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Optimization of a Low-Cost Corona Dielectric-Barrier Discharge Plasma Wastewater Treatment System through Central Composite Design/Response Surface Methodology with Mechanistic and Efficiency Analysis

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Abstract: Water pollution, which is intensified by the release of hard-to-degrade pollutants, poses severe threats to ecosystems, human health, and economic development. The existing advanced oxidation processes often involve high operational costs and can potentially result in secondary pollution, highlighting the necessity for innovative and more sustainable solutions. To address these challenges, our study introduces a cost-effective and eco-friendly corona dielectric-barrier discharge for wastewater treatment. Using the central composite design/response surface methodology, a high decolorization rate of 98% of methylene blue (MB) was achieved within 10 min by optimizing parameters such as pH and voltage. Furthermore, the mechanisms underlying the generation of reactive oxygen species through this device were discussed in detail and the degradation pathways of MB were elucidated. Moreover, this device is very energy-efficient, exhibiting a low energy density and electrical energy per order of 0.15 watt/mL and 5.79 kWh/m³/order, respectively. In conclusion, the plasma discharger developed in this study provides a cost-effective and environmentally sustainable solution for dye wastewater treatment. This research contributes significantly to the advancement of sustainable dye wastewater management practices, offering an innovative method that meets both environmental and economic objectives.

Keywords: water purification; non-thermal plasma; reactor design; advanced purification systems



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1. Introduction

Water pollution remains one of the most severe environmental challenges of the modern era, with its impact further exacerbated by the release of hard-to-degrade pollutants, posing significant threats to ecosystems, human health, and economic development. Artificial organic dyes, extensively used in the textile and leather industries, are major contributors to water pollution. Currently, the market offers over 10,000 different dyes, with global production exceeding 700,000 metric tons each year, 5% to 10% of which end up in industrial wastewater [1]. A dye concentration range of 10 to 50 mg/L can significantly affect water transparency, disrupt aesthetic qualities, and reduce the solubility of gases in water, thereby influencing the ecological balance of aquatic systems [2]. Moreover, the infiltration of these dyes into ecosystems contributes to water quality degradation and poses enduring environmental and health risks, given their toxicity, resistance to biodegradation, and accumulation in water, soil, and the aquatic food chain. Methyl blue (MB), a cationic dye with a triphenylmethane structure, is prevalent in various industries and medical practices. It is employed for dyeing textiles such as wool and cotton, and in paper production for coloring and coating. In the medical field, MB is used as an antiseptic

and diagnostic aid, aiding in tissue staining and visualization during surgical procedures. Despite its utility, MB poses health risks to humans and animals; it is generally safe in therapeutic doses, but overexposure can lead to eye irritation, dry mouth, tachycardia, nausea, vomiting, abdominal pain, diarrhea, visual disturbances, hemolytic anemia, and methemoglobinemia [3]. Moorthy et al. also reported that MB can be categorized as toxic to aquatic organisms according to EU-Directive 93/67/EEC [4]. Consequently, the development of effective methods to eliminate MB from industrial wastewater is critical to safeguarding both environmental and public health.

Traditional methods for treating dye wastewater, such as coagulation, flocculation, membrane filtration, adsorption, and ion exchange, have demonstrated initial effectiveness in decolorizing wastewater. These methods, however, often entail high capital and recurring costs, making them economically unsustainable for many industries [5,6]. Additionally, they frequently result in the formation of sludge or require the regeneration of adsorbent materials, thereby limiting their broader application. Advanced oxidation processes (AOPs), including techniques like the ozone peroxide advanced oxidation process ($O_3-H_2O_2$), have emerged as promising alternatives. AOPs operate by generating reactive species, such as hydroxyl free radicals, which effectively break down water pollutants into carbon dioxide and water through mineralization [7,8]. These processes are particularly good at decomposing recalcitrant materials and toxic contaminants. However, AOPs often require the extensive use of oxidants and other chemicals, raising concerns about secondary pollution and their broader environmental impact [9]. Furthermore, they are not always cost-effective due to the need for additional equipment such as ozone generators, hydrogen peroxide storage and injection facilities, and comprehensive monitoring and control systems [10,11]. This need for additional equipment and chemical use has led to ongoing research aimed at developing more cost-effective and efficient methods for the single-step production of reactive oxygen and nitrogen species, with the goal of improving wastewater treatment processes.

In recent years, non-thermal plasma technology has gained significant attention for its ability to degrade complex and stubborn organic compounds. This technology has found extensive applications in environmental clean-up, particularly in the treatment of pollutants that are otherwise difficult to break down using conventional methods [12]. Non-thermal plasma operates efficiently at breaking down a wide range of hazardous substances, making it a versatile tool in tackling environmental challenges. The effectiveness of non-thermal plasma stems from its ability to generate a variety of reactive species that can attack and decompose complex molecular structures found in various pollutants [13]. Its applications extend beyond environmental remediation to include air purification, surface treatment, and even in the medical field for sterilization and therapy. Its efficiency and adaptability have led to its adoption across multiple sectors for the sustainable management and treatment of complex pollutants. One major concern with plasma technology, despite its advancements, is its high energy consumption. Additionally, while numerous studies have indicated pH fluctuations during the discharge process due to the formation of various ionic species, there remains a research gap in understanding the effect of initial pH on the degradation of organic pollutants.

