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Research Article

Methylene blue concentration and pH-induced photocatalytic degradation of methylene blue without photocatalyst under visible light

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Abstract **–** Among the wastewater treatments, the advanced oxidation process (AOP) is one of the most popular techniques, due to its advantages in comparison with the other conventional physical and chemical processes. It is well known that photocatalysis is the most well-organized and appealing method for the degradation of organic toxins utilizing nano-sized semiconducting matter in the existence of solar radiation. There are many operational parameters that highly impact the photocatalytic activity of photocatalysis. Therefore, in this study, the influences of the operational parameters like pH and concentration of methylene blue (MB) on the photodegradation of the MB were investigated. It was observed that variation in the pH values of the dye solution led to an important change in the photocatalytic efficiency of the MB, especially at pH value 11. On the other hand, it is found that with decreased MB concentration the degradation time was reduced. These outcomes are very important for removing organic dyes with relatively inexpensive routes.

Keywords – Methylene Blue Concentration, Photocatalytic Degradation, Photocatalyst Under Visible Light

I. INTRODUCTION

Methylene blue is known as a chemical compound with the formula $C_{16}H_{18}ClN_3S$, which is an organic chloride salt, methylthionine chloride or Swiss blue. It is also a toxic compound and certain substances in drinking water corrosive (irritating) to the skin when at some level human health disorders and organisms even death. Common side effects headache, vomiting, high blood pressure, confusion, allergic reactions, shortness of breath, red blood cell destruction, serotonin syndrome [1]. It's average in different industrial liquid wastes concentration of approximately 25 to 4000 mg/L varies between Acceptance in drinking water MM density 1 mg/L, oil and gas and it is 2.0 mg/L in wastes [2]. International Environment Conservation Authority phenol in river and lake water has set a threshold of 0.2-2 mg/L for its content.

Liquid wastes containing such organic dye compounds, environmentally friendly if disposed of without waste will not pollute the environment. Organic paint waste method used in processing can be done, one of which is adsorption or photo removal methods such as degradation. Recently, this method, which is quite effective to degrade the methylene blue (MB). This method is also easy to separate requires and waste dye molecules simple can be simply broken down into radical molecules like hydroxide, peroxide, etc. [3].

Photocatalytic degradation of organic dyestuffs to decompose with the help of sun/UV light is a usable method. This method is the same with the Advanced Oxidation Process (AOP), known as innovative for wastewater treatment, and relatively new method. So, it was developed to meet the increasing demand for an efficient wastewater treatment. AOP is mainly oxidizing radicals that react, that is, in the environment based on temporary creation of OH*, $O2^{\bullet -}$, H_2O_2, O_3. Through these products the organic fossilization of complexes was occurred, therefore the wastewater gets cleaned [4]. Under light illumination of organic MB dye Possible redox reactions were given as below.

$$MB + h\nu \rightarrow h^+ + e^- \quad (1)$$

$$h^+ + H_2O \rightarrow {}^*OH + H^+ \quad (2)$$

$$h^+ + OH^- \rightarrow {}^*OH \quad (3)$$

$$h^+ + pollutant \rightarrow (pollutant)^+ \quad (4)$$

$$e^- + O_2 \rightarrow {}^*O^{2-} \quad (5)$$

$$^*O2^- + H^+ \rightarrow {}^*OOH \quad (6)$$

$$2{}^*OOH^+ \rightarrow O^2 + H_2O_2 \quad (7)$$

$$H_2O_2 + {}^*O^{2-} \rightarrow {}^*OH + OH^- + O^{2-} \quad (8)$$

$$H_2O_2 + h\nu \rightarrow 2{}^*OH \quad (9)$$

$$MB + ({}^*OH, h^+, {}^*OOH/O^{2-}) \rightarrow \text{degraded product} \quad (10)$$

Basically, photocatalysis can be compartmentalized in to several. One of the divisions is heterogeneous catalysis, the second is homogeneous catalysis. First, different toxic compounds profitably for the decay of groups used. Biological treatment, chemical decomposition and wastewater treatment methods such as activated carbon absorption. There are many advantages of photodegradation compared to its use [5, 6]. In this regard, photocatalysis is very low waste. hazardous waste even at water concentrations It has many activities that can eliminate it. UV/solar radiation for the destruction of pollutants the most suitable process for wastewater use. can be accepted as well. Also, photocatalysis In the process, all oxidation of organic pollutants, possibly in homemade reactor organization highly effective and economical used secondary safe, using catalysts beyond forming non-matter, very small several hours or even at the degree of concentration sometimes it happens in less than an hour. Above all, it eliminates toxic wastes from wastewater. can be a superior process to remove and the last twenty years, it attracts great attention [7].

