

Treatment of simulated printing and dyeing wastewater using ozone microbubble

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Abstract. Owing to its widespread and persistent usage, methylene blue (MB) is an environmental substance, mostly found in the printing and dyeing industry that raises concerns in the environment recently by posing significant threat to human life and the ecosystem as a whole. Thus, there is the need to effectively manage and treat the wastewater from these industries before reaching to the available water sources. Ozonation treatment is very efficient in treating printing and dyeing wastewater (MB) and can be greatly improved by using micro-bubble technology. Microbubble dissolution is an effective way to improve the rate of ozone mass transfer. To discover these properties, a method was used to improve the mass transfer of ozone microbubbles, which was used to effectively treat simulated printing and dyeing wastewater. We investigated the effects of pH, water temperature, ozone flow, and other conditions on the dissolution and attenuation properties of ozone in methylene blue microbubble solutions. Treatment of simulated printing and dyeing wastewater (methylene blue) was investigated under various initial pH and ozone flow rates. A catalytic exhibition was performed towards the decolorization of methylene blue (MB) concentrations and the corresponding COD removal efficiency. Ozone depletion and pH levels played key roles in MB degradation. Under high pH level of 11.01, the rate of removal of COD was 93.5%. Ozone dosage also has direct effect on COD removal efficiency and decolorization. Higher ozone flow rates, 0.4 L/min and 0.5 L/min recorded more than 94% degradation of COD thus very effective and efficient. Also, ozone flow rates 0.3 L/min, 0.4 L/min and 0.5 L/min with initial pH, 7.03, 6.63 and 6.36 decreased to 3.43, 3.49 and 3.44 after reaction processes which clearly shows that with high ozone dosage, pH reduces considerably.

1 Introduction

One inalienable quality of man is the quality of procreation and as procreation proceeds, there is an unabated need to enhance, conserve and preserve the available resources to sustain the progeny of man. Thus, the quest of nations and the human race to better their living and national development has resulted in several issues of Environmental pollution, especially water pollution which is detrimental to human health as well as the sustainability of the Environment. Water pollution remains a major issue to be addressed by improving wastewater treatments. Printing and dyeing wastewater from the textile printing and dyeing industry is a high concentration of organic wastewater, complex ingredients, strong alkaline, color, depth, containing toxic and harmful substances that causes serious pollution on the environment. Methylene blue wastewater is very difficult to treat on its own and can cause harm to other clean water bodies and as a matter of fact threatens human body so as vigorously pollutes the water environment thus it is imminent to dispose of them

(Jack Clifton and Leikin, 2003). Therefore, dyeing wastewater comprehensive treatment theory has become one of the problems that need to be tackled at present. Among all the different water treatment, oxidation technology is almost the best method, especially in refractory wastewater treatment. Ozone oxidation processes can achieve disinfection, color removal and degradation of organic pollutants in a single unit process [4]. Recently, the use of ozone microbubble generator in wastewater treatment results of interest basically because ozone has strong oxidizability hence is widely used in drinking water and wastewater treatment. However, due to the low solubility and selective oxidation of ozone, the traditional ozone oxidation technology has the problems of slow gas-liquid mass transfer rate, weak oxidation capacity and low ozone utilization rate, which limits its application [2,5,6]. Furthermore, ozone is not effective in the mineralization of organic substances. In many cases, ozonation cannot completely oxidize organic substances into carbon dioxide, leading to the production of oxidation by-products [3]. To improve the efficiency of ozonation process, few novel techniques, have been

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tested which include catalytic ozonation. Undoubtedly, efficient technique for ozone transfer rate improving is especially desired for the treatment of wastewater containing high concentrations of organic pollutants.

Microbubbles are small bubbles with a diameter of less than 50 microns. Compared with traditional bubbles, microbubbles with a diameter of 10-50 μ m can enhance the gas-liquid mass transfer process [1,3]. Also associated with conventional bubbles with a diameter of several millimeters, microbubbles have a huge interface area, high bubble density, low rising velocity and high internal pressure, which can effectively dissolve ozone into the solution [14] and optimize the ozone oxidation process [15]. Ozone microbubble technology has been widely studied and applied in wastewater decolorization, deodorization, sterilization, and pollutant removal [16,17], but there are few studies on the mass transfer and attenuation characteristics of ozone microbubble in water.