To address these issues, this study introduces an innovative wastewater treatment method through the development of an ultra-low-cost corona dielectric-barrier discharge (cDBD). The central composite design/response surface methodology (CCD/RSM) was employed to investigate the effect of the initial pH and voltage and to optimize the degradation efficiency. This study provides a thorough analysis of the mechanisms driving the generation of reactive oxygen species (ROS) and the breakdown of MB, along with a detailed exploration of the chemical mechanisms by which pH and voltage influence pollutant removal efficiency. These insights can help in achieving low energy consumption in large-scale operations, thereby improving the sustainability and effectiveness of this treatment method.

2. Materials and Methods

2.1. Experimental Setup

A schematic diagram of the cDBD plasma microreactor is shown in Figure 1. The reactor's main body was constructed using a 20 mL scintillation vial, with a working volume of 10 mL and an outer diameter of 28 mm. An 18-gauge copper wire served as the live electrode, while a 0.1 mm thick, 0.5-inch-long copper tape was coiled around the glass tube as the ground electrode. The discharge gap between the electrodes was 1 mm. An Adjustable 24V DC dual display fixed current power supply was used to test the optimal voltage range. The amplified voltage that was applied to the reactor varied between 28 and 33 kV. The working frequency was 0.3 Hz with a 50% duty cycle, while the initial dye concentration was 10 mg/L, and the treatment time was 10 min (with an effective working time of 5 min).

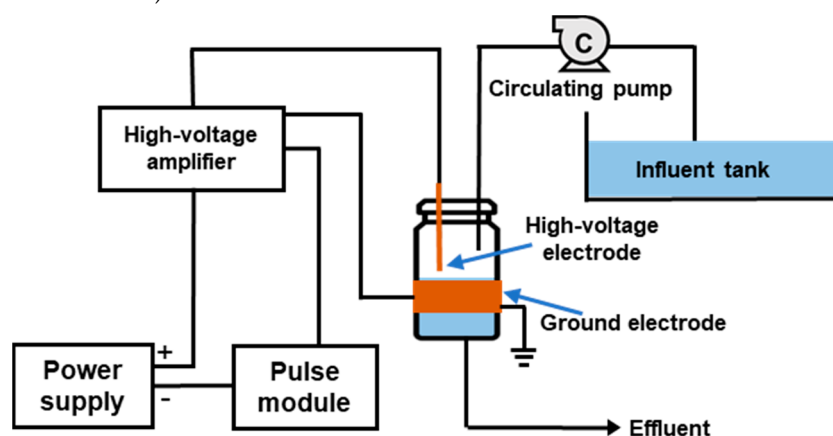


Figure 1. Schematic diagram of the cDBD reactor.

2.2. Methods and Analysis

All chemicals used were analytical grade and were used without any further purification. MB (1% *w/v*) was purchased from BeanTown Chemical Inc. (Hudson, NH, USA) and was diluted to 10 mg/L. Sulfuric acid (95–98%) and sodium hydroxide ($\geq 97.0\%$; beads) were purchased from VWR International (Radnor, PA, USA). The pH of the solution was determined using a PHS-25 digital-display pH meter (XL 600, Fisher Scientific, Hampton, NH, USA).

To assess the dye concentration throughout the treatment process, samples were regularly collected and analyzed for absorbance at approximately 664 nm ($\lambda_{\max}$) using a SpectroVis® Plus Spectrophotometer from Vernier Software & Technology (Beaverton, OR, USA) with a 10 mm plastic cuvette. The breakdown of the dye was quantified based on the decolorization rate, and the decolorization rate of the samples was calculated as:

$$\text{Decolorization rate}\% = \left(1 - \frac{C_{ci} - C_{cf}}{C_{ci}}\right) \times 100\% \quad (1)$$

where C_{ci} and C_{cf} are the MB concentrations at time $t = 0$ and treatment time t , respectively.

2.3. Experimental Design

CCD/RSM is favored for its efficiency and flexibility in optimizing responses, providing comprehensive data on variable effects and experimental errors, even with fewer experiments [14]. In this study, the pH of the MB solution and the voltage applied were selected as independent variables to determine their effects on the performance of the plasma discharger, where the decolorization rate was used as the response variable. Each independent variable ranged over five levels, including $\pm\alpha$ (α , $\alpha = 1.4142$), ± 1 (high and low), and 0 (medium). The actual values of the high and low levels were 4 and 9 for pH and 28 and 33 kV for voltage. These levels were chosen based on preliminary

trials. Experimental design was conducted using the RSM through the CCD in the statistical software Design-Expert (version 13.0.1.0, Stat-Ease Inc., Minneapolis, MN, USA) to generate the experimental runs and determine the optimal combination of these two independent variables to maximize the efficiency for the degradation process according to the experimental results. A total of 13 ($2k + 2k + cp$, where k is the number of factors and cp is the number of center points) experiments for the two factors with five center points were conducted. Table 1 shows the independent experimental factors and their levels in the CCD.

