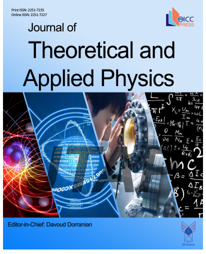

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Degradation of diazinon and endosulfan pesticides using surface dielectric barrier discharge cold plasma employing $Ar/H_2O/H_2O_2$ working gas

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Original Research

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Abstract:

Water refinement from stable organic compounds has faced challenges in conventional approaches. Non-thermal plasma technology as an advanced oxidation process (AOP) is an eco-friendly water and wastewater treatment solution. In this study, the capability of the dielectric barrier discharge (DBD) plasma was examined to degrade diazinon and endosulfan pesticides from an aqueous solution by employing a combined gas of $Ar/H_2O/H_2O_2$. This approach introduces the synergistic effect of the DBD plasma and hydrogen peroxide oxidant for the pesticide degradation method. This study compared the effects of $Ar/H_2O/H_2O_2$ gas without plasma running, Ar plasma, and $Ar/H_2O/H_2O_2$ SDBD plasma in pesticide reduction. The results demonstrated that combining Ar and H_2O/H_2O_2 cold vapor in SDBD plasma significantly enhances pesticide degradation compared to using either method alone. While the reduction efficiency of the hydrogen peroxide oxidant was 17% and 18% for diazinon and endosulfan, it was enhanced by the Ar SDBD to 30% and 37%, respectively after 15 minutes of indirect treatment. Moreover, introducing H_2O/H_2O_2 vapor into the Ar SDBD plasma ($Ar/H_2O/H_2O_2$ SDBD) achieved a 60% and 65% reduction in diazinon and endosulfan, respectively, after 15 minutes of treatment, highlighting its potential as a sustainable and efficient method for pesticide removal from water. The energy yield (G_{50}) as a measure of the efficiencies of the removal of the diazinon and endosulfan pesticides are 225 and 220 mg/kWh, respectively for $Ar/H_2O/H_2O_2$ SDBD. The study also found that running frequency, dielectric thickness, treatment time, and working voltage can significantly affect the degradation efficiency. Reactive oxygen species (ROS) such as O_3, H_2O_2, OH^*, aquas electrons, and other plasma species are responsible for the degradation of these pesticides. This research generally indicates the high potential of the $Ar/H_2O/H_2O_2$ SDBD plasma as an alternative approach for rapidly reducing agriculture activity-related chemicals in water.

Keywords: Atmospheric pressure non-thermal plasma; Diazinon; Endosulfan; Hydrogen peroxide; Surface dielectric barrier discharge(SDBD)

1. Introduction

Pesticides are extensively utilized in modern agriculture to control crop contamination. Using these pesticides can result in lower product loss and higher yield per unit of land area. However, these chemicals are accompanied by serious health threats to humans, animals, and the environment. These pesticides generally enter the surface and groundwater as runoff. Studies have shown that even trace amounts of these pesticides (ng/day) can result in toxicity and enhance the health risks of chronic diseases due to their bioaccumulative effects. The environmental fate of pesticides has not been fully understood and the introduction of new materials in the formulation of pesticides has further added to the complexity of this issue [1–7]. So far, more than 1500 pesticides have been recorded and more than 500 types of pesticides are currently used worldwide. The production and consumption of pesticides have experienced a 12-fold increment in the last 50 years [8]. Based on the Environmental Protection Agency (EPA), agricultural activities are responsible for releasing at least 46 types of pesticides into the groundwater [9]. Chemical pesticides can be divided into four groups: organochlorides, organophosphorus, carbamates, and pyrethroids. The organophosphorus compounds include various types accounting for 40% of the commercial pesticides. Depending on their application, pesticides can be classified into herbicides, insecticides, fungicides, rodenticides, nematicides, and growth regulators of plants and insects [10]. Here, the degradation mechanism of two types of insecticides (organophosphorus and organochlorine) will be addressed.

