



Analysis of the degradation mechanism of methylene blue by atmospheric pressure dielectric barrier discharge plasma

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ABSTRACT

The degradation of a methylene blue solution using the dielectric barrier discharge (DBD) technique is proposed in this paper. The effect of pH on the degradation rate is also investigated. The concentration of oxidants in the liquid phase is tested through iodimetry. The key factors that affect the degradation rate of the methylene blue solution are analyzed. The intermediate and final products are also investigated. The discharge process is studied by analyzing the radical species in both gas and liquid phases. The degradation mechanism of methylene blue is investigated according to the bond energy theory. The results show that the degradation rate in acidic solutions is higher than that in alkaline solutions. The lowest degradation rate is obtained from the neutral solution. The existence of OH^- in the liquid phase can promote the generation of hydroxyl radicals during the degradation process. Radical species (e.g., O_3 and $\cdot\text{OH}$) are the key factors during the degradation process of methylene blue. NO_3^- , SO_4^{2-} , and Cl^- are discovered in the liquid phase through ionic chromatogram testing. The methylene blue molecules are oxidized into inorganic ions by DBD plasma.

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1. Introduction

According to statistics, 15% of the world's total output of dye products is discharged into the environment as dye wastewater, which seriously pollutes groundwater resources [1]. A large number of new organic products (such as alizarin red [2] and methylene blue [3]) cannot be effectively degraded by conventional wastewater degradation methods because of their stable molecular structures. The development of a new and efficient wastewater treatment technique for such dyes is thus necessary. Dielectric barrier discharge (DBD) plasma technology [4] is a new technology that has attracted the interest of scientists in recent years because of its unique advantages. It is widely used in research regarding catalyst treatment [5,6], surface treatment [7,8], volatile organic compound (VOC) degradation [9], and many other fields. The application of DBD technology in the degradation of wastewater [10,11] is a new approach in wastewater treatment. There has been some research on DBD technology for wastewater degradation. For example, Mok et al. [12] proposed a gas phase DBD reactor to degrade the azo dye Orange II. They concluded that the chromaticity of the synthetic wastewater rapidly disappeared and that the ring structures in the dye molecule were effectively destroyed by DBD plasma. However, the destruction of the ring structures in the dye molecule was quite refractory to further oxidation. Tang et al. [13] applied gas phase

DBD to treat AR88 acid and concluded that the DBD system was an effective technology for the treatment of AR88 solution. They also concluded that hydroxyl radicals were the major reaction species when 100% relative humidity (RH) air was used as a gas source, while O_3 was the major reaction species when pure oxygen was used. Due to the complexity of the degradation process, however, the degradation mechanism remains in the exploratory stage.

In this study, methylene blue was selected as the model organic contaminant because of its stable molecular structure (Fig. 1). This paper focuses on exploring the reaction mechanism between DBD plasma and methylene blue molecules by analyzing the degradation process of a methylene blue solution.

2. Experimental apparatus and methods

2.1. Reagents

Analytical-grade methylene blue was obtained from the Institute of Xinchun Reagent in Tianjin. The pH of the methylene blue solutions was controlled by NaOH – NaH_2PO_4 buffer solutions. Iodimetry was used to determine the oxidants' concentration in the liquid phase.

2.2. Apparatus

Fig. 2 shows a diagram of the experimental apparatus, which included an AC power supply and a DBD reactor. The power frequency was adjustable to 10–20 kHz, while the voltage was

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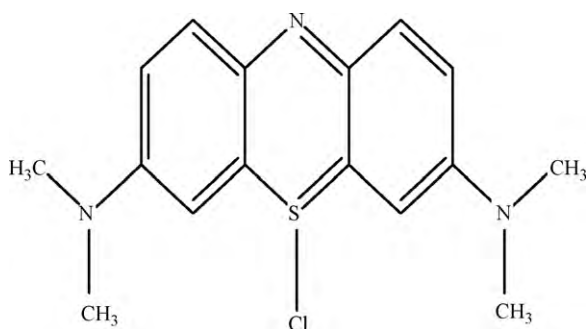


Fig. 1. Chemical structure of a methylene blue molecule.

adjustable to 0–25 kV. During the discharge process, the power was automatically cut off when the current was overloaded.

