




Article

A Study of the Performance of Dielectric Barrier Discharge under Different Conditions for Nitrobenzene Degradation

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Abstract: Water scarcity and water contamination due to the extensive use of organic compounds in industries trigger us to adopt modern techniques for wastewater treatment. In this research, we developed a new dielectric barrier discharge (DBD) system which was evaluated for the degradation of nitrobenzene in water under different experimental arrangements. DBD produces an enormous amount of active species like O_3 , $\bullet O$, O_2^+ and O_2^- and $\bullet OH$ to degrade the pollutants. In this study, NB (Nitrobenzene) was treated from wastewater by changing the gas flow rate, adopting different carrier gas, by adding inhibitors and promoters and the effect of applied voltage on the production of active species to check the effectiveness of the DBD system. The DBD system was evaluated based on input power, degradation efficiency and energy yield compared with other advanced oxidation processes. The energy yield of the DBD system was 1.253 mg/kWh for the degradation of 20 mg/L of NB to 75% in 60 min with the discharge power of 0.538 W, which displays better results in comparison with the other AOPs regarding energy yield and the degradation efficiency of the pollutant. The results illustrate the significance of the system and further suggest its application to industrial-scale treatment.

Keywords: dielectric barrier discharge; active species; advanced oxidation processes; nitrobenzene; energy yield

1. Introduction

Water scarcity and water pollution are major issues in the world at present. Persistent organic pollutants (POPs) are compounds that have alarming concerns because of their toxicity, bioaccumulation and perseverance among the ecosystems. Many compounds have high threats to human and ecological health at small concentrations [1]. Nitro-aromatic compounds are extensively being used as solvents and intermediates for the production of explosives, pesticides, plastics and many other chemical products. Nitrobenzene (NB, Figure 1) is one of the nitro-aromatic compounds that has been used to produce aniline, dyes, explosives and various pharmaceutical products [2]. It is used as an organic solvent in water and soil because of its dispersive nature. It has a significant environmental concern because of its toxicity, the quantity of production and difficult biodegradation [3–5].

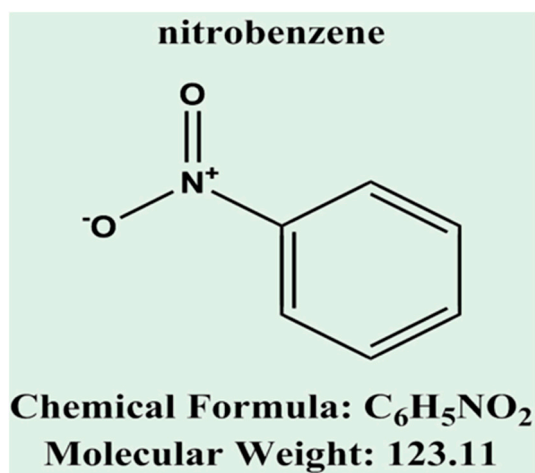


Figure 1. The molecular structure of Nitrobenzene (NB).

The nitro-group in NB has a robust electron-withdrawing property that hinders the traditional chemical oxidation and the biological treatment methods [6]. In this perspective, advanced oxidation processes (AOPs) exhibit advantages over conventional treatment methods because of the generation of strong oxidants. These oxidants have the capability to eliminate the problems associated with bio-resistant organic compounds [7]. DBD is one of the AOPs that has received enormous attention for the removal of organic pollutants in recent years [8,9]. It is broadly used in the study for surface treatment [10,11], volatile organic compound (VOC) degradation [12,13], catalyst treatment [14] and in several other areas. The use of DBD technology for wastewater degradation [15–17] is a novel approach towards wastewater treatment. DBD plasma systems produce active species such as O₃, •OH, oxygen atom radicals and H₂O₂ that allow the organic pollutants to decompose [16,18–23]. These active species act as powerful oxidizing agents that can prompt chain reactions in pollutant molecules and are expected to degrade wastewater pollutants. Due to their high oxidizing strength, many complex and toxic organic pollutants could be converted to less or even non-toxic products and degraded fully into CO₂ and H₂O, thus giving an eventual solution for wastewater treatment [24]. As compared to other treatment methods, DBD produces a stable, uniform and diffuse discharge. Furthermore, DBD has a small footprint in the environment, a high treatment efficiency, a short processing cycle and no effects of secondary pollution [23].

We focused to evaluate the DBD plasma reactor for the removal of NB applying different experimental conditions such as the effects of changing the gas flow rate, the frequency of the input gas, the effects of different inhibitor and promoter and effects of adding methanol. The novel approach was adopted to get efficient results at lower discharge power inputs. The DBD system was evaluated based on the degradation efficiencies and by comparing the reaction kinetics and energy yield with other published works to know the effectiveness of this system.