Organophosphorus (OP) pesticides are among the vital compounds that significantly impact public and environmental health due to their lipophilicity, bioaccumulation factor (BAF), and presence in the food chain. Various research efforts have focused on these pesticides' toxic environmental effects. The World Health Organization (WHO) classified this type of pesticide as class II, which was found to be moderately dangerous. Endosulfan and diazinon are among the common pesticides in Iran [11, 12]. Diazinon ($C_{12}H_{21}N_2O_3PS$) is an OP pesticide with acute toxicity in mammalians and aquatic creatures whose accumulation in water has posed a serious environmental challenge. According to the WHO and the Environmental Protection Agency of the US (USEPA) report the maximum allowed level of diazinon in drinking water and soil should be 0.1 and 0.17 µg/L, respectively. Regarding its environmental challenges and current level of contamination in many countries, diazinon was selected for this research. Like other pesticides and herbicides, several researchers have addressed the degradation and modification of diazinon. These studies have addressed diazinon degradation through heterogeneous catalysts, photocatalysts, sonochemical processes, hydrodynamic cavitation, UV illumination, electrochemical procedures, bioremediation, and cold plasma. With the help of more stabilized methods such as heterogenous catalysts, these approaches have been concentrated on a combination of catalysts with ultrasound waves, and visible and UV lights as the degradation rate of a single method is often less than the hybrid ones [13]. Endosulfan is an organochlorine insecticide whose bioaccumulation has seriously threatened human health. This chemical is commonly used in agricultural activities. This insecticide has shown good outcomes against some insects with difficult control; however, it can enter the surface and groundwater through runoff, posing serious challenges to the ecosystems. The latest European Union (EU) report on the quality of water and pesticide-induced contamination stated that the environmental quality standard (EQS) of endosulfan has exceeded the allowed level in 35% of the monitored rivers. Studies have revealed that contaminating water resources with pesticides is an environmental issue. Regarding the increasing growth of agriculture in most provinces of Iran, this phenomenon is increasing, endangering freshwater resources. The level of pesticide residues in the water resources is directly correlated with the use of pesticides in these areas. If not controlled, the use of pesticides can seriously endanger the public health. For instance, Golshani et al. (2022) examined the concentration of diazinon, malathion, and azinphos methyl pesticides in the water samples and sediments from five rivers (Sefidrood, Chaloos, Babolrood, Tajan, and Gorganrood) along the Caspian Sea shore. The samples were collected from the surface water and sediments from summer to winter. The pesticide contents were analyzed by gas chromatography-mass spectroscopy (GC-MS). The results indicated the higher salinity ($2-8\%$) and turbidity ($1-9\%$) of Gorganrood. Higher diazinon (water 0.08 ± 0.06, sediment 0.04 ± 0.01), malathion (water: 0.09 ± 0.06 and sediment 0.05 ± 0.01), and azinphos-methyl (water 0.1 ± 0.08, sediment 0.06 ± 0.02) were observed in Tajan river. The average level of these three pesticides was higher in the summer compared to the fall. The content of azinphos-methyl was above the sediment quality guideline (SQGs), suggesting continuous monitoring. Their studies broaden our insight into the presence of OPs in the rivers ending in the Caspian Sea [14]. The general results of the studies have shown that the current concentration of pesticides in the region's waters (exceeding the MRLs set by the European Union) and neglecting to control the use of pesticides and regular monitoring of water sources seriously endanger public health. Considering the importance of environmental protection and the role of chemical pesticides, this study examines the use of pesticides in the agricultural sector and the risks associated with using these chemicals for society, agriculture, freshwater resources, and the environment.

