

Article

Electrically Enhanced Hydroxyl Radicals Degrading Malachite Green in Water: A Study by DFT Calculation and Experiment

Yingjian Li ^{1,2}, Hanzeng Wang ³, Yong Han ^{4,*} and Tifeng Jiao ^{1,*} 

¹ State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China

² Hebei Key Laboratory of Power Electronics for Energy Conservation and Drive Control, Yanshan University, Qinhuangdao 066004, China

³ Smart Distribution Network Center, State Grid Jibei Electric Power Company Limited, Qinhuangdao 066004, China

⁴ School of Electrical Engineering, Yanshan University, Qinhuangdao 066004, China

* Correspondence: hanyong@ysu.edu.cn (Y.H.); tfjiao@ysu.edu.cn (T.J.)

Abstract

Here, density functional theory (DFT) simulations and experimental studies were conducted to explore the effect and mechanism of an external electric field (EF) on the decolorization efficiency and degradation rate of malachite green (MG) in water by hydroxyl radicals generated in the discharge plasma process. The simulation results indicated that the external EF had a significant impact on the degradation rate. Under the action of the EF along the reaction axis direction, the free energy barrier of the reaction decreased and the reaction rate increased. As the EF strength increased from 0 to 0.002 a.u., the free energy barrier of reaction 1 decreased from 9.164 kcal/mol to 7.097 kcal/mol, and the reaction rate increased from $1.499 \times 10^6 \text{ s}^{-1}\text{M}^{-1}$ to $4.764 \times 10^7 \text{ s}^{-1}\text{M}^{-1}$; the free energy barrier of reaction 2 decreased from 2.318 kcal/mol to -1.262 kcal/mol , and the reaction rate increased from $1.313 \times 10^{11} \text{ s}^{-1}\text{M}^{-1}$ to $5.457 \times 10^{13} \text{ s}^{-1}\text{M}^{-1}$; the free energy barrier of reaction 3 decreased from 7.755 kcal/mol to 7.011 kcal/mol, and the reaction rate increased from $1.764 \times 10^7 \text{ s}^{-1}$ to $6.242 \times 10^7 \text{ s}^{-1}$. Under the action of the EF in the opposite direction along the reaction axis, the opposite effect was presented. In addition, we analyzed the surface electrostatic potential, dipole moment, condensed Fukui function and spin density under different-strength EFs to explore the mechanism of the influence of the external EF on the reaction and further clarified the feasibility of an external EF promoting the degradation of MG in water by hydroxyl radicals. The experimental study results showed that EF can promote the degradation of MG under a discharge plasma process. This is consistent with the trend of the results obtained from DFT simulations under the action of a positive EF with higher electric field intensity, verifying the feasibility of the method of EF-assisted discharge plasma degradation. In addition, we experimentally explored the changes in the decolorization efficiency of MG under different initial conditions.

Keywords: hydroxyl radical; malachite green; density functional theory; degradation; electric field



Academic Editor: Christos Argiris

Received: 14 May 2026

Revised: 21 June 2026

Accepted: 24 June 2026

Published: 30 June 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

MG, a triphenylmethane-class dye, serves dual industrial functions as both a coloring agent and a biocide commonly used in aquaculture to treat parasites in water and inhibit bacterial growth [1,2]. However, MG is a potent toxicant exhibiting teratogenic,

carcinogenic, and mutagenic properties, presenting significant risks to human health and ecological safety [3]. MG is widely present in various industrial wastewaters due to its extensive application. MG has a complex molecular structure and a high ratio of chemical oxygen demand to biochemical oxygen demand, making it difficult to degrade and posing a huge threat to the environment. Thus, the treatment of MG wastewater has attracted wide attention.

The traditional wastewater treatment methods include three types: physical methods, chemical methods and biological methods. The physical methods are mostly applied in the initial treatment stage, but their application scope is rather limited and the removal rate is relatively low. The chemical methods may lead to the generation of toxic by-products, posing a risk of secondary pollution to the water body. Because the 5-day biochemical oxygen demand (BOD₅) of MG is nearly zero, conventional biological treatment methods cannot effectively degrade MG [4,5]. Advanced oxidation processes (AOPs), such as hybrid ultrasonic–electrochemical approaches [6], photocatalytic degradation [7], and Fenton oxidation [8], have emerged as promising alternatives for the treatment of organic wastewater. However, challenges including secondary pollution, high energy consumption, and low degradation efficiency persist [9]. Therefore, developing a treatment strategy for MG wastewater that combines low environmental impact with high degradation efficiency is of great significance.

As an AOP, discharge plasma technology (DPT) mainly generates ultraviolet light, shock waves, free radicals ($\bullet\text{OH}$, $\text{HO}_2\bullet$, $\bullet\text{O}$, etc.), H_2O_2 , O_3 and other oxidizing species through various physical and chemical effects, which can effectively degrade organic pollutants in water [10–12]. Among them, $\bullet\text{OH}$ exhibits the most prominent degradation effect because it can non-selectively degrade various organic pollutants in water [13,14]. In addition, DPT operates effectively under ambient temperature and pressure conditions and is characterized by low cost and environmental friendliness. Rodrigues Júnior et al. [15] studied the removal of diazinon from water using cold plasma. Their results showed that cold plasma achieved a high degradation efficiency for diazinon and could rapidly degrade it within a short period. Chandani Vaigankar et al. [16] compared various methods including plasma treatment. They emphasized the synergistic effect of catalyst-assisted free radical generation in accelerating the degradation of pollutants. This provides guidance for selecting appropriate advanced oxidation methods to effectively treat pollutants in water. The dielectric barrier discharge plasma system can effectively remove multiple pollutants such as benzene, toluene and p-nitrophenol simultaneously [17]. Furthermore, discharge plasma has demonstrated excellent degradation ability for several dyes in water, including methylene blue [18], Rhodamine B [19], and cochineal dye [20]. Despite its promising potential, the practical implementation of DPT for pollutant degradation still faces challenges. Specifically, the highly active species generated by discharge plasma have a short lifespan, which results in relatively low energy efficiency when discharge plasma participates in the degradation process [21].

To improve the efficiency of discharge plasma in the degradation stage, researchers have combined DPT with other catalytic technologies. Among these combined approaches, applying an external EF during the degradation process is a simple and efficient method. The external EF can affect the reaction pathway and activity of chemical reactions. Ramanan et al. [22] studied the changes in the Menshutkin reaction when an external EF was applied. The study result showed that when the EF is aligned with the reaction axis direction, the activation energy of the reaction can be reduced, thereby accelerating the reaction. The EF being in the opposite direction may suppress the reaction. Yang et al. [23] studied the reaction process of the Diels–Alder reaction through the method of single-molecule electrical detection. The results indicated that a strong external EF significantly

lowers the energy barriers for both concerted and stepwise reactions and could catalyze the Diels–Alder reaction. Tao et al. [24] studied the molecular structure of trichloroethylene based on DFT. The research results indicated that the C–Cl bond of trichloroethylene was prone to dissociation when an external EF was applied. The external EF made trichloroethylene more likely to participate in chemical reactions.

