

Reduction of Methylene Blue by Using Direct Continuous Ozone

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Abstract

The reduction of Methylene Blue using continuous ozone is directly investigated in this paper. The effects of the initial concentration of the solution, the initial pH of the solution, the time of treatment by using direct continuous ozone, the volume of the solution and the concentration of ozone given were examined. The experimental results show that the proposed direct ozone method is quite effective in reducing MB levels in solution. The reduction level of MB in the solution gets higher along with the addition of ozone capacity given to the solution. MB concentrated solutions with large volumes require a long ozonation time with a constant ozone concentration. Under basic conditions (pH 12), the MB reduction level is quite high for all ozonation treatments.

Keywords: Direct continuous ozone, methylene blue, reduction, decolorization, advanced oxidation process.

DOI: 10.7176/JEES/10-4-07

Publication date: April 30th 2020

1. Introduction

In the dyeing industrial liquid waste there contains a large amount of organic pollutants. This pollutant in the form of coloring molecules has a complex and stable structure due to the presence of auxochromes (water-soluble bonding compounds) and chromophores (coloring compounds) (Hasan Nembr 2017). These compounds are toxic, recalcitrant, and difficult to degrade by traditional physical, chemical, and biological treatments. Methylene Blue has toxic and dangerous properties. The content of methylene blue in water can cause health problems for humans such as the effects of burns in the eyes, vomiting, nausea, diarrhea, shortness of breath and allergic reactions (Olajire *et al.* 2014), (Al-Anber 2018).

Disposal of liquid waste with high levels of methylene blue into the water flow will cause serious environmental pollution (Jin *et al.* 2014).

Various methods were developed to reduce the content of methylene blue in textile wastewater starting from biological, chemical and physical methods (Al-Anber 2018). Biological methods are often used to treat textile liquid waste because of its low cost and simple application. However, this biological method requires quite a long time, gives rise to deposits and is less effective for decomposing high levels of methylene blue in liquid waste (Olajire *et al.* 2014).

The ozone oxidation process is a suitable and effective method to reduce the content of methylene blue in liquid waste (Hasan *et al.* 2017). Ozone is a molecule with very strong oxidizing properties. Thus, ozone is an alternative method that can be used to reduce the content of methylene blue in liquid waste. This ozonation method is suitable for dealing with large quantities of liquid waste at high flow rates. In addition, this method is more economical and easier and safer to use. This method also does not cause deposits in the final stages of wastewater treatment (Al-Anber 2018).

In this study, the performance of the direct ozonation method for liquid waste was evaluated using a methylene blue solution as a liquid waste model. The ozone concentration, the concentration of the methylene blue solution, the volume of the methylene blue solution, the ozonation time of the methylene blue solution and the pH level of the solution were varied to obtain the reduction level of the methylene blue dye in the textile liquid waste.

2. Methods

2.1. Material and Equipment

This research uses an ozone generator produced by Dipo Technology. Concentrate produced by the generator is measured using the titration method and a maximum concentration of 93.60 mg/L is obtained and an ozone capacity of 112.32 grams/hour with an air flow rate of 20 L/minute. Methylene blue (MB) NaOH, 37% HCl that have been used in this experiment are MB produced by Merck. To get MB solutions with certain concentrations, aquades have been used. The pH of the solution is measured by the universal pH measurement method. MB concentration measurements before and after the ozonation treatment were used based on the absorbance of waves from UV-Vis Spectrophotometer (Genesys 150). Dissolution and ozonation were carried out in a standard glassware Herma, Pyrex. Ozonation is carried out on the MB solution in a glass beaker and stirred using, Hot Plate Magnetic Stirrer (MS300). The chemical compounds used in this experiment were weighed using Analytical Balance,

2.2. Experimental Set Up

The experimental platform is shown in figure 1. The output ozone concentration from generator is measured using the iodometric titration method. Ozone is captured with 0.2 M KI solution for 2 minutes. Then, KI solution is titrated with 0.4 M Na₂S₂O₃ solution. Ozone concentration is calculated using the equation (Yulianto *et al.* 2019), (Chasanah *et al.* 2019):

$$C_o = \frac{24000 \times V_t \times N_t}{\text{flow rate} \times \text{time}} \quad (1)$$

C_o is the ozone concentration (gr/L), V_t is the titrant volume (L), N_t is the titrant normality (mol/L).