2. Materials and Methods

2.1. Experimental Setup

The experimental system comprises of a DBD reactor, an oxygen source equipped with a pressure gauge, a 45 L water barrel containing the NB polluted water, a pump to regulate the water flow in the system, high voltage power supply with an oscilloscope, mixing reaction tank and a gas-liquid separator. DBD configuration and experimental design are illustrated in Figure 2. The water container was filled with tap water followed by the mixing of specific amounts of NB and other chemicals to yield synthetic wastewater. Before initiating the DBD reactor, the solution was pumped with a flow rate of 1.0 m³/h for 3 min to mix it thoroughly and regulate the flow in the system. Oxygen was then

supplied to the DBD reactor, and the concentration was set to 3 L/min. A pressure of 0.1 MPa was maintained and monitored throughout the experiment. High voltage power (1–1.8 kV) was applied to the DBD reactor which ionized the oxygen molecules to produce a huge number of highly active species. An ammeter and an oscilloscope (WaveJet 354A, LeCory, Mansfield, TX, USA) were used to monitor the power parameters. The run time duration of the system was 60 min. Samples were taken after specific intervals (such as 0, 5, 10, 20, 30, 40, 50 and 60 min) to monitor the degradation rate of nitrobenzene. All the conditions for the operation of the DBD reactor are reported in Table 1.

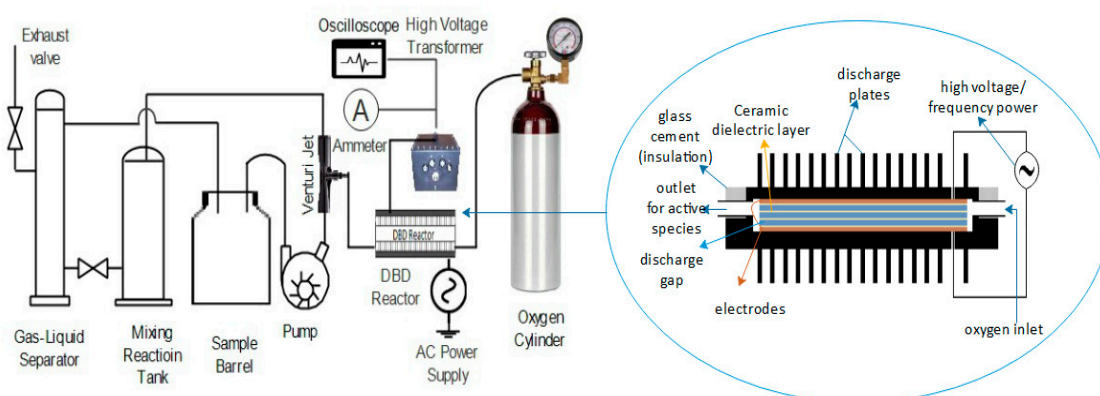


Figure 2. The schematic illustration of the experimental setup for the dielectric barrier discharge (DBD) system assisted nitrobenzene degradation with the illustration of the DBD reactor assembly.

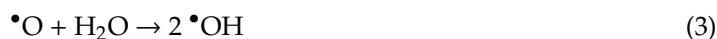
Table 1. The main characteristic conditions of the Dielectric Barrier Discharge (DBD) system.

Parameters	Values
Oxygen Concentration	3 L/min
Gas pressure	≥0.1 MPa
Water circulation flow rate	1.0 m ³ /h
Voltage range	1.0–1.8 kV
Average electron energy	>0 eV
Sample barrel volume	40 L
Water temperature	20 °C

The DBD's configurations and principles depend on the presence of a dielectric barrier in the discharge path which is based on quartz, alumina, glass, plastics, ceramics, mica, Teflon, rubber or silica. To generate plasma at a normal pressure and high voltage amplitudes, the discharge gap is normally kept between 0.1 mm to 10 mm [25].

The internal assembly of the DBD reactor consists of two sintered silver electors attached to dielectric plates of ceramics. The ceramic plates are separated by insulating tapes to maintain a plate clearance of about 0.2 mm, as shown in the DBD reactor's assembly (Figure 2). The main base of the DBD reactor consists of sintered silver metal painted with a thin layer of α -Al₂O₃ on its external surface. This base contains an array of outward-extended plates that work as a heat sink providing a large surface area to the system to absorb heat. When oxygen is provided, high voltage power is applied to the DBD reactor, O₂ molecules get excited and produce a strong discharge in the displacement between the two dielectric layers. As a result, both the physical and chemical reactions occur simultaneously, producing a huge quantity of active species with a high activity [22,23,26]. Hydroxyl radicals (\bullet OH) are produced, when the active species like O₃, \bullet O, O₂⁺ and O₂⁻ enter the water. These active species and hydroxyl radicals react with the pollutants and degrade them into stable or less active by-products. The detailed mechanism of the production of active species in the DBD reactor and their percolation into water is described in the following chemical reactions.





2.2. Materials Used

We used the following analytical grade reagents in the experiments containing nitrobenzene $\text{C}_6\text{H}_5\text{NO}_2$ (99.0%), hydrogen peroxide H_2O_2 (30%), ferrous sulphate heptahydrate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, anhydrous sodium carbonate Na_2CO_3 (99.8%), sodium hydrogen carbonate NaHCO_3 (99.5%), isopropyl alcohol $\text{C}_3\text{H}_8\text{O}$ (IPA) (99.7%) and tert-Butanol $\text{C}_4\text{H}_{10}\text{O}$ (TBA) (98%). All these reagents were purchased from Sinopharm Chemical Reagent Co. Ltd, Shanghai. Distilled water was used to prepare the stock solutions for all the experiments.