The main challenge indeed involves finding a way to obtain more freshwater sources and purified water. To achieve this goal, many studies have been conducted on water treatment using various methods such as ozonation, ultraviolet (UV) radiation, filtration, boiling, and advanced oxidation processes (AOP) or their combinations [15, 16]. The results indicated that the systems for reducing water toxins have their advantages and disadvantages. Conventional water treatment only destroys particles and bacteria, and industrial and agricultural wastewater toxins are not directly removed. Researchers have conducted extensive studies on advanced oxidation processes, such as photo-Fenton and non-thermal plasma techniques to overcome these issues. Plasma methods have significant advantages over AOPs which require the use of chemicals as they can operate with no chemicals, so they can be employed to treat wastewater in marine facilities and environmental waters in remote areas.

Reactive particles are formed only during discharge thus, they quickly react with water-soluble pollutants due to their high reactivity. Moreover, the plasma process has a long life in removing water pollution. Therefore, plasma could be a cost-effective and comprehensive tool for producing OH radicals. It can also be effectively combined with ultraviolet, active chemicals, and high electric fields to reduce water and wastewater pollutants efficiently [17, 18]. Numerous technologies have been developed to degrade pesticides. The choice of degradation method depends on the type of pesticide, the extent of water pollution, and environmental conditions. Regarding the limitations of each technology, integrated approaches could often be more effective in resolving pesticide contamination. Research efforts have focused on using non-thermal water treatments, including cold plasma, ultrasound, pulsed electric field, electrolyzed water, and UV irradiation, as novel approaches for reducing water and wastewater toxins. These technologies have offered promising potential in the degradation of pesticides and other endocrine disruptors, with the advantage of operating at room temperature and lower cost.

Aziz et al. (2023) conducted a study on the treatment of organic pollutants to investigate the current challenges associated with the use of Water Falling Film (WFF) reactors for wastewater treatment through Advanced Oxidation Processes (AOPs). Their findings indicated that WFF has the potential to enhance the efficiency of wastewater treatment and increase production capacity when combined with AOPs. This phenomenon is achieved through high mass transfer rates, reduced residence time, a high surface-to-volume ratio, and low-pressure drop, which collectively enhance the efficiency of pollutant removal and decrease energy consumption. Combining various AOPs in WFF reactors can significantly increase organic pollutant removal efficiencies. They stated that the design of the WFF reactor facilitates the mass transfer of reactive species to the treated solution, enhancing degradation efficiency [17].

The proposed technique of this study involves the combination of atmospheric pressure SDBD of Ar with cold vapors of hydrogen peroxide (H_2O_2) and water (H_2O) to degrade diazinon and endosulfan pesticides. This approach enhances the production of RONS species for pesticide mitigation and oxidation in aqua solutions. For this purpose, the effects of effective variables such as frequency, dielectric thickness, H_2O/H_2O_2 presence, treatment time, and applied voltage were explored to reduce the organic pesticides (diazinon and endosulfan) from aqueous solution using atmospheric cold plasma. In the following, the plasma treatment and the details of the structures will be described.

2. Materials and methods

2.1 Sample preparation

Commercial diazinon(endosulfan) with a volume of 50 µL was dissolved in 1000 mL of deionized water to prepare samples with a concentration of 0.005% by volume. For each pesticide, 60 mL from the prepared samples were poured into the Petri dish with a 90 mm diameter. This concentration was selected as recommended for the product application and represents the maximum diazinon concentration in the environment. Furthermore, this concentration allows proper detection of diazinon by gas chromatography and reduces extraction and detection errors. The treatment time was increased from 5 min to 30 by 5 min increments. Four groups were prepared to investigate the separate impact of different schemes on the degradation efficiencies. The first group was a negative control sample (without plasma and working gas), the second group was dedicated to the SDBD of Ar plasma (Ar SDBD), the third group was treated only with $Ar/H_2O/H_2O_2$ gas (plasma-off group), and the last group belonged to $Ar/H_2O/H_2O_2$ SDBD. All the samples similarly contained 2.84 and 2.95 mg/L for diazinon and endosulfan pesticides, respectively. Each sample contained 60 mL of the prepared solution for treatment and the corresponding volume percentage of the pesticides was 0.005% by volume.