Motivated by these findings, we propose that an EF can enhance the degradation of MG in wastewater by hydroxyl radicals. In this study, DFT was employed to investigate the variation in the reaction rate between MG and the hydroxyl radical (the primary reactive species generated in discharge plasma) under various applied EFs. The underlying mechanism was elucidated by calculating the surface electrostatic potential, dipole moment, condensed Fukui function, and spin density of the reaction system. In addition, experiments were conducted to examine how initial conditions influence the decolorization efficiency of MG in water during the discharge plasma process. The experimental results further confirmed the promotional role of the applied EF in MG removal.

2. Methodology

2.1. Quantum Chemistry Simulation

Quantum chemical calculations were performed via the Gaussian 09 package [25]. Under the attack of active free radicals, MG undergoes multiple degradation reactions, including addition, N-demethylation and ring-opening processes, with dominant pathways involving amino demethylation and central carbon hydroxylation [2,6,26,27]. To explore the external EF effect on DPT-mediated MG degradation, reactions along the x -axis EF (aligned with the reaction axis, defined as the chemical bond electron density recombination direction [22,28,29]) were simulated (reaction steps: Figure S1a; DFT models: Figure S1b). The connection line between the two atoms involved in the reaction was set parallel to the x -axis, and the x -axis direction was the direction of chemical bond breaking or formation, so that the influence of the EF on the reaction could be analyzed more accurately. MG* (reactant of reaction 1) represents the MG structure after aqueous dissolution and Cl[−] dissociation [30]. Under the action of hydroxyl radicals, through electron nucleophilic rearrangement and nucleophilic addition reactions, it generates the reactant of reaction 2. For reaction 1, this paper focuses on the addition reaction of hydroxyl radicals.

Stable molecular configurations and transition states (TSs) were searched via the DFT-based Berny algorithm [31]. The geometries of reactants, TSs and products were optimized at the M06-2X/6-31G(d,p) level, with rationality verified by frequency analysis: stable species had positive vibrational frequencies, while TSs featured a single imaginary frequency (first-order saddle point). The imaginary frequencies of the TSs and the tunneling effect correction coefficient for the three-step reaction are shown in Table S1. By observing the vibration patterns corresponding to the imaginary frequency, it was confirmed that they connected the reactants and products along the reaction coordinate direction. The simulation calculation adopted the default convergence criteria of Gaussian: the maximum force was less than 0.00045; the root mean square force was less than 0.00030; the maximum displacement was less than 0.00180; the root mean square displacement was less than 0.00120. During the calculation process, the reactant of reaction 1 adopted the singlet state (spin multiplicity = 1), while the TS and the hydroxyl radical both adopted the doublet state (spin multiplicity = 2). The reactants of reaction 2 were in the singlet state, and the TS was in the doublet state. The reactant and TS of reaction 3 were both in the doublet state. Intrinsic reaction coordinate (IRC) calculations (Gonzalez–Schlegel method) further confirmed the TSs' connectivity to correct reactants and products [32]. Single-point energy was computed at the B2PLYPD3/def2TZVP level, and free energy was calculated via the Shermo program [33]. We set the temperature to 298.15 K, the pressure to 1 atm,

and the zero point energy frequency scale factor to 0.97. The structural optimization adopted the PCM solvent model, and the single-point energy calculation adopted the SMD solvent model.

The Multiwfn program [34,35], a versatile wavefunction analysis tool, was adopted to acquire and analyze the molecular dipole moment, spin density, condensed Fukui function and surface electrostatic potential.

2.2. Experiment

2.2.1. Experimental Materials and Setup

The MG employed in this study was purchased from Fangzheng Reagent Factory (Tianjin, China). The selected standard solutions were HCl and NaOH, purchased from Thermo Fisher Scientific (Shanghai, China). All chemical reagents were of analytical reagent grade. Figure S2 shows the experimental setup diagram. The voltage output of the discharge plasma power supply was applied to the two metal electrodes of the dielectric barrier discharge (DBD) plasma generator, generating discharge plasma through gas-phase discharge. The metal electrodes were circular with a diameter of 4.5 cm. The distance between the two metal electrodes during discharge was 4 cm. The glass insulating medium between the electrodes not only prevented the generation of an arc caused by excessive discharge current but also ensured uniform discharge between the electrodes. The voltage and current of the discharge plasma power supply were adjustable, which could be used to calculate the input power. In the experiment, the input current was set at 1 A, and the input power was changed by adjusting the input voltage. The controllable DC power supply was connected to two identical electrode plates to provide a stable external EF. The peristaltic pump was connected to the double-bottom beakers and DBD plasma generator to circulate the water solution in the system.

2.2.2. Experimental Methods

Four independent experiments were performed to investigate the effects of initial conditions on discharge plasma-mediated MG decolorization efficiency in aqueous solution.

Experiment 1: MG solution (pH = 5, 50 mg/L) was treated at 65 W, 80 W and 95 W input power, with the MG concentration monitored over 60 min.

Experiment 2: MG solutions (50 mg/L, pH = 3, 5, 7) were degraded at 65 W, and MG concentration changes were recorded within 60 min.

Experiment 3: MG solutions (pH = 5, 50, 70, 90 mg/L) were treated at 65 W, with the MG concentration tracked during the 60 min reaction period.

Experiment 4: To explore the effect of EF strength on MG degradation, 50 mg/L MG solution (pH = 5) was treated at 65 W with external EF intensities of 8×10^3 , 1.2×10^4 and 1.6×10^4 V/m, and the MG concentration was monitored over 60 min.

In all experiments, 350 mL MG solution was degraded with a peristaltic pump flow rate of 50 mL/min. Samples were collected at 5, 10, 15, 30, 45 and 60 min, and the MG concentration was determined via UV-visible spectrophotometry at MG's maximum absorption wavelength of 617 nm [36]. Standard curves were established using 1, 5 and 10 mg/L MG solutions, with absorbance measured at 617 nm, which is shown as

$$C = 19.19A + 0.188 \quad (1)$$

In the formula, C represents the concentration of MG solution, and A represents the absorbance of MG solution.

The calculation formula for the decolorization efficiency during the degradation process is as follows:

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\% \quad (2)$$

In the formula, C_0 and C_t represent the concentrations of MG solution at time 0 and time t respectively.