Table 1. Factors and their levels for the central composite design.

Factors	Code	Coded and Actual Levels				
	X_i	$-1.414 (-\alpha)$	-1 (Low)	0 (Center)	1 (High)	$1.414 (+\alpha)$
Voltage (kV)	X_1	27	28	30.5	33	34
pH	X_2	3.0	4.00	6.5	9	10.0

3. Results and Discussion

3.1. Model Evaluation and Statistical Analysis

This study utilized CCD coupled with RSM to comprehensively analyze and optimize the conditions for MB dye degradation in the microreactor, which are crucial for understanding the interactions between variables and their combined effect on the response. Table 2 illustrates the design matrix and the outcomes of experiments assessing the effectiveness of MB dye degradation in the microreactor over a treatment period of 10 min. Using CCD, the Design-Expert software developed a quadratic model based on the experimental data in Table 2, focusing on two independent variables: voltage (X_1) and pH (X_2). The resulting models demonstrated a proficient capability in predicting the dye decomposition rate. Additionally, analysis of variance (ANOVA) was employed to evaluate the quadratic models, further confirming the significant correlations between the independent variables and the observed responses. The best-fit regression model, which was established based on actual factors for the response parameter, was determined by Design-Expert as follows:

$$\text{Decolorization rate}(Y\%) = 0.3456 + 0.0682X_1 - 0.2627X_2 - 0.0125X_1X_2 + 0.0978X_1^2 + 0.1428X_2^2 \quad (2)$$

Table 2. The CCD design matrix for experimental design, observed and predicted response for MB removal.

Run	Voltage (kV)	pH	Decolorization Rate%
1	30.5	6.5	28.1
2	28.0	9.0	36.4
3	33.0	9.0	43.0
4	34.0	6.5	61.1
5	30.5	6.5	40.2
6	27.0	6.5	36.2
7	30.5	6.5	32.9
8	30.5	6.5	33.5
9	33.0	4.0	94.5
10	28.0	4.0	81.6
11	30.5	10.0	18.1
12	30.5	6.5	37.5
13	30.5	3.0	97.9

Table 3 presents the results of the analysis of variance (ANOVA), a statistical method used to ensure the significance and reliability of the models developed in this study [15]. With an F value of 29.59 and the corresponding p value of 0.0001, the model was considered significant according to the goodness-of-fit tests, and there was a very low chance (0.02%)

that the F value could occur due to noise. In addition, the results from the insignificant lack of fit analysis results, with an F value of 4.27 and the corresponding p of 0.0972, indicated the adequacy of the model. The coefficients of determination (R^2), adjusted R^2 , and predicted R^2 for the decolorization rate were 0.9531, 0.9226, and 0.7384, respectively. The difference between adjusted R^2 and predicted R^2 is less than 0.2, suggesting that the predicted R^2 is in reasonable agreement with the adjusted R^2 . Furthermore, the linear correlations between the observed and predicted data for the decolorization rate were evident, as shown in Figure 2a. The R^2 of 0.9531 implied that the model of the decolorization rate has a high degree of correction and could explain 95.31% of the total variation. The coefficients of variation for the decolorization rate (14.68%) demonstrated clear agreement between the experimental and model results. Additionally, the adequate precision value (15.11, which measures the signal to noise ratio) for the model was larger than 4.0, indicating that the signals of the model were all adequate. In conclusion, all these statistical results showed that the developed model was able to predict the experimental data and adequately describe the relationship between the variables and responses. To be more specific, this quadratic model was validated for describing the decolorization rate under different pH and voltage within the range used in this study.

Table 3. Analysis of variance (ANOVA) results for model terms.

Source	Sum of Squares	df	Mean Square	F-Value	p -Value	
Model	0.7750	5	0.1550	29.59	0.0001	significant
X_1 -Voltage	0.0368	1	0.0368	7.03	0.0329	
X_2 -pH	0.5520	1	0.5520	105.37	<0.0001	
$X_1 X_2$	0.0006	1	0.0006	0.12	0.7399	
X_1^2	0.0646	1	0.0646	12.33	0.0098	
X_2^2	0.1421	1	0.1421	27.13	0.0012	
Residual	0.0367	7	0.0052			not significant
Lack of Fit	0.0280	3	0.0093	4.27	0.0972	
Pure Error	0.0087	4	0.0022			
Cor Total	0.8117	12				

R^2 , 0.9531; adjusted R^2 , 0.9226; predicted R^2 , 0.7384; adequate precision, 15.11; CV%, 14.68; standard deviation, 0.0724; Predicted Residual Error Sum of Squares (PRESS), 0.2124.