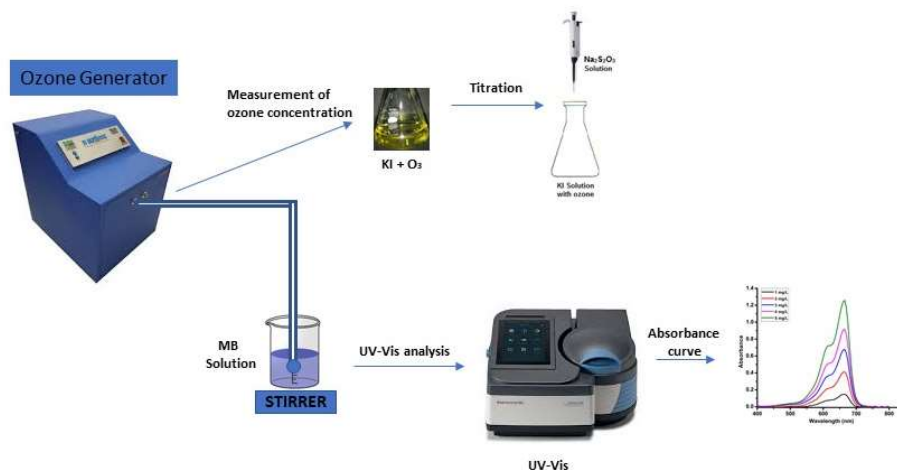


Figure 3. Experiment set up

2.3. Experimental Procedure

One gram of blue methylene powder is dissolved in 1000 mL distilled water to obtain 1000 mg/methylene blue mother liquor. It is continued by dilution according to the desired concentration of the methylene blue solution. To get the absorbance of methylene blue, using UV-Vis first calibrate the maximum wavelength of the methylene blue solution. The absorbance of the sample solution was measured at wavelength intervals from 400 nm to 800 nm. The maximum wavelength for MB was obtained at 665 nm. The ozonation process was carried out with a solution of methylene blue sample with a concentration variation of 10, 20, 30 and 40 mg/L each of 100 mL. The sample solution was ozonized with ozone contact time variation parameters of 15, 30, 45 and 60 minutes at pH 7, then absorbance measurements of methylene blue with a UV-Vis spectrophotometer. The curve calibration of absorbance the MB is presented in the figure 2

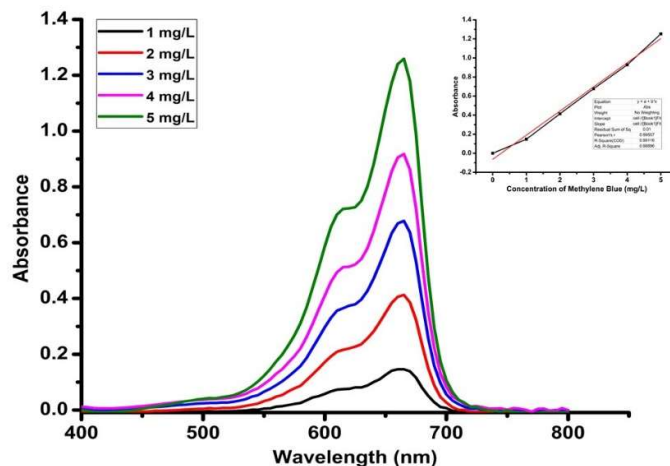


Figure 2. Calibration curve of absorbance MB solution by using UV-Vis Analysis by spectrometer

To a certain voltage applied can be inferred to have a mean value of the current with small error bars. At the same graph, the effect of voltage applied to electrical current is very easy to find, the electrical current was greater with the increasing voltage applied. By using the average current value for each flow rate and applied voltage, the average input power can be determined for each flow rate. Input power (IP) can be determined by using the following equation (Muhammad *et al.* 2017).

$$\text{Input Power (IP)} = \text{Applied Voltage (V)} \times \text{Average Capacitive Current (I)} \quad (2)$$

Besides Input Power, an ozone generator can determine the capacity of the ozone produced by a generator. Ozone capacity is determined by the following formula (Muhammad *et al.* 2017).

$$\text{Ozone capacity (g/h)} = \text{ozone concentration (g/L)} \times \text{air flow rate (L/h)} \quad (3)$$

The ozonation process is carried out with a 20 mg/L methylene blue sample solution. The sample solution was ozonized with the volume variation parameters of the blue methylene solution, 200, 400, 600, 800 and 1000 mL with ozone contact time variations of 20, 40 and 60 minutes in pH 7, then measurements of absorbance of methylene blue with UV-Vis spectrophotometer.