3. Results and Discussion

3.1. DFT Calculations

3.1.1. Free Energy Barrier and Reaction Rate

The reaction rate directly reflects the speed of the reaction, which can be calculated by the TST formula [37]:

$$k^{TST} = k\sigma \frac{k_B T}{h} e^{-\Delta G^\ddagger / (RT)} \quad (3)$$

where k represents the tunneling effect correction coefficient, σ represents the degeneracy of the reaction pathway, k_B represents the Boltzmann constant, T represents the temperature of the reaction, h represents the Planck constant, R represents the ideal gas constant, and $\Delta G^\ddagger$ represents the activation energy of the reaction.

The free energy barrier, defined as the TS free energy minus the reactant free energy, determines the reaction difficulty and correlates inversely with the reaction rate. Thus, we computed the free energy barriers and reaction rates of reaction 1 under x -axis EFs of varying intensities.

Tables 1 and 2 list the corresponding data for positive and negative x -axis EFs, respectively. The results revealed that strengthening the positive EF gradually lowered the free energy barrier and accelerated the reaction rate, whereas the negative EF exerted the opposite effect, indicating that a positive EF promotes reaction 1 while a negative EF suppresses it. This is because the positive electric field preferentially stabilizes the transition state with a larger dipole moment, thereby reducing the energy difference between the reactants and the transition state, lowering the energy barrier and accelerating the reaction [38].

Table 1. The free energy barrier and reaction rate of reaction 1 when a positive EF was applied.

EF Strength (a.u.)	Free Energy Barrier (kcal/mol)	Reaction Rate ($s^{-1}M^{-1}$)
0	9.164	1.499×10^6
0.0002	8.832	2.615×10^6
0.0005	8.628	3.678×10^6
0.001	8.232	7.127×10^6
0.002	7.097	4.764×10^7

Table 2. The free energy barrier and reaction rate of reaction 1 when a negative EF was applied.

EF Strength (a.u.)	Free Energy Barrier (kcal/mol)	Reaction Rate ($s^{-1}M^{-1}$)
0	9.164	1.499×10^6
0.0002	9.314	1.167×10^6
0.0005	9.569	7.603×10^5
0.001	9.938	4.106×10^5
0.002	10.381	1.961×10^5

Tables S2 and S3 display the free energy barriers and reaction rates of reaction 2 under positive and negative x -axis EFs, respectively. Strengthening the positive EF reduced the free energy barrier and accelerated the reaction rate of reaction 2, while the negative EF exerted irregular effects, revealing that a positive EF promotes reaction 2, with unstable

negative EF impacts. Tables S4 and S5 list the corresponding data for reaction 3, showing that an EF exerts the same effect on reaction 3 as on reaction 1.

The analysis results show that an EF applied along the reaction axis promotes degradation. Moreover, when the EF is enhanced, the promoting effect increases.

3.1.2. Dipole Moment

The dipole moment is a vector used to describe the asymmetry of charge distribution, and it is calculated by the following formula [39]:

$$\mu = \begin{bmatrix} \mu_x \\ \mu_y \\ \mu_z \end{bmatrix} = \sum_A q_A \begin{bmatrix} X_A \\ Y_A \\ Z_A \end{bmatrix} - \int \begin{bmatrix} x \\ y \\ z \end{bmatrix} \rho(r) dr \quad (4)$$

where q_A represents the nuclear charge of atom A, and X_A , Y_A , and Z_A represent the three Cartesian coordinates of atom A. x , y and z represent the three Cartesian coordinates of the electron position.

Figure 1 depicts the dipole moment variation of the TS in reaction 1. It can be seen that the dipole moment rises with strengthening positive EF and declines under enhanced negative EF. The positive EF elevates the TS's dipole moment, enhancing its stability, lowering the activation energy and thus facilitating the reaction [40,41], whereas the negative EF inhibits the reaction conversely.

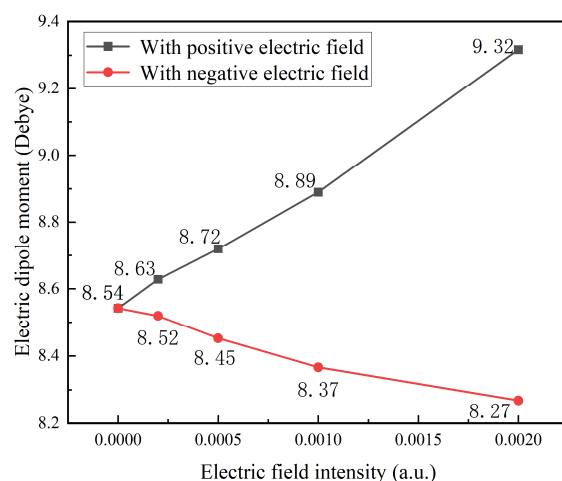


Figure 1. The change in dipole moment of the TS of reaction 1 under the action of the EF in the x -axis direction.

Figure S3 presents the TS dipole moment variation of reaction 2. Strengthening the positive EF increases the dipole moment, while a negative EF triggers irregular changes, revealing that a positive x -axis EF promotes reaction 2, with unstable negative EF effects. Figure S4 depicts the TS dipole moment changes for reaction 3 under an x -axis EF, which follow the same rule as those for reaction 1: a positive EF facilitates reaction 3 and a negative EF suppresses it.

3.1.3. Electrostatic Potential

The molecular van der Waals surface electrostatic potential (ESP) can be used to predict nucleophilic and electrophilic reaction sites [42]. To investigate the effect of an external EF on reactivity, we plotted the system's ESP maps via Multiwfn and calculated the reactive atom ESP using the efficient algorithm from Refs [43,44]. Figure 2 displays the ESP plot of reaction 1's TS without an EF: the ESPs of the C12 and O51 atoms are 62.548 kcal/mol and

27.885 kcal/mol, respectively. ESP magnitude links to atomic charge and electron density, and a positive ESP signifies dominant nuclear charge effects.

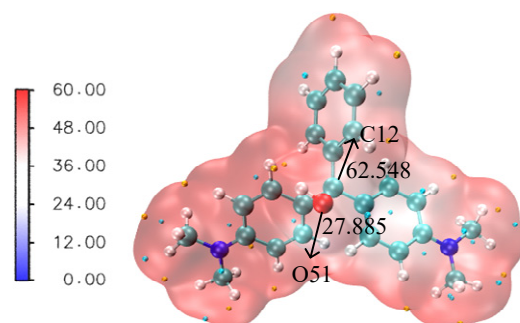


Figure 2. ESP diagram of reaction 1 without external EF effect. The red ball represents O, the white ball represents H, the green ball represents C, and the blue ball represents N.

With EF intensity, the ESP of C12 declines while that of O51 rises. The reduced C12 ESP signifies a higher electron cloud density, rendering it more vulnerable to $\bullet\text{OH}$ attack; the increased O52 ESP indicates lower electron density and stronger electrophilicity. Thus, a positive EF boosts reactivity and accelerates the reaction.

