

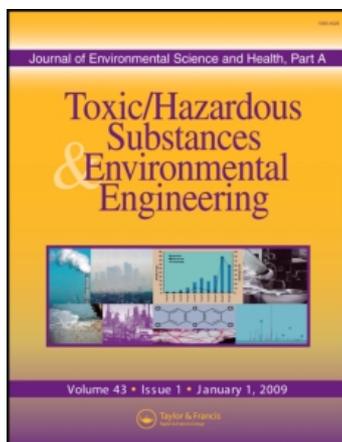
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Journal of Environmental Science and Health, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597268>

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First published on: 17 March 2010

To cite this Article Baek, Mi-Hwa , Ijagbemi, Christianah Olakitan and Kim, Dong-Su(2010) 'Spectroscopic studies on the oxidative decomposition of Malachite Green using ozone', Journal of Environmental Science and Health, Part A, 45: 5, 630 – 636, First published on: 17 March 2010 (iFirst)

To link to this Article: DOI: 10.1080/10934521003595779

URL: <http://dx.doi.org/10.1080/10934521003595779>

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Spectroscopic studies on the oxidative decomposition of Malachite Green using ozone

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Spectroscopic studies on the oxidative decomposition of Malachite Green (MG) using ozone were investigated. Parameters such as color removal, initial dye concentration, COD reduction, reaction temperature and pH were studied to determine optimum conditions for complete MG decomposition. Complete removal of MG color was achieved within 10 min of reaction with ozone. The ozone oxidation reaction time increased as concentration of MG increases, inferring, there would be increase in MG removal as concentration decreases. COD reduction was observed as reaction time increases and the rate of reaction monotonically increased as temperature increases. From the spectroscopic analysis of the intermediates and the by-products of MG reaction with ozone, a tentative mechanistic approach of MG decomposition was postulated. It was also observed that after five minutes of ozone oxidation, color removal rate in the wastewater containing Malachite Green obtained from a small scale local dyeing industry reached almost 90%.

Keywords: Spectroscopic analysis, Malachite Green, decomposition characteristics, ozone oxidation

Introduction

Malachite Green (MG), also known as C.I. Basic Green 4, is a toxic chemical primarily used as dye for materials like silk, leather, and paper.^[1] Though, it is an extremely effective weapon against fungus and parasitic infections in fish, but its metabolites have serious side effects on aquatic life and as well in humans. MG is classified as Class II Health Hazard and has been found toxic in human cells leading to liver tumor formations.^[2] Several countries have banned the use of MG in food and food processing, also the US Food and Drug Administration does not approve its use, but MG applications are still be found in many parts of the world due to its low cost, availability, and efficacy for some desired purposes.^[3] The oral consumption of MG is hazardous and its toxicity such as carcinogenesis, mutagenesis, teratogenesis and reduced fertility has been reported.^[2–6] Therefore, the removal of MG in dye wastewater before being discharged to the environment is necessary and as well very important.

Large fractions of dyes are wasted during dyeing processes as most dye effluents still contain considerable dye concentrations.^[7] Over the years, a great deal of studies

has also been done on dye removal by adsorption processes. Adsorption technique has played a very significant role in removing toxic dyes from industrial effluents using waste materials from industrial and agricultural waste products such as de-oiled soya, red mud, bagasse fly ash, peat moss, rice husk, wool, bottom ash from thermal plants and residue of animal bones.^[7–11]

Adsorption and aerobic biodegradation have been found to be inefficient for complete decomposition and elimination of many reactive dyes.^[3] Recently, research work on wastewater treatment has been channeled towards complete elimination and decomposition of reactive dyes. Dye decomposition techniques such as advanced oxidation processes e.g. sonolysis and Fenton processes; chemical oxidation and reduction; photocatalytic and electrochemical treatment have been considered promising, efficient, cleaner and greener approaches. The advanced oxidation processes (AOPs) is linked to oxidative reactions by hydroxyl radical ($\cdot\text{OH}$) generated in treatment methods such as O_3/UV , $\text{H}_2\text{O}_2/\text{UV}$, $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ photolysis, photoassisted $\text{Fe}^{3+}/\text{H}_2\text{O}_2$, and TiO_2 -mediated photocatalytic processes.^[3,13–16]

Ozone oxidation is one of the most effective methods of producing the free radicals in AOPs. The attraction to ozone oxidation process (ozonation) over other chemical oxidation methods is the provision of two possibility degradation routes: (1) the reaction of ozone by mass transfer from the gas phase with the substrate in the bulk solution and (2) ozone auto decomposition, which gener-

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Received September 3, 2009.

ates radicals that react with the substrate. Literature has shown that ozone oxidation process has been successfully employed to decompose reactive dyes.^[13] One of the advantages of the process over other dye treatment processes is that ozone can revert to oxygen through autolysis without yielding harmful compositions. Ozone oxidation methods have been developed to economically generate ozone using atmospheric oxygen.

