

Removal of Diethylene Glycol from Wastewater by Photo Aeration

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Received: 18 May 2024 | Revised: 30 May 2024 | Accepted: 2 June 2024

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ABSTRACT

Photo air oxidation combines the use of ultraviolet (UV) light and air as an oxidant to degrade diethylene glycol (DEG) in wastewater. DEG is well known for its high chemical oxygen demand and has raised some serious environmental issues, since the conventional biological treatment package in plants may not be able to treat the waste in an effective manner. UV light generates highly reactive species, such as hydroxyl radicals ($\bullet\text{OH}$), which can react with DEG and break it down into smaller, less harmful compounds. Air, specifically oxygen (O_2), can act as an additional oxidant in the process, assisting in the degradation of DEG. The UV light source, such as low-pressure mercury lamps that emit at around 254 nm, is still needed to initiate the generation of hydroxyl radicals. The presence of oxygen in wastewater allows the hydroxyl radicals to react with DEG more effectively, improving the oxidation process. In the present research work, the effect of airflow rate, UV light intensities, oxygen partial pressure, and initial DEG concentration on photo-oxidation of DEG in wastewater was examined. We have also performed a kinetic study, from which the reaction order and the rate constant were determined.

Keywords-formatting; photo oxidation; aeration; diethylene glycol (DEG); rate constant; chemical oxygen demand

I. INTRODUCTION

Diethylene glycol (DEG) is a typical industrial chemical that is used in the production of solvents, antifreeze, and resins [1]. However, due to its possible toxicity to both people and the environment, DEG is considered a hazardous material [2]. Therefore, before wastewater is released into water bodies or used again in industrial operations, it is crucial to remove DEG from it. Photo-air oxidation is a useful technique for removing DEG from wastewater. By combining the power of light and oxygen, a process known as photo-air oxidation can break down and eliminate organic contaminants from water. When it comes to DEG, this procedure involves exposing wastewater that has been contaminated with DEG to ultraviolet (UV) light when oxygen is present. Highly reactive hydroxyl radicals ($\bullet\text{OH}$) are formed through chemical processes triggered by UV radiation. DEG molecules react with these radicals, resulting in their breakdown into smaller, less toxic chemicals.

There are several benefits in eliminating DEG using photo-air oxidation. Initially, this approach is non-invasive and does not necessitate the use of sophisticated machinery or the inclusion of chemicals. Continuous treatment is possible by the easy installation of UV lights in wastewater treatment plants. Furthermore, depending on the initial concentration and reaction conditions, DEG degradation can occur within minutes to hours, making the process rather fast. Generally, photo-air oxidation is a widely applicable technique that may efficiently

eliminate not only DEG, but also other organic contaminants found in wastewater.

Various solutions for the oxidation and removal of DEG or similar molecules from wastewater have been presented [3]–[7]. For example, monoethylene glycol was treated with ozone, which acted as an oxidant [3]. The authors suggested combining ozone with hydrogen peroxide in the presence of $\text{S}_2\text{O}_8^{2-}$ to circumvent the problem of low ozone solubility. This study investigated how the treatment method affected the Chemical Oxygen Demand (COD). The main intermediates found in the oxidation of ethylene glycol are glycolaldehyde, oxalic acid, and formic acid. More recently, the authors in [4] explored the degradation of ethylene glycol by photo-oxidation in the presence of activated hydrogen peroxide and persulfate anion. The researchers performed a comparative study of both photo-oxidation by hydrogen peroxide in the presence of UV light and photo oxidation in the presence of persulfate anions. It was found that the latter is more effective. The researchers investigated the process based on initial ethylene glycol concentration, reaction duration, oxidant dosage, and other parameters. The researchers also investigated the process kinetically. The reaction was found to follow first-order reaction kinetics. The rate constants for hydrogen peroxide in the presence of UV light and photo oxidation in the presence of persulfate anion were found 0.070 min^{-1} and 0.243 min^{-1} respectively.

In the present work, an economical and new method was developed for the treatment of wastewater containing DEG. The DEG was treated by photo aeration [8]. The treatment process was explored at different initial DEG concentrations, different air flow rates, and different intensities of UV radiation. Finally, the order of the reactions and the rate constants were estimated via a kinetic study.

II. MATERIALS

The aqueous solution of DEG used in this experiment was synthetically prepared and had varying amounts of DEG. DEG with a purity of 98% was used to prepare the test solution, which was then diluted with distilled water. A DR-6000 Hach UV-visible spectrophotometer was used to analyze the change in DEG concentration during the oxidation process. The concentration of DEG was determined from the COD using the DR-6000 Hach UV-visible spectrophotometer.