Recently there have been many photocatalyst to destroy the organic dyes such as ZnO, Fe_2O_3, TiO_2, SnS, ZnS, CZTS, $LaSrMnO_3$, CuO, Sb_2S_3, etc. [8-16]. But Amongest all, the TiO_2 is considered as the best one. However, its photocatalytic efficiency remains insufficient due to low absorption ratio of UV and visible radiation. So, the scientists have focused on different methods and materials to obtain more efficient photocatalysts. It is costly and takes a lot of effort. For this purpose, in this study without photocatalyst. Destruction of MB without photocatalyst intended by changing operational parameters like pH and concentration of organic dyes.

II. Materials and Method

All chemicals used during the experiment of analytical purity and provided from the German company Merck. Ultrapure water, Sodium hydroxide (NaOH, 0.01n/L)/glacial acetic acid (GAA) and MB in the whole experiment were used as the solvent, pH regulator and organic dye, respectively. During the absorption experiments MB was used as an absorbent as it is known a basic cationic dye. The other known names of this basic dye other are C16H18ClN3S and 319.85 g/mol, methylthioninium chloride, CI 52015 and basic blue 9. The molecular structure of this structure and [3] its corresponding energy levels were presented in Fig. 1.

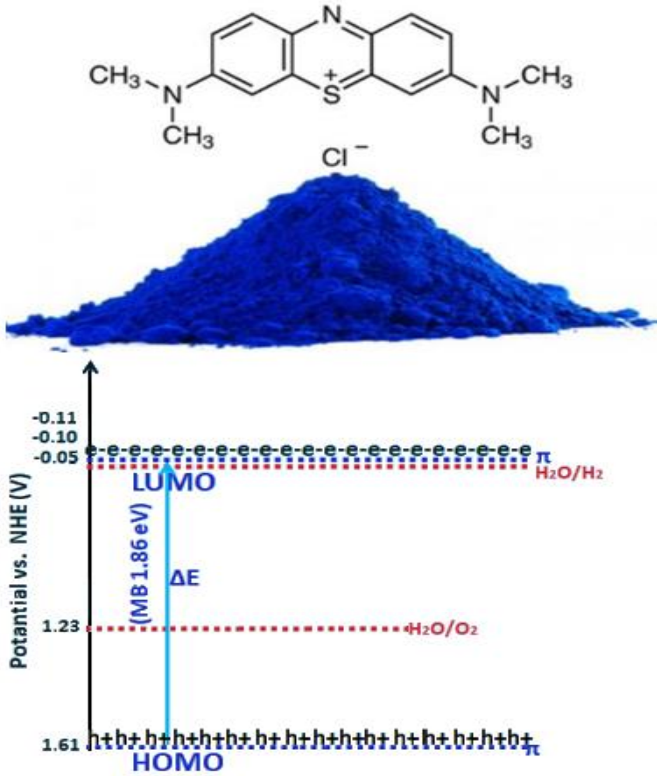


Fig. 1 The molecular structure and corresponding energy levels of MB.

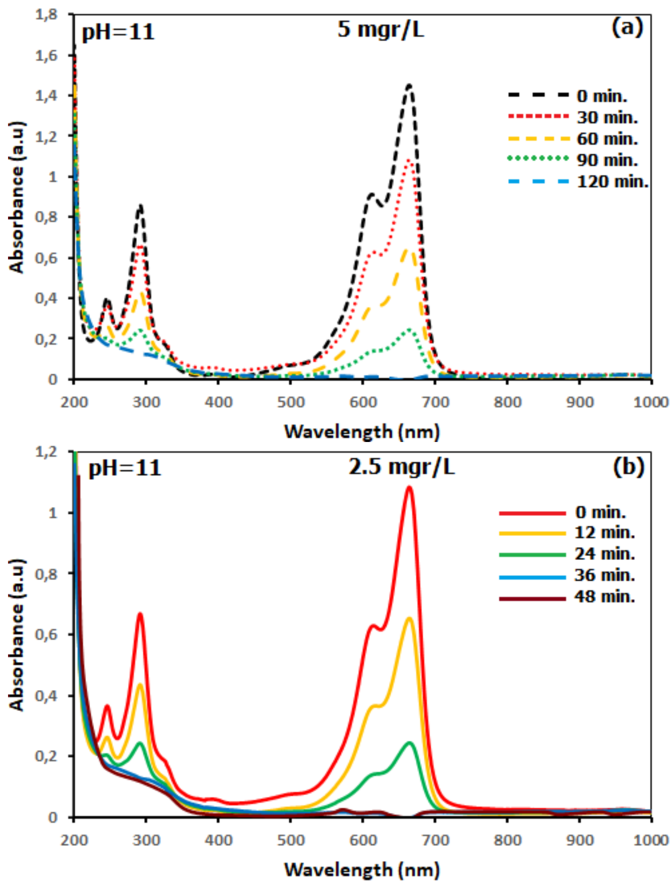
For the preparation of the MB solutions, 5 mgr/L, 2.5 mgr/L and 1.25 mg/L mgr MB were dissolved in 100 ml pure water by using a magnetic mixer at room temperature. Then it was stirred until dissolved accordingly. The pH (Hanna pH meter was used (HI2211 pH/ORP meter)) of the mixture was regulated via the desired content of NaOH. According to literacy, the MB has the best photodegradation at a pH value of 11 [17, 18]. However, to investigate the effect of pH 4, 7 and 11 values, the MB solution pH values were regulated by Therefore, the pH value was adjusted by NaOH and GAA.