Figure 3 shows the ESP of the TS of reaction 1 when a positive EF is applied. We can conclude from Figure 3 that when the EF is enhanced, the ESP of the C12 atom decreases, while the ESP of the O51 atom increases. The decrease in the ESP of the C12 atom indicates an increase in its electron cloud density, making it more susceptible to attack by $\bullet\text{OH}$. The increase in the ESP of the O51 atom indicates a decrease in its electron cloud density and an increase in its electrophilicity. This indicates that a positive external EF can enhance reaction activity and promote the progress of the reaction.

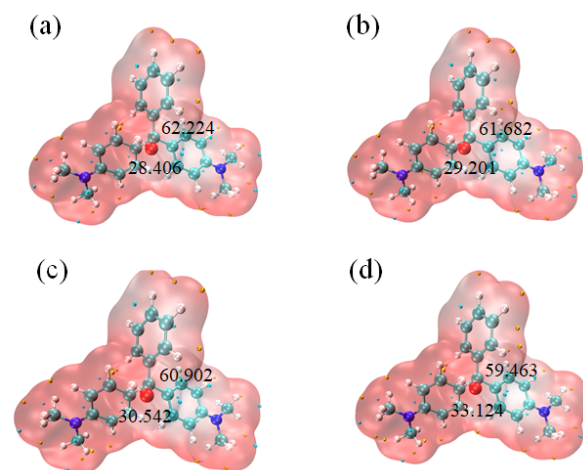


Figure 3. ESP diagrams of reaction 1 under the action of an EF in the positive x -axis direction, with EF strength of (a) 0.0002 a.u., (b) 0.0005 a.u., (c) 0.001 a.u., or (d) 0.002 a.u. The red ball represents O, the white ball represents H, the green ball represents C, and the blue ball represents N.

Figure 4 shows ESP diagrams of the TS of reaction 1 when a negative EF is applied. We can conclude from Figure 4 that when the EF is enhanced, the ESP of the C12 atom increases, the electron cloud density of the C12 atom decreases, the ESP of the O51 atom decreases, the electrophilicity of the O51 atom weakens, and the activity of the reaction decreases. This indicates that a negative external EF suppresses the progress of the reaction.

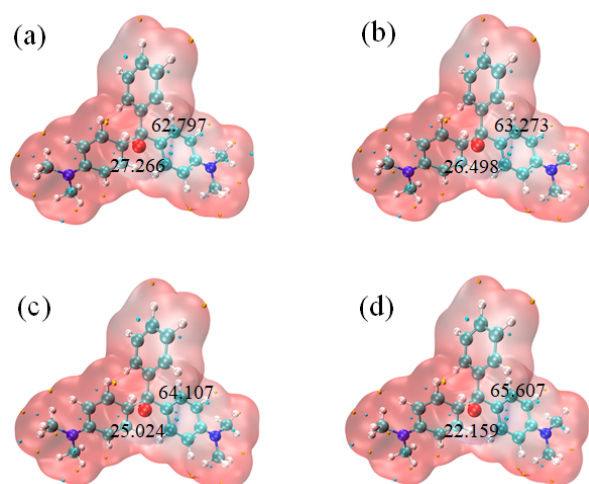


Figure 4. ESP diagrams of reaction 1 under the action of an EF in the negative x -axis direction, with EF strength of (a) 0.0002 a.u., (b) 0.0005 a.u., (c) 0.001 a.u., or (d) 0.002 a.u. The red ball represents O, the white ball represents H, the green ball represents C, and the blue ball represents N.

We calculated the ESP of the TS reaction site for reaction 2 but failed to obtain the ESP of the embedded bonding C13 atom, thus analyzing the reactant ESP instead. Figure S5 depicts the reactant ESP of reaction 2 without an EF, while Figure S6 shows that under a positive x -axis EF, C13 has negative ESP with increasing absolute value under stronger EFs, indicating higher electron cloud density and stronger nucleophilicity that facilitates $\bullet\text{OH}$ attack. Conversely, Figure S7 reveals that an enhanced negative EF reduces the absolute value of the C13 ESP, lowering the electron density and nucleophilicity to inhibit reaction 2.

For reaction 3, Figure S8 shows the ESP without an EF, and Figure S9 illustrates that an enhanced positive EF enlarges the ESP absolute value difference between C1 and C13, intensifying electron density unevenness to promote bond cleavage and boost reactivity. Figure S10 demonstrates that an enhanced negative EF narrows this difference, hindering bond breaking and reducing the reactivity of reaction 3.

3.1.4. Spin Density

Spin density is used to describe the spatial distribution of unpaired electrons in the open shell system. For a molecule, the spin density at a certain point in space is equal to the alpha electron density minus the beta electron density at that point, which can be expressed by the following formula [45]:

$$\rho = \rho_{\alpha} - \rho_{\beta} \quad (5)$$

where ρ_{α} , ρ_{β} represent the densities of alpha and beta electrons, respectively.

Figure 5 presents the spin density between C12 and O51 in reaction 1's TS under varying x -axis positive EFs. Strengthening the EF raises the absolute spin density values of both atoms, indicating more unpaired electrons. This enhances atomic interaction and boosts reaction activity.

Figure 6 shows the spin density between the C12 atom and O51 atom in the TS of reaction 1 when different strengths of negative x -axis EFs are applied. We can conclude from Figure 6 that when the EF is enhanced, the absolute values of the spin density of the C12 and O51 atoms both decrease. This indicates that the negative external EF reduces the number of unpaired electrons of the two bonding atoms, reduces the interaction between the two atoms, and lowers the activity of the reaction.

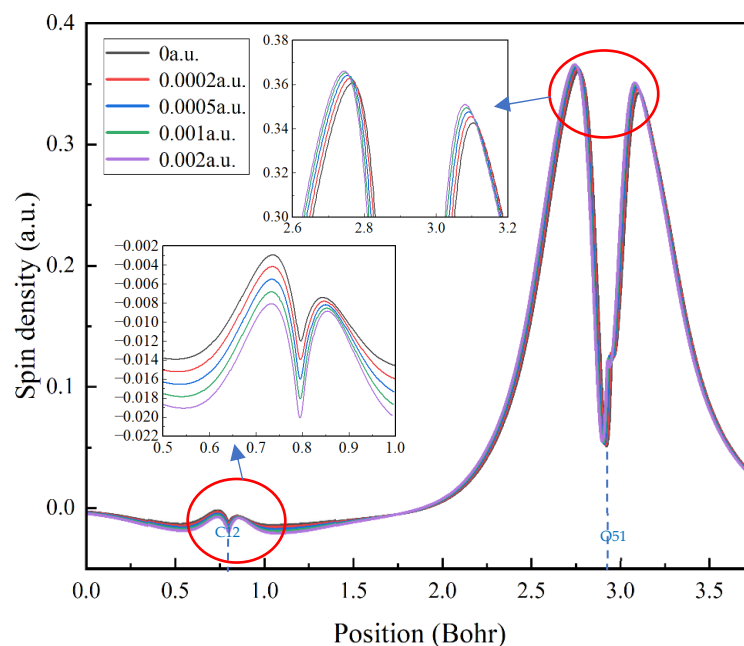


Figure 5. The spin density plot of reaction 1 under the action of a positive EF.