Argon gas (99.999%) was used as the carrier gas to transfer H_2O/H_2O_2 (1:0.3) cold vapors into the plasma reactor. The upper limits for mole fractions of hydrogen peroxide and water vapors at 30 °C based on Giguere and Maass's findings [19] were estimated to be 25, 492, and 856 ppm (part per million) inside the plasma reactor, respectively [20]. Hydrogen peroxide was chosen because more experimental data are available for this species comparing others such as hydroxyl radicals and hydrogen and molecular oxygen. H_2O_2 is a useful but imperfect indicator of hydroxyl radicals in plasma systems. Furthermore, in some plasma systems, hydrogen peroxide can be closely related to hydrogen and molecular oxygen formation. Therefore, although hydrogen peroxide can be affected by many factors, it is relatively easy to measure and can provide good insight into plasma activity. The required electric power was also supplied by a homemade variable frequency high-voltage AC power source with the frequency and peak-to-peak voltage range of 6 to 14 kHz and 0 to 15 kV, respectively. The current was tailored up to 140 mA peak-to-peak.

2.1.1 Measurement of the pesticide concentration

A GC/MS mass spectrometer(GC-Mass 6890N, Agilent company, USA) and a CMOS Spectrometer with a wavelength coverage of $180 - 1100$ nm and a resolution of $0.1 - 5$ nm were utilized to analyze and investigate the reduction of organic toxins. The GS-MS analyzer assayed the prepared samples of diazinon and endosulfan; the corresponding concentrations were 2.84 and 2.95 mg/L, respectively. The samples in Petri Dishes were transferred to the lab for GC-MS tests.

2.2 Experimental set-up

A schematic picture of the experimental setup is presented in Figure 1. The electrode arrangement of the SDBD consists of copper strips glued edge to edge on the top and back surfaces of the glass dielectric. The dimensions of the copper strips are 2 cm × 25 cm and with a thickness of 0.2 mm, spaced at a 2−cm distance. Glass dielectric is also made as one of the influential variables in the investigation of the reduction of organic toxins, in thicknesses of 1 to 6 mm. Wide and thin Kapton strips were glued on the upper surface of the SDBD structure as a strong dielectric to prevent the corona phenomenon and loss of electrical power. The applied AC high voltage and the corresponding frequency were from 1 to 15 kV and 6 to 14 kHz, respectively. To place the components of the plasma source next to each other (electrodes and dielectric), a 10−mm thick clear plexiglass chamber with respective lengths and widths of 254 and 164 mm was considered. Two 9−mm openings were also placed on both sides of the main chamber for gas injection. After mixing and sampling, the sample-containing