3. Results and Discussion

3.1. Influence of Ozone Concentration

When ozone applied direct continuously into aqueous media so it will be produce new reactive species products, OH and H₂O₂. The reactive species can also help the MB reduction process through the oxidation mechanism. The high ozone concentrations indicate a high number of moles of ozone per liter. Its correlates with an increase in the number of new reactive species formation and reduction processes through oxidation. This is confirmed by results of the study presented in figure 3.

Figure 3 shows the reduction of methylene blue as a function of ozone concentration for several volumes of methylene blue solution with an ozonation time of 60 minutes. For all volumes of methylene blue solution, the reduction of methylene blue increases with increasing concentration of ozone given into the solution. This happens because the higher the concentration of ozone, the collision between ozone molecules and methylene blue substances in the water increases so that the level of reduction also increases.

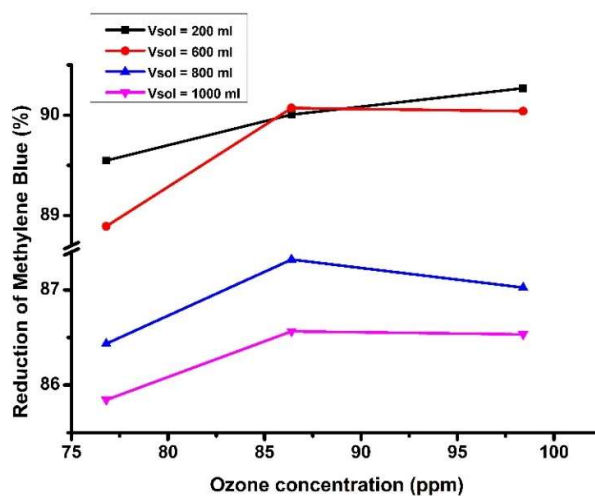


Figure 3. The trend of reduction Methylene Blue as function of ozone concentration with treatment time of 60 minutes

In addition to ozone concentration, the volume of solution also influences the MB reduction level. Figure 4 shows the reduction of methylene blue as a function of the volume of methylene blue solution for some ozone concentrations given with an ozonation time of 60 minutes. For all ozone concentrations, the reduction level of methylene blue decreases with increasing volume of the methylene blue solution. An increase volume of the solution with a constant ozone concentration make the level of interaction between ozone molecules and MB lower so that the reduction level decreases.

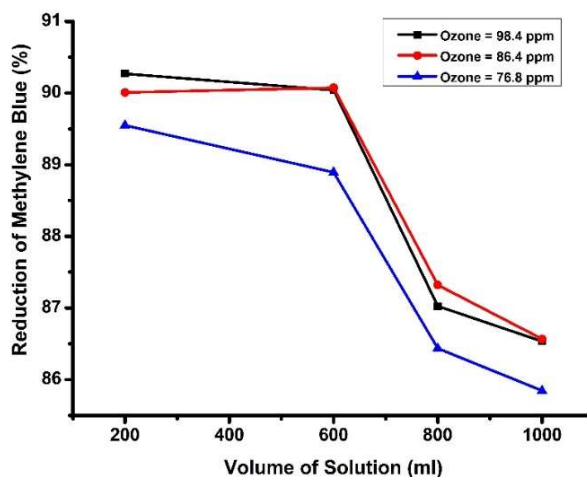


Figure 4. The Trend of reduction MB as function of solution with treatment times of 60 minutes