The absorption of MB solutions before and after various 30 minutes radiation time was directed and scrutinized using a UV–Vis spectroscopy (PerkinElmer Lambda 25) dependent on the distinctive absorption of the MB top at 664 nm [17]. The photocatalytic activity (η) of the degradation of MB without using any photocatalyst was tabulated via the following formula; $\eta = [(1-(C/C0))]x100$ where C_0 and C are the main absorption top of MB, representing density of the MB before and after photocatalysis, respectively [3].

III. Results

According to the UV-Vis spectrum of the methylene blue solution, depended on the MB concentration and pH, the highest peak corresponding to the wavelength of 664 nm was taken as the C_0 as starting concentration. On the other hand, the intensity of C_0 was decreased by time under visible the light and denoted as C. The decreased C_0 by different interlude times depended on different MB concentrations were demonstrated in Fig.2a-c. As the time increased the main MB peak concentration decreased and the initial MB concentration effects the decay time of the MB. As the concentration of the MB decreased the degradation of MB time reduced linearly.

Fig.3a-c shows the pH dependent of the the absorbance spectra of the MB under visible light with different radiation times. As can be seen from them the pH has important impact on the degradation of MB under visible radiation. Therefore, at the pH=11 value, the highest reduced main absorbance summit of MB was observed (see Fig. 3a). However, at the pH value of 7 the significant reduction in main was not observed as seen in Fig. 3b. Moreover, the slight decreasing in



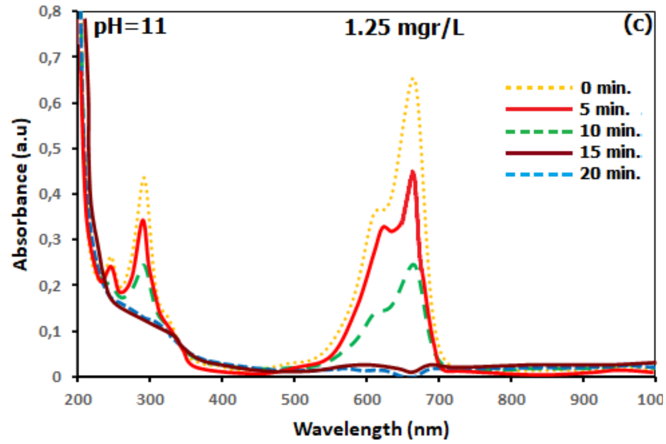
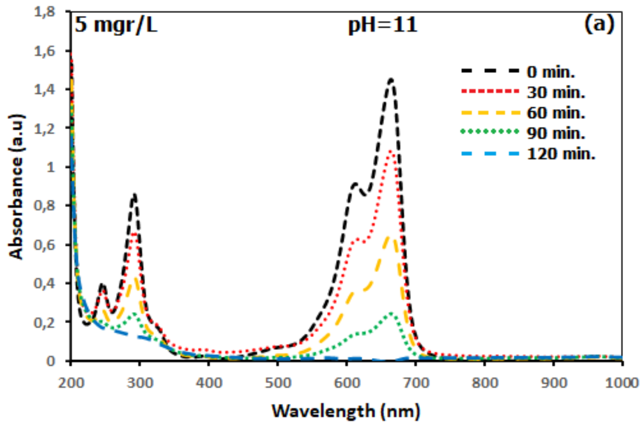
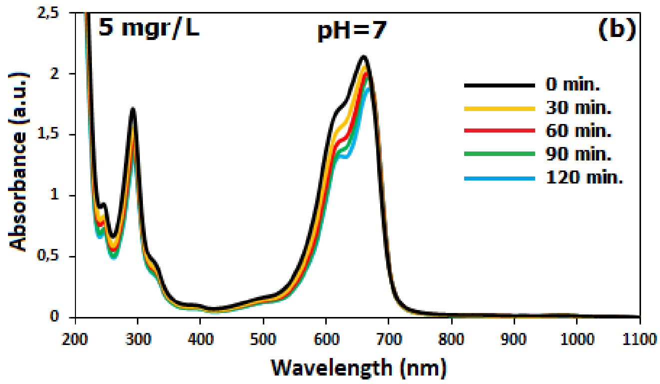