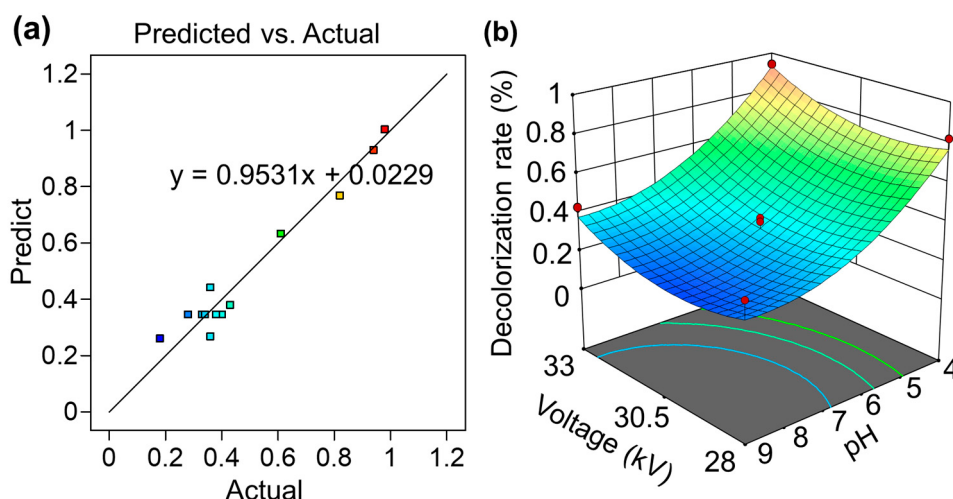


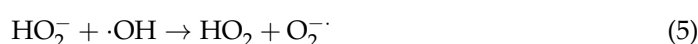
Figure 2. (a) Linear correlations between the observed and predicted data for decolorization rate, and (b) response surface plots of decolorization rate with respect to voltage and pH.

Figure 2b presents a surface response plot illustrating the decolorization rate as a function of pH and voltage. These plots are instrumental in determining the optimal conditions for the response variable within the selected experimental ranges, focusing

specifically on a pH range of 4 to 9 and a voltage range of 28 to 33 kV, represented as -1 to $+1$. The analysis reveals that the maximal decolorization efficiency, quantified at 94.0%, was achieved at an optimal pH of 4 and a voltage of 33 kV in the high and low levels. Furthermore, while experimental data pointed out that conditions of a pH of 3 and a voltage of 30.5 kV led to a decolorization efficiency of 97.9%, the CCD/RSM analysis suggested that a 100% removal rate is achievable at a pH of 3 and a voltage of 33 kV. This finding underscores the greater influence of pH over voltage in determining the degradation efficiency. The figure also clearly showed a substantial enhancement in the decolorization rate with increasing voltage, underscoring its pivotal role in plasma treatment. Furthermore, a comparison of experimental runs 6 and 9 in Table 2 indicated that the decolorization rate improved from 36% to 61% with a voltage increment from 27 kV to 33 kV, highlighting the significant effects of both pH and voltage on the treatment process.

Equation (3) presents a coefficient of -0.2627 for the pH term, indicating a substantial inverse relationship with the degradation rate. Such a coefficient implies that an acidic environment enhances the rate of degradation more effectively than neutral or alkaline conditions. This correlation is also graphically illustrated in Figure 2b. MB degradation was lower than 40% at a solution pH of 9, and increased to 94% at a solution pH of 4.

The enhanced degradation capability with decreasing pH is primarily due to the following reasons. First, the pH of the solution critically impacts the ionization potential of target pollutants, thereby affecting their reactivity and degradation. In aqueous environments, MB predominantly exists in its cationic form (MB^+). Under acidic conditions, MB transitions into a protonated form (MBH^{2+}), which alters its electronic structure. The increased protonation of the dimethylamino groups in acidic media enhances the susceptibility of the methyl groups to dissociation [16]. This protonation potentially facilitates the oxidative degradation of MB, making acidic conditions more conducive to its breakdown. Second, the presence of the hydroxyl anion (OH^-) in alkaline conditions may interfere with the effective reaction of the hydroxyl radical ($\cdot\text{OH}$) [17]. In addition, the decomposition of hydrogen peroxide (H_2O_2) leads to the formation of hydroperoxide anion (HO_2^-), which can act as a quenching agent for $\cdot\text{OH}$ [18]. It is important to note that the superoxide anion (O_2^-) generated in Equation (5) is a relatively weak nucleophile and reducing agent, which can reduce MB to a colorless reduced form but is not capable of decomposing the MB molecules.