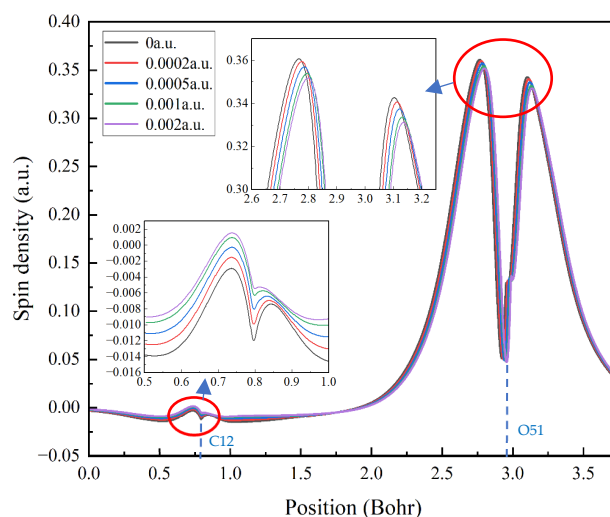


Figure 6. The spin density plot of reaction 1 under the action of a negative EF.

Figure S11 presents the spin density between C13 and •OH-derived O53 in reaction 2's TS under a positive x -axis EF. Strengthening the EF raises the spin density of both atoms, increasing unpaired electrons and boosting reaction activity. Figure S12 shows the corresponding spin density under a negative x -axis EF, with irregular changes in atomic spin density as the EF intensifies. For reaction 3, Figure S13 displays the spin density between C1 and C13 under a positive EF: C1 has a positive spin density while C13 shows negative values, and their absolute values rise with a stronger EF. As spin density reflects the unpaired electron distribution linked to bond activity and cleavage [46], the increased absolute spin density signifies promoted C-C bond breaking and an accelerated reaction. Figure S14 reveals that an enhanced negative EF reduces the absolute spin density of C1 and C13, cutting unpaired electrons and suppressing reaction activity.

3.1.5. Fukui Function and Reactive Site Activity

The Fukui function [47] is used to describe the changes in electron density at different positions in a molecule during a chemical reaction, and to predict the reactive sites. The Fukui function is expressed as follows:

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{V(r)} \quad (6)$$

In the formula, $\rho(r)$ represents the electron density, N represents the number of electrons, and $V(r)$ represents the attractive potential generated by the atomic nucleus for electrons.

The Fukui function has three forms, $f^+(r)$, $f^-(r)$, and $f^0(r)$, corresponding to nucleophilic, electrophilic and free radical reactions, respectively. The specific formulas are as follows:

$$f^+(r) = \rho_{N+1}(r) - \rho_N(r) \quad (7)$$

$$f^-(r) = \rho_N(r) - \rho_{N-1}(r) \quad (8)$$

$$f^0(r) = \frac{1}{2}[f^+(r) + f^-(r)] \quad (9)$$

In the formulas, $\rho_{N+1}(r)$, $\rho_N(r)$ and $\rho_{N-1}(r)$ represent the electron density of the molecule at $N + 1$, N , and $N - 1$ electrons, respectively.

Due to the nature of the Fukui function it is not possible to quantitatively examine the distribution of Fukui functions on each atom. Therefore, we calculate the condensed Fukui function (CFF) [48] to quantitatively analyze the activity of different atoms in the reaction. The CFF describes the active sites of molecules in nucleophilic, electrophilic, and radical reactions through changes in atomic charge. The three forms of the CFF are defined as:

$$f_k^+ = q_k(N) - q_k(N + 1) \quad (10)$$

$$f_k^- = q_k(N - 1) - q_k(N) \quad (11)$$

$$f_k^0 = \frac{1}{2}(f_k^+ + f_k^-) = \frac{1}{2}[q_k(N - 1) - q_k(N + 1)] \quad (12)$$

In the formulas, $q_k(N + 1)$, $q_k(N)$, and $q_k(N - 1)$ represent the charges of the atom at $N + 1$, N , and $N - 1$ electrons, respectively.

Based on the Hirshfeld atomic charge method, we calculated the CFFs of reactants in three reactions under x -axis EFs with different intensities. Tables 3 and 4 list the CFFs of C12 in reaction 1's reactant under positive and negative EFs, respectively. The results show that strengthening the EF causes no obvious changes in Fukui functions, indicating that an external EF has negligible effect on the CFF of reaction 1's reactive sites.

Table 3. CFF of C12 atom of reaction 1 under external positive x -axis EF.

EF Strength (a.u.)	$q_k(N)$	$q_k(N + 1)$	$q_k(N - 1)$	$f^-(r)$	$f^+(r)$	$f^0(r)$
0	0.0642	−0.0250	0.0747	0.0105	0.0893	0.0499
0.0002	0.0642	−0.0251	0.0747	0.0105	0.0893	0.0499
0.0005	0.0640	−0.0252	0.0746	0.0106	0.0892	0.0499
0.001	0.0638	−0.0253	0.0744	0.0106	0.0891	0.0499
0.002	0.0631	−0.0257	0.0739	0.0108	0.0889	0.0498

Table 4. CFF of C12 atom of reaction 1 under external negative x -axis EF.

EF Strength (a.u.)	$q_k(N)$	$q_k(N + 1)$	$q_k(N - 1)$	$f^-(r)$	$f^+(r)$	$f^0(r)$
0	0.0642	−0.0250	0.0747	0.0105	0.0893	0.0499
0.0002	0.0644	−0.0250	0.0749	0.0105	0.0894	0.0500
0.0005	0.0645	−0.0249	0.0750	0.0105	0.0895	0.0500
0.001	0.0648	−0.0248	0.0752	0.0105	0.0896	0.0500
0.002	0.0651	−0.0247	0.0756	0.0105	0.0898	0.0502

Tables S6 and S7 present the CFFs of C13 in reaction 2's reactant under positive and negative x -axis EFs, respectively. Strengthening a positive EF raises the $f^-(r)$, $f^+(r)$, and $f^0(r)$ values, boosting C13's reactivity in various reactions; an enhanced negative EF reduces these values and inhibits C13's reactivity. For reaction 3, the CFF of C13 (Tables S8 and S9) shows no obvious changes under x -axis EFs, meaning that its reactivity remains stable. Tables S10 and S11 display the CFFs of C1 in Reaction 3: an increasing positive EF elevates its $f^-(r)$, $f^+(r)$, and $f^0(r)$ values to enhance its reactivity, while a stronger negative EF lowers these values and weakens its reactivity. Thus, a positive EF accelerates reaction 3 and a negative EF suppresses it.