The insulating DBD reactor was comprised of a reaction space and a cooling space. A pair of silver papers with diameters of 60 mm was used to parallel-cover the outer surfaces of the reaction space; one was used as a high-voltage electrode, and the other was used as a ground electrode. The discharge distance was 8 mm, and 25 mL of a 100 mg/L methylene blue solution was treated in each run.

2.3. Methods and analysis

Methylene blue solution was prepared as the model wastewater. Atmospheric air, which was considered as the gas phase, was used to fill the reaction space. Active species were produced in the gas phase during the discharge process. These species were subsequently transferred into the liquid phase and reacted with the methylene blue molecules. The concentration of the methylene blue solution was quantitatively analyzed by spectrophotometric methods in accordance with the Lambert–Beer law. Meanwhile, the concentration of oxidants in the liquid phase was quantitatively analyzed by iodimetry.

The input voltage was controlled at 22 kV with a frequency of 10.5 kHz. The absorption spectra of the methylene blue solution were measured by a U-3010 UV spectrophotometer (Hitachi Co., Japan). The concentration of the methylene blue solution was measured by a VIS-723G visible spectrophotometer (Beijing Rayleigh Analytical Instruments Co., China) at 670 nm. The pH of the methylene blue solution was tested by a PHS-25 pH meter (Shanghai Hong Yi Instrument Co., Ltd., China). The degradation products were characterized by a GCMS-QP2010 (SHIMADZU Corporation, Japan) instrument, and acetone was chosen as the solvent. The analytical conditions are listed in Table 1. The functional groups of the products were investigated by a Vector 33 Fourier transform infrared spectrometer (Bruker Co., Germany). Here, potassium bromide was chosen as the reference material. Inorganic ions in the degradation products were determined using a 792 Basic ionic chromatographer (Switzerland Metrohm Co., Switzerland). The plasma active species

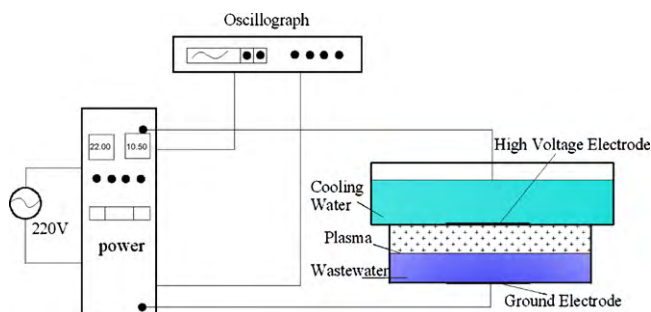


Fig. 2. Diagram of the experimental apparatus.

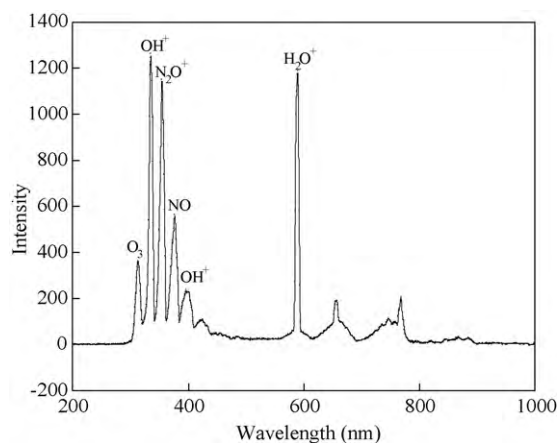


Fig. 3. Emission spectrum of methylene blue during the DBD process.

generated during the DBD process were tested using a QE 65000 optical emission spectroscopy (OES) with a spectral resolution of 1 nm. The light emitted by the micro-discharges was collected by an optical fiber located close to the glass vessel wall of the reactor in a dark room to avoid external light interferences. The integration time was 1 s.

3. Results and discussion

In this section, the discussion of the results obtained will focus on the following: the relationship between the concentration of oxidants and the degradation rate of methylene blue molecules; the investigation of the reactions in either the air or liquid phases during the discharge process; the degradation mechanism of methylene blue molecules.