Malachite Green was chosen as a model substrate for this study as its decomposition by ozone has not yet been reported. To date, various techniques including ultrasound irradiation,^[14] UV and visible irradiation over Sn-doped TiO₂ film^[15] and Fe³⁺-catalyzed electro-Fenton process^[16] have been reported to decompose MG.

In this work, the decomposition of MG in aqueous solution using ozone oxidation process was investigated. Operating parameters such as color removal, initial dye concentration, COD reduction, reaction temperature and pH were studied to determine optimum conditions for complete decomposition, discoloration, and total oxidation of the MG dye. Based on UV-Vis, FT-IR and ¹H-NMR analyses, a tentative mechanistic approach of MG decomposition was postulated with a proposition on the possible MG degradation pathway.

Materials and Methods

Materials

The dye, Malachite Green oxalate salt with the IUPAC name, *N, N, N, N*-Tetramethyl-4,4'-diaminotriphenylcarbenium oxalate and molecular formula C₅₂H₅₄N₄O₁₂ (MW 927) was obtained from Sigma-Aldrich. The stock solution of ca. 1 mM was prepared in a 50 mL volumetric flask and stored in a cold and dark environment to prevent light degradation. All solutions were prepared using triple distilled water (>18 MΩ). Ozone as an oxidizing agent was generated from dried oxygen by feeding atmospheric air into a discharge-type ozone generator (Ozonias Co., LAB2B) with oxygen intake fixed at 6 L min⁻¹. The amount of ozone generated (0.80 mg hr⁻¹) was controlled by varying the voltage with a variable dispenser. Figure 1 shows the schematic diagram of the reactor.

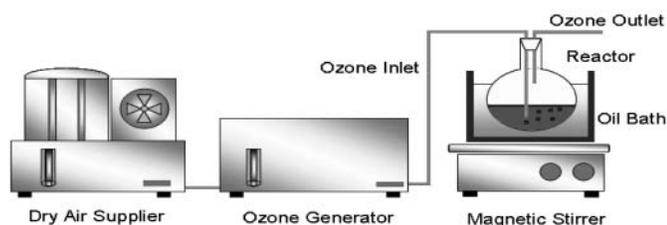


Fig. 1. Schematic diagram of reactor.

Table 1. Chemical assay of real wastewater.

| Items | Real wastewater |
|-------------------------------------|-----------------|
| pH | 4 ~ 5 |
| COD(mg L ⁻¹) | 400 ~ 450 |
| BOD(mg L ⁻¹) | 300 ~ 350 |
| SS(mg L ⁻¹) | 100 ~ 120 |
| Concentration (mg L ⁻¹) | 550 |

Procedures and analyses

A Pyrex flask was used as the reactor and the experiment was performed with 500 mL of MG solution with needed samples drawn out at regular intervals. In the course of the study, reduction in COD, effects of initial MG concentration, reaction temperature and pH were investigated. The study on effect of concentration entails varying the initial concentration (7, 14 and 21 mg L⁻¹) of MG by dilution using distilled water at 25°C. Temperature effects were measured with the reactor temperature controlled between 0°C and 46°C and observations at 0.1°C were recorded during an ice bath of the reactor. For high temperature effects the reactor was placed in a silicon oil bath. Using standard methods of COD analysis,^[17] changes in COD was observed by drawing out samples at 0 min, 5 min, 40 min, 180 min and 720 min of ozone addition. The initial pH of MG was controlled by the addition of dilute 0.1 M of H₂SO₄ and NaOH solutions.