III. METHODOLOGY

A glass-jacketed reactor was used to carry out photo-oxidation of DEG. The reactor capacity was 2.5 L. A pH probe, an air supply tube with a sparger, a thermometer, and a UV emitting lamp inside a quartz tube made up the reactor. The light was kept at a distance of 25 centimeters. The quartz tubes used served two purposes. To evenly distribute UV light across the reactor solution and shield the UV lamp from the liquid. The power of the UV emitting lamp was set at 4, 8, and 12 W. The lamp produced UV radiation mainly at 255.2 nm. The sparger's primary objective was to ensure an even and efficient air distribution within the reactor. The experiments were carried out by testing different air flow rates, initial DEG concentration, and UV light intensity. Throughout the experiment, the stirrer speed was kept at 1000 RPM. Similar equipment and methodology have been used for the removal of sulfides and thiosulfates from wastewater [9].

IV. RESULTS AND DISCUSSION

A. Effect of Initial DEG Concentration

Figure 1 shows the effect of the initial DEG concentration on DEG photo-oxidation.

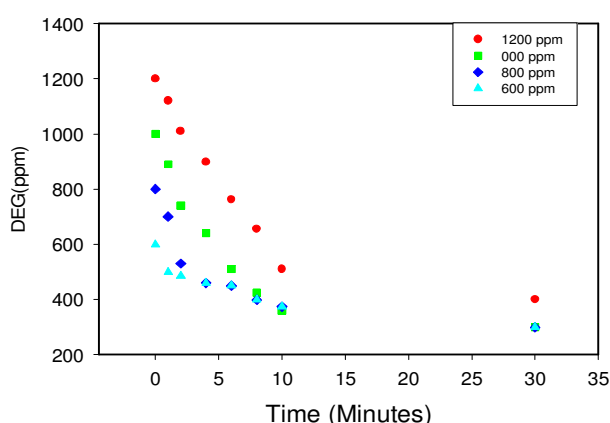


Fig. 1. DEG concentration decline for initial DEG concentrations of 600, 800, 1000, and 1200 ppm at 4L/min of airflow rate and 4 W of UV light power.

Air at a flow rate of 4 L/min was used to treat four distinct initial concentrations of 600, 800, 1000, and 1200 ppm. The power of UV light irradiation was 4 W during the photo-oxidation process. As shown in Figure 1, the higher initial DEG concentration resulted in a faster rate of DEG oxidation. The photo-oxidation procedure took 30 min to oxidize about 50% of the 400 ppm of DEG, while it took 60 min for the 1200 ppm concentration. Higher intensity UV light absorption may be the cause of the excited DEG ion production, which may explain the higher rate of photo oxidation.

B. Effect of Air flow Rate

Figure 2 shows that as airflow rate increased, DEG's oxidation rate also increased noticeably. An increase in the air flow rate is expected to make more oxygen available for the oxidation process. The air flow of 8 L/min exhibited the highest DEG photo-oxidation, which could be associated with the formation of activated oxygen species, such as singlet oxygen (1O_2) in the presence of ultraviolet radiation, reducing the energy barrier for oxidation [10]. The 1O_2 could have initiated a radical chain reaction that would have caused DEG to oxidize in solution. However, we were unable to confirm the presence of 1O_2 .

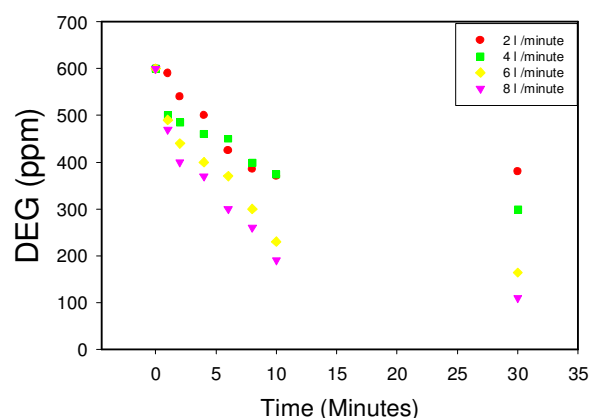


Fig. 2. Effect of air flow rate on DEG photo-oxidation. The UV light power was at 4 W and the initial DEG concentration was 600 ppm.