3.1. Determination of oxidants during the degradation process

The existent species in the gas phase were investigated by OES testing during the DBD process (as shown in Fig. 3). A collection of species was produced in the discharge space during the DBD process. The results show that these species were mainly O_3 , OH^+ , N_2O^+ , NO , and H_2O^+ . According to their lengths of survival, the species were divided into ground state species and active state species. The concentrations of the active state species, such as OH^+ and N_2O^+ , were difficult to test because these species were in transient energy states and their survival times were only about 10^{-8} s. Ground state species, such as O_3 , are easier to test because of their longer survival times. Compared to OH^+ and N_2O^+ , O_3 exhibited a more steady energy state and a longer survival time. The concen-

Table 1
Analytical conditions for GC/MS.

GC condition		MS condition	
Injection mode	Split	Ion source temperature	200 °C
Split rate	20:1	Interface temperature	250 °C
Carrier gas	Helium (99.9999%)	Solvent out time	3 min
Sample volume	270 °C	End time	18.33 min
Temperature program		Start (m/z)	20
50 °C (2 min)		End (m/z)	600
220 °C (30 °C/min)			
260 °C (6 °C/min)			
220 °C for 3-min holding			
260 °C for 10-min holding			

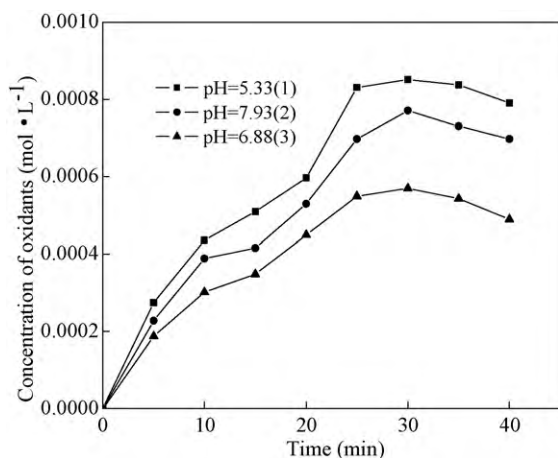


Fig. 4. Variation of concentrations of oxidants in the solution at different discharge times.

tration of the ground state species is a reflection of the quantity of all the species generated in the gas phase.

In this experiment, species were produced in the gas phase and subsequently dissolved in the aqueous phase. After discharge, ground state species, which contained some oxidants, survived for a certain length of time. The concentration of the oxidants was determined by iodimetry, the results of which are shown in Fig. 4.

Fig. 4 shows that the concentration of oxidants achieved a constant value of 30 min after discharge, with the highest concentration found in the acidic solution. Thirty minutes after discharge, the concentration of oxidants was 0.85 mmol/L in the alkaline solution and 0.77 mmol/L in the alkaline solution and 0.57 mmol/L in the neutral solution. The concentration of oxidants showed a decreasing trend in the acidic, alkaline, and neutral solutions. Oxidants are thus found to be critical to the degradation process; the degradation rate decreases with decreasing concentrations of oxidants. Oxidants generated in the reaction space play major roles during the degradation process, such that the higher the concentrations of oxidants in the liquid phase are, the higher the degradation rate of the methylene blue solution is.

Taking O_3 as an example because it is a major oxidant, methylene blue molecules are degraded by O_3 in the following reactions [12]:

(1) O_3 , as a strong oxidant, can directly oxidize methylene blue molecules:



(2) O_3 triggers a series of decomposition reactions and generates hydroxyl radicals. These radicals have greater oxidation potentials than O_3 through reactions (2) and (3). Methylene blue molecules are oxidized by the hydroxyl radicals. Because of their high oxidative potential, other organic molecules could even be directly mineralized by hydroxyl radicals.



3.2. Effect of solution pH

The methylene blue solutions were treated by DBD at different times. The color of the methylene blue solution gradually faded as the degradation reaction proceeded (as shown in Fig. 5). This indicates that the methylene blue concentration steadily decreased.