Using the UV-Vis spectrophotometer (Jasco, V-550), the absorbance of the MG solution before and after ozone oxidation process were obtained at the maximum absorbance frequency ($\lambda_{max} = 617$ nm) of MG. Study on structural changes using FT-IR (Jasco, 300E) was carried in the region of 600–4200 cm⁻¹. To further elucidate structural changes in the dye's solution, observations on ¹H-NMR (Bruker, 250 MHz) was carried out.

Dye wastewater, containing Malachite Green, obtained from a small scale local dyeing industry was used in the study; the assay is presented in Table 1. Fifty times dilution of the real wastewater was made to obtain the similar concentration of dye solution in distilled water.

Result and Discussion

Decomposition of MG by ozone

The ozone consumption rate was fixed at 0.80 mg hr⁻¹ with 14 mg L⁻¹ and 25°C as initial concentration and temperature of the MG solution respectively. Within 10 min of the wastewater reaction with ozone, the initial green color of the dye was completely removed. Figure 2 shows the changes in UV-Visible spectra of MG during ozone oxidation at different ozone addition times. The decrease in the peak of MG at the maximum absorbance frequency indicates a rapid decomposition of the dye i.e.,

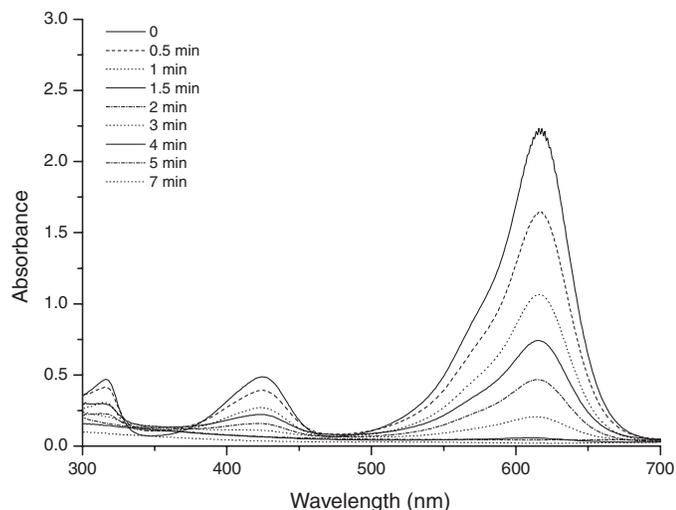


Fig. 2. UV-Vis spectra of MG according to ozone oxidation time (initial concentration of MG: 14 mg L^{-1} , ozone dosage: 0.80 mg hr^{-1} , initial pH: 4.4).

the destruction of MG conjugated structure by ozone. For 7 min of ozone addition, the maximum absorbance wavelength shifted from 617 nm to 605 nm. As displayed in Figure 2, the hypsochromic shift observed in the UV-Vis spectra, is an *N*-demethylation process.^[14,18]

Reduction in COD

Changes in COD were measured in order to provide information on the susceptibility of MG towards chemical oxidation. COD removal (%) during ozone addition was determined in 0, 5, 40, 180 and 720 min of ozone addition (Fig. 3). It was observed that COD reduction was

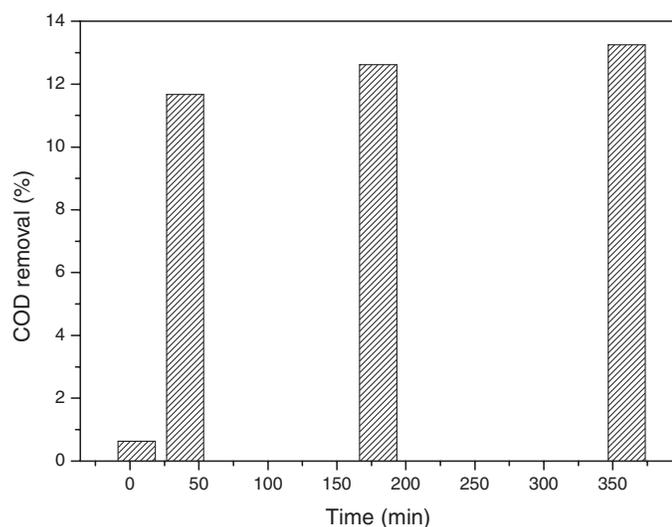


Fig. 3. COD removal with ozone oxidation time (initial concentration of MG: 8.4 g L^{-1} , ozone dosage: 0.80 mg hr^{-1}).

approximately 12% after 40 min of ozone addition. It has been reported^[19] that ozone oxidation process is efficient for dye decomposition and non-efficient for COD removal as the reduction in COD after 6 h of ozone addition was just 13.2%. Similar results of 11–29% and 5–20% reduction in COD have been obtained and reported.^[20,21] Reduction in COD monotonically decreased as ozone addition time increases (Fig. 3).

