



Degradation of Methylene Blue Using Microplasma Discharge – A Relative Study with Photodegradation

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Received: 8-03-2021, Revised: 16-05-2021, Accepted: 18-05-2021, Published: 23-05-2021

Abstract: Large-scale production and application of synthetic dyes have become a matter of concern as it is a major factor responsible for environmental pollution. Most dyeing effluents are discharged into water bodies and lands without being treated, which ultimately pollutes the groundwater making it unfit for consumption. The present study explains the degradation of one of such synthetic dyes Methylene blue (MB), using non-thermal Microplasma treatment. The aqueous solution of MB was treated with an array of air microplasma discharge at atmospheric pressure. Different concentrations (10 ppm, 20 ppm) of MB solution were treated for various treatment time and chemical parameters like pH, electrical conductivity, total dissolved solids and salinity was measured. The degradation percentage reached 100% in 15 min of treatment for 10 ppm MB solution, and 20 min of treatment for 20 ppm MB solution indicated by the color change from blue to a clear solution. The reactive oxygen species (ROS) and reactive nitrogen species (RNS) formed during the microplasma treatment are responsible for MB degradation. Same volume of MB solution was irradiated by direct sunlight for photodegradation and was found to degrade the solution of 10 ppm by 96% and 20 ppm by 93% in 10 hours of treatment. Experimental results indicated that microplasma treatment was effective for dye degradation, without the need of pretreatment process or chemicals.

Keywords: Non-thermal Plasma, Microplasma, Methylene Blue, Dye Degradation, Photodegradation.

1. Introduction

The rapid growth of textile industry has caused environmental pollution throughout the world. Wastewater from textile and various other industries consists of dyes and other detrimental organic pollutants. Almost 50,000 tons of dyes are produced from various industries of which about 10% of it ends up as wastes [1]. Various industries discharge the effluents directly

into water bodies; which makes it imperative for the treatment of wastewater. Based on industrial processes, wastewater contains different types of solids, salts, detergents, etc. among which dyes are most harmful to the environment [2]. Textile wastewater when released to water bodies may affect the quality of the water, increases chemical and biochemical oxygen demand, causes bioaccumulation in aquatic organisms [3]. Release of industrial pollutants not only affect the aquatic life but also bio accumulates in soil affecting the soil quality, underground water, which further used for public water supply system will affect human life [4].

There are numerous methods for dye treatment of wastewater. The conventional methods include physiochemical methods such as adsorption, membrane filtration, ion exchange and coagulation, biological methods such as anaerobic process, adsorption by microbes, etc. [5]. Advanced oxidation processes (AOPs) are another effective method for wastewater treatment. AOPs such as Non-thermal plasma (NTP) treatment are one of the efficient methods for organic dye degradation [5], particularly, microplasma is a method for the treatment for wastewater. Microplasmas are NTPs that are confined to the micro range. They have a high surface-to-volume ratio and high collision rate between plasma species and hence high average energy exchange making it advantageous over other plasma discharges [6]. In NTP treatment, reactive species such as hydroxyl radicals ($\bullet\text{OH}$), hydrogen peroxide (H_2O_2), and ozone (O_3) are generated. These reactive species are capable of degrading various organic pollutants including dyes in wastewater [7].

Some of the researchers has already reported the degradation of MB using plasma method, such as Gracia *et al* [8], studied the degradation of MB in aqueous solution as a model dye using a non- thermal microwave plasma jet at atmospheric pressure. The effect of gas flow and concentration of dye was analyzed. A 50 ml of solution was degraded in 30 min of treatment time. Chandana *et al* [7], studied the atmospheric pressure non-thermal plasma jet method for the degradation of MB in aqueous medium. MB solution of 100 mg/L was treated with the discharge and showed that degradation efficiency decreased with increase in concentration of MB. Magureanu *et al* [9], studied the degradation of MB using dielectric barrier discharge (DBD) in coaxial configuration under pulsed regime. The solution was treated with air and oxygen as plasma gas. The effect of input voltage, gas flow rate and solution flow rate is studied. The study showed 95% degradation in 30 min of treatment. Reddy *et al* [10], explained the degradation of MB in DBD plasma. A high AC voltage of 14-18kV was used to generate plasma. A 100 mg/L MB solution treated with air as plasma gas was degraded to 100 % at 25 min treatment time.