2.3. Analysis Methods

The concentration of NB was determined by using the equation obtained by the calibration curve of nitrobenzene solutions with the help of UV-vis spectrophotometer (UV-9600 Rayleigh, Beijing, China) throughout the experiments [27,28]. The absorbance of several known concentration samples of NB was determined at 262 nm wavelength. Calibration curve between absorbance (at 262 nm) and the concentration was plotted as shown in Figure 3. Total organic carbon (TOC) was measured by a TOC analyzer (TOC-L/CPN, Shimadzu Corporation, Kyoto, Japan). Ozone concentration in the air stream as produced by the DBD reactor was determined by Ozone Monitor (KEN-2000, Evergreen, Carnate, Italy) and the ozone concentration in the water was determined by a D. Ozone Microprocessor Controller (CL7685, B & C electronics, Carnate, Italy). The NB degradation efficiency was calculated by the following equation

$$\eta = \frac{C_t - C_0}{C_0} \times 100 \quad (8)$$

where η is the degradation and removal efficiency of NB, C_t is the NB concentration at interval time t and C_0 is the NB initial concentration.

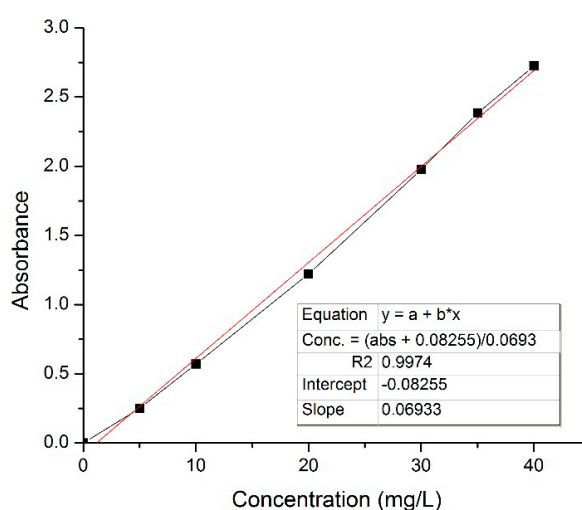


Figure 3. A plot of the calibration curve between different concentrations (at time intervals) and absorbance (at 262 nm of wavelength) values of nitrobenzene (NB).

3. Results and Discussions

3.1. The Effect of Applied Voltage on the Production of Active Species

Discharge voltage is the main electrical parameter to judge the performance of the DBD reactor because it has a vital role in the production of plasma (such as O_3 and $\bullet OH$) [29]. Researchers have mentioned that at higher voltages, the power of the DBD system is higher to produce ozone [30,31]. Eventually, it would increase the degradation efficiency of the pollutants due to the production of a huge number of active species. Therefore, the effect of voltage on the production of ozone was investigated in this study and the results are shown in Figure 4a. Four levels of voltages 1.2, 1.4, 1.6 and 1.8 kV were investigated at the oxygen flow rate of 3 L/min. Ozone concentrations were measured for 30 min and an average value was opted to analyze the results. It was found that the ozone production increased with the increase in voltage.

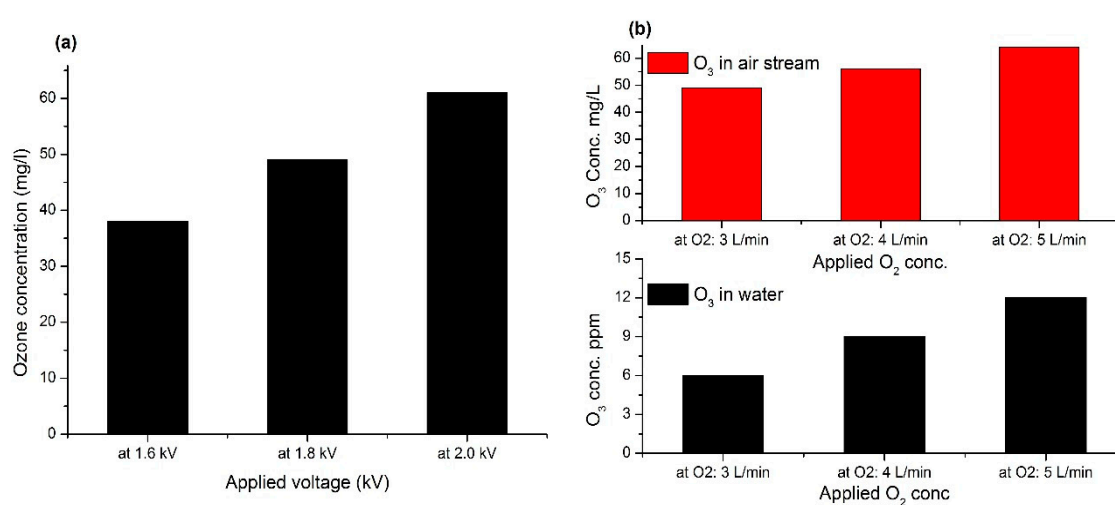


Figure 4. (a) The effect of voltage on the production of ozone, (b) The variation in the ozone concentrations in air and water streams.