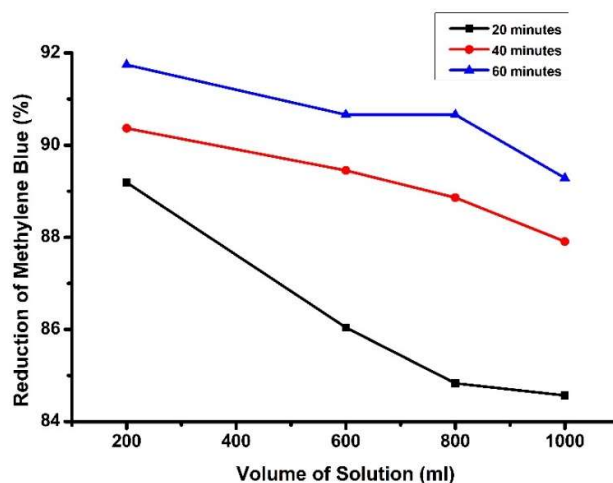


Figure 5. The trend of reduction MB as function of solution for several treatment times and ozone concentration of 98.4 ppm

In other hand, reduction of MB as function of solution for several treatment times with ozone concentration of 98.4 ppm as in figure 5 shows that the MB reduction rate decreases with increasing volume of the MB solution.

3.2. Influence of Treatment Times and MB Solution

The effect of ozonation time on the MB reduction rate was investigated by varying the ozonation time for 15, 30, 45 and 60 minutes at an ozone concentration of 98.4 ppm for some MB concentrations. The results are presented in Figure 6. According to Figure 6, MB removal increases with an increase in ozonation time for some MB concentrations.

According to Figure 6, it can be seen that MB concentrations also affect the level of MB reduction for some ozonation times. The initial concentration of MB solution affects the rate of ozone decomposition in the solution (Desai & Mehta 2014). The higher the MB concentration level, the ozonation time needed to increase the MB reduction for longer with a constant ozone concentration. The MB reduction efficiency at higher initial MB concentration was lower than that at lower initial MB concentration. This is shows that for the constant energy input, the amount of plasma active species formed in the discharge process was maintained at a specific concentration level (Wu *et al.* 2019). Thus, the degradation efficiency would be reduced at higher MB concentration. It proved that the proposed plasma reactor is effective for MB degradation.

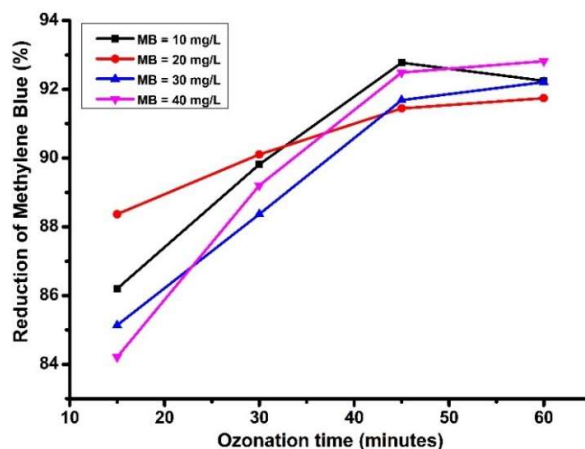


Figure 6. The trend of reduction MB as function of treatment times for several MB concentration with ozone concentration of 98.4 ppm

The decrease of MB concentration by using direct continuous ozone takes place exponentially with time as shown in figure 7. The overall reduction of the MB contained in the wastewater using direct continuous ozone is a complex process with many reactions, which cannot be individually distinguished (Sevimli *et al.* 2002). By assuming that the reaction between ozone and methylene blue follow first-order kinetics with respect to the concentration of MB solution, yielding an overall second-order kinetics, may be written as (Wu *et al.* 2019), (Sevimli *et al.* 2002):

$$\ln \frac{C}{C_0} = -kt \quad (4)$$

The rate constant k was defined by the graph slope using the kinetic equation for first order reaction ($\ln C = -k.t + const$).