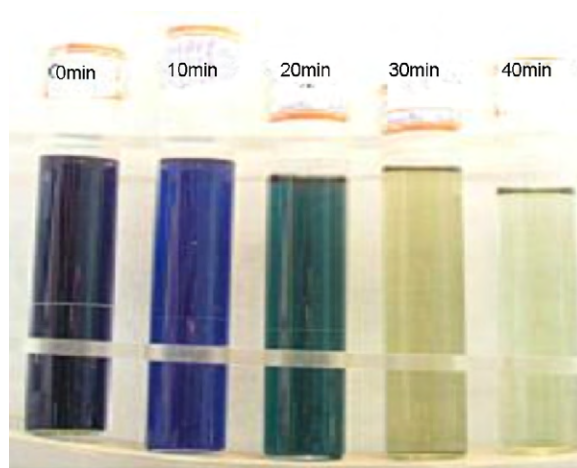


Fig. 5. Color variation of different methylene blue solutions at different treatment times.

Buffer solutions were used to control the pH of the methylene blue solution. Discharge experiments were carried out on samples with different pH values. The degradation rates of methylene blue in acidic, neutral, and alkaline solutions were investigated by testing the concentration of methylene blue in these solutions, the results of which are shown in Fig. 6. A maximum degradation rate of 99.79% was obtained in the acidic solution; while degradation rates of 91.46% and 75.58% in the alkaline and neutral solutions, respectively, were obtained 40 min after treatment. We can thus conclude that the degradation rates of methylene blue solutions vary with different pH at similar degradation times. The degradation rates show a decreasing trend in acidic, alkaline, and neutral solutions. Xue et al. [2] and Feng et al. [14] obtained the same results in their experiments.

The degradation rate of the methylene blue solution may be affected by the pH in the following ways:

First, methylene blue molecules and their intermediate products show different existence states in solutions with different pH [15]. These states include the dissociated and undissociated states. At different pH, the dissociated portion (P_1) of methylene blue molecules, their undissociated portion (P_2), and other portions with other states (P_n) exhibit different proportions. The different states of methylene blue molecules show different reaction rate constants (K_1, K_2, \dots). The degradation rate (R) of a methylene blue solu-

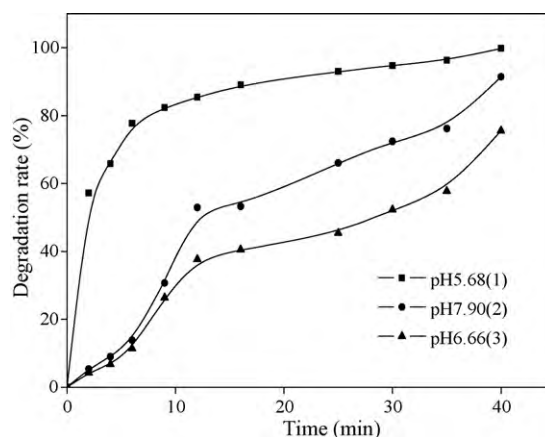


Fig. 6. Variation of degradation rates of methylene blue at different discharge times.

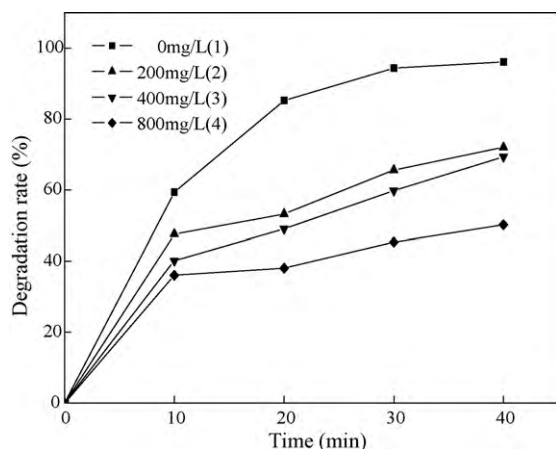


Fig. 7. Variation of degradation rates with the addition of sodium carbonate.

tion can be given by the following equation at a given treatment time (t).

$$R = \sum_{i=1}^n (K_i P_i) t \quad (4)$$

In methylene blue solutions with different pH values, the different values of $K_1, P_1, K_2, P_2, \dots, K_n, P_n$ produce different values of R . As such, it is difficult to determine the exact value of R .