The present work aims at the degradation of Methylene blue in aqueous solution using array microplasma discharge and a comparative analysis on photodegradation of MB dye by the irradiation of direct sunlight.

2. Experimental procedure

2.1 Materials

Methylene blue, titanium (IV) oxysulfate, and sulphuric acid of analytical grade were procured from Sigma aldrich. The aqueous solution of MB with a concentration of 20 ppm was prepared by dissolving 20 mg of Methylene Blue in 1L of distilled water. A 10 ppm solution was prepared by diluting the stock solution. 50 ml of prepared solution was used for the treatment.

2.2 Experimental setup

The degradation of Methylene Blue (MB) was carried out using an array of microplasma at atmospheric pressure. The detailed description of the experimental set up is provided in previous publications [11,12]. A fixed input high AC voltage was applied to generate the air microplasma. A solution of 50 ml volume with a concentration of 20 ppm and 10 ppm was prepared and is treated using microplasma at a treatment time of 5, 10, 15 and 20 mins. The degradation under microplasma treatment is indicated by the color change of blue solution to a clear solution. A volume of 50 ml of 20 ppm and 10 ppm aqueous solution of MB was allowed to undergo degradation under direct sunlight. The samples were kept in open Sunlight for solar radiation on successive days between 10:30 am to 5:30 pm (IST) with temperature ranging between 29°C to 32°C.

2.3 Analysis

Chemical parameters like pH, electrical conductivity, total dissolved solvents (TDS) and salinity were measured using Eutech instrument. The concentration of hydrogen peroxide (H_2O_2) was determined using colorimetric method. Titanium (IV) oxysulfate and sulphuric acid react with H_2O_2 to form a yellow-colored pertitanic acid complex, whose concentration is directly proportional to the concentration of H_2O_2 . This is determined by the absorbance of the complex at 407 nm [12].

The degradation of MB dye is analyzed using Optical emission spectrometer: Oceanoptics-HR4000CG-UV-NIR and the degradation efficiency η of MB is determined using the equation [12]:

$$\eta(\%) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where, A_0 is the absorbance of untreated sample and A_t is the absorbance at time t .

3. Results and discussion

3.1 Chemical parameters

Chemical parameters of the MB solution are measured at various treatment time is given in Table 1. The pH of the solution is found to decrease with the increase in treatment time. This is due to the acidic nature of RNS such as nitrous and nitric acid that are formed from nitrogen

present in the air during the microplasma discharge [11]. The variation of pH as a function of treatment time is given in Figure 1. The electrical conductivity of the solutions increased with increase in treatment time. This is due to the generation of charged species and various intermediate products formed during the dye degradation [12].

Table 1. Chemical parameters for 10 ppm and 20 ppm of MB solution

Concentration (ppm)	Microplasma Treatment time (min)	pH	Conductivity ($\mu\text{S}/\text{cm}$)	TDS (ppm)	Salinity (ppm)
10	0	7.94	95	67	51
	5	4.61	119	85	63
	10	3.06	316	225	154
	15	2.88	443	315	216
20	0	8.39	115	82	61
	5	6.66	202	144	100
	10	3.80	262	188	130
	15	2.96	501	356	244
	20	2.76	640	457	315