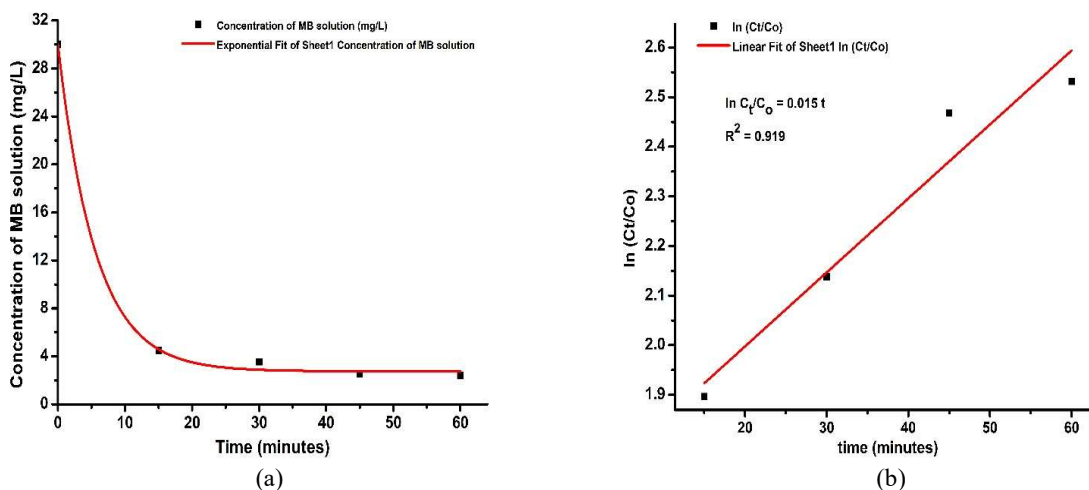


Figure 7. a) Exponentially decrease in MB concentration, b) Linear regression

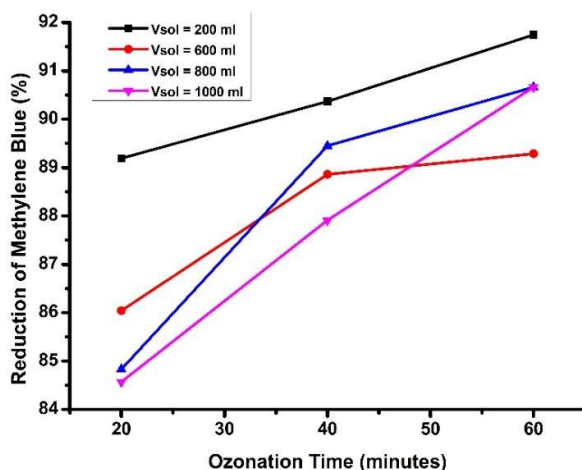


Figure 8. The trend of reduction MB as function of treatment times for several volume of MB with ozone concentration of 98.4 ppm

Figure 8 shows the effect of the initial volume of the solution on the MB reduction rate and the treatment time of the solution. A large volume of solution requires a longer treatment time than a smaller volume of solution. The level of MB reduction in the volume of more solution is also lower than the level of MB reduction in the volume

of the solution being smaller.

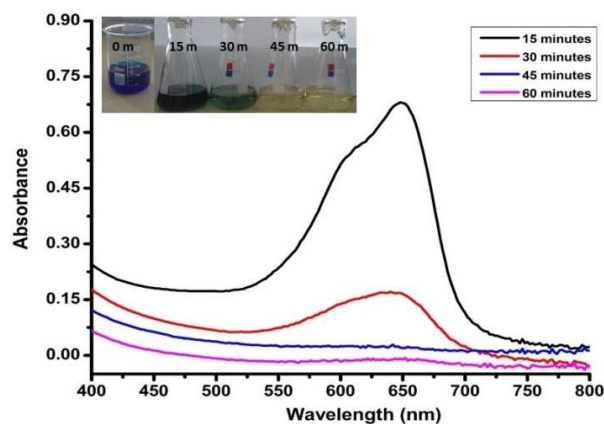


Figure 9. The absorbance curve of MB with initial concentration of 40 mg/l, volume 100 ml, and ozone concentration of 98,4 ppm

Figure 9 shows the visible absorption spectrum of the MB solution during the treatment process using direct continuous ozone. The absorption peak at 650 nm clearly decreases with increasing exposure time, indicating the MB dye molecules are reduced by treatment using direct continuous ozone. MB molecules break down after 30 minutes of treatment. Even at the time of treatment 45 and 60 minutes the MB molecule has completely decomposed. This can be used as a reference for treatment time with MB concentration, MB solution volume and certain ozone concentrations. Because the MB concentration is linear with the absorbance value, so the smaller the absorbance value, the smaller the MB concentration in the solution. So from this graph, it can be seen that the optimal MB reduction treatment time is at least 30 minutes with an initial concentration of 40 mg / l, a volume of 100 ml, and an ozone concentration of 98.4 ppm. From the graph it can be seen that in the treatment above 30 minutes the absorbance value approaches the value 0 which indicates that the MB content has been optimally reduced.