Second, the existence of OH^- species can enhance the decomposition of O_3 into the hydroxyl radical, which exhibits an oxidative potential of 2.80 V in an alkaline solution. Ozone, on the other hand, exhibits an oxidative potential of 2.07 V [13]. This may be the reason why the degradation rate is higher in alkaline solutions than in neutral ones. As discussed in Section 3.1, the concentration of oxidants in the acidic solution is higher than in the alkaline solution. The concentration of oxidants has a significant effect on the degradation rate, such that the higher the concentration of oxidants, the higher the degradation rate in the acidic solution. The degradation rate in neutral solutions is the lowest due to the low concentration of oxidants in such solutions.

3.3. Influence of sodium carbonate addition on the degradation process

An experiment was designed to analyze the relationship between the concentrations of radical species and the degradation rates of the methylene blue solution.

Sodium carbonate solutions of 0 mg/L, 200 mg/L, 400 mg/L, and 800 mg/L were each added into separate flasks containing 100 mg/L methylene blue solution, and the degradation rates of the samples were tested after DBD treatment. The results are shown in Fig. 7. The degradation rate after 30 min of treatment was 94.4% when no sodium carbonate (0 mg/L) was added to the methylene blue solution. Those for 200 mg/L, 400 mg/L, and 800 mg/L of sodium carbonate were 65.6%, 59.8%, and 45.4%, respectively. The degradation rate of methylene blue decreased with increasing amounts of added sodium carbonate. Gao et al. [16] and Wang et al. [17] obtained the same results in their experiments. Sodium carbonate solutions of 0 mg/L, 200 mg/L, 400 mg/L, and 800 mg/L without methylene blue were prepared as blank samples. The concentrations of the oxidants in the blank samples were tested after DBD treatment, as shown in Fig. 8. In the solution with 0 mg/L sodium carbonate, the concentration of the oxidants 30 min after DBD treatment was 0.207 mmol/L. The oxidant concentrations of the solutions with 200 mg/L, 400 mg/L, and 800 mg/L sodium carbonate were 0.169 mmol/L, 0.104 mmol/L, and 0.086 mmol/L, respectively.

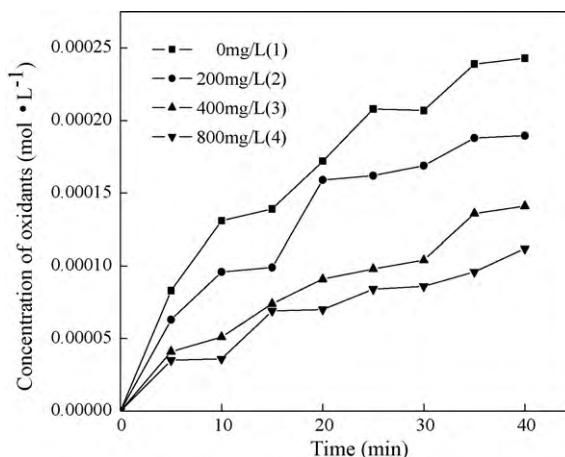


Fig. 8. Variation of concentrations of oxidants with the addition of sodium carbonate.

The concentration of oxidants decreased with increasing concentrations of sodium carbonate. The degradation rate also decreased with decreasing concentrations of oxidants.

Sodium carbonate is a type of free radical species scavenger. During the DBD degradation of methylene blue, the OH^- radical is formed as a component of the oxidants and plays an important role in the process. The reaction between the OH^- radical and sodium carbonate occurs more easily than others, and their reaction rate is faster than that for the reaction between the OH^- radical and methylene blue. Most of the OH^- radicals react with the sodium carbonate, instead of with the methylene blue molecules. Thus, the collision probability between OH^- radicals and methylene blue molecules is reduced. The results show that the degradation rate decreases with decreasing concentrations of oxidant. Thus, the presence of oxidants is a key factor that controls the degradation process.

3.4. Discharge mechanism analysis

DBD treatment was carried out on pure water to test its conductance, the results of which are shown in Fig. 9. The conductance of pure water was found to increase with increasing discharge times, indicating that the amount of inorganic ions in pure water increased during the DBD process.