3.2. Experimental Results

This section explores the impacts of diverse initial conditions on discharge plasma-induced MG degradation in aqueous solution and verifies the feasibility of an external electric field (EF) for boosting this degradation process via experiments under variable input power, pH, initial MG concentration and EF strength.

Regarding input power (Figure S15, 50 mg/L MG, pH = 5), 65 W, 80 W and 95 W all achieved 100% MG degradation within 60 min, and the decolorization rate rose with increasing power, attributed to the elevated oxidizing species generation from DBD plasma at higher power. For pH effects (Figure S16, 50 mg/L MG, 65 W), alkaline conditions were excluded due to distorted UV absorption of MG [49]. Acidic environments drastically accelerated degradation: pH = 3 reached nearly 100% efficiency in 15 min, pH = 5 hit 100% in 60 min, while pH = 7 only yielded 56.5% in 60 min. The rate decline with rising pH stems from the stronger oxidation potential of $\bullet OH$ (the key reactive species) under acidic conditions.

As shown in Figure S17 (65 W, pH = 5), increasing the initial MG concentration suppressed both the decolorization efficiency and rate. This is because higher MG concentrations intensified competition for oxidizing species between parent molecules and intermediates [50–52], limiting DPT's performance for high-concentration MG wastewater. For EF strength (Figure S18, 65 W, 50 mg/L MG, pH = 5), strengthening the EF accelerated the decolorization rate; despite opposite effects of EF directions in simulations, a positive EF exerted a dominant promotion, and the boosting effect intensified with increasing EF strength, confirming that an external EF effectively facilitates discharge plasma-induced MG degradation.

This paper used DFT to simulate the three-step degradation reaction of MG under the action of the EF. Through calculations and analyses of the free energy barrier, reaction rate, dipole moment, spin density, electrostatic potential and condensed Fukui function of the degradation reaction, the internal mechanism of an external EF enhancing the degradation of MG by discharge plasma in water was revealed. Experiments on the degradation of MG by an EF and discharge plasma were conducted, confirming the promoting effect of the external EF on the degradation of MG by discharge plasma.

4. Conclusions

This study combined quantum chemical simulations and experiments to explore the microscopic mechanism of EF-enhanced MG degradation by hydroxyl radicals generated by a discharge plasma process. We simulated key degradation reactions, calculating free energy barriers and reaction rates. A positive EF along the reaction axis reduced energy barriers and accelerated reactions, while a reverse EF exerted the opposite effect, proving that a positive EF promotes MG degradation in a strength-dependent manner. Further analyses of the dipole moment, spin density, CFF and surface ESP revealed that a stronger positive EF boosts bonding atom activity and facilitates reactions, clarifying the enhancement mechanism. Macroscopic experiments investigated factors including the input power, initial MG concentration, pH and EF intensity. The results showed that increasing the EF and DBD input power raised decolorization rates, while a higher MG concentration and pH lowered the efficiency. It is worth noting that when the effect of a negative EF was simulated, the changes in reaction 2 did not follow a regular pattern with the variation of EF intensity. There are mainly two reasons for this. One is that we adopted the implicit solvent model, whose inherent drawback is that it cannot represent the strong interaction between the solvent and the solute, resulting in certain errors in the calculation results. This error may have been more significant in reaction 2. Secondly, unlike that of reaction 1, the reaction site of reaction 2 is the C atom on the benzene ring. This may have led to more complex changes when it was affected by the EF, which need to be deeply studied in the future. In addition, although the DFT result is consistent with the experimental trend, the difference in the EF intensity used by the two is obvious. In fact, in most of the current literature that simulates the effect of an EF, the magnitude of EF intensity is mostly 1 V/nm [53,54]. However, such a strong EF is difficult to achieve in actual experiments. Therefore, the DFT calculation results under the influence of the EF are only qualitative, rather than quantitative. The degradation of MG in water by an external EF in cooperation with discharge plasma was presented in this paper. It is hoped that in the future, this method can be explored for application in the degradation of wastewater containing various types of pollutants, and it can be utilized in practical engineering.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/coatings16070776/s1>.

Author Contributions: Conceptualization, data curation and writing—original draft preparation, Y.L.; visualization and investigation, H.W.; methodology, software, and validation, Y.H.; supervision and writing—reviewing and editing, T.J. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by the Natural Science Foundation of Hebei Province (grant no. B2025203025) and S&T Program of Hebei (grant no. 216Z3601G).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding authors.

Conflicts of Interest: Hanzeng Wang is affiliated with Smart Distribution Network Center, State Grid Jibei Electric Power Company Limited, but did not receive any financial support from the company for the present study. The remaining authors declare no conflicts of interest.