Kinetics and effect of initial MG concentration

Figure 4 presents the remaining concentration of MG at different initial dye concentrations for varying ozone oxidation time. Temperature was 23°C and ozone dosage was fixed at 0.80 mg hr^{-1} . With increase in concentration of MG, ozone oxidation time increases, this connotes, there would be increase in MG removal as concentration decreases. The half-life of molecular ozone varies from few seconds to few minutes and as well depends on substrate solution's pH, temperature and concentration. At low concentrations, molecular ozone can actively attack dye composition, and as such can be very unstable in water due to its high reactivity.^[22] Ozone half-life time in this study was 0.6 min, 1.0 min and 1.8 min at initial MG concentrations of 7, 14 and 21 mg L^{-1} respectively. The kinetics of the reaction of MG with ozone was therefore studied under these conditions, with the rate of dye decay determined at various concentrations. The results obtained from calculations as presented in Table 2, portray the reactions to be of the first-order mechanism.^[23] The first-order reaction rates were acquired using Equation 1.

$$\ln(C / C_0) = -k_1 t \quad (1)$$

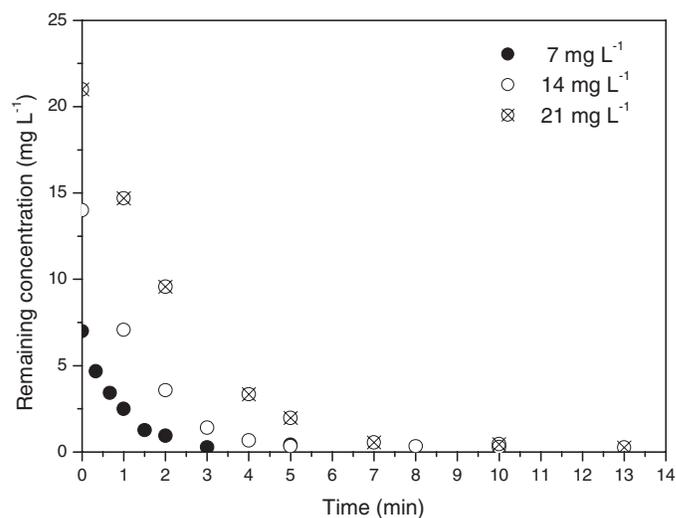


Fig. 4. Remaining concentration of MG at different initial concentrations for varying ozone oxidation time (ozone dosage: 0.80 mg hr^{-1} , temp.: 23°C).

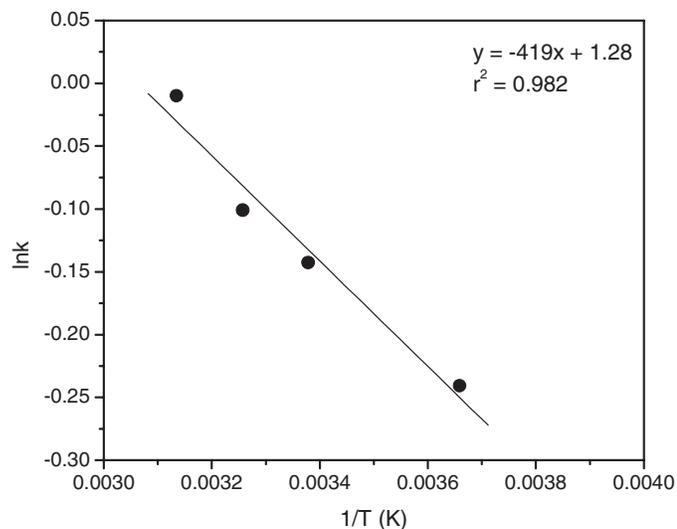


Fig. 5. Plot of $\ln k$ vs. $1/T$ (initial concentration of MG: 14 mg L^{-1} , ozone dosage: 0.80 mg hr^{-1}).

where, C is the concentration of MG in the dye wastewater after ozone oxidation, C_0 , the initial concentration of MG before ozone oxidation, k_1 is the first order rate constant and t is the reaction time.