The experiment was designed to determine the concentration of the ions in pure water treated by DBD, the results of which are shown in Fig. 10. The main inorganic ions found in water are NO_3^- . The concentration of NO_3^- was found to increase with increasing

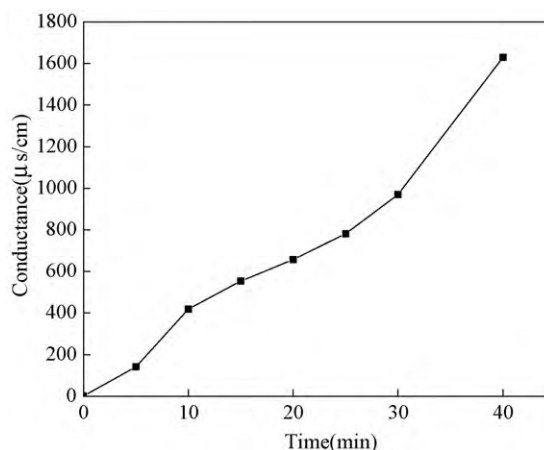


Fig. 9. Variation in conductances of pure water at different discharge times.

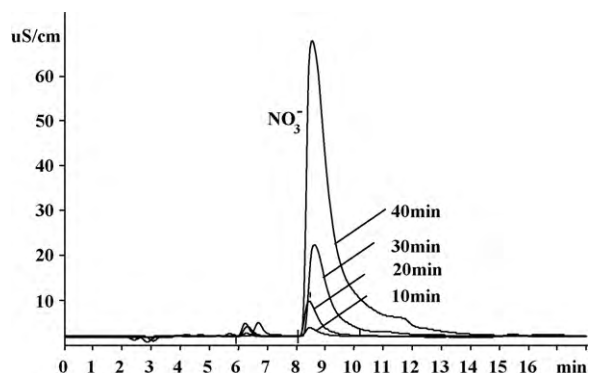


Fig. 10. Ion chromatogram of pure water treated by DBD.

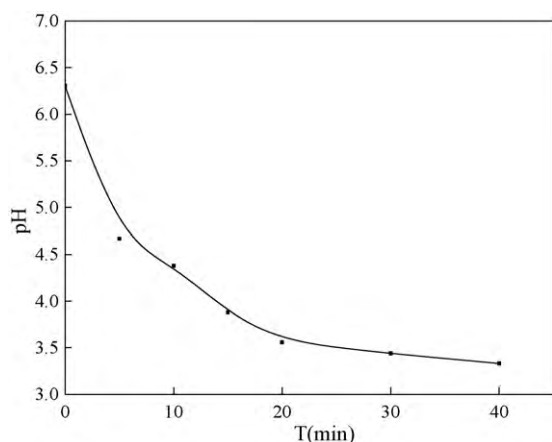


Fig. 11. Variation of pH with discharge times.

discharge times. During the DBD process, a large amount of NO and NO₂ was produced because the gas source was atmospheric air. NO and NO₂ were transferred from the gas phase to the liquid phase and reacted with water molecules. NO₃⁻ was produced from the following reactions [18]:



The production of NO and NO₂ is harmful to the degradation of methylene blue. Some of the oxygen in the system was consumed in this way, and the generation of some oxidants, such as O₃, was limited. Tang et al. [13] discovered that the degradation rate is higher when the gas source is pure oxygen compared to when it is atmospheric air. This is because more O₃ can be generated when the gas source is pure oxygen. Reactions (3)–(9) could be expected to lower

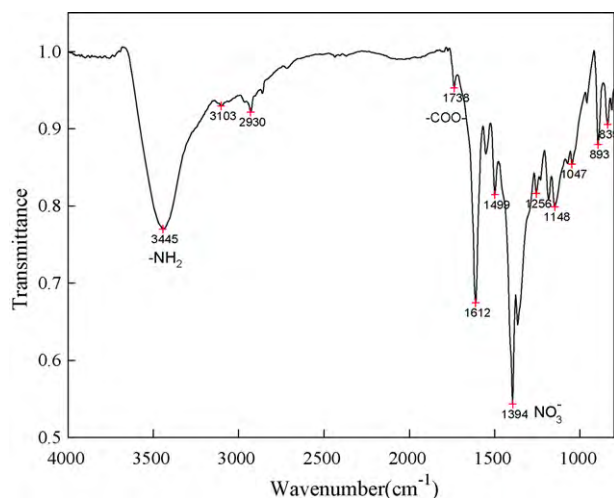


Fig. 13. FTIR of treated methylene blue.