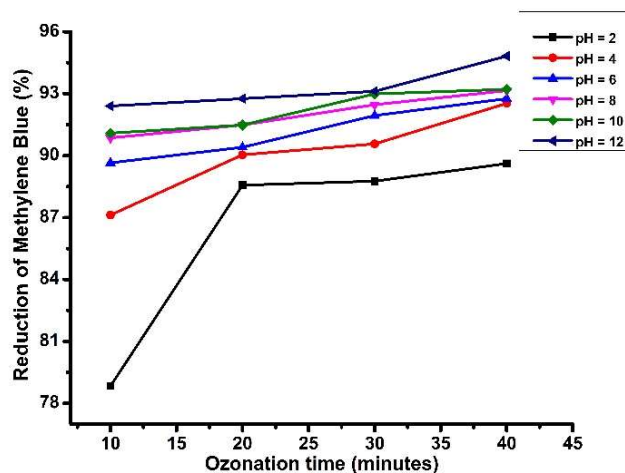


Figure 10. The trend of reduction MB as function of treatment times for several PH of MB with ozone concentration of 98.4 ppm

Figure 10 shows the trend of MB reduction as a function of treatment times for some initial pH of MB solution. The rate of ozone decomposition is favored by the formation of hydroxyl radicals at higher pH values [11]. so it can be seen that at high pH values ozonation time is less than at low pH. It can be seen that the ozonation time decreases with increasing initial pH of the solution. A high initial pH of the solution also provides a faster MB

reduction rate than a low initial pH of the solution.

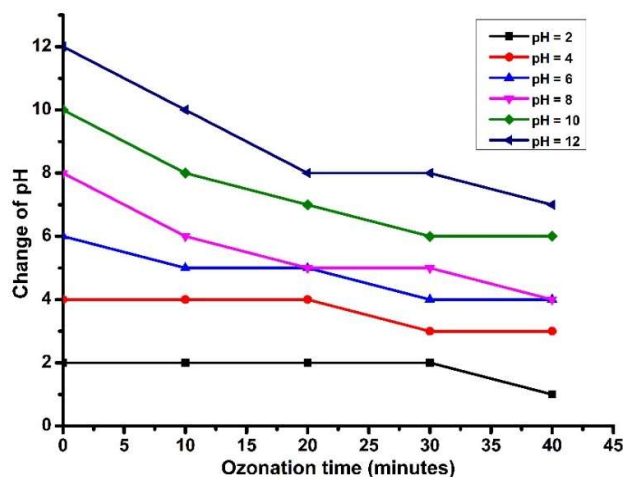
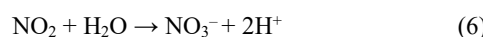


Figure 11. The change of methylene blue's pH as function of treatment times for several initial pH of MB and ozone concentration of 98.4 ppm

On the other hand, increasing the treatment time of MB solution causes the pH of the initial MB solution to change as shown in Figure 11. All the initial pH of the solution has decreased during the treatment time. The pH values of all the MB solutions gradually reach a certain level in the range of acidic conditions. That may be due to some special acid compounds such as nitrous acid and nitric acid, which are derived from nitrogen in the air during the release process as given in equation (2)-(6). In addition, carboxylic intermediates produced in the MB degradation process can also contribute to certain pH variations in solution. The reason is that more hydroxyl radicals are produced in the acidic atmosphere and increase the decomposition of O₃ to hydroxyl radicals in the presence of OH⁻ (Wu *et al.* 2019). So the pH value of the solution decreases as shown in Figure 11.