Effect of temperature

The influence of temperature on the rate of MG decomposition was investigated and the results as displayed in Table 2 imply that the rate of reaction monotonically increases as temperature increases. The decomposition after 5 min of reaction was in the range of 96–98% under a temperature range of 0–46°C. Equally, from Table

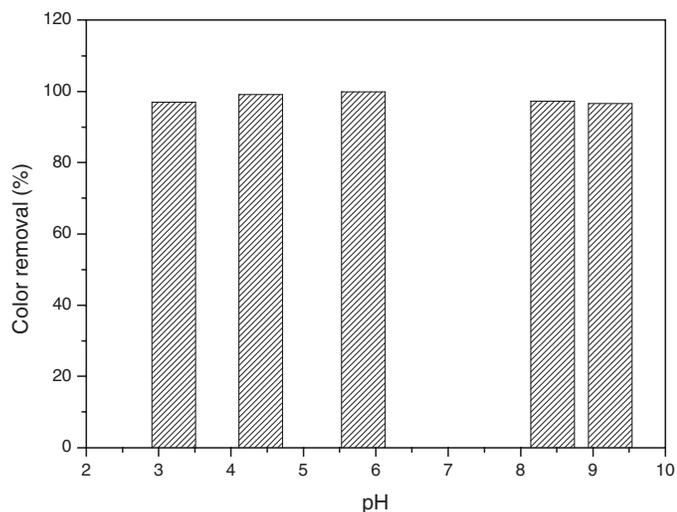


Fig. 6. Effect of pH on the reaction of MG with ozone (initial concentration of MG: 14 mg L^{-1} , ozone dosage: 0.8 mg hr^{-1} , temperature: 23°C).

Table 2. Reaction rate constants for MG decomposition at different initial concentrations and temperatures.

| Initial conc. (mg L^{-1}) | k_1 (min^{-1}) | Temp. | | k_1 (min^{-1}) | r^2 |
|---|-----------------------------|-------|----------------------|-----------------------------|-------|
| | | r^2 | ($^\circ\text{C}$) | | |
| 7 | 1.31 | 0.996 | 0 | 0.786 | 0.993 |
| 14 | 0.867 | 0.992 | 23 | 0.867 | 0.992 |
| 21 | 0.528 | 0.995 | 34 | 0.904 | 0.997 |
| | | | 46 | 0.990 | 0.998 |

2, as the reaction temperature increases, the rate of decomposition also increases. Similar behavior has been reported for some chemical processes that are chemical reaction dependent.^[24] The Arrhenius equation (Equation 2) is

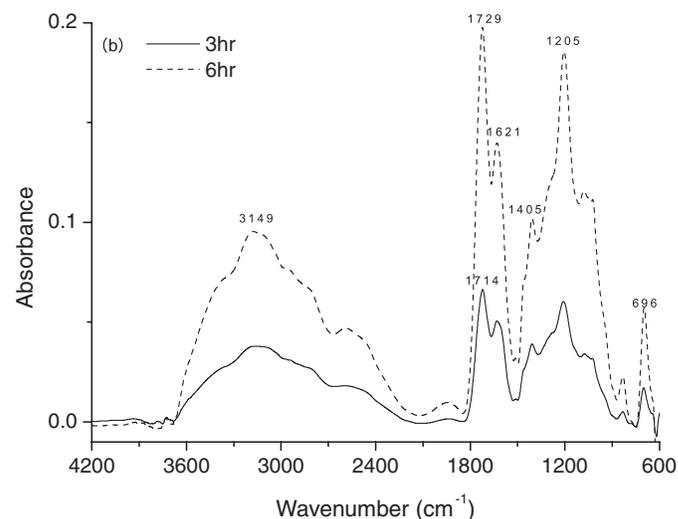
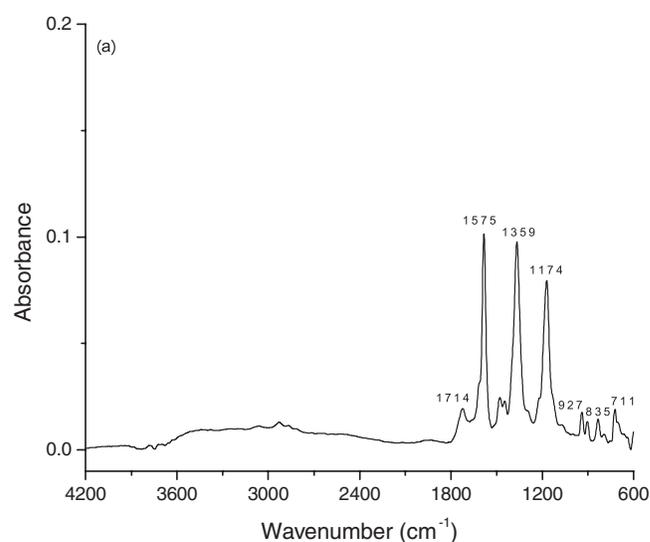


