidic medium and it was measured with combined electrode connected to Calimatic (model Knick) pH-meter. Concentrations of methylene blue were followed by visible spectrophotometric techniques using curve of calibration which showed good linearity between concentration and optical density at $\lambda_{\text{max}} = 668 \text{ nm}$. The spectrophotometer was ThermoSpectronic Biomate3 and cells were plastic model and have 1cm as optical length.

Chemical structure of MB is shown in Figure 1.

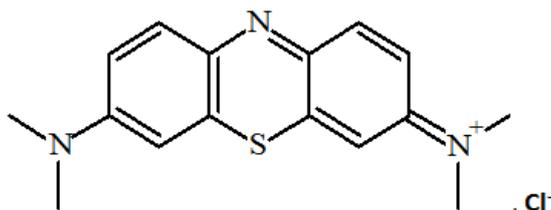


Fig. 1. Molecular structure of MB

The disappearance efficiency of Methylene Blue was calculated as follows (Eq. (1)):

$$\text{Disappearance efficiency (\%)} = (1 - [\text{MB}]_t / [\text{MB}]_0) \times 100 \quad (1)$$

Where $[\text{MB}]_0$ is the initial concentration of Methylene Blue, and $[\text{MB}]_t$ is the concentration of Methylene Blue at reaction time t .

3 RESULTS AND DISCUSSION

3.1 EFFECT OF SUNLIGHT

Four solutions of MB at different pH were prepared in Pyrex graduated flasks and exposed to solar rays. Disappearance of MB in each solution was followed by using curve of calibration. Established kinetics curves (Figure 2), showed important disappearance after 140 min at basic pH.

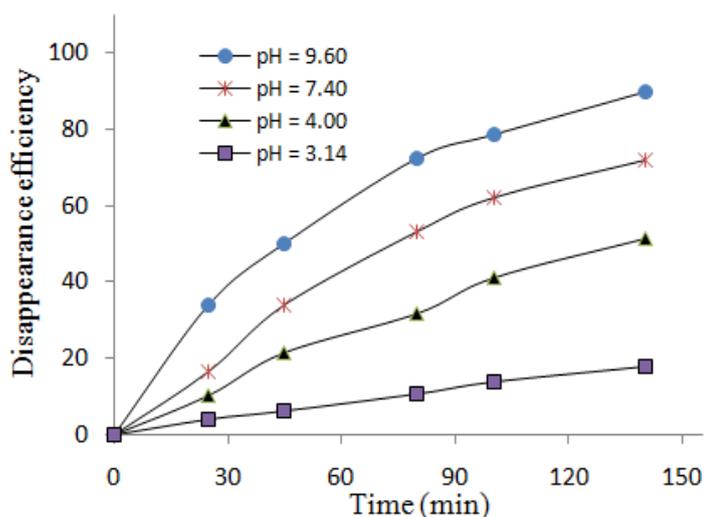


Fig. 2. Effect of sunlight on the disappearance of Methylene blue. Reaction conditions: $[\text{dye}]_0 = 5 \mu\text{M}$ and temperature = 30°C

Initial reaction rate (Table1) and consequently the percentage of disappearance by molecule photolysis process depended on pH of treated solution. This was probably due the solar photons are captured by dye, resulting in the breaking of chemical bonds between the various constituent atoms of Methylene Blue.

Table 1. Initial rate Measured of MB disappearance under sunlight, at different pH values

pH	Initial rate (r_0)($\mu\text{M}/\text{min}^{-1}$)
3.14	0.0127
4.00	0.0309
7.40	0.0479
9.60	0.0958

3.2 EFFECT OF FREE CHLORINE

For appreciating the effect of free chlorine on MB, same concentration of Methylene Blue (MB) which was mixed with progressive concentrations of diluted chlorine in five flasks (from 42 μM to 212 μM).

After 10 min of contact time, and at pH = 2.56, residual concentrations of MB were measured and presented in Figure 3. The graph showed that MB concentrations decreased with increasing ratio [free chlorine]/[MB].