3.4. Influence of Initial Solution pH

pH is one of the important parameters that control water quality because pH is able to determine the rate of reaction of substances in water (Mundadan *et al.*, 2017). Because the dyeing of wastewater ranges from acidic to basic conditions (Pavithra *et al.* 2019), (Wu *et al.* 2019), it is necessary to investigate the effect of the pH of the initial solution on the MB reduction efficiency. Figure 12 shows the tendency of pH variations to the level of MB reduction for some ozonation time. The increase in the initial pH solution with the concentration of ozone and MB that remains constant is proportional to the reduction level of MB in the solution which also increases.

At basic pH, ozone quickly decomposes to produce hydroxyl radicals and other radical species in solution (Desai & Mehta 2014). So the MB reduction level at low pH shows a significant increase than the upper pH. This can be seen in Figure 12.

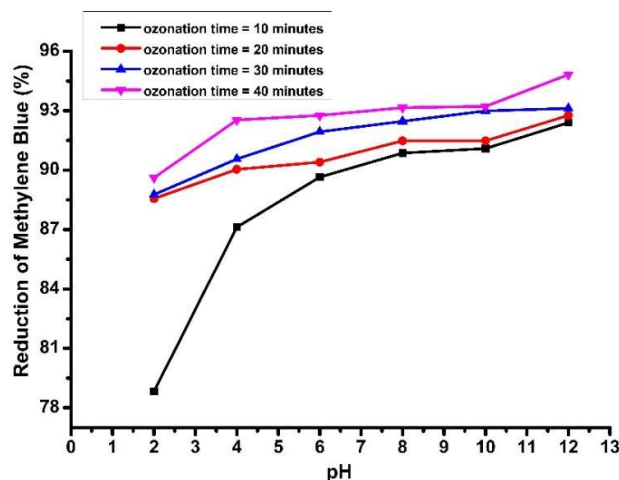


Figure 12. The reduction of methylene blue as function initial pH for several treatment times and ozone concentration of 98.4 ppm

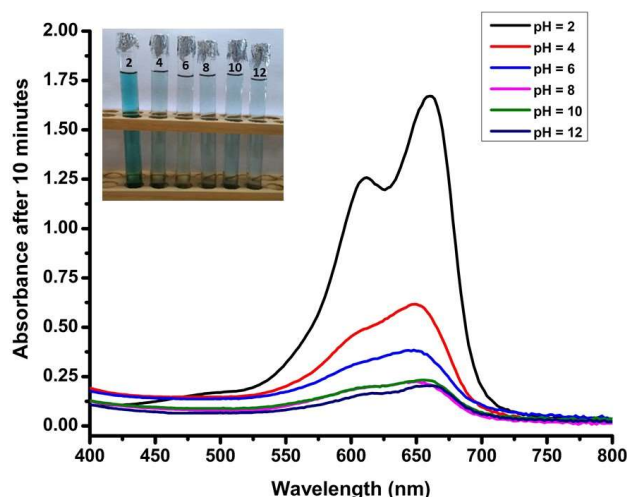


Figure 13. The absorbance curve of methylene blue as function of wave length for several pH of MB

Figure 13 shows the absorption spectrum seen from the MB solution during the treatment process using direct continuous ozone. The absorption peak at 665 nm obviously decreases with increasing initial pH value of the solution. This shows that the MB dye molecules are reduced by the treatment process using direct continuous ozone. Almost all MB molecules decompose with the pH value of the solution reaching pH 12. Thus, this value can be used as a reference to the initial pH value of the solution for the treatment process using direct continuous ozone. Because the MB concentration is linear with the absorbance value, so the smaller the absorbance value, the smaller the MB concentration in the solution. So from this graph, it can be seen that the optimal MB reduction pH is at least 8 with an initial concentration of 40 mg / l, a volume of 100 ml, and an ozone concentration of 98.4 ppm. From the graph it can be seen that in the treatment above pH value is 8 the absorbance value significant decreases which indicates that the MB content has been optimally reduced when compared to pH value under 8.

3.5. Reduction Mechanism

The reduction mechanism of MB can be investigate use LC-MS to explore the possible reduction intermediates. A possible pathway was put forward as shown in figure 14 by Lihang Wu, *et.al* (2019), with development from

results were reported by Wang, *et.al* (2017).