References

- Zhu, H.; Zou, H.M. Ultra-efficient catalytic degradation of malachite green dye wastewater by KMnO₄-modified biochar (Mn/SRBC). *RSC Adv.* **2022**, *12*, 27002–27011. [\[PubMed\]](#)
- Diao, Z.H.; Li, M.Y.; Zeng, F.Y.; Song, L.; Qiu, R.L. Degradation pathway of malachite green in a novel dual-tank photoelectrochemical catalytic reactor. *J. Hazard. Mater.* **2013**, *260*, 585–592. [\[CrossRef\]](#) [\[PubMed\]](#)
- Srivastava, S.; Sinha, R.; Roy, D. Toxicological effects of malachite green. *Aquat. Toxicol.* **2004**, *66*, 319–329. [\[CrossRef\]](#) [\[PubMed\]](#)
- Bai, C.P.; Xiao, W.S.; Feng, D.X.; Xian, M.; Guo, D.; Ge, Z.X.; Zhou, Y.S. Efficient decolorization of Malachite Green in the Fenton reaction catalyzed by [Fe(III)-salen]Cl complex. *Chem. Eng. J.* **2013**, *215*, 227–234. [\[CrossRef\]](#)
- Li, Y.; Gao, Z.Q.; Ji, Y.F.; Hu, X.B.; Sun, C.; Yang, S.G.; Wang, L.H.; Wang, Q.G.; Fang, D. Photodegradation of malachite green under simulated and natural irradiation: Kinetics, products, and pathways. *J. Hazard. Mater.* **2015**, *285*, 127–136. [\[CrossRef\]](#)
- Ren, Q.G.; Kong, C.C.; Chen, Z.H.; Zhou, J.D.; Li, W.M.; Li, D.Y.; Cui, Z.J.; Xue, Y.; Lu, Y.H. Ultrasonic assisted electrochemical degradation of malachite green in wastewater. *Microchem. J.* **2021**, *164*, 106059. [\[CrossRef\]](#)
- Putri, E.M.; Rachimoellah, M.; Rahendaputri, C.S.; Adisti, Y.; Zetra, Y. Photocatalytic degradation of malachite green using TiO₂ and O₂/UV. *AIP Conf. Proc.* **2018**, *2049*, 020092. [\[CrossRef\]](#)
- Oturan, M.A.; Guivarch, E.; Oturan, N.; Sirés, I. Oxidation pathways of malachite green by Fe³⁺-catalyzed electro-Fenton process. *Appl. Catal. B Environ.* **2008**, *82*, 244–254.
- Wei, Y.; Lu, G.L.; Xie, D.R.; Sun, T.Y.; Liu, Y.; Zhang, Y.; An, J.T.; Li, M.H.; Guo, H. Degradation of enrofloxacin in aqueous by DBD plasma and UV: Degradation performance, mechanism and toxicity assessment. *Chem. Eng. J.* **2022**, *431*, 133360. [\[CrossRef\]](#)
- Wang, B.W.; Wang, C.; Yao, S.M.; Peng, Y.P.; Xu, Y. Plasma-catalytic degradation of tetracycline hydrochloride over Mn/ γ -Al₂O₃ catalysts in a dielectric barrier discharge reactor. *Plasma Sci. Technol.* **2019**, *21*, 065503. [\[CrossRef\]](#)
- Rodrigues, F.E., Jr.; Fernandes, F.A. Diazinon degradation in water applying glow discharge plasma technology. *Braz. J. Chem. Eng.* **2025**, *42*, 109–121. [\[CrossRef\]](#)
- Jiang, N.; Qiu, C.; Guo, L.J.; Shang, K.F.; Lu, N.; Li, J.; Zhang, Y.; Wu, Y. Plasma-catalytic destruction of xylene over Ag-Mn mixed oxides in a pulsed sliding discharge reactor. *J. Hazard. Mater.* **2019**, *369*, 611–620. [\[PubMed\]](#)
- Zhang, H.; Huang, Q.; Ke, Z.G.; Yang, L.F.; Wang, X.Q.; Yu, Z.L. Degradation of microcystin-LR in water by glow discharge plasma oxidation at the gas–solution interface and its safety evaluation. *Water Res.* **2012**, *46*, 6554–6562. [\[PubMed\]](#)
- Jiang, B.; Zheng, J.T.; Qiu, S.; Wu, M.B.; Zhang, Q.H.; Yan, Z.F.; Xue, Q.Z. Review on electrical discharge plasma technology for wastewater remediation. *Chem. Eng. J.* **2014**, *236*, 348–368. [\[CrossRef\]](#)
- Júnior, F.E.R.; Fernandes, F.A. Degradation of diazinon by dielectric barrier discharge plasma. *J. Environ. Chem. Eng.* **2024**, *12*, 111539.
- Vaigankar, C.; Agadyekar, V.G.; Kakodkar, E.; Kunkalekar, R.; Joshi, N. Comparative evaluation of plasma-assisted and photochemical advanced oxidation processes for p-nitrophenol degradation in water. *J. Photochem. Photobiol. A Chem.* **2026**, *478*, 117237.
- Agadyekar, V.G.; Kakodkar, E.; Barretto, D.A.; Barni, R.; Riccardi, C.; Joshi, N. Concurrent removal of benzene, toluene, and P-nitrophenol from water using dielectric barrier discharge plasma. *Clean. Eng. Technol.* **2025**, *27*, 101042. [\[CrossRef\]](#)
- Chandana, L.; Reddy, P.M.K.; Subrahmanyam, C. Atmospheric pressure non-thermal plasma jet for the degradation of methylene blue in aqueous medium. *Chem. Eng. J.* **2015**, *282*, 116–122. [\[CrossRef\]](#)
- Ganzallo, F.J.; Su, X.D.; Yatom, S.; Vasilev, M.; Mededovic, S. Characterization and treatment performance of an atmospheric pressure plasma jet-operated spinning disc reactor for the treatment of rhodamine B dye. *Plasma Chem. Plasma Process.* **2023**, *43*, 1685–1708. [\[CrossRef\]](#)
- Quispe-Quispe, A.; Pérez-Falcón, L.F.; Quispe-Marcatoma, J.; Landauro, C.V.; Peña Rodríguez, V.A. Removal of cochineal dye color through atmospheric pressure plasma discharge jet. *Appl. Sci.* **2024**, *14*, 680. [\[CrossRef\]](#)
- Dong, J.Q.; Lv, J.; Yang, G.Y. Dielectric barrier discharge combined with Fe (III)-NTA activated persulfate for efficient degradation of enrofloxacin in water. *Environ. Pollut. Bioavailab.* **2024**, *36*, 2319250.
- Ramanan, R.; Danovich, D.; Mandal, D.; Shaik, S. Catalysis of Methyl Transfer Reactions by Oriented External Electric Fields: Are Gold-Thiolate Linkers Innocent? *J. Am. Chem. Soc.* **2018**, *140*, 4354–4362. [\[PubMed\]](#)
- Yang, C.; Liu, Z.T.; Li, Y.W.; Zhou, S.Y.; Lu, C.X.; Guo, Y.L.; Ramirez, M.; Zhang, Q.Z.; Li, Y.; Liu, Z.R.; et al. Electric field-catalyzed single-molecule Diels-Alder reaction dynamics. *Sci. Adv.* **2021**, *7*, eabf0689. [\[PubMed\]](#)
- Tao, Y.P.; Su, M.Z.; Duan, Z.X.; Han, L.G.; Sun, K.X. Structural and physical properties of trichloroethylene under an external electric field. *J. Phys. Org. Chem.* **2021**, *34*, e4269. [\[CrossRef\]](#)
- Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R. *Gaussian 09W, Revision A 02*; Gaussian, Inc.: Wallingford, CT, USA, 2009.
- Gao, G.D.; Zhang, A.Y.; Zhang, M.; Chen, J.L.; Zhang, Q.X. Photocatalytic degradation mechanism of malachite green under visible light irradiation over novel biomimetic photocatalyst HMS-FePcs. *Chin. J. Catal.* **2008**, *29*, 426–430. [\[CrossRef\]](#)