Moreover, the equilibrium between H_2O_2 and $\cdot\text{OH}$ is pH-dependent, being more favorable in acidic solutions. The electrons generated by plasma can interact with water to produce hydrogen radicals ($\cdot\text{H}$), which subsequently react with oxygen to form hydroperoxyl radicals ($\cdot\text{HO}_2$) and superoxide anion radical ($\text{O}_2^{\cdot-}$) intermediates (Equations (6) and (7)) [19]. These intermediates can further enhance the generation of H_2O_2 production (Equations (8)–(10)) [20]. Furthermore, in acidic conditions, H_2O_2 can decompose into $\cdot\text{OH}$ (Equation (11)), which possesses an exceptionally high oxidative potential (E_0) and is recognized as one of the most potent oxidizing agents available, surpassed only by fluorine. Thus, it can be concluded that a reduction in pH significantly enhances the degradation efficiency of MB.





3.2. Reaction Order and Kinetics

The degradation of organic compounds in aqueous solutions through plasma treatment is predominantly characterized by first-order kinetics. Assuming the degradation of MB aligns with the pseudo-first-order reaction model, the experimental data can be appropriately fitted to the corresponding first-order kinetic equation.

$$\ln\left(\frac{C}{C_0}\right) = k_0 * t \quad (12)$$

where k_0 is the observed rate constant, and C_0 and C are the initial dye concentration and the concentration after time t , respectively. Figure 3 presents the pseudo-first-order kinetic plot, demonstrating a linear relationship of $\ln(C/C_0)$ over time obtained at a pH of 3 and a voltage of 31.5 kV. The plot reveals a high correlation coefficient (R^2) of 0.9858 for the degradation process. This value indicates that the decomposition of MB aligns well with the characteristics of a pseudo-first-order reaction.

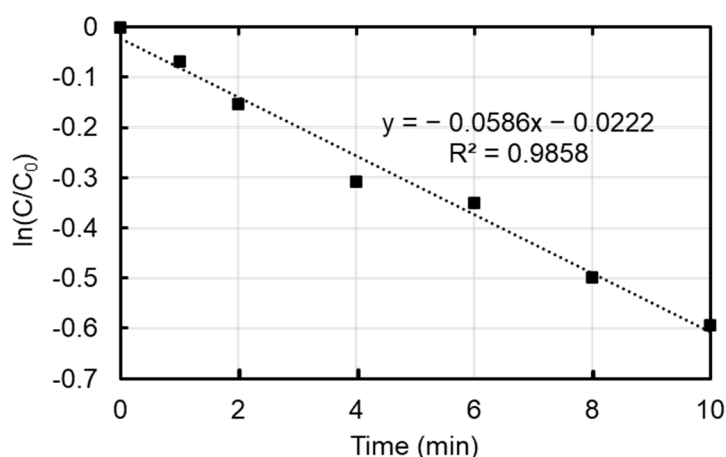


Figure 3. First-order linear plot of $\ln(C/C_0)$ versus time of MB degradation by non-thermal plasma.

3.3. Mechanism Analysis

Wastewater treatment through plasma-induced reactions is facilitated by three distinct methods, each influencing the design of the reactors used [21]. The direct discharge approach involves immersing electrodes in water, creating a filamentary streamer discharge at high electric fields (around 1 MV/cm), which generates reactive oxygen species and produces OH radicals, hydrogen, and hydrogen peroxide. This method also induces shockwaves and UV radiation, aiding in the decomposition of organic contaminants and microorganisms. An alternative, the indirect discharge approach, generates plasma above the water surface, relying on the diffusion of plasma-produced species into the water, a process governed by Henry's law and requiring lower initiation voltage. Lastly, the bubbling method introduces plasma within injected bubbles in the water, effectively increasing the contact surface area between plasma and liquid and allowing for tailored chemical reactions, illustrating the diverse methodologies underlying plasma water purification systems. In this study, the indirect discharge method was used, owing to its higher energy efficiency [22].

In this indirect discharge process, plasma is generated between the anode tip and the water surface, forming a bright streamer discharge. This plasma interacts with the water surface, causing slight movements or small ripples due to the electro-hydrodynamic effect, which leads to surface deformation [23]. The primary mechanism for degrading pollutants in water through non-thermal plasma involves the production of a variety of reactive species after the collisions between accelerating electrons and neutrals. Primary

reactive species with fleeting lifespans (1–3 μ s) are formed in the gas phase immediately after the collision, including ionized neutrals and gas (M^+), excited neutrals and gas (M^*), N, O, atomic H, NO, and O_2^{*-} [24–26]. Then, some reactive species generated in the plasma process are subject to immediate radiative decay, while others would react with additional reactive species, neutral molecules, and water to form secondary reactive species like hydrogen peroxide (H_2O_2), nitrogen dioxide (NO_2), nitric oxide (NO), and ozone (O_3) in the surrounding air [27,28]. These secondary reactive species, once generated in the gas phase, would migrate into the liquid phase or other substrates, where the formed tertiary reactive species expand their lifetimes from milliseconds to several days. These tertiary reactive species are more stable, including O_3 , H_2O_2 , nitrate (NO_3^-), peroxyxynitrite ($ONOO^-$), and nitrite (NO_2^-). Figure 4 visually summarizes the reactive species formation process from the discharge region through the gas phase to the target substrate.