Fig. 2a-c the absorbance spectra of the MB were taken at different interlude timer for various MB concentrations.

the main absorbance top of MB was detected as detected in Fig. 3c.





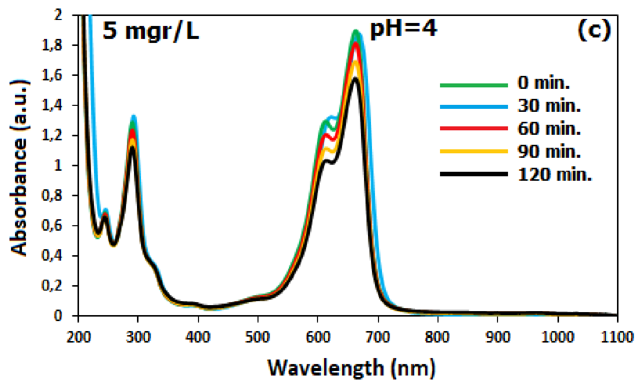


Fig. 3a-c The absorbance spectra of the MB were taken at different interlude timer for various pH values.

IV. DISCUSSION

The results as observed from Figs. 2a-c and 3a-c showed that the methylene blue (MB) dye can be mainly degraded at certain conditions without any photocatalyst. As can be seen in Figs. 2a-c the MB degraded totally within 120 min. for pH=11 and MB concentration of 5 mgr/L. As the MB dye concentration decreased the MB decay time was decreased from 120 min. to 20 min. Especially, at a certain pH value of 11 it completely removed for 120 min as compared to the other pH values. This is mainly because of the high molar ratio OH^- generated as the pH=11 value relatively higher than pH=4 and 7. Creating more OH^- ions leads to more hydroxyl radicals (*OH^-), which degrade MB according to equation 10.

The photocatalytic efficiency of the degradation of the MB was calculated according to the followed equation:

$$\eta=((C-C_0/C_0)\ x100) \qquad (11)$$

The η was computed as 99. 84 at. % for degradation of MB having variant concentration as at 120 min. seen in Figs 2a-c. On the other hand, the computed photocatalytic yield was reduced to 5. 12 at. % from 99. 84 at. % when the pH value of the MB solution reduced to 7 from 11. However, at neutral region with pH value 4 the η was calculated as 12.25 at. %. These results impressively reflect the effective impact of pH on the photocatalytic degradation of MB under visible light. Our findings are highly consistent with the literature [19-25], where photocatalysts were used. But in the present study any photocatalyst was not used, making this study comprehensive research in this field because of reducing the cost of process. So, this research has a potential of opening groundbreaking work in photocatalysis process.

V. CONCLUSION

In this study, methylene blue (MB), having high potential as being in wastewater as common organic dye, was studied for the first time to degrade without any photocatalyst under sun light radiation. The degradation of it was carried out according to the Uv-Vis analysis under the main conditions like certain pH value and MB concentration. It was observed an important decay of MB under visible light with pH=11 value and various MB concentration of 5 mgr/L, 2,5 mgr/L, and 1,25 mgr/L.

The fastest degradation of MB was occurred at pH=11 value and MB concentration of 1,25 mgr/L compared to other pH values and MB concentrations. In addition to, with reduced MB concentration, the degradation time also reduced. Moreover, as increased pH value from 4 to 11, the decay ratio of MB was increased due to enhanced OH^- amount in the medium. The efficacy of the degradation of MB was computed as 99, 84 at. % for the pH value of 11 in 120, 48, and 20 min. with MB concentrations of 5 mgr/L, 2,5 mgr/L, and 1,25 mgr/L, respectively. It was expected that these valuable outcomes will be useful for the reduction of cost of the wastewater around the world.

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