Fig. 7. FT-IR spectra: (a) before ozone oxidation and (b) after ozone oxidation (initial concentration of MG: 8.4 g L^{-1} , ozone dosage: 0.80 mg hr^{-1}).

given as:

$$\ln k = -E_a / RT + \ln A \quad (2)$$

where, k is the rate constant (min^{-1}) and T is the temperature (K). From Equation 2, a plot of $\ln k$ versus $1/T$ was drawn (Fig. 5), the slope E_a , yielded activation energy of 3.48 kJ mol^{-1} indicating that the process of MG decomposition by ozone is a spontaneous reaction process (Fig. 5). The positive E_a value is in agreement with reported literature.^[23]

Effect of pH

The influence of pH on color removal from the dye wastewater is shown in Figure 6. Color removal was observed in the alkaline medium and this behavior reveals that partial mineralization of MG is more pronounced when color removal takes place. The fact that degradation is more pronounced when ozone oxidation is carried out in the alkaline medium is a consequence of the oxidation potential presented by the hydroxyl radical. As the ozone oxidation reaction progresses, there is a corresponding decrease in pH value of the dye wastewater.^[25–27] Shu and Chang^[26] observed a decreasing pH in dye solutions during ozone oxidation and it was reported that ozone oxidation process rarely produces complete mineralization to CO_2 and H_2O , but leads to production of partial oxidation products such as organic acids, inorganic acids, aldehydes and ketones during the ozone oxidation process. Also from Figure 6, as from the pH of 4.4, color removal reduces as pH decreases; similar observation has been reported by Styliidi et al.^[25]

FT-IR and $^1\text{H-NMR}$ spectroscopic analysis

FT-IR and $^1\text{H-NMR}$ spectra were evaluated to elucidate structural change during the decomposition of MG by ozone. Figure 7 displays the FT-IR spectrum of the MG solution acquired before and after 3 hr and 6 hr ozone oxidation process. From Figure 7 (a), MG presents several bands in the region $600\text{--}4200 \text{ cm}^{-1}$, which can be ascribed as follows: The band at 1714 cm^{-1} corresponds to the carbonyl ($\text{C}=\text{O}$) stretching vibrations in carboxylic acids, and the intense peak at 1575 cm^{-1} can be linked to $\text{C}=\text{C}$ aromatic skeletal vibration. The bands situated at 927 cm^{-1} , 835 cm^{-1} , and 711 cm^{-1} were characteristics of the C-H bond located close to N in the aromatic ring while the peak located at 1359 cm^{-1} could be ascribed to C-H bonding in the $\text{CH}_3\text{-N}$ and peak at 1174 cm^{-1} shows the presence of the C-N bond. Important changes in the band intensities were observed after 3 hr and 6 hr of ozone addition (Fig. 7b).

The intense band at 3149 cm^{-1} , assigned to the N-H bond, can be proposed to be N -demethylation while the broad peak could signify the presence of the hydrogen bond between N-H and H_2O .^[28] The intense band that appeared near 1714 cm^{-1} in the FT-IR spectrum for 3 hr of ozone addition (Fig. 7 b), may have occurred due to the stretching vibrations in the carbonyl group, leading to formation of carboxylic acid after ozone addition. The C-O band of the carboxylic acid was displayed at 1205 cm^{-1} , while the $\text{C}=\text{C}$ and C-H band of the aliphatics which resulted from the breaking down of the aromatic rings, appeared at 1621 cm^{-1} and 696 cm^{-1} respectively. The band of CH_3 appeared at 1405 cm^{-1} .