C. Effect of UV Radiation Intensity

Figure 3 illustrates how quickly DEG oxidation occurs in response to increased UV irradiation. Almost 50% of DEG oxidizes in around 30 minutes when exposed to 4 W of UV radiation, but nearly 70% of DEG oxidizes when exposed to 12 W of UV radiation. The intensity increased from 0.06 mW/cm² to 1.7 mW/cm², when the power increased from 4 to 12 W. Increased generation of singlet oxygen species may be the cause of the accelerated DEG oxidation observed under a higher UV radiation intensity. In agreement with our results, an increase in the rate of oxidation by increasing the intensity of the UV light has been observed in a previous study [11].

D. Effect of Oxygen Partial Pressure

Figure 4 shows that a higher partial pressure of oxygen accelerated the oxidation of DEG. 50% of DEG was found to be oxidized in 30 minutes under 4 W of UV irradiation and

21% of the the O₂ content. However, 600 ppm of DEG were completely oxidized after 30 minutes when the O₂ content increased to 30 and 40%. It is obvious that the increase in the partial pressure of oxygen also led to an increase in the conversion of DEG. The conversion under 4 W UV irradiation with 21, 30 and 40% O₂ was 50, 100, and 100%, respectively. This observation can be associated with a higher probability of singlet oxygen formation with the higher oxygen content.

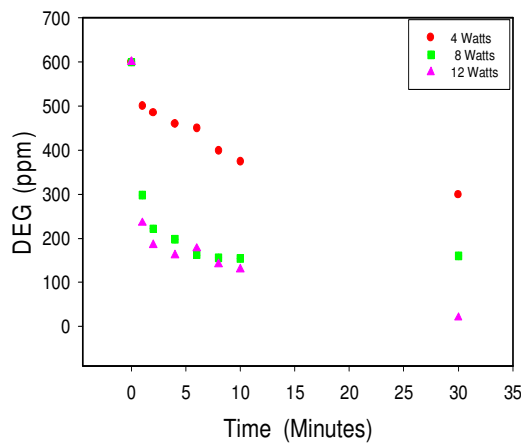


Fig. 3. Effect of UV light intensity in DEG photo-oxidation at 4 L/min of airflow rate and 600 ppm of initial DEG concentration.

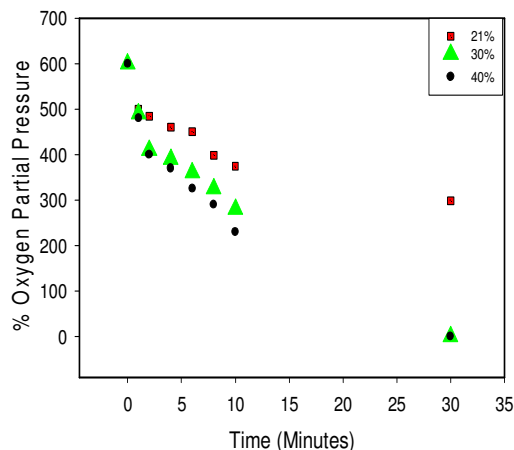


Fig. 4. Effect of the partial pressure of oxygen at 4 L/min of airflow rate and 600 ppm of DEG concentration

E. Kinetics Study

The order of the reaction and the reaction rate constant for the photo-oxidation process were found from the kinetic analysis in relation to the DEG concentration and the partial pressure of oxygen. A power-law kinetic model was used to quantify the rate at which dissolved oxygen oxidizes DEG [12]. We suggest the following rate equation for DEG oxidation:

$$r_{DEG} = k[DEG]^X [O_2]^Y \tag{1}$$

where k is the reaction rate constant and X and Y are the order of the oxidation reaction with respect to the DEG concentration and oxygen, respectively. Using the ideal gas

law, the partial pressures of oxygen were converted to the corresponding concentrations. The order of reaction with respect to both the DEG concentration and the oxygen was determined at constant air flow and UV light radiation from the linear plots between the reaction rate and the initial DEG concentration, as shown in Figures 5 and 6. The rate constant was determined from the linear plot between the reaction rate and the product of the partial oxygen pressure and the DEG concentration, as shown in Figure 7.

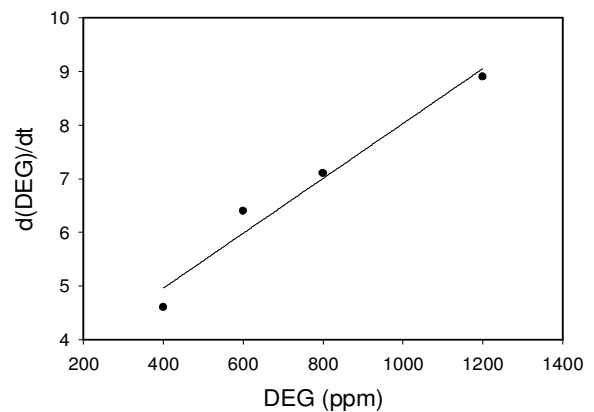


Fig. 5. Plot between the rate of reaction and the initial concentration of DEG.