Keiji et al. [18] reported that microbubble technology can improve the mass transfer rate of gas, but ozone will be affected by gas-liquid flow parameters and environmental conditions in the dissolution process. In this work we propose to assess the discoloration rate of methylene blue (dye) concentration as a function of different pH levels so as varied ozone flow rates coupled with its respective COD removals under different retention times. This is strictly centered on using ozone microbubble generator as a tool to effectively measure the removal rates of chemical oxygen demand (COD) in a simulated printing and dyeing wastewater so as check for the decolorization and degradation effect.

Therefore, this article using the microbubbles generating device, developed by ozone is studied under different water (pH, temperature) and operating conditions (gas flow rate and pressure) system of liquid phase concentration of ozone, ozone, decomposition coefficient of mass transfer coefficients and the effects of parameters such as half-life, micro air bubble technology for ozone in water purification applications provide a theoretical basis.

2. Methods and Materials

2.1 Experimental device

The experimental device is shown in Figure 1 and 2. Ozone gas is produced by ozone generator (Zhejiang Saige Environmental Protection Technology Co., Ltd) with oxygen as gas source. The gas flow was controlled by flowmeter, and the ozone production was measured by ozone concentration detector. Ozone is mixed with the circulating liquid in the reactor into the microbubble generator (Self-Made). The reactor is sealed with an effective volume of 800ml MB concentration.

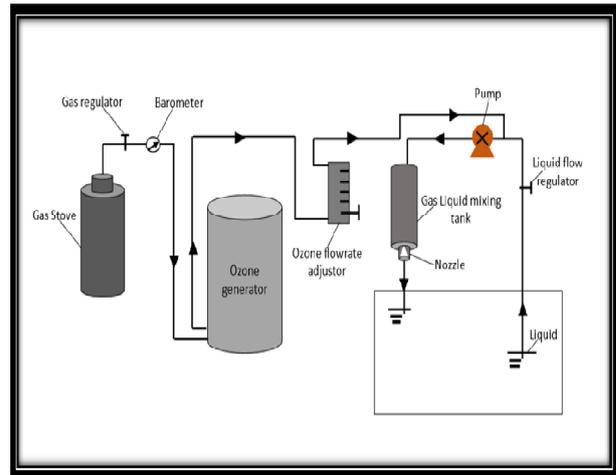


Fig.1. Schematic diagram of experimental apparatus



Fig.2. A photograph of the experimental setup in the lab

2.2 Parameter analysis method

The parameter test methods are showed in table 1.

Table 1. Test detection indicators and test methods

Parameter	Detection Method
pH	Portable Meter
Chemical Oxygen Demand (COD)	Potassium dichromate method (Photometric Colorimetric Determination Equipment (PCD))
Dissolved Oxygen	DO instrument
Temperature	Portable thermometer
Decolorization	Ozone (O ₃)

2.3 Materials

The main experiment materials are showed in table 2.

Table 2. Main experiment materials

<i>Chemical Name</i>	<i>Chemical formula</i>
Methylene blue trihydrate	$C_{16}H_{18}ClN_3S \cdot 3H_2O$ F.W.373.90
Potassium Iodide Solution	KI
Sulfuric Acid Solution	H_2SO_4
Starch Solution	$(C_6H_{10}O_5)_n$
Sodium Hydroxide	NaOH
Sodium Carbonate	Na_2CO_3
Hydrogen Sulphate	$H_2Na_2O_4S_2$
Sodium Thiosulfate Pentahydrate	$H_2Na_2O_4S_2$

2.4 COD measurement method and instrument

COD tends to measure the organic matter in the samples taken by using a chemical oxidant. It's critical that a strong enough oxidant is used to react with virtually all organic material in the collected samples. The underlined steps were systematically followed in the measurement of the COD levels during the entire experimental and analytical processes.