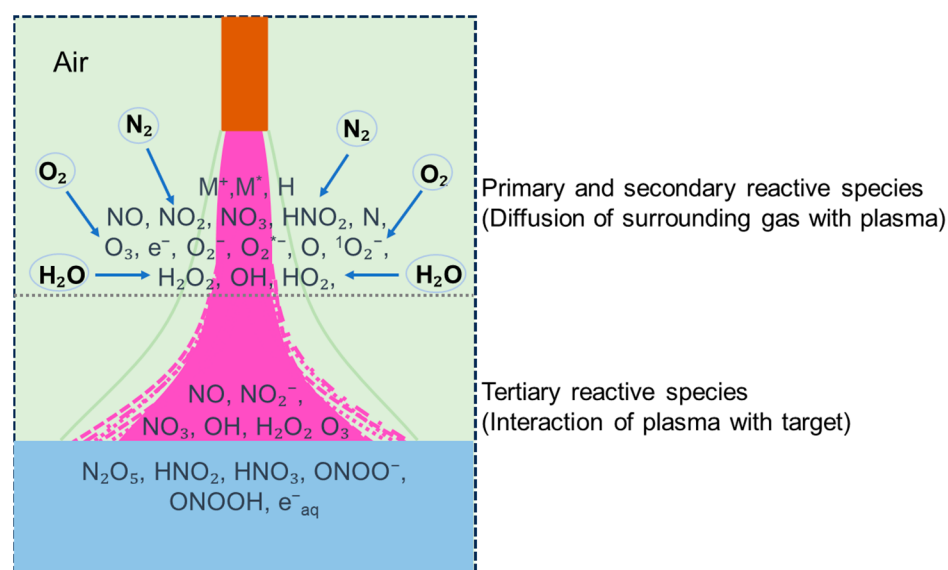
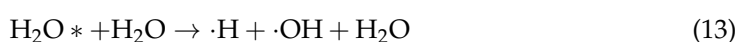


Figure 4. Schematic diagram representing the formation of various reactive species in the non-thermal atmospheric pressure plasma. The M-symbol indicates atoms or molecules (excited (*)) or ionized (+)).

In the plasma-treated substrate, the electrolytic dissociation of water is also facilitated by plasma-generated electrons, yielding H_2O_2 , as demonstrated in Equations (13) and (14). Hydrogen peroxide is a stable oxidizing agent formed not only via direct electron impact with water molecules but also through the dimerization of hydroxyl radicals. The in situ generation of H_2O_2 serves as a proxy for the presence and reactivity of hydroxyl radicals within the plasma-mediated process [29]. Additionally, the peroxyxynitrous acid, a reactive nitrogenous intermediate, undergoes homolysis to yield $\cdot NO$ and $\cdot OH$ [30], which are integral to the oxidative degradation pathway.



The reactive species produced can engage in various mechanistic pathways when interacting with organic dye molecules. These pathways include electrophilic addition, hydrogen abstraction, and the initiation of radical chain reactions. Photochemical dissociation by ultraviolet (UV) photons, as well as electron and ion-induced fragmentation, contributes to the multitudinous routes of MB molecular decomposition. UV radiation can also dissociate hydrogen peroxide molecules present in aqueous solution to further improve the formation of highly reactive hydroxyl radicals [31]. This results in the disruption of conjugated chromophoric systems and the oxidative opening of aromatic ring

structures, ultimately leading to conversion into innocuous end-products like carbon dioxide and water.



The initial step of MB degradation is characterized by the homolytic cleavage of the N–CH₃ bond, which is the least energetically stable, with a bond dissociation energy of 70.8 kcal/mol [3]. This process yields thionin acetate and methyl radicals that are subsequently oxidized to methanol (CH₃OH), formic acid (HCOOH), or formaldehyde (HCHO) [32]. The carbon–sulfur (C–S) bond and carbon–nitrogen (C–N) bond are the most active parts of the remaining structure, which means that they are more likely to be attacked by reactive radicals or ozone due to their lower bond dissociation energies compared to other molecular bonds present, and thus form phenol and aniline-2-sulfonic acid [33]. The degradation intermediates generated can undergo further oxidation reactions, leading either to complete mineralization or to the formation of less complex organic species, as shown in Figure 5.