3.2. Effect of Varying Oxygen Flow on the Concentration of O₃ in Water and Air Stream

The ozone produced by the DBD reactor was introduced to the system containing polluted water. Further, it was mixed with the polluted water to react with the pollutants present in it and degrade them eventually. Ozone produced by the DBD reactor was introduced to the system to further produce hydroxyl radicals and to enhance the degradation of the pollutants. The more the ozone produced, the greater would be the treatment efficiency of the system. In view of this concept, the ozone concentration in the air stream produced directly by the DBD reactor and its concentration after mixing it in water were investigated and the results are presented in Figure 4b.

3.3. The Effect of Different Carrier Gases on NB Degradation

Different carrier gasses produce different active species and in varying amounts. The production of ozone and the hydroxyl radical is associated with the specific carrier gas and ultimately results in the higher or lower degradation efficiencies of the available pollutant depending on these carrier gases. N_2 is an inert gas that does not participate in most of the reactions and the bond dissociation energy of O_2 (5.12 eV) is less than that of N_2 (9.82 eV). Therefore, O_2 is easily dissociated as compared to N_2 , producing more active species. To investigate the effect of different carrier gases, O_2 , N_2 and air were provided to the DBD reactor at the same flow rate and same experimental conditions. The results showed that the degradation efficiency of NB is much higher when O_2 was the carrier gas as compared to the air and N_2 as shown in Figure 5. Moreover, the active species produced by oxygen are O_3 and $\bullet OH$, which are more reactive as compared to the species produced by N_2 , that is, N , N_2^+ and N^+ [29].

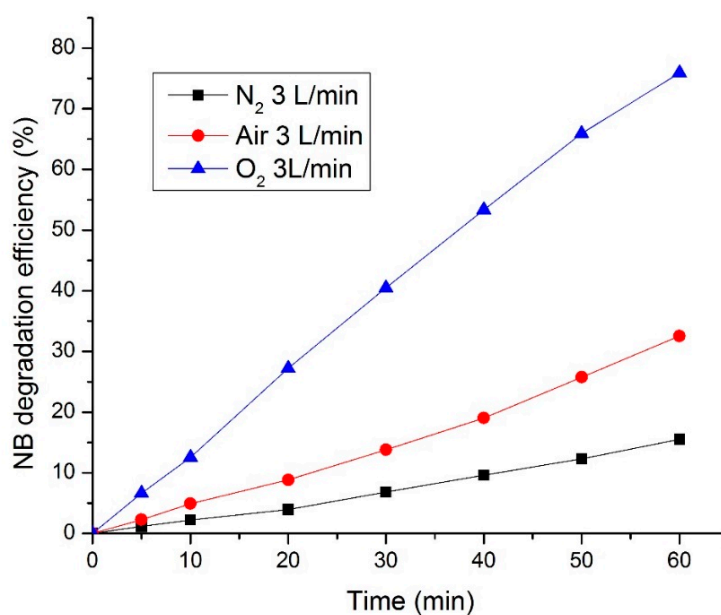


Figure 5. The effect of different carrier gases on the degradation of NB in the DBD reactor, at NB concentration of 20 mg/L, gas flow rate of 3 L/min and an applied voltage of 1.8 kV.

3.4. The Influence of Oxygen Flow Rate on NB Degradation

The effect of oxygen flow was investigated on the O₃ production. NB degradation at different oxygen flow rates such as 3, 4 and 5 L/min was adopted. Other conditions were 20 mg/L of NB, voltage and water flow rate was considered similar to the previous reactor setup, i.e., 1.8 kV and 1 m³/h, respectively. The results illustrated a remarkable difference while providing a higher flow rate of oxygen, increasing the degradation efficiency, as shown in Figure 6. Since, at higher flow rates more oxygen flows into the system, resulting in a lot of active species being generated. Therefore, active species help the degradation process to incline. A study by Reddy et al. (2013) constructed similar arguments [7].

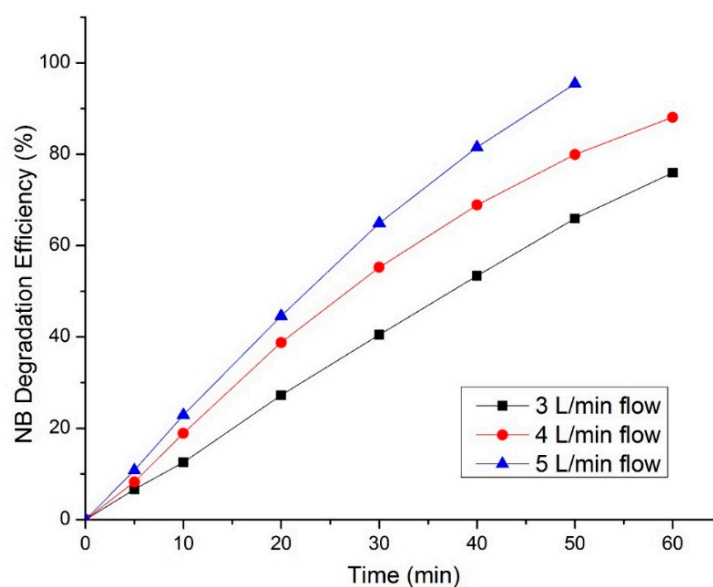


Figure 6. The effect of different oxygen flow rates on the degradation of NB in the DBD reactor, at NB concentration of 20 mg/L and an applied voltage of 1.8 kV.