27. Sanjay, B.P.; Sandeep, S.; Santhosh, A.S.; Karthik, C.S.; Varun, D.N.; Swamy, N.K.; Mallu, P.; Nithin, K.S.; Rajabathar, J.R. Unprecedented 2D GNR-CoB nanocomposite for detection and degradation of malachite green—A computational prediction of degradation pathway and toxicity. *Chemosphere* **2022**, *287*, 132153. [PubMed]
28. Shaik, S.; Danovich, D.; Joy, J.; Wang, Z.F.; Stuyver, T. Electric-Field Mediated Chemistry: Uncovering and Exploiting the Potential of (Oriented) Electric Fields to Exert Chemical Catalysis and Reaction Control. *J. Am. Chem. Soc.* **2020**, *142*, 12551–12562. [CrossRef] [PubMed]
29. Shaik, S.; Mandal, D.; Ramanan, R. Oriented electric fields as future smart reagents in chemistry. *Nat. Chem.* **2016**, *8*, 1091–1098. [CrossRef] [PubMed]
30. Sarmiento, A.P.; Borges, A.C.; de Matos, A.T.; Romualdo, L.L. Phenol degradation by Fenton-like process. *Environ. Sci. Pollut. Res.* **2016**, *23*, 18429–18438. [CrossRef]
31. Marti, K.H.; Reiher, M. Haptic quantum chemistry. *J. Comput. Chem.* **2009**, *30*, 2010–2020. [CrossRef] [PubMed]
32. Maeda, S.; Harabuchi, Y.; Ono, Y.; Taketsugu, T.; Morokuma, K. Intrinsic reaction coordinate: Calculation, bifurcation, and automated search. *Int. J. Quantum Chem.* **2015**, *115*, 258–269. [CrossRef]
33. Lu, T.; Chen, Q.X. Shermo: A general code for calculating molecular thermochemistry properties. *Comput. Theor. Chem.* **2021**, *1200*, 113249. [CrossRef]
34. Lu, T.; Chen, F.W. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, *33*, 580–592. [PubMed]
35. Lu, T. A comprehensive electron wavefunction analysis toolbox for chemists, Multiwfn. *J. Chem. Phys.* **2024**, *161*, 082503. [CrossRef] [PubMed]
36. Ma, A.S.; Qian, H.L.; Liu, H.X.; Ren, S.L. Degradation of malachite green by g-C₃N₄-modified magnetic attapulgite composites under visible-light conditions. *Environ. Sci. Pollut. Res.* **2023**, *30*, 96360–96375.
37. Tian, L. TST Calculator. Available online: <http://sobereva.com/310> (accessed on 1 December 2024).
38. Hoffmann, N.M.; Wang, X.; Berkelbach, T.C. Linear free energy relationships in electrostatic catalysis. *ACS Catal.* **2022**, *12*, 8237–8241. [CrossRef]
39. Galego, J.; Climent, C.; Garcia-Vidal, F.J.; Feist, J. Cavity Casimir-Polder forces and their effects in ground-state chemical reactivity. *Phys. Rev. X* **2019**, *9*, 021057.
40. Bhattacharyya, K.; Karmakar, S.; Datta, A. External electric field control: Driving the reactivity of metal-free azide–alkyne click reactions. *Phys. Chem. Chem. Phys.* **2017**, *19*, 22482–22486. [PubMed]
41. Song, Z.X.; Liang, C.Y.; Gong, K.; Zhao, S.P.; Yuan, X.; Zhang, X.X.; Xie, J. Harnessing the high interfacial electric fields on water microdroplets to accelerate Menshutkin reactions. *J. Am. Chem. Soc.* **2023**, *145*, 26003–26008. [CrossRef] [PubMed]
42. Politzer, P.; Murray, J.S. Molecular electrostatic potentials and chemical reactivity. In *Reviews in Computational Chemistry*; John Wiley & Sons, Ltd.: Hoboken, NJ, USA, 1991; pp. 273–312.
43. Zhang, J.; Lu, T. Efficient evaluation of electrostatic potential with computerized optimized code. *Phys. Chem. Chem. Phys.* **2021**, *23*, 20323–20328. [CrossRef] [PubMed]
44. Lu, T.; Chen, F.W. Quantitative analysis of molecular surface based on improved Marching Tetrahedra algorithm. *J. Mol. Graph. Model.* **2012**, *38*, 314–323. [CrossRef] [PubMed]
45. Zhao, C.X.; Lu, Y.X.; Zhu, Z.D.; Liu, H.L. Theoretical Exploration of Halogen Bonding Interactions in the Complexes of Novel Nitroxide Radical Probes and Comparison with Hydrogen Bonds. *J. Phys. Chem. A* **2018**, *122*, 5058–5068. [CrossRef] [PubMed]
46. Sheka, E. Stretching and breaking of chemical bonds, correlation of electrons, and radical properties of covalent species. *Adv. Quantum Chem.* **2014**, *70*, 111–161. [CrossRef]
47. Parr, R.G.; Yang, W.T. Density functional approach to the frontier-electron theory of chemical reactivity. *J. Am. Chem. Soc.* **1984**, *106*, 4049–4050. [CrossRef]
48. Yang, W.T.; Mortier, W.J. The use of global and local molecular parameters for the analysis of the gas-phase basicity of amines. *J. Am. Chem. Soc.* **1986**, *108*, 5708–5711. [CrossRef] [PubMed]
49. Chen, C.C.; Lu, C.S.; Chung, Y.C.; Jan, J.L. UV light induced photodegradation of malachite green on TiO₂ nanoparticles. *J. Hazard. Mater.* **2007**, *141*, 520–528. [CrossRef] [PubMed]
50. Reddy, P.A.K.; Raju, B.R.; Karuppiiah, J.; Reddy, E.L.; Subrahmanyam, C. Degradation and mineralization of methylene blue by dielectric barrier discharge non-thermal plasma reactor. *Chem. Eng. J.* **2013**, *217*, 41–47. [CrossRef]
51. Feng, J.W.; Zheng, Z.; Sun, Y.B.; Luan, J.F.; Wang, Z.; Wang, L.H.; Feng, J.F. Degradation of diuron in aqueous solution by dielectric barrier discharge. *J. Hazard. Mater.* **2008**, *154*, 1081–1089. [CrossRef] [PubMed]
52. Yu, J.M.; Yan, W.W.; Zhu, B.; Xu, Z.M.; Hu, S.H.; Xi, W.H.; Lan, Y.; Han, W.; Cheng, C. Degradation of carbamazepine by high-voltage direct current gas-liquid plasma with the addition of H₂O₂ and Fe²⁺. *Environ. Sci. Pollut. Res. Int.* **2022**, *29*, 77771–77787. [PubMed]

53. Jiang, Q.G.; Ao, Z.M.; Chu, D.W.; Jiang, Q. Reversible transition of graphene from hydrophobic to hydrophilic in the presence of an electric field. *J. Phys. Chem. C* **2012**, *116*, 19321–19326. [[CrossRef](#)]
54. Han, Y.; Ma, S.R.; Ma, J.; Guiraud, P.; Guo, X.Q.; Zhang, Y.J.; Jiao, T.F. In-situ desorption of acetaminophen from the surface of graphene oxide driven by an electric field: A study by molecular dynamics simulation. *Chem. Eng. J.* **2021**, *418*, 129391. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.