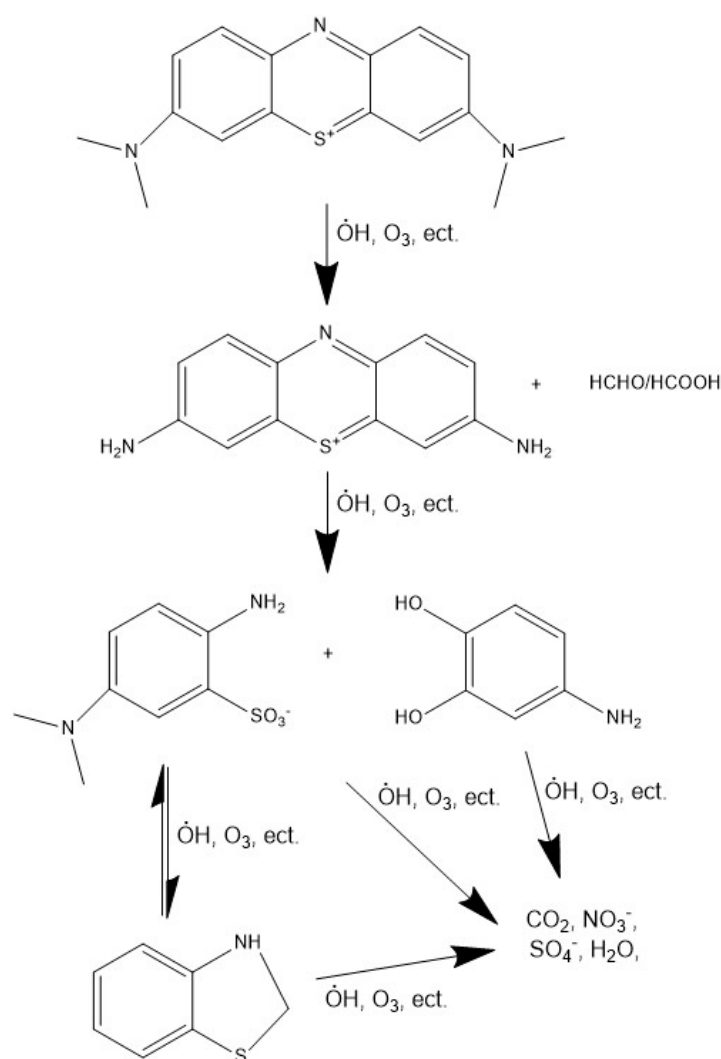


Figure 5. Proposed degradation mechanism pathway of methylene blue dye in the cDBD system.

3.4. Practical Analysis

Evaluating the efficiency of AOPs in wastewater treatment is very important and often characterized by kinetic rate constants. However, these constants alone do not encompass other aspects of AOP efficiency, especially the operational costs. To fill this gap, Bolton et al. [34] introduced the Electrical Energy per Order (EE/O), defined by Equation (16). EE/O measures the electrical energy required per reactor volume to decrease a target

contaminant's concentration by one order of magnitude, a critical metric in evaluating energy consumption, which constitutes a significant portion of AOP operating costs. This metric is especially relevant for scenarios with low initial pollutant concentration (C_0) and is a critical measure of operational costs and instrumental in effectively scaling up treatment designs and estimating costs. The calculated EE/O value provides a benchmark for assessing the energy efficiency of the plasma treatment relative to other AOPs. A lower EE/O signifies greater energy efficiency and cost-effectiveness in contaminant reduction.

$$EE/O = \frac{P_{\text{elec}} * t * 1000}{V * 60 * \log(C_0/C)} \quad (16)$$

where P_{elec} is the system power (kW), V is the volume of water treated (L) in time t (min), C_0 is the initial contaminant concentration (EE/O is valid for low initial concentrations, typically <100 mg/L), and C is the final concentration [35].

For the non-thermal plasma treatment process in this study, the total electrical energy utilized was 2.78 watts for treating a volume of 10 mL over 20 min, with a 50% duty cycle. The process successfully reduced the initial concentration of the contaminant from 20 ppm to 0.7 ppm. According to Equation (16), the EE/O = $(0.00278 \times (20 \times 50\%) \times 1000) / (0.01 \times 60 \times \log(20/0.7)) = 31.82 \text{ kWh/m}^3/\text{order}$ for an initial concentration of 20 mg/L.

The plasma treatment system, requiring no oxidants, has a cost advantage over other AOPs and is competitive in the market. A brief economic comparison of different AOPs, such as ultrasonication (U/S), O_3 , and UV treatments, is provided in Table 4. Notably, this moderate EE/O number is even lower than other existing efficient systems in low initial concentration.

Table 4. A comparison of plasma technologies with other AOPs employed for dye removal.

AOPs	C_0	C	Chemicals Cost (USD)	Energy Density Used (watt/mL)	EE/O (kWh/m ³ /order)	Total Capital Cost (USD)	Reference
US	20	2	NA	0.50	10,964.69	1.83×10^{10}	[36,37]
O_3	20	2	NA	0.03	103.91	4.53×10^5	[36,37]
U/S + UV	20	2	NA	0.53	3698.09	5.86×10^9	[36,37]
U/S + O_3	20	2	NA	0.53	1215.02	1.92×10^9	[36,37]
UV + O_3	20	2	NA	0.06	111.56	1.12×10^7	[36,37]
U/S + UV + O_3	20	2	NA	0.56	989.9	1.50×10^9	[36,37]
U/S + H_2O_2	100	45.65	2.06×10^5	0.03	43.07	5.33×10^8	[36,38]
UV + H_2O_2	100	84.35	2.06×10^5	0.01	559.2	9.09×10^7	[36,38]
U/S + UV + H_2O_2	100	9.13	2.06×10^5	0.04	39.76	7.99×10^7	[36,38]
Photocatalysis	402.6	40.26	2.52×10^4	0.71	3654.68	2.67×10^8	[36,39]
U/S + photocatalysis	402.6	40.26	6.98×10^3	0.76	1059.08	1.11×10^8	[36,39]
Plasma	20	0.7	NA	0.33	31.82	62	This study
Plasma	10	0.1	NA	0.15	5.79	62	This study