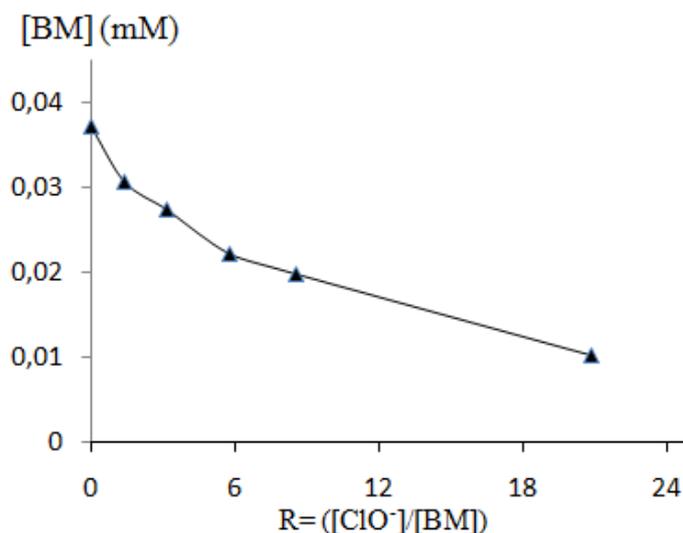


Fig. 3. Effect of [free chlorine]/[MB] ratio on the disappearance of Methylene blue. Reaction conditions: Contact time= 10 min, [dye]₀= 0,037 mM, pH= 2,56 and temperature= 25°C

On the other hand, one of the last experiment was also conducted at different pH values for appreciate its effect on kinetic. The results were reported on the graph (Figure 4) which showed that the rates of chlorination reactions that occurred at basic pH were slowed.

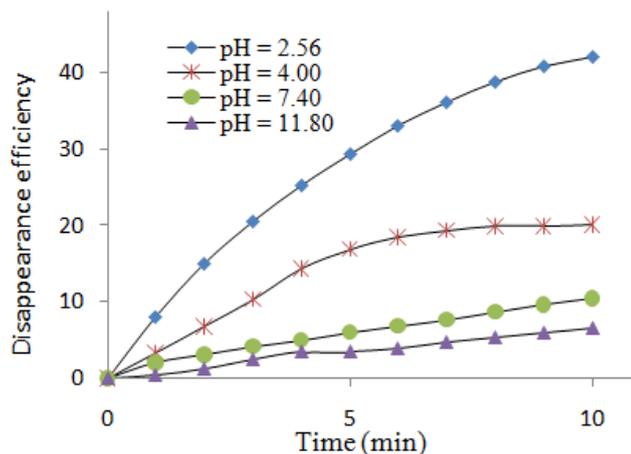


Fig. 4. Effect of free chlorine on the disappearance of Methylene blue. Reaction conditions: $[ClO^-]_0 = 53 \mu M$, $[dye]_0 = 5 \mu M$, and temperature = 25°C

In contrast, at acidic pH, important speed was observed and about 40% of MB was disappeared after 10 min of contact at pH=2,56. Table 2 resumes the obtained initial reaction rate in each attempt.

Table 2. Initial rate Measured of MB disappearance with free chlorine, at different pH values

pH	Initial rate (r_0)($\mu M/min^{-1}$)
2.56	0,035
4.00	0,116
7.40	0,093
11.80	0,023

3.3 EFFECT OF FREE CHLORINE/SUNLIGHT SYSTEM

For attempts to observe effect of pH medium on the system free chlorine/solar rays on Methylene Blue (MB) disappearance, flasks contained a mixture of MB and diluted chlorine and then exposed to sunlight. The Figure 5, which assembled kinetics of MB disappearance, showed that the phenomenon became faster at higher pH values.

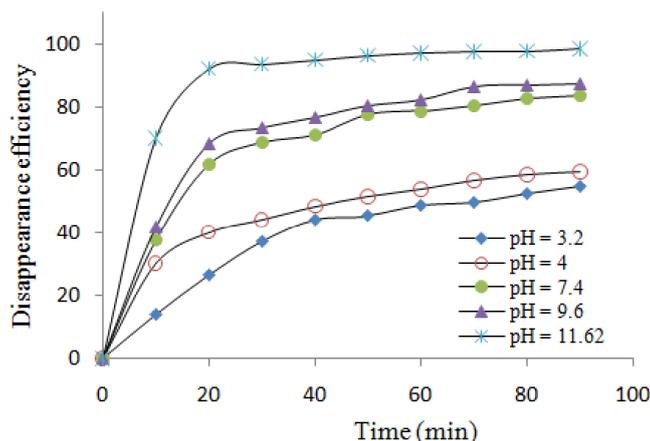


Fig. 5. Effect of free chlorine/sunlight system on the disappearance of Methylene Blue. Reaction conditions: $[ClO^-]_0 = 53 \mu M$, $[dye]_0 = 5 \mu M$, and temperature = 30°C

The initial reaction rates are assembled in the Table 3.

Table 3. Initial rate Measured of MB disappearance with free chlorine/sunlight system, at different pH values

pH	Initial rate (r_0)($\mu\text{M}/\text{min}^{-1}$)
3.20	0.629
4.00	1.815
7.40	1.826
9.60	1.850
11.62	4.561

In addition and as reported by researchers [9], [10], [11], [12], UV light can decompose hypochlorous acid and hypochlorite anions which absorb energy in the 292 to 380 nm region.