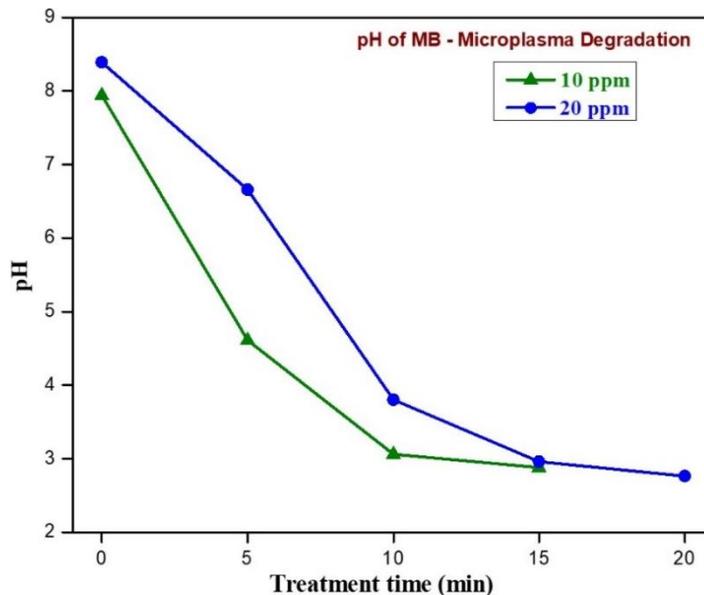


Figure 1. Variation of pH of Methylene blue solution during microplasma discharge

3.2 Quantification of hydrogen peroxide (H_2O_2)

The formation of H_2O_2 during the degradation of MB is determined by colorimetric method through the formation of pertitanic acid which showed a peak at 407 nm. The variation of H_2O_2 concentration with different treatment time is shown in Figure 2. A concentration 0.816 mM of H_2O_2 was generated during 20 min treatment of 20 ppm solution and 1.068 mM on 15 min treatment of 10 ppm solution. The production of OH radicals are mainly responsible for the formation of H_2O_2 in treatment medium. From Figure 2, the concentration of H_2O_2 increased according to the treatment time for 10 ppm due to more number of OH radicals. But in the case of 20 ppm, upto 15 min concentration of H_2O_2 were increased afterthat a decline in the concentration was exhibited which is due to the interaction between more number of radicals with more number of dye molecules compared with the 10 ppm dye solution. Microplasma serves as a source for the formation of reactive species that degrades the dye efficiently. Microplasma discharges has the property of high electron density and high reactivity. Hence, it can generate active species such as H_2O_2 , relatively higher than other plasma discharges [13, 14].

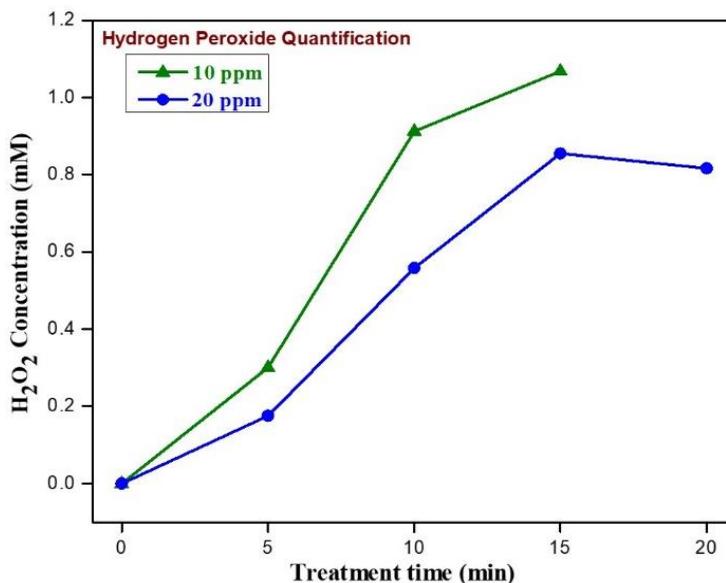
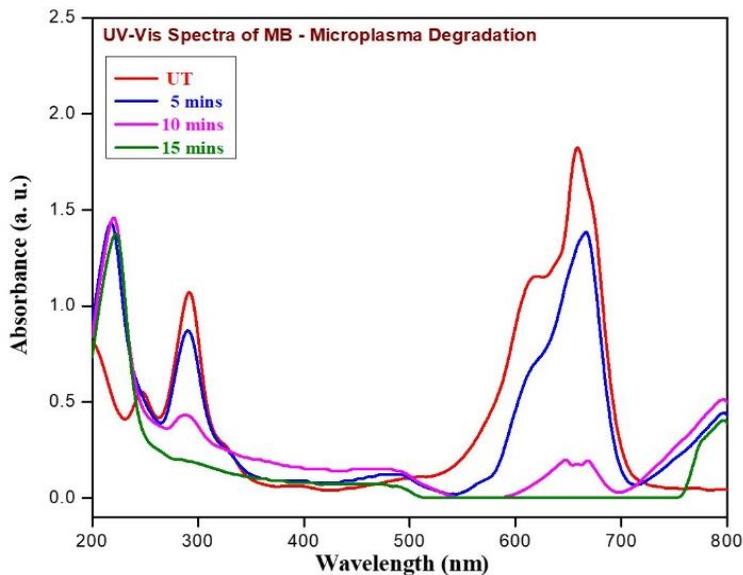