the pH of the pure water. Thus, water pH was measured and used as an indicator of the discharge process. The results of such measurements are shown in Fig. 11. The pH of water dropped rapidly during the early stages of DBD treatment, and reached a steady value after 30 min. The DBD process could be described as follows: radical species are produced in the gas phase and then transferred to the liquid phase. These radicals then react with the substances in the liquid phase. Both the discharge and the transfer processes are complicated processes. Better degradation effects may be attained if the two processes were enhanced. Further studies are expected to focus on the investigation of these two processes.

3.5. Degradation mechanism of methylene blue

In order to analyze the degradation mechanism of methylene blue molecules during the DBD process, its intermediate and final products were determined.

3.5.1. GC–MS analysis

GC–MS analysis showed that phenyl thiophene was formed in the methylene blue solution 20 min after treatment via DBD (as shown in Fig. 12).

3.5.2. FTIR analysis

FTIR analysis showed that the intermediate products of methylene blue contain –NH₂, –COO– and NO₃⁻ groups, as can be seen in Fig. 13.

3.5.3. Ion chromatography analysis

After treating for 40 min, the methylene blue solution was analyzed by ion chromatography (as shown in Fig. 14). The ions SO₄²⁻, NO₃⁻, and Cl⁻ were found, indicating that methylene blue molecules oxidize into SO₄²⁻, NO₃⁻, and Cl⁻ during the degradation process.

Hi#: 1 Entry:5986 Library: NIST27.LIB
SI: 93 Formula: C7H5NS CAS:95-16-9 Mol Weight: 135 RetIndex:0
CompName: Benzothiazole

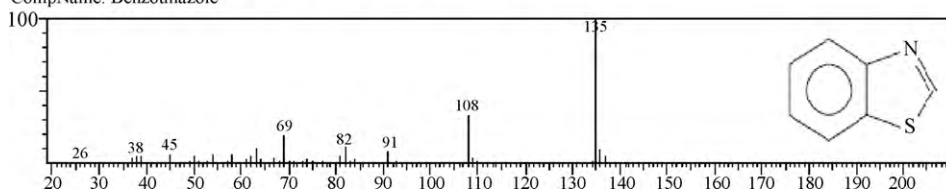


Fig. 12. Phenyl thiophene.

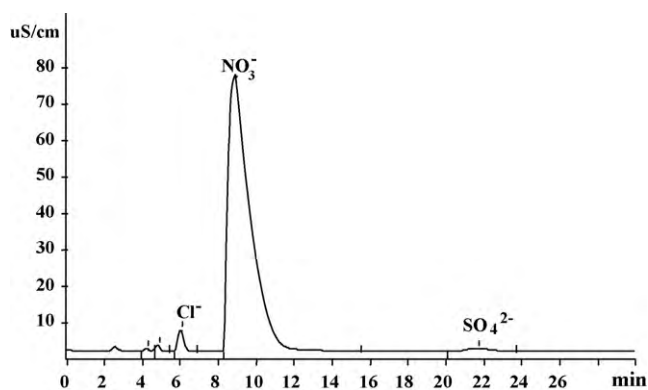


Fig. 14. Determination of inorganic ions in the methylene blue solution after 40 min of treatment.

Table 2
Chemical bonds energies in a methylene blue molecule [19].

Molecule bonds	Bond energy (kcal/mol)
CH ₃ -N (CH ₃) C ₆ H ₅	70.8
N (CH ₃) ₂ -C ₆ H ₅	93.2 ± 2.5
C ₆ H ₅ -NH-C ₆ H ₅	87.4
C ₆ H ₅ -S-C ₆ H ₅	76 ± 2
C ₆ H ₅ -NH ₂	102.6 ± 1.0

The chemical bonds corresponding to the given bond energies are shown as “-”.