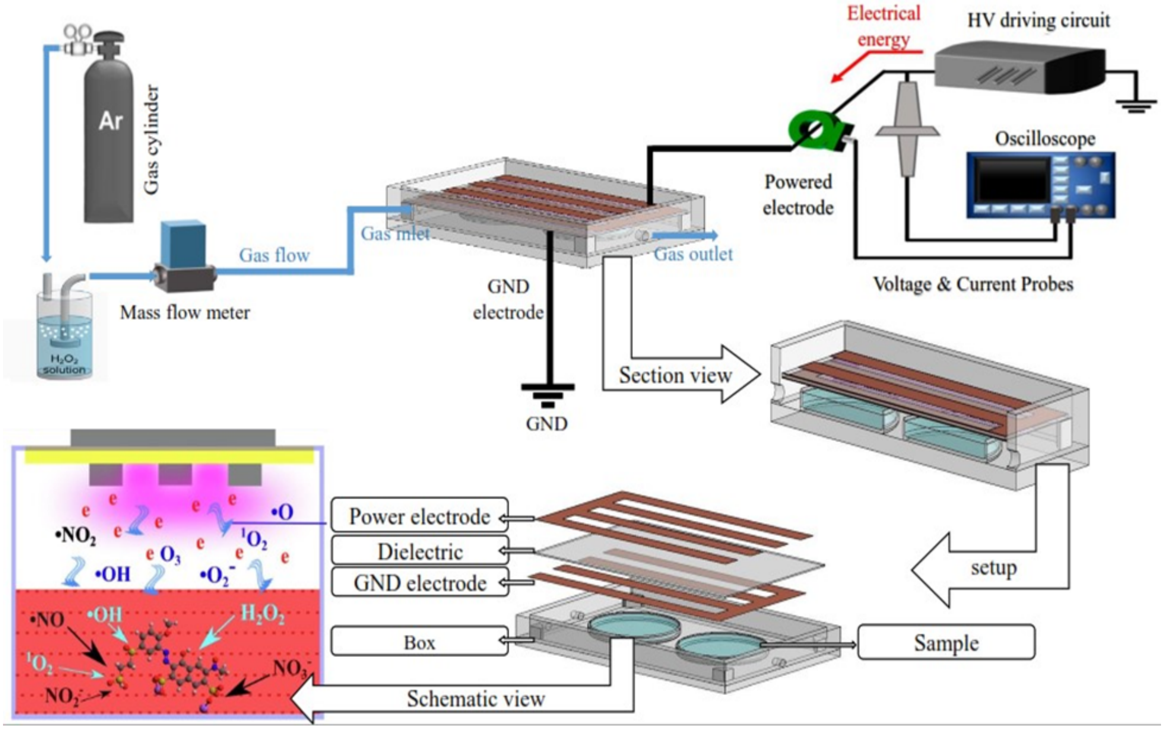

Figure 1. Schematic picture of the setup.

petri dish and the electrodes were also placed in the main chamber. Then, pure argon gas (99.99%) was injected into the H_2O/H_2O_2(1:0.3)-containing container with a gas flow rate of 20 L/min to transfer H_2O/H_2O_2 into the plasma reactor throughout the experiment. At this stage, the dielectric discharge system is ready to produce plasma and treat water contaminated with organic pesticides, with the help of H_2O/H_2O_2 vapor plasma. The organic pesticide reduction apparatus with the $Ar/H_2O/H_2O_2$ SDBD method and the diagnostic tool is shown in Figure S1.

2.2.1 Electrical measurements

The voltage applied to the electrodes was also monitored by a high voltage probe (Tektronix high voltage probe P6015A) to record the voltage wave shape by an oscilloscope (GW Instek GDS-2104E oscilloscope). A current monitor(Pearson Inc., 110A) was also employed to record the time evolutions of the current signals. The sinusoidal voltage waveform with a frequency of 9.57 kHz at a peak-to-peak voltage of 14.4 kV and a peak-to-peak current of 114 mA is depicted in Figure 2. The corresponding root-mean-square of the voltage and current signals were 5.27 kV and 40 mA, respectively.

The electrical discharge characteristics depend on operation parameters such as voltage, discharge gap, and frequency. Dielectric serves as a charge trapper, limiting the carried charge, hence, preventing electrical sparks [21, 22].

2.3 Initial evaluations of pesticide reduction

The reduction of diazinon and endosulfan organic pesticides was explored using quantitative (GC-MS analysis) and qualitative (UV-Vis analysis) methods. Plasm-off samples were also treated only with $Ar/H_2O/H_2O_2$ cold vapor to ensure the participation of plasma in the degradation of pesticides and any other effects. Regarding several repeats of the tests and influencing variables, a spectrophotometric method was adopted for the qualitative analysis of the process to analyze and investigate the reduction of pesticides. The UV-Vis spectrometer was used to measure the absorption of the samples versus wavelength between 190 nm and 600 nm. The reference covet was chosen deionized water as a reference for the samples. The difference in the absorption percentage at the maximum absorption peak around $\lambda = 200$ nm for the negative control and treated samples is proportional to the reduced pesticide by the treatment schemes. According to Figure S2(a) in the supplementary file, the absorption of the negative control sample and treated endosulfan samples by the Ar SDBD are 87% and 63%, respectively. The ab-