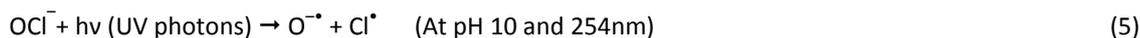
The reactions occurring in the UV photolysis of aqueous species of free chlorine can generate hydroxyl radicals (OH^\bullet) and chlorine radicals (Cl^\bullet) as follows (Eqs. (2), (3)):



At higher pH such as pH 10 all of the chlorine is present as OCl^- which can be decomposed into chloride ions (Cl^-) and oxygen atoms (O) by UV radiation of 350 nm (Eq. (4)):



However, when OCl^- is irradiated at 254nm, the primary photoprocess is as follows (Eq. (5)):



At this wavelength, OH^\bullet radicals can be generated by the reaction (Eq. (6)):



As a result, the observed enhancement by using free chlorine/sunlight can be due to the association of the above facts and also to the generated radicals which oxidise efficiently organic matter.

3.4 EFFECT OF FENTON'S REAGENT

The choice of Fenton's reagent is important, in order to generate enough radicals to oxidize Methylene Blue (MB). No reaction was observed with MB additional to solutions contained only Fe^{2+} ions or H_2O_2 . Therefore, Disappearance of MB became possible when a mixture of solutions of H_2O_2 and Fe^{2+} ions was added to solution of MB at acidic pH (Fenton reaction). As showed in Figure 6 and as reported in Table 4, weak reaction of MB disappearance was occurred when pH medium was basic comparing the same fact when medium became highly acidic.

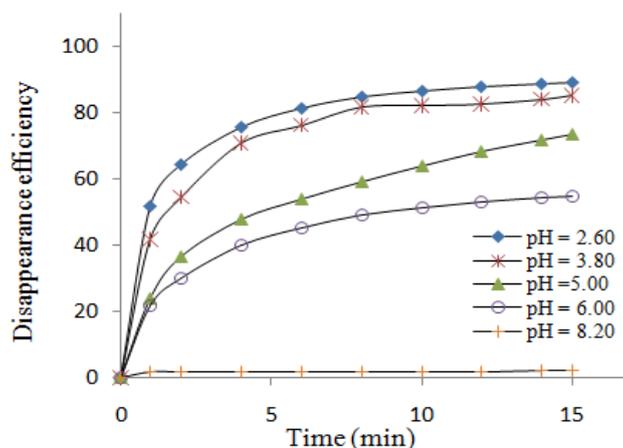


Fig. 6. Effect of Fenton's reagent on the disappearance of Methylene Blue. Reaction conditions: $[\text{dye}]_0 = 25 \mu\text{M}$, $[\text{H}_2\text{O}_2]_0 = 0,4 \text{ mM}$, $[\text{Fe}^{2+}]_0 = 0,14 \text{ mM}$ and temperature = 25°C

Table 4. Initial rate Measured of MB disappearance with the Fenton's reagent system, at different pH value

pH	Initial rate (r_0)($\mu\text{M}/\text{min}^{-1}$)
2.60	11.321
3.80	9.832
5.00	4.957
6.00	5.150
8.20	0.442

According to researchers papers [13], [14], MB can be destroyed, as in other AOPs, by initiated hydroxyls radicals (OH^\bullet) which have a high reactive potential. Fenton reaction, one more time, takes place at very low pH for keeping the iron in solution, until the H_2O_2 is fully consumed. At high acidic medium, the following reactions resume the steps of initiation of hydroxyl radicals and regeneration Fe^{2+} ions (Eqs. (7)-(8)) [15], [16]:



4 CONCLUSION

This work can be a first step to extend major advanced oxidation processes to aim to degrade dyes such as Methylene Blue (MB). The obtained results showed that classic oxidant like sunlight, free chlorine, free chlorine/sunlight and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ systems can remove the dye at different initial pH in acceptable time. Kinetics curves showed that disappearance percentage of MB under sunlight increased with increasing pH values. By contrast, disappearance of MB became faster at acidic pH when only free chlorine was added to the aqueous solution of MB. However in case to apply the system sunlight/free chlorine to MB aqueous solutions, important level of MB disappearance was achieved in only 20 min at basic pH. The system containing H_2O_2 and Fe^{2+} ions was also tested to remove MB in terms of kinetic curves at different pH values. Important reaction initial rate and consequently high removal level were obtained at acidic pH within a reduce time comparing to the preceded reactions.

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