- With the use of a pipette gun, 2.5ml each of the original samples (wastewater) were taken with same amount of distilled water as a blank.
- 0.7ml of COD LH-D reagent (oxidant, potassium dichromate mercuric sulphate solution) is added to all samples and shaken thoroughly to form a uniform mixture.
- Addition of 4.8ml, COD LH-E reagent (catalyst, sulfuric acid silver sulfate solution) to all samples again and also shaken very well to form a uniform mixture.
- Sample tubes are carefully wiped and placed under 165°C of thermal digestion for 10 minutes.
- Samples are then removed to cool down for 2 minutes.
- 2.5ml of distilled water is added to all samples and shaken thoroughly to form a uniform mixture.
- Samples are placed in water to cool down for 2 minutes.
- Determination of COD content takes place with the use of the photometric colorimeter equipment (Lianhua Technology).



Fig.3. A picture of COD equipment (left) and thermal digestion equipment(right)

2.5 Experiment and Test Method

To facilitate the treatment of simulated printing and dyeing wastewater using ozone microbubble generator, the experiment made use of equipment, as captured in fig.1 and also a pH device (Sartorius PB-10) which was basically used to check for both pH and temperature of the wastewater. Sulfuric acid (H_2SO_4) and Sodium hydroxide (NaOH) were used to adjust the initial pH value for the start of each level. A “Before” sample is taken before reaction process starts then subsequent samples follows within stipulated retention times (3mins, 5mins, 8mins and 10mins). Different experiments were conducted under varied pH levels and ozone flowrates after which samples gathered went through laboratory analysis to check for the efficiency and removal rate of COD.

3 Results and Discussion

3.1 Effect of ozone microbubble on the decolorization of Mb concentration.

The effect of ozone on the decolorization and decomposition of Mb concentration by the use of magnetic stirrer is vividly shown in Fig.4. This was carried out during the preliminary stages to carefully detect how ozone can effectively remove the dye from the concentration. Methylene blue of 0.094g was measured and poured into a conical flask and then filled with distilled water to 1000ml. The concentration is thoroughly shaking to form a uniform mixture after which a sample of 800ml is taken and used for the experiment. Sample (0-Before Stirring) is taken down before the reaction process begins. Under an ozone flow rate of 0.4 L/min, mb concentration is then left to undergo reaction process where samples were taken after 3mins, 5mins, 8mins and 10mins respectively. It can be seen that the decolorization of mb can reach close to 100% within the space of 10mins as clearly shown in fig.3 below. Under ozone condition, the decolorization reaction is really accelerated hence significantly higher

and faster. The color goes through series of changes and completely decolorizes as time increases.



Fig.4. Decolorization effect of MB solution treated with ozone microbubble solution for 0~10min

3.2 Influence of pH on decolorization rate and COD removal efficiency of Mb.

The influence of pH on decolorization rate and COD removal efficiency of Mb is clearly shown in Fig. 5 below. In order to assess the direct influence of pH on COD removal so as the rate at which decolorization takes effect, we set the experimental conditions for the respective initial pH under an ozone dosage (OF) of 0.4 L/min. pH levels ranges between 3 and 11. COD degradation rate gradually increases under different conditions of pH.

With the exception of pH levels, 3.03 and 5.02 which recorded removal efficiencies of 87.4% and 88.2% respectively, the rest saw a drastic increase in COD removal. pH levels, 4.26, 7.03, 9.05 and 11.01 recorded significant and effective removal rates of COD, 90.2%, 91.2%, 92.8% and 93.5% respectively. This clearly depicts that under the ozone flow rate of 0.4 L/min, methylene blue (mb) concentration with pH 11.01 recorded the highest removal of COD. Hence the higher the pH, the higher the degradation rate of COD. The lower the pH level, the higher and faster decolorization effect and the higher the pH, the lower and slower decolorization effect. Mb concentration under low pH (less than 3) with ozone dosage 0.4 L/min, through reaction process, records fast decolorization within the space of 10 minutes as compared to pH levels higher than 5 which decolorizes slowly, hence taking more than 10 minutes to completely change color (become colorless).