3.5. The Effect of Different Inhibitors on NB Degradation

In order to know the role of hydroxyl radicals in the DBD plasma treatment and the degradation of NB, the effects of different inhibitors were investigated here. Tertiary butyl alcohol (TBA) and Isopropyl alcohol (IPA) are known to have the best scavenging effect for hydroxyl radicals [32]. Despite these two scavengers, carbonate and bicarbonate ions were also used to check the scavenging effect of hydroxyl radicals for the treatment of NB. The results of NB degradation with scavengers and without scavengers were compared. The results shown in Figure 7 reports that the degradation of NB was significantly decreased by the addition of these scavengers. However, increasing the concentration of these inhibitors decreased the efficiency of the NB removal, which demonstrates the hydroxyl radicals are scavenged. We confirmed the role of hydroxyl radicals for NB degradation. Carbonate and bicarbonate anions were shown to have a smaller scavenging effect compared to TBA and IPA. Similar results were investigated by many other researchers [32–34].

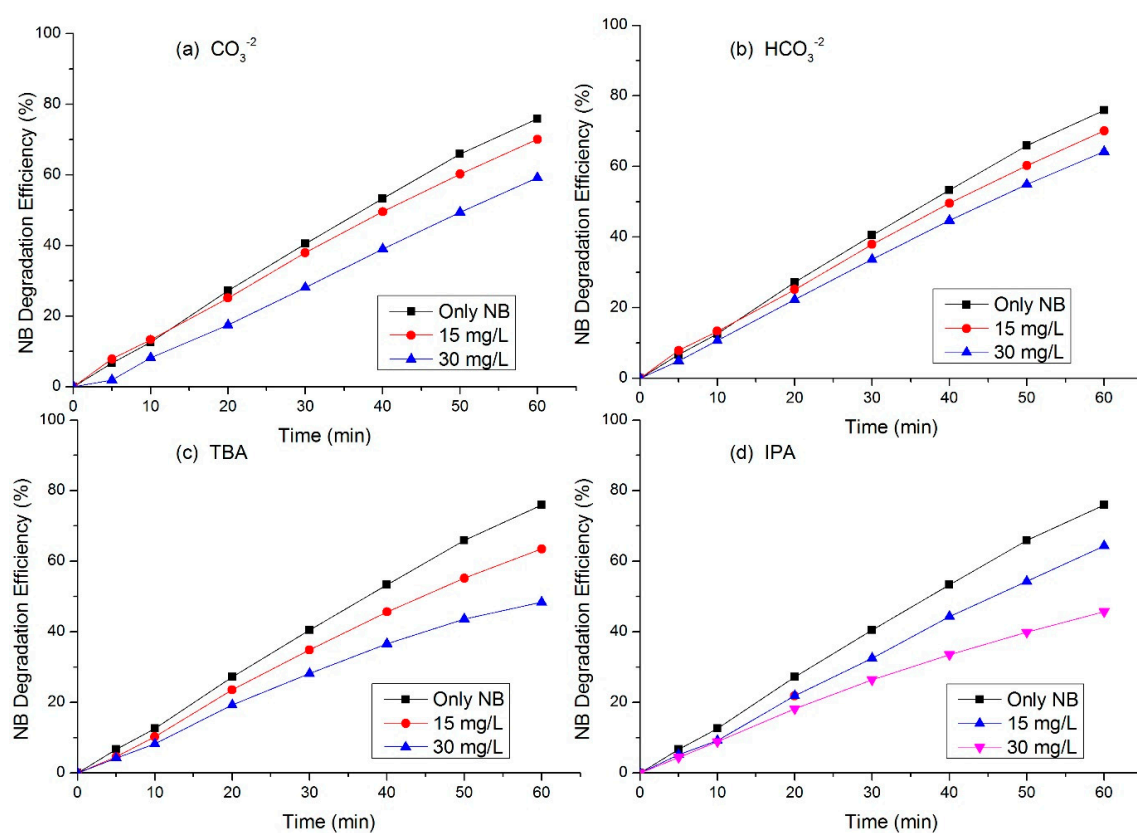


Figure 7. The effect of different hydroxyl radical scavengers on the degradation of NB, at an NB concentration of 20 mg/L, an oxygen flow rate of 3 L/min, and an applied voltage of 1.8 kV. (a) Effect of carbonate ions; (b) Effect of bicarbonate ions; (c) Effect of tertiary butyl alcohol (TBA) and (d) Effect of isopropyl alcohol (IPA).

3.6. Effect of Promoters

H_2O_2 and Fe^{2+} were used as the promoters to check the degradation efficiency of NB. The DBD reactor produces a large quantity of active species and the most important active species in this study are the hydroxyl radical and H_2O_2 . Different concentrations of 50, 100 and 200 mg/L of hydrogen peroxide were added to the system in different batches. In the first batch, hydrogen peroxide was added in a single lump at the start of the experiment while in the second batch, the hydrogen peroxide was used intermittently by adding 20 mg/L after every 10 min. The results showed that the addition of hydrogen peroxide with definite intervals gave better results compared to the addition at once, as shown in Figure 8. This can be explained because the oxidation potential of the hydroxyl radical