Figure 2. Concentration of H_2O_2 formed during microplasma discharge of MB solution with different treatment time

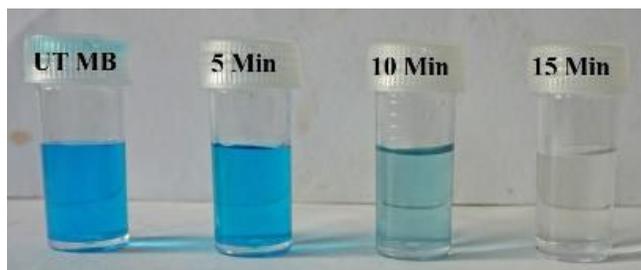
3.3 UV-Vis absorption analysis

The aqueous solution MB dye was treated using an array of microplasma discharge and the degradation efficiency was analyzed by UV-Vis spectrum. Figure 3 (a-b) represents the absorption spectra and images of degraded MB during various degradation time for 10 ppm concentration. The maximum absorption with the characteristic peak of the dye is obtained at a wavelength of 664 nm [14]. The characteristic peak reduced as the treatment time increased.

The same effect was also obtained for 20 ppm MB solution. The peak was found to disappear at 15 min treatment for 10 ppm and 20 min treatment for 20 ppm solution.



(a)



(b)

Figure 3. (a) UV-Vis absorption spectra, and (b) image of methylene blue degradation of 10 ppm concentration at different treatment times

The degradation percentage of 10 ppm and 20 ppm MB solution is shown in Figure 4. Both the dye solutions achieved 100 % degradation within 15 min and 20 min of treatment time which indicates the direct influence of treatment time on the degradation percentage. This suggests the complete degradation of MB from the aqueous solution indicated by the color change from blue to a clear solution. The disappearance of the peak is due to the degradation of MB by various reactive species like hydroxyl radicals, ozone, hydrogen peroxide, RNS, and so on [12]. The possible reactions for the formation of such reactive species are [12, 16]:



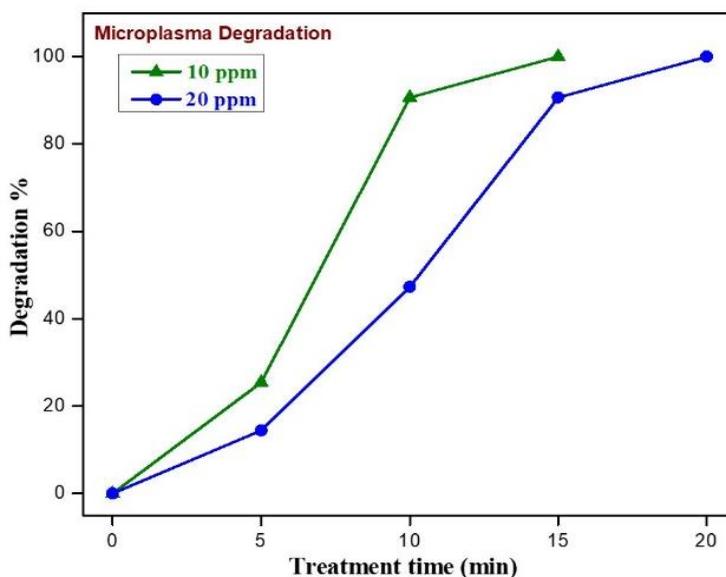
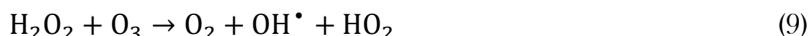
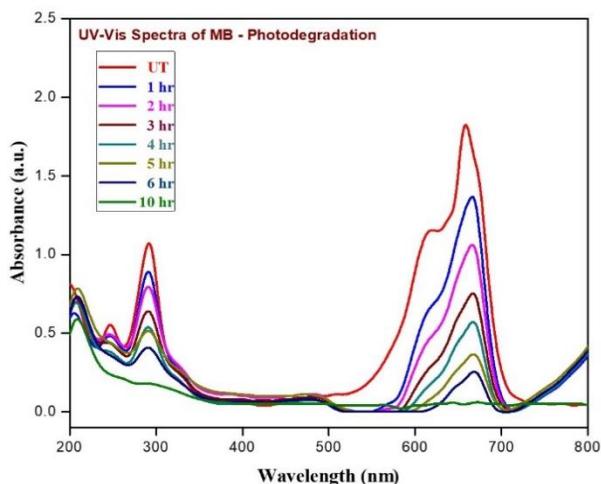