In addition to operational costs, a comprehensive assessment of the economic viability of our novel plasma-based AOP technology necessitates a thorough understanding of the capital cost. This is essential not only for a complete economic analysis but also for making informed decisions about technology adoption and scalability. For our demonstration microreactor, the total capital cost is primarily composed of basic components, crucial for its operation. These include copper wire as the live electrode, copper tape as the ground electrode, a circulating pump priced at USD 15, necessary piping, a high voltage amplifier costing USD 10, a pulse module valued at USD 12, and a power supply for USD 15. It is important to emphasize that our capital cost estimation for the microreactor is a rough approximation, focusing mainly on these fundamental components. This approach differs from the more comprehensive cost analyses often associated with larger-scale AOP systems, which include additional cost elements like infrastructure, labor, and maintenance. These findings suggest that this plasma-based AOP approach, despite being a micro-level demonstration, is promising for larger scale applications due to its cost-effective scalability.

This aspect is particularly relevant in wastewater treatment, where cost-efficiency and scalability are critical. Therefore, our system emerges as a viable option for large-scale wastewater treatment scenarios, offering a balance of economic and operational benefits.

The comprehensive data from various AOPs, as summarized in Table 4, elucidate the relative economic and efficiency profiles of each method. The findings indicate that while standalone methods like U/S are cost-intensive, their integration with other AOPs can yield more economically viable solutions. For instance, U/S treatment alone exhibits a higher EE/O of 10,964 kWh/m³/order, which significantly diminishes to 989 kWh/m³/order when combined with UV or O₃ treatments. This suggests that non-thermal plasma may similarly benefit from integration with other technologies to further enhance wastewater treatment efficiency.

The elevated total water treatment cost observed in this study is primarily attributed to the limited capacity of the employed reactor. Notably, the reactor operated without the introduction of any gases and featured a straightforward experimental setup, indicating substantial potential for future enhancements and optimization. Furthermore, the overall treatment efficiency could be further increased if the process were scaled up [40]. Additionally, a study by Fahmy et al. [41] provided valuable insights into optimizing the removal of Acid Orange 142 dye. They achieved an 88.87% removal efficiency in treating 100 mL of wastewater with a 20 mg/L dye concentration, using a 12.5 kV voltage and a 5 mm gap between the solution surface and the high-voltage electrode over 90 min. Their energy consumption under these conditions was 2.025 kWh, equating to 30.375 W/mL. In contrast, our study recorded a substantially lower energy consumption rate of 0.33 W/mL, while achieving a higher decolorization rate of 96.5%, indicating a more efficient process for dye decolorization. These results clearly showed the effectiveness of this reactor.

In comparison to other AOPs utilized for water treatment, the efficiency and cost of the current plasma-based technology are quite competitive. These findings suggest that plasma technology not only holds broad application prospects but also, when integrated with other AOPs, can lead to further cost reductions. The potential for cost-effective scalability and the ability to integrate seamlessly with other treatment methods make plasma technology a promising option in advancing sustainable water treatment strategies.

4. Conclusions

In conclusion, this study introduced an ultra-low-cost cDBD plasma device, offering an affordable and efficient solution to wastewater treatment. Through CCD/RSM optimization, this study identified that the optimal operational conditions within the low and high levels were achieved at a pH of 4 and a voltage of 33 kV, resulting in a 94.0% decolorization efficiency. Furthermore, the CCD/RSM optimization revealed a trend indicating better efficiency with a lower pH and higher voltage. The performance of the plasma discharger was optimized using CCD/RSM with the initial pH and applied voltage as independent variables. The prediction model achieved a high correlation coefficient ($R^2 = 0.9763$) between the experimental data and the model's predictions. This research fills a crucial gap by analyzing the effects of initial pH and voltage on the degradation efficiency of organic pollutants and, specifically, by detailing the mechanisms of ROS generation and the degradation pathways of MB. The practical viability and efficiency of the plasma device to degrade MB were demonstrated by a low energy density and EE/O of 0.15 watt/mL and 5.79 kWh/m³/order, respectively. This research not only demonstrates that plasma is a promising and environmentally friendly option for dye wastewater treatment, but also establishes a foundation for ongoing innovation in non-thermal plasma applications.

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