($E = 2.02$ V) is higher than that of hydrogen peroxide ($E = 1.78$ V) [32], the species with a higher oxidation potential has a greater strength to degrade the pollutant molecules. Therefore, the addition of hydrogen peroxide at once increased its concentration compared to hydroxyl radicals in the system which resulted in a declining trend of degradation efficiency. On the other hand, if hydrogen peroxide was added with intervals and with smaller amounts, it showed significant results. This is because, at higher concentrations, hydrogen peroxide exhibits a self-scavenging effect. Similarly, hydroxyl radicals were scavenged by excess H_2O_2 resulting in the HO_2^\bullet and H_2O production as described in Equation (9). Figure 8 shows the results for both promoters and it was obvious that the degradation of NB was accelerated and inhibited with the addition of H_2O_2 depending on the mode of dosage. Similar results were described by Jiao et al. [35] for the degradation of nitrobenzene and by Feng et al. for the degradation of diuron [36]. Ferrous ions Fe^{2+} were added to the solution to check the effect of NB degradation in the DBD system which further reacted with hydrogen peroxide to produce hydroxyl radicals as described in Equation (10) [7]. The addition of Fe^{2+} ions produced hydroxyl radicals that eventually increased the degradation of the pollutants as shown in Figure 8.

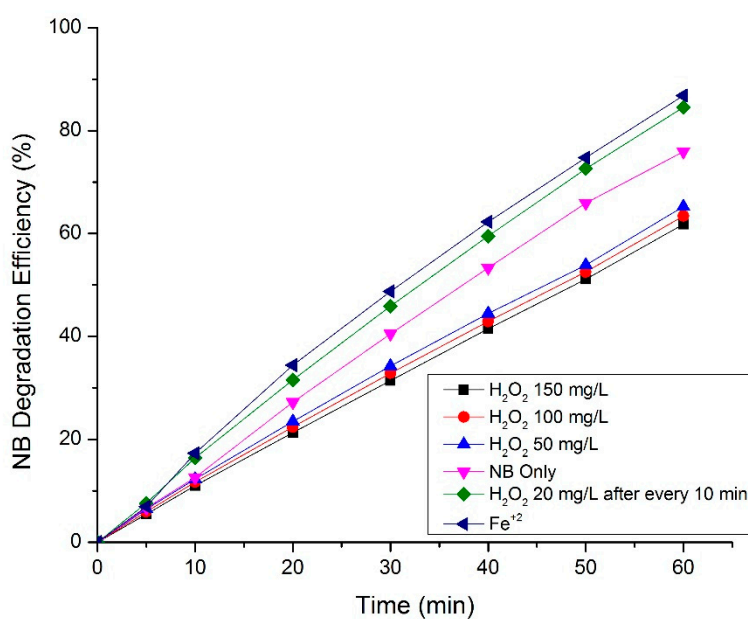


Figure 8. The effect of the addition of different promoter on the degradation of NB, at an NB concentration of 20 mg/L, an oxygen flow rate of 3 L/min, and an applied voltage of 1.8 kV.

3.7. Effect of Addition of Methanol on the Degradation of NB

Methanol acts as a hydroxyl radical scavenger. We added methanol to check its effect on the degradation efficiency of NB. Figure 9 shows the degradation of NB with and without the addition of methanol. The degradation of nitrobenzene is greatly influenced by the addition of methanol. By adding 10 mL of methanol in the system, the degradation decreases from 75% to 21% compared to the system without methanol (NB only in Figure 9). Increasing the methanol concentration showed a significant decrease in the NB degradation efficiency. These results indicate that the free radicals were the main active species for degradation. Duan et al. (2016) [37] also reported that these free radicals are scavenged by the addition of methanol. We are in good agreement that by adding methanol to the solution, free radicals will be scavenged, hence, reducing the NB degradation efficiency.

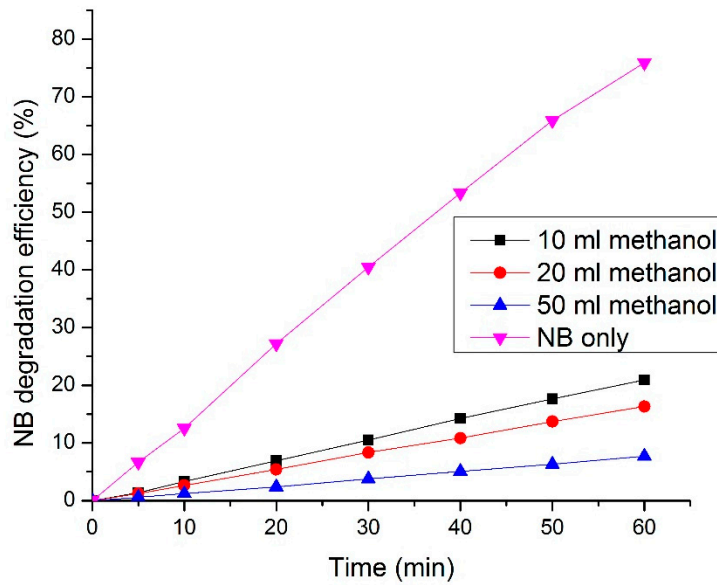


Figure 9. The effect of the addition of different methanol concentrations of NB degradation at an NB concentration of 20 mg/L, an oxygen flow rate of 3 L/min, and an applied voltage of 1.8 kV.