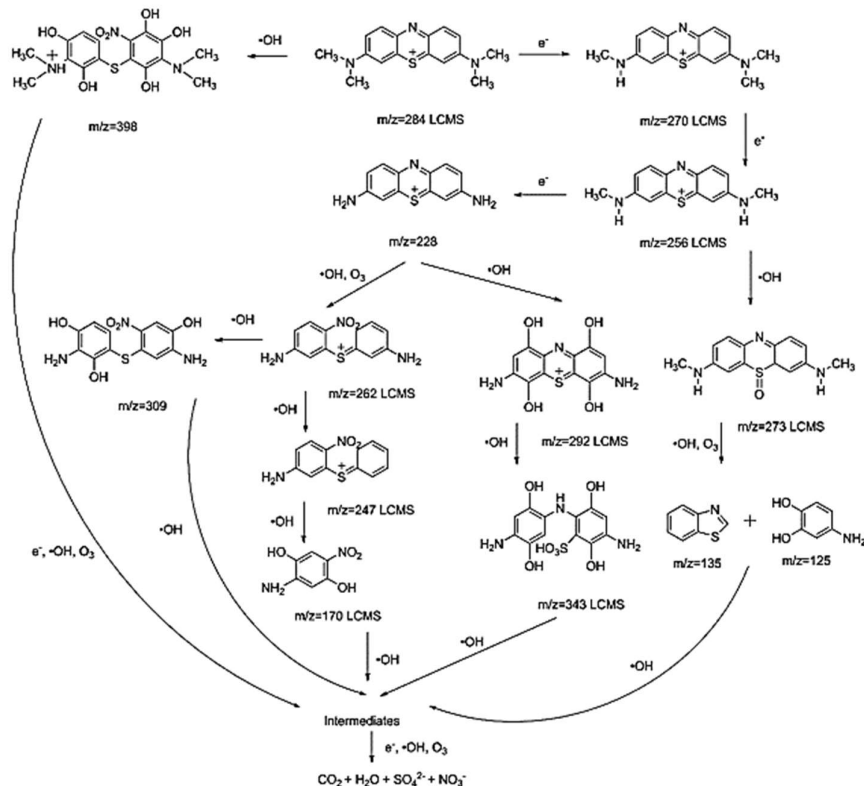


Figure 14. Possible pathway of MB reduction (Ling Wu, 2019)

The intermediates were mainly generated by high energy electron attack, ozonation and hydroxylation process. The existence of MB molecule was confirmed by peak at m/z of 284. With the presence of high-energy electrons which were attributed to demethylation, the presence of hydroxyl radical as the main species which was attributed to hydroxylation process, the bond energy and the possible ring breaking products which can be arised from hydroxyl radicals and ozone, so the possible intermediates of MB decomposition can be ionic by-products such as acetate, oxalate, and sulfate. And the finally, all of the intermediates were decomposed and mineralized into $\text{CO}_2, \text{H}_2\text{O}, \text{SO}_4^{2-}$ and NO_3^- .

4. Conclusion

In this study, the aqueous solution of a model basic textile dye and the Methylene Blue as the model compound, was treated using direct continous ozone. An experimental investigation was carried out to evaluate the effectiveness of direct continous ozone occuring by radical-type reactions for enhancing the degradability of aqueous solutions of the model recalcitrant pollutant on a laboratory scale. That shows that the concentration of methylene blue in the reduced solution after treatment uses direct continous ozone. The results with the basic dye, MB, show that the reduction in MB concentration and decolorization is quite extraordinary under basic conditions (pH 12). High ozone concentrations are effective for reducing MB concentrations in solution. Increasing the concentration of ozone will increase the concentration of dissolved ozone, making decolorization faster. While high pH values encourage a greater reduction rate. This shows that high pH values encourage more effective ozone decomposition in water.

Acknowledgment

All members of group of research thanks to Ministry of Research, Technology and High Education for financial support of this research in the scheme High Education Innovation Programe (IPT Programe) of the year 2019 with contract number 09/PKS/IPT/INSENTIF/IV/2019. The facilities of this project had been used for plas research and its application at Diponegoro University

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