As shown in Figure 8, the aromatic peaks in the benzene ring appeared at 6.5–7.6 ppm and the methyl peaks in the $\text{N}(\text{CH}_3)_2$ near benzene ring appeared at 3.04, 3.14 ppm.

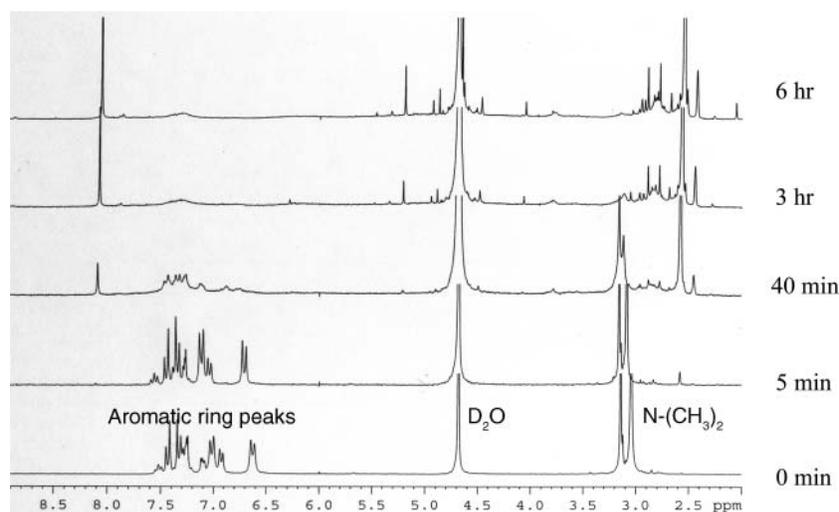


Fig. 8. $^1\text{H-NMR}$ spectra of MG according to ozone oxidation time (initial concentration of MG: 8.4 g L^{-1} , ozone dosage: 0.80 mg hr^{-1}).

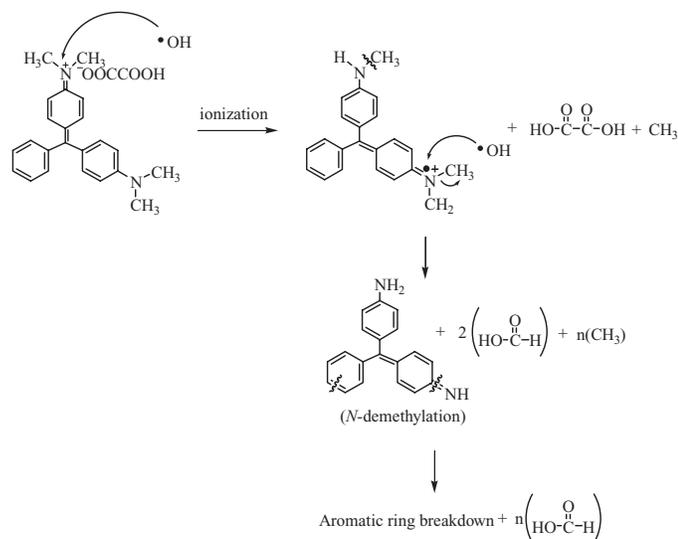


Fig. 9. Proposed degradation pathway of MG decomposition by ozone oxidation process.

As the decomposition reaction progresses, these peaks disappear. It can be said that the decomposition of MG by ozone took place due to the broken down of the benzene rings which resulted in a new peak at 8.1 ppm. This peak is the H peak of the carboxylic acid. The peak increases as ozone oxidation time increases. Also, the complex peaks at 2.0–3.0 ppm show the presence of the aliphatic compounds produced during decomposition process.

From Figures 2, 7 and 8, it can be said that the decomposition of MG by ozone might have occurred via two competitive processes: the decomposition of the conjugated structure and *N*-demethylation process. It has been assumed that ozone reaction in aqueous solution with target substrates could be a combination of two bi-molecular