3.8. TOC Removal and NB Degradation Results

Karuppiah et al. (2019) reported the total organic carbon (TOC) removal along with the pollutant degradation to evaluate the process efficiency [38]. In our study, we have picked TOC as a parameter to check its removal efficiency as compared with the NB degradation efficiency. Figure 10 displays the TOC removal efficiency and NB degradation efficiency of the DBD system. The results indicate a remarkable NB degradation efficiency while the TOC removal was not significant. The similar results for TOC removal were expressed by Shen et al. (2006) [39].

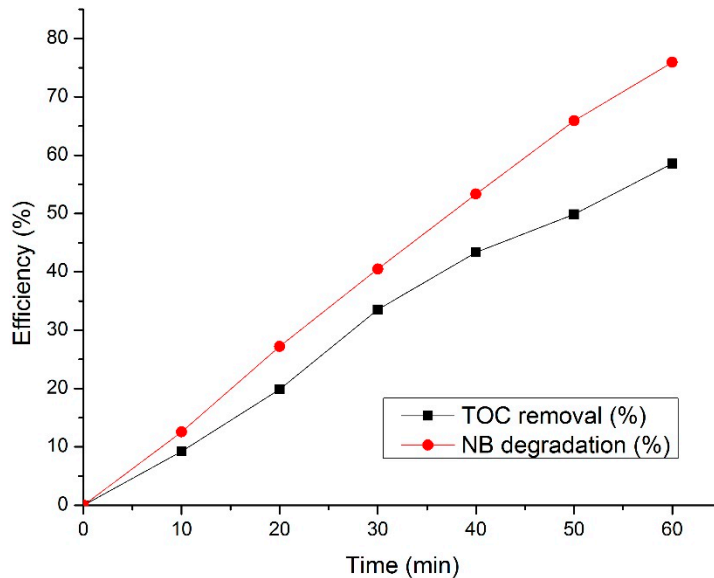


Figure 10. The total organic carbon (TOC) removal efficiency and NB degradation efficiency by the BDB system at an NB concentration of 20 mg/L, an oxygen flow rate of 3 L/min, and an applied voltage of 1.8 kV.

3.9. Degradation Kinetics

Yin et al. (2012) [40] studied the first order kinetics model to evaluate the NB degradation process. We adopted a similar approach to study the first order kinetic model as given in Equation (11). The basic aim to study reaction kinetics was to investigate the reaction process of NB degradation.

$$\ln\left(\frac{C_t}{C_0}\right) = -kt \quad (11)$$

where C_t is the NB concentration at a given time t (min) and C_0 is the initial NB concentration and k is the reaction rate constant. The kinetic constant k for the degradation of NB in the DBD reactor was reported to be 0.0237 min^{-1} with an R^2 of 0.9983 which was compared with the other AOPs in Table 2.

Table 2. The reaction kinetics comparison with other advanced oxidation processes (AOPs).

Treatment System	Type of Water	Initial Conc. (mg/L)	Treatment Time	Degradation (%)	K (min^{-1})	R ²	References
DBD reactor	Nitrobenzene	20	60 min	75	0.0237	0.9983	current work
ZVI reduction	Nitrobenzene	25	8 h	56	0.0165	0.1038	[40]
Pyrite Fenton system	Nitrobenzene	20	5 h	77	0.0113	0.9644	[3]
Catalytic ozonation	Nitrobenzene	100	120 min	55	0.0065	-	[41]
UV/TiO ₂ /O ₂ photocatalysis	Lindane	40	90 min	55	0.60	-	[42]
TiO ₂ /UV photocatalysis	2,4-dibromophenol	25–126	30 min	53–14	0.025–0.0056	-	[43]
Photo-Fenton/O ₃	Atrazine	35	5 min	66	0.24	-	[44]

3.10. Energy Yield

Energy yield is an important parameter to study the degradation efficiency of nitrobenzene (NB). By measuring the energy yield we mean the NB degradation efficiency per unit of energy used by the DBD reactor. Energy yield (Y in mg/kWh) for the degradation of NB was calculated by the following formula [7,45]

$$Y = \frac{C_0 \times V \times D}{P \times t \times 100} \quad (12)$$

where C_0 is the NB initial concentration in mg/L, V is the total volume (in L), D is the degradation efficiency (%), P is the discharge power of the DBD reactor in kW and t is time (in h). Discharge power (P) used by the DBD reactor was calculated by the charge (Q) and voltage (V) Lissajous method [7,46,47]. Where charge Q (i.e., time-integrated current) was measured from the capacitor voltage across the $4.7 \mu\text{F}$ capacitor connected in series with the ground electrode of DBD. Voltage was measured by connecting a high voltage probe (P6015A, Tektronix, Beaverton, OR, USA) and the V and Q waveform was plotted by connecting a Digital Oscilloscope (WaveJet 354A, Mansfield, TX, USA) across the high voltage supply to get the V - Q Lissajous curve as shown in Figure 11. The area of the V - Q Lissajous curve represents the energy (E) dissipated in the system and the discharge power was obtained by multiplying the area of this curve with the frequency, i.e., $P = f \times E$ [48]. A comprehensive comparison of power, energy yields and degradation efficiencies with the other works are depicted in Table 3. From the comparison, we found that our DBD system shows significant removal efficiencies of up to 75% in 60 min of the time interval at 0.538 watts, while all other AOPs, even with higher powers, have lower degradation efficiencies. Although some studies mentioned a higher energy efficiency, they used more power and higher power leads to greater degradation efficiencies. Our DBD system modification reduces the power consumption and still reaches the significant NB degradation efficiencies.