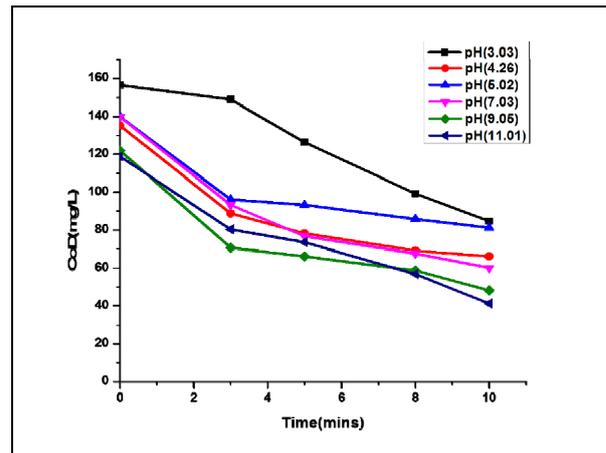


Fig.5. COD degradation rate under different pH conditions

3.3 Effect of varied ozone dosage on COD removal.

Ozone is the major player in this simulated printing and dyeing wastewater treatment processes, thus the dosage of O_3 has significant effect on the degradation of COD and decolorization of the concentration. This is clearly shown in Fig.6. With test conditions: pH (6-7), temperature ($19^{\circ}C-20^{\circ}C$), the degradation rate of COD changes at different flow rates of ozone. With increasing dosage of ozone, COD removal increases after 10 minutes. The reaction almost reach equilibrium in the process where dosages are 0.4 L/min and 0.5 L/min. There are 6 different dosages of ozone, 0.05 L/min, 0.1 L/min, 0.2 L/min, 0.3 L/min, 0.4 L/min and 0.5 L/min with corresponding removal of COD, 88.4%, 89.3%, 91.2%, 93.7%, 94.1% and 96.1%. When the amount of ozone flow is relatively small, there is slow changes in the removal efficiency of COD. From the experimental results shown in Fig.6, after reaction period of 10 minutes, the concentrations with ozone dosage of 0.3 L/min, 0.4 L/min and 0.5 L/min recorded more than 93% COD removal hence very effective and efficient. Thus, taking into account, 0.4 L/min is chosen as the best dosage of ozone in all the subsequent experimental processes.

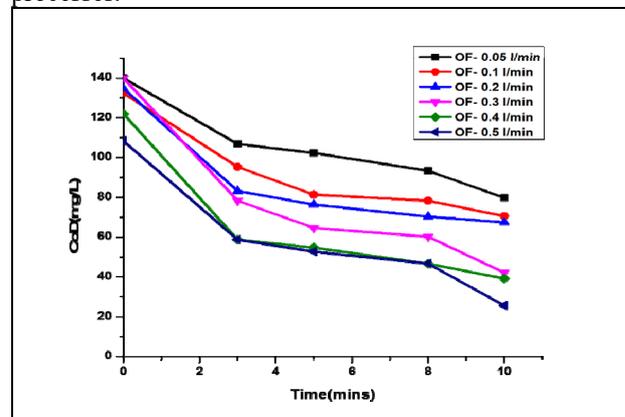


Fig.6. Effect of ozone dosage on the degradation rate of COD

3.4 Temperature variation under different ozone dosages.

To assess the variations of temperature under different ozone flow rates, experiment was carried out under conditions of initial pH ranging from 6-7 and ozone dosages of 0.05 L/min, 0.1 L/min, 0.2 L/min, 0.3 L/min, 0.4 L/min and 0.5 L/min and the results are shown in Fig. 7.