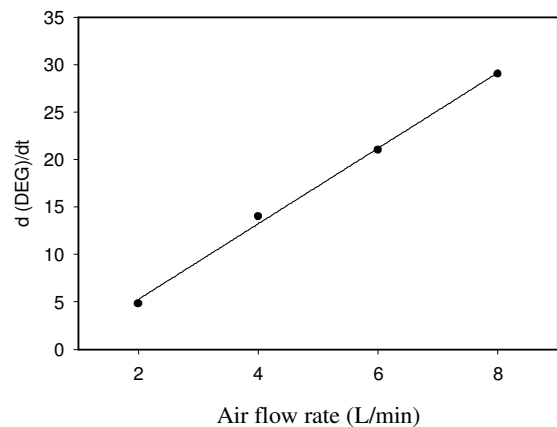


Fig. 6. Plot between the reaction rate and the air flow rates.

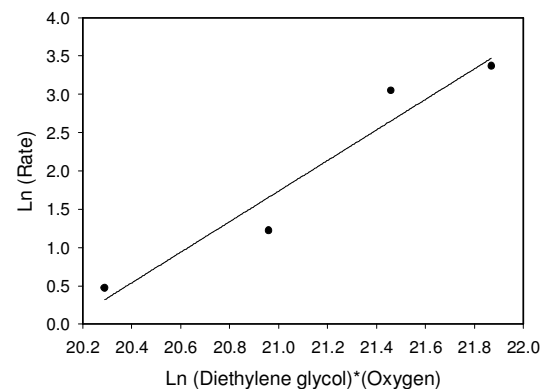


Fig. 7. Plot between the rate of reaction and the product of the DEG concentration and the partial oxygen pressure.

Table I provides details of the data for the reaction orders and the rate constants. It was found that the photo-oxidation reaction followed almost 1st order (1.4) for DEG concentration and slightly over 1st order (1.5) for oxygen concentration. Thus, the entire oxidation proceeded nearly according to the third-order reaction kinetics. Other investigators have also observed a similar reaction sequence on the oxidation of inorganic contaminants [11]. This implies that the concentration of unreacted species in the solution was a major determinant of the rate of the oxidation process.

TABLE I. KINETIC DATA OF DEG PHOTO-OXIDATION.

Oxidation	Order of reaction	Rate constant ($\text{Lmol}^{-1}\text{min}^{-1}$)	Overall order of reaction
DEG	1.4	3.6	3 rd Order
Areal Oxidation	1.5		

V. CONCLUSIONS

Photo-oxidation was used to remove DEG from an aqueous solution. Complete removal of DEG was achieved by photo aeration using 12 W of UV light. In conclusion, the oxidation of Diethylene Glycol (DEG) exhibits an approximate first-order dependence on both the oxygen and DEG concentrations, with an overall third-order reaction rate. This suggests that the reaction rate is directly proportional to the concentration of both oxygen and DEG, indicating a bimolecular mechanism. Moreover, it was found that when UV light and partial pressure rise, so does the reaction rate. This suggests that both elements are essential for improving the kinetics of the reaction. The creation of reactive species is probably sparked by UV light radiation. These species then react more rapidly with oxygen and DEG, accelerating the reaction rate. The increase in the partial oxygen pressure further promotes the availability of oxygen molecules, facilitating the oxidation process. The combined effect of UV light radiation and increased partial oxygen pressure results in a higher reaction rate, indicating a synergistic relationship between these two factors. It is crucial to comprehend the kinetics of DEG oxidation for a variety of purposes, including environmental research and industrial operations.

Our results indicated the order of the process as well as the effects of oxygen partial pressure and UV light radiation, offering important new information for adjusting reaction conditions and creating effective oxidation systems. However, the precise mechanisms by which partial pressure of oxygen and UV light affect the rate of reaction should be investigated further. Also, the investigation of the impact of additional variables such as temperature and a catalyst would advance our understanding of the kinetics of DEG oxidation.

ACKNOWLEDGMENTS

The author extends his appreciation to the Deanship of Scientific Research at Northern Border University, Arar, KSA for funding this research work through the project number "NBU-FFR-2024-2148-01".

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