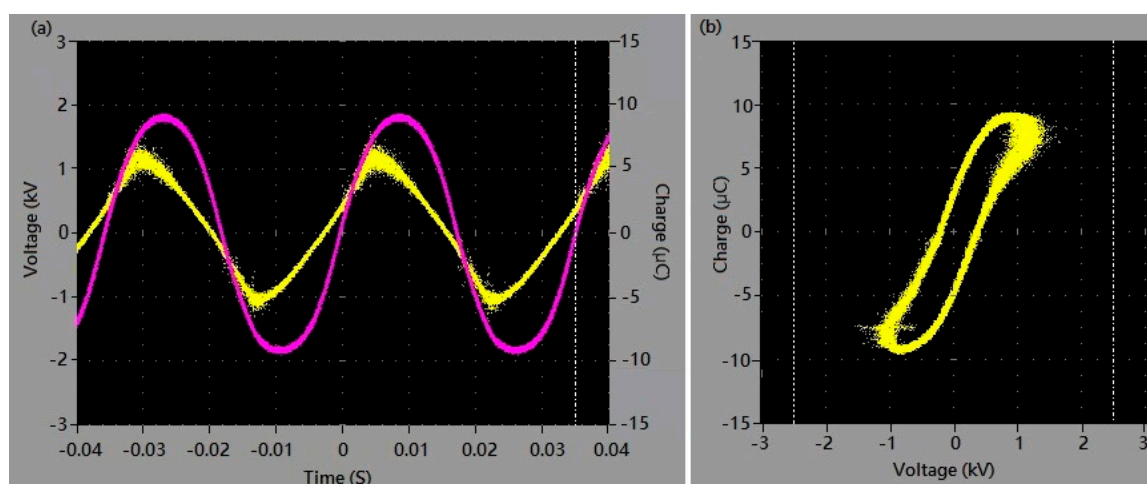


Figure 11. (a) The Charge-Voltage (Q-V) waveform and (b) Lissajous curve at 1.8 kV and 50 Hz.

Table 3. The comparison of the DBD system with other AOPs for power, energy yield and degradation efficiency.

Treatment System	Type of Water	Initial Conc. (mg/L)	Treatment Time (min)	Power (W)	Energy Yield (mg/kWh)	Degradation (%)	References
DBD reactor	Nitrobenzene	20	60	0.538	1.25	75	current work
Glow discharge plasma	Nitrobenzene	50	60	-	0.1512	50	[49]
PCD Reference reactor	Nitrobenzene	10	60	66	0.067	35	[50]
PCD Hybrid-series reactor	Nitrobenzene	10	60	66	0.030	65	[50]
Pyrite Fenton system	Nitrobenzene	20	300	-	-	77	[3]
Classic Fenton system	Nitrobenzene	20	300	-	-	30	[3]
DBD reactor	Atrazine	0.03	20	27	2.25	50	[51]
TiO ₂ photocatalysis	diclofenac	10	240	9	82.6	85	[52]
Corona with liquid shower	b-Oestradiol	3	30	120	1400	70	[53]
Contact glow discharge reactor/point-plate	phenol	100	30	44	340	61	[54]
Pulsed liquid discharge	phenol	100	15	55	570	40	[55]
Gas/liquid gliding arc discharge	4-Chlorophenol	40	76	230	1020	89	[56]

* PCD: Pulsed corona discharge.

4. Conclusions

In this study, the DBD system was developed for the degradation of nitrobenzene and its effectiveness was evaluated on the basis of different parameters. The results showed that the degradation of NB was significantly improved by increasing the voltage, gas flow rate and with the addition of promoters to the system while it was decreased with the addition of inhibitors and also decreased with the presence of methanol. Oxygen was the best carrier gas out of air and nitrogen gave the maximum degradation efficiencies of NB. Increasing the flow rate of oxygen further increase the degradation efficiency by producing more active species. Ozone and hydroxyl radicals were found to be the promising active species governing the efficiency trends in the DBD system. These active species were scavenged greatly by the addition of methanol, decreasing the NB degradation efficiency. Addition of promoters H₂O₂ and Fe²⁺ the NB degradation was inclined. Comparison of this system

with other AOPs for the degradation efficiency, input power, reaction kinetics, treatment time and energy yield verified the importance of this system and its effectiveness. This study demonstrated that DBD plasma is an effective technology for the degradation of nitrobenzene and further suggest its application to industrial-scale treatment.

Author Contributions: Conceptualization, M.I.N.; Data curation, M.I.N., T.G. and H.W.; Formal analysis, M.A.; Funding acquisition, C.Y.; Investigation, P.J.A. and H.W.; Methodology, M.I.N. and T.G.; Project administration, C.Y.; Resources, C.Y.; Supervision, C.Y.; Visualization, P.J.A. Writing—original draft, M.I.N.; Writing—review & editing, M.I.N.; A.M.Z. and A.A.

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