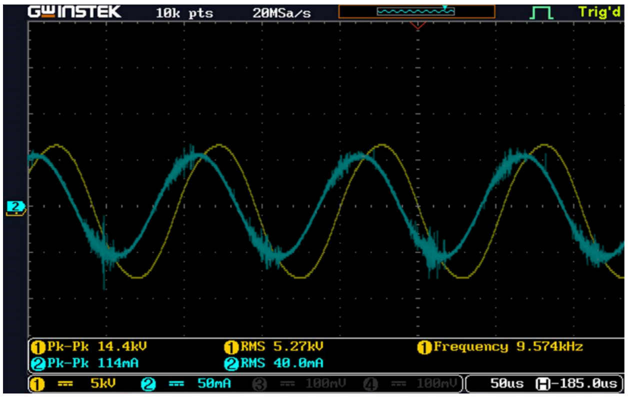

Figure 2. Voltage-Current evolution of the SDBD at 9.57 kHz, and 14.4 kV peak-to-peak. The peak-to-peak current is 114 mA.

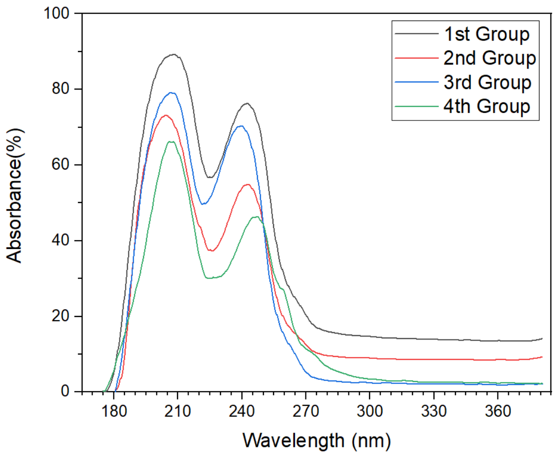

Figure 3. Absorption spectra of the negative control sample (1-st group, black color)), Ar SDBD (2-nd group, red color), plasma-off for $Ar/H_2O/H_2O_2$, (3-rd group, blue color) and $Ar/H_2O/H_2O_2$ SDBD (4-th group, green color) for degradation of diazinon with a dielectric thickness of 2 mm. The concentration of the samples was 0.005% by volume in 60 mL solution. The treatment time, driving frequency, and, applied voltage were 15 min, 9.5 kHz, and 14 kV, respectively.

sorption for negative control and treated diazinon samples was 90% and 65%, respectively, as seen in Figure S2(b). Gas chromatography and mass spectrometry (GC-MS) were employed for all groups to evaluate the efficiencies of the degradation. Denoting the removal efficiency of the pesticide by η, it was quantitatively determined by the following equation:

$$\eta = \frac{c_0 - c}{c_0} \tag{1}$$

where c denotes the remaining pesticide after treatment, and c_0 represents the initial pesticide concentration. To validate the qualitative method for each parameter and explore the effect of each variable, four groups were examined by UV-Vis spectrometer whose results are reported in the following sections.

3. Results

In this section, the effective variables for diazinon and endosulfan reduction by $Ar/H_2O/H_2O_2$ SDBD including excitation frequency, treatment time, applied voltage, electrode distance from the surface of the substrate, and dielectric thickness are qualitatively and quantitatively analyzed as will be discussed in detail in this section.