Figure 4. Degradation % of methylene blue in 10 ppm and 20 ppm concentration during different microplasma treatment times

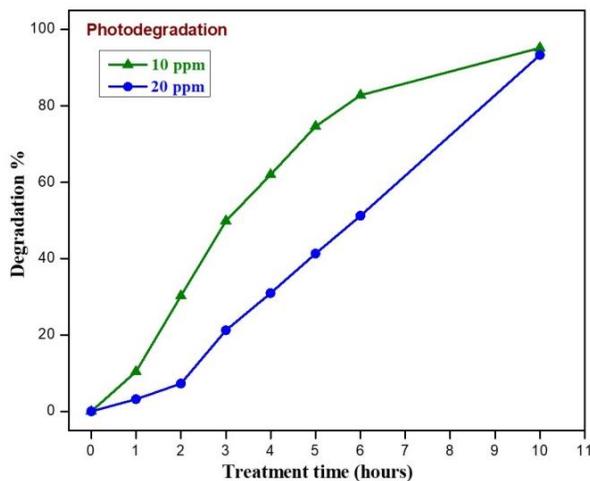
3.4 Photodegradation

A 10 ppm and 20 ppm aqueous solution of MB was allowed to undergo degradation under direct sunlight. The degradation was analyzed at every 1 hour interval using UV-Vis spectrophotometer. The absorbance peak was found to reduce in each analysis. The characteristic peak almost diminished at 10-hour irradiation time. The degradation of MB under

sunlight for 10 ppm concentration is shown in Figure 5 (a). The same effect was also obtained for 20 ppm MB solution. Figure 5(b) shows the degradation percentage of 10 ppm and 20 ppm are 96% and 93%, respectively after 10 hours.



(a)



(b)

Figure 5. (a) UV-Vis absorption spectra of photodegradation of 10 ppm MB solution, (b) Degradation % of MB solutions (10 ppm and 20 ppm) with different time under sunlight

4. Conclusion

The Methylene Blue (MB) degradation was carried out under microplasma discharge with air as plasma generating medium. The chemical parameters such as pH and conductivity of MB solution indicated the formation of radicals and reactive species which are responsible for

dye degradation. The formation of H_2O_2 in microplasma treatment media is the prime factor responsible for dye degradation within a short duration. Microplasma treatment was able to degrade (100%) the MB dye of 10 ppm in 15 min and 20 ppm in 20 min. A comparative study of dye degradation was done with photodegradation under direct sunlight which degraded the MB dye of same volume and concentration of 10 ppm and 20 ppm in 10 hours, 96% and 93%, respectively. The results showed that microplasma treatment is efficient and environment-friendly method, which does not require any additional methods and catalysis for the complete degradation of dyes.

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Acknowledgements: This work was partially supported by the Rashtriya Uchchar Shiksha Abhiyan (RUSA_2.0) grant No.BU/RUSA/BEICH/2019/299-2, Bharathiar Entrepreneur, Innovation and Career Hub (BEICH) received from MHRD, Government of India. Ms. Kavitha, acknowledges the University Research Fellowship (No. C2/18369/2021) received from Bharathiar University, Coimbatore.

Conflict of interest: NIL

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