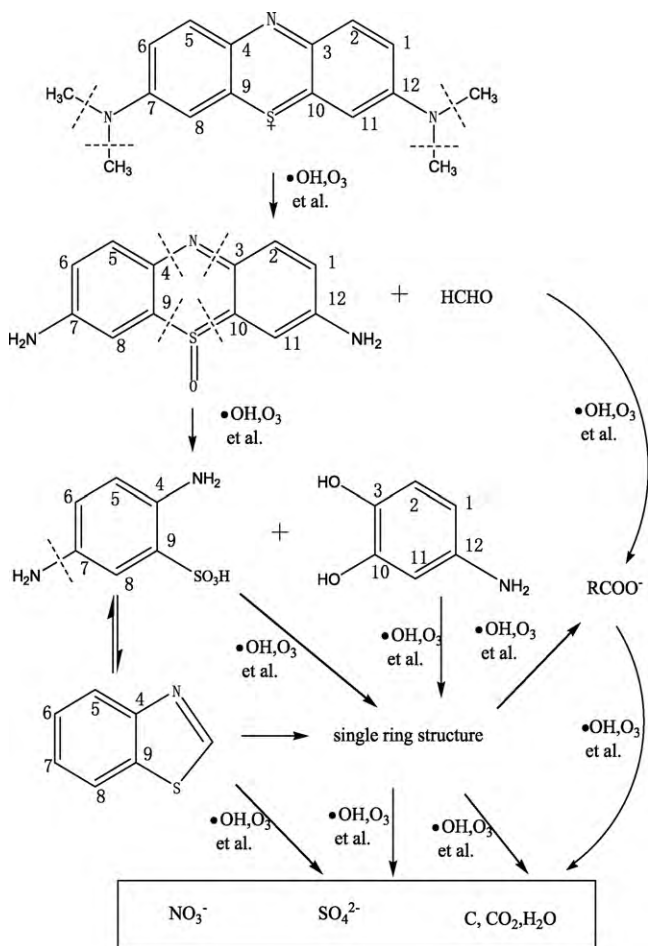


Fig. 15. The degradation path of the methylene blue molecule.

3.5.4. Degradation mechanism analysis

Chemical reactions consist of the breaking of old bonds and the formation of new ones. According to the bond dissociation energy (BDE) theory, the lower the BDE is, the more active the chemical bond is [19] and the easier it is for old bonds to break and new bonds to form. The main bond energy data of methylene blue molecules are shown in Table 2.

Based on the intermediate and final products detected, the degradation mechanism for methylene blue is analyzed and described, as shown in Fig. 15. During the dissolution of the methylene blue molecule, Cl⁻ is first ionized and exists in the detached state. N-CH₃, which is connected to ⁷C or ¹²C, has the lowest BDE value in the methylene blue molecular structure. During the bombardment of the radical species, the N-CH₃ bond is first broken and the -CH₃ is oxidized into HCHO or HCOOH. C-S and C-N are the most active parts of the remaining structure of the methylene blue molecule. During the bombardment of •OH and O₃, the two bonds are broken more easily. At the same time, phenyl thiophene and other molecular structures determined during the GC-MS analysis are formed. In the latter period of the DBD process, an abundance of radical species in the methylene blue solution is generated. These oxidize organic molecular structures until they are finally transformed into inorganic ions, such as CO₂, H₂O, Cl⁻, SO₄²⁻, and NO₃⁻. These ions were discovered during ion chromatography analysis.

4. Conclusion

The results obtained in this study show that the degradation of the methylene blue solution using the DBD technique is feasible and proceeds effectively. The degradation rates of the methylene blue solution varied as a function of the solution pH at similar degradation times. The degradation rates showed a decreasing trend in acidic, alkaline, and neutral solutions. The concentration of free radicals can be reduced by adding sodium carbonate to the solution; thus, the collision probability between radical species and methylene blue molecules can also be reduced. Ozone and other active species generated in the reacting space play major roles during the degradation process. The discharge process was analyzed. The radical species (O₃, OH⁺, N₂O⁺, NO, and H₂O⁺) were produced in the gas phase and transferred to the liquid phase, where they reacted with the substances in it. Based on the BDE theory, the degradation mechanism of the methylene blue was analyzed, and it showed perfect conformity with the experimental results.

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