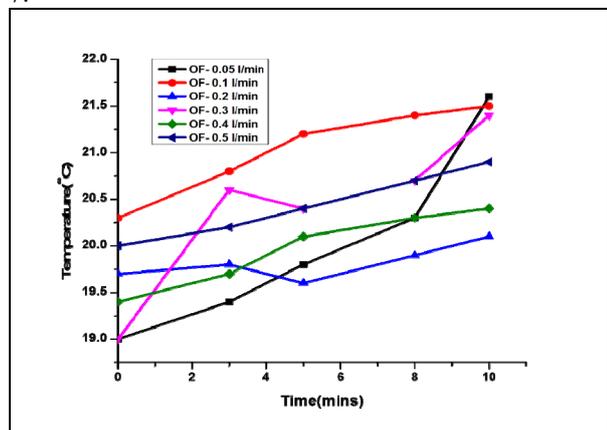


Fig. 7. Influence of ozone dosages on reaction temperatures

As shown in Fig. 7, under all the different ozone dosages, the initial temperatures were between 19°C – 20°C. Temperatures persistently increased throughout the stipulated retention times under ozone flow rates, 0.05 L/min, 0.1 L/min, 0.4 L/min and 0.5 L/min with the exception of O₃ flow rates, 0.2 L/min and 0.3 L/min which recorded a bit of fluctuations within retention times, 3 minutes and 5 minutes, where for 0.2 L/min, there was an increase in temperature from initial 19.7°C to 19.8°C and later saw a decrease in temperature to 19.6°C before increasing to the end. Ozone flow rate 0.3 L/min also recorded same trend of rise, fall and rise under the same times where initially the temperature was 19°C, rose to 20.6°C within 3 minutes and then dropped to 20.4°C in 5 minutes before increasing to 20.7°C and 21.4°C under 8 and 10 minutes respectively.

3.5 Influence of ozone dosage on pH values.

In order to critically analyze how ozone flow rate affect the values of pH, another experiment was conducted with test conditions: initial pH ranging from 6-7 with ozone dosages, 0.01 L/min, 0.1 L/min, 0.2 L/min, 0.3 L/min, 0.4 L/min and 0.5 L/min. The temperature ranges were between 19°C – 21°C and the reaction time of 10 minutes. Ozone flow rates had influence on the respective initial pH values of the methylene blue (mb) concentration and the result is shown in Fig.8.

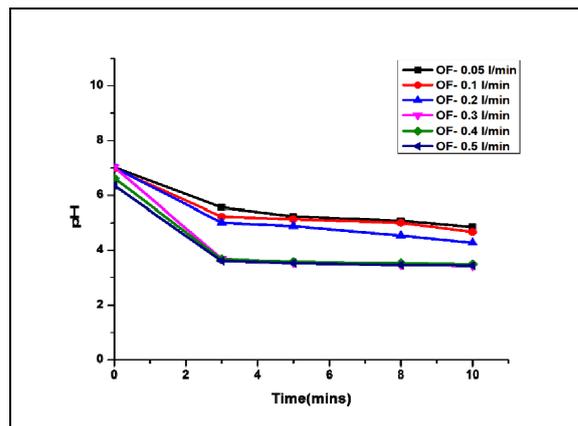


Fig.8. Influence of Ozone flow rates on pH levels

Fig. 8 clearly shows that with increasing dosage of ozone, pH levels decrease after 10 minutes of reaction period. Mb concentrations with ozone flow rate, 0.01 L/min, 0.1 L/min and 0.2 L/min, under initial pH of 7.03, 6.98 and 7.01 respectively recorded a slight decrease in levels after 3 minutes of reaction period where concentrations with ozone flow rate 0.01 L/min decreased from 7.03 to 5.56 under 3 minutes and 4.86 after 10 minutes. Flow rates 0.1 L/min and 0.2 L/min also recorded a bit similar decrease in pH levels after reaction period of 10 minutes. Ozone dosages, 0.3 L/min, 0.4 L/min and 0.5 L/min had greater influence on the pH levels of Mb concentration where it recorded about 50% decrease in pH levels under 3 minutes and slowly decreases after 10 minutes. Ozone flow rates 0.3 L/min, 0.4 L/min and 0.5 L/min with initial pH, 7.03, 6.63 and 6.36 decreased to 3.69, 3.68, 3.61 under 3 minutes respectively and a corresponding decrease to 3.43, 3.49 and 3.44 after reaction period of 10 minutes. Thus, when ozone dosage is high, pH values decreases drastically and when it is low, it records a bit slower decrease.