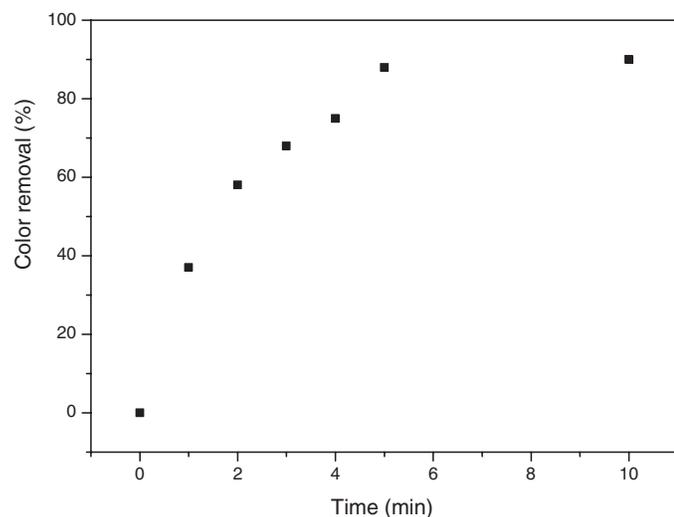


Fig. 10. Change in color removal with ozone oxidation time for real wastewater.

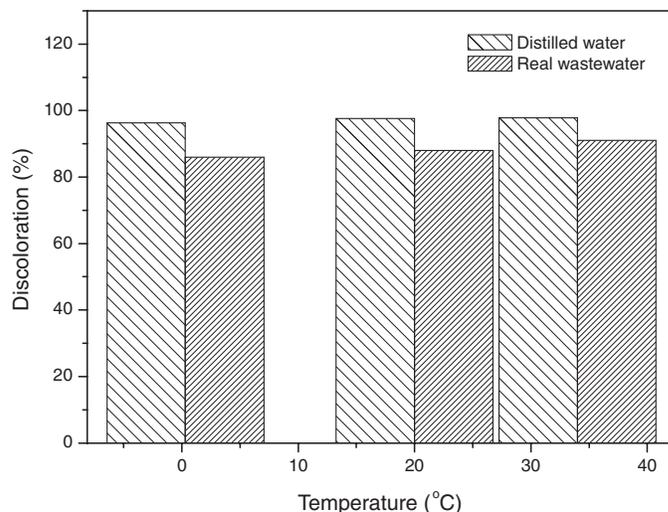


Fig. 11. Discoloration of dye in distilled water and real wastewater at different temperatures.

reactions, namely, a direct or indirect manner via reactions with its free radical decomposition products.^[24] The decomposition of MG can be said to have occurred by:^[28] a slightly partial degradation via the direct molecular ozone mechanism, which is highly solute selective, slow and very suitable for the opening of the aromatic rings by means of ozone cycloaddition; and a major degradation via a radical type reaction involving $\cdot\text{OH}$ induced by ozone's self-decomposing nature in aqueous solutions as shown in Figure 9.^[16,26,28]

Treatment of dyeing industry wastewater containing Malachite Green

Figure 10 shows the change in color removal with ozone oxidation time for real wastewater containing Malachite Green. After 5 minutes of ozone oxidation, color removal rate in the wastewater reached almost 90%. This discoloration behavior in the real wastewater can be explained by the same mechanism of discoloration with the synthetic dye solution. To examine the discoloration efficiency according to temperature, Figure 11 presents the discoloration of the dye when prepared with distilled water in comparison with real wastewater at different temperatures. Based on these results, ozone oxidation process showed a fairly high efficiency as discoloration after five minutes of reaction was 86%, 88% and 91% at temperatures of 0.3°C, 20°C and 34°C, respectively, which is applicable to real dye wastewater treatment.

Conclusions

Results obtained from the study indicate that ozone oxidation process can effectively be used in removing the initial

green color of MG from aqueous solutions. Information on determination of optimum conditions for complete decomposition of the dye can be deduced from studied parameters such as color removal, COD reduction, initial dye concentration, reaction temperature and pH. Complete color removal was achieved in 10 min of MG reaction with ozone. Color removal increases as concentration decreases and a COD reduction of 12% was observed in 40 min of the dye wastewater oxidation by ozone. Studies on temperature effects revealed that rate of reaction monotonically increases as temperature increases while the results from the spectroscopic analyses revealed that MG decomposition by ozone may have occurred principally by the breaking of the benzene rings. Therefore, the decomposition of MG by ozone might have occurred via two competitive processes of: decomposition of the conjugated structure and *N*-demethylation process. It can be suggested that ozone oxidation process could be a way out of the current environmental problems of industrial dye pollution.

Acknowledgement

This work was supported by the National Research Foundation (NRF) grant funded by the Korean government (No. 2009-0093-461).

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