3.6 Effect of pH value on temperature.

Under different initial pH values, another set of experiment is set to figure out how pH influences the degree of hotness and coldness in the process of ozone degradation of methylene blue (mb). Fig. 9 shows how the variation in pH values affect temperature levels during reaction period.

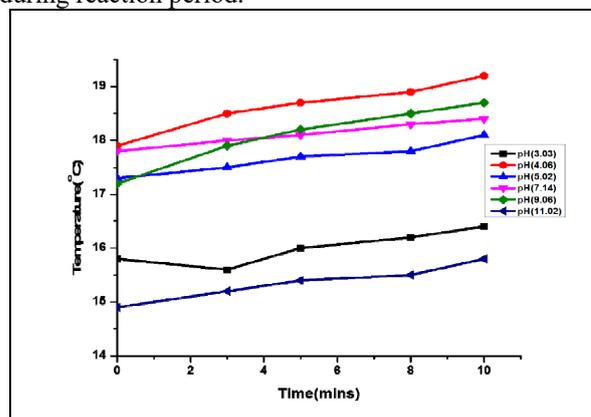


Fig. 9 Variation of concentration pH and its effect on temperature

As shown in Fig. 9, pH levels are set to be 3.03, 4.06, 5.02, 7.14, 9.06 and 11.02 with initial temperatures: 15.8°C, 17.9°C, 17.3°C, 17.8°C, 17.2°C and 14.9°C respectively. With 800ml of methylene blue concentration and ozone dosage of 0.4 L/min, the temperature levels persistently increased throughout the reaction time of the experiments under each level. Unlike pH- 3.03 which recorded a decrease in temperature right after reaction period of 3 minutes and subsequently increased to finish, i.e., initial temperature of 15.8°C before experiment and later dropped by 0.2°C after 3 minutes before increasing to 16°C after 5 minutes and consequently 16.4°C within 10 minutes. Therefore, pH values don't adversely affect temperature levels as temperature goes through its normal state of rise which helps to speed up reaction process.

4 Conclusion

In this study, a new type of ozone microbubble generation system was established by using the method of enhancing the mass transfer of ozone microbubbles to effectively treat a simulated printing and dyeing wastewater. The effects of pH, water temperature, ozone flow rate and other conditions on the dissolution and attenuation characteristics of ozone in microbubble methylene blue solution were investigated.

The study was strictly centered on using ozone microbubble generator as a tool to effectively remove the chemical oxygen demand (COD) in a simulated printing and dyeing wastewater so as check for the decolorization and degradation effect.

With an ozone dosage of 4 L/min and methylene blue (mb) concentration of 800ml, there was a higher exhibition of catalytic towards the degradation and decolorization of mb concentration within the space of 10 mins. The color goes through series of changes and completely decolorizes as time increases, COD removal rate was very effective too. Mb under low pH (less than 3) with ozone dosage 0.4 L/min by reaction process, records fast decolorization in the space of 10 minutes as compared to higher pH levels (above 5) which decolorizes slowly hence take 10 minutes to fully change color.

The possible degradation mechanisms were greatly influenced by pH values and ozone dosages. Under high pH levels, COD removal efficiency of simulated printing and dyeing wastewater (mb concentration) treated by ozone microbubble oxidation, were significantly higher and effective. The removal rate of COD is 93.5% with pH of 11.01.

Notwithstanding the above, the main player of this experiment is ozone and its level of dosage has direct effect on COD removal so as decolorization rate. It was revealed that the higher the flow rate, the faster the changes in decolorization and a corresponding increase and effectiveness in COD removal efficiency. Ozone dosages of 0.4 L/min and 0.5 L/min recorded more than 94% degradation rate of COD hence very effective and efficient.

This study presents relevant data demonstrating that the treatment of printing and dyeing wastewater through the utilization of ozone microbubble increases the removal efficiency of some organic pollutants from industrial wastewater basically from the textile industries. Also, this technique is not only effective, feasible, inexpensive, energy saving, reduction of wastewater treatment cost and environmentally friendly but it also serves as a source of resource utilization and reuse. Furthermore, it provides alternative textiles wastewater recycling for both developing and developed countries thereby reducing their environmental and health impact.

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