3.1 Synergistic method and frequency effect

It is well-known that an integrated approach of several methods is often more effective in combat against pesticides. Therefore, a combination of Ar SDBD and cold vapor of H_2O/H_2O_2 was adopted in this research to produce an effective cold plasma for treating diazinon and endosulfan solution samples. As hydrogen peroxide is physiologically dangerous, the use of this method can resolve the concerns. Regarding the ease of H_2O_2 measurement, it can offer a proper insight into the plasma activity. The absorption spectrum of the negative control sample (1-st group), Ar SDBD (2-nd group), samples treated by the $Ar/H_2O/H_2O_2$ (plasma-off) (3-rd group), and $Ar/H_2O/H_2O_2$ SDBD(4-th group) with a dielectric thickness of 2 mm was shown in Figure 3 for diazinon reduction in 15-minute treatment.

As can be seen in Figure 3, a 13.3% decline at the absorption peak (around $\lambda = 200$ nm) upon using only H_2O/H_2O_2 cold vapor carried by argon gas($Ar/H_2O/H_2O_2$ as the third group, blue color) with a flow rate of 20 L/min to the chamber in the absence of plasma. The absorption percentage showed a further decrement of 21.2% for Ar SDBD employing only argon plasma (Ar SDBD only as the second group, red color) at the respective voltage and current of 14.4 kV and 114 mA. Furthermore, a combination of Ar SDBD and $Ar/H_2O/H_2O_2$ SDBD (the fourth group,green color) led to a 26.23% decrement in absorption, suggesting the synergistic effect of the mentioned approaches.

The effect of the excitation frequency was given in Figure 4 for diazinon and endosulfan for groups 2 and 4 to show the impact of H_2O/H_2O_2 cold vapor plasma on the degradation efficiencies with plasma running at 15 minutes of treatment. As can be seen in Figure 4, the addition of H_2O/H_2O_2 increased the reduction of the diazinon and endosulfan almost equally in all excitation frequencies from 6 to 14 kHz, mainly due to the formation of hydroxyl radicals. At the frequency of 9.5 kHz, the reduction in the pesticides was maximum for Ar SDBD and $Ar/H_2O/H_2O_2$ SDBD for both pesticides. At 9.5 kHz, the reduction of endosulfan was efficient compared with that of diazinon. For simplicity, the reduction in the peak absorption of the samples at around 200 nm was denoted by $\Delta_{\rm abs}^{\rm max}$ (%), as depicted in Figure 4. The results indicated the prominent role of frequency in the formation of plasma reactants and mechanisms that led to diazinon and endosulfan decomposition efficiencies.

Table 1 presents the effect of running frequency and the presence of H_2O/H_2O_2 in the Ar SDBD on the efficiency reduction of diazinon and endosulfan for 15 minutes of

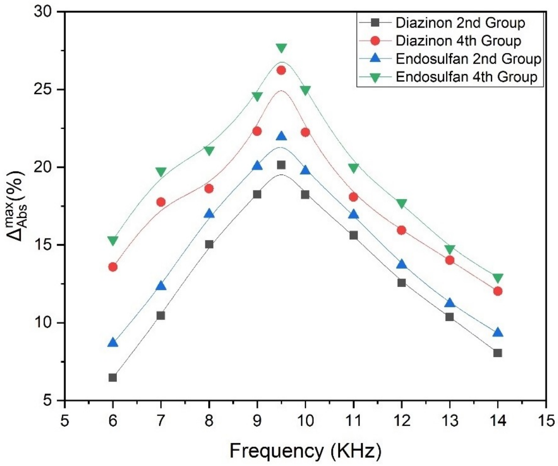

Figure 4. Variation of diazinon and endosufan reduction by Ar SDBD and $Ar/H_2O/H_2O_2$ SDBD employing different frequencies from 6 to 14 kHz. The dielectric thickness was 2 mm and the treatment time was 15 minutes.

treatment.

3.2 Treatment time

Plasma application in humid air forms ozone, peroxides, singlet oxygen, and some nitrogen oxides, which are all water-soluble. The mass transfer from the gas phase plasma to water requires time. To explore the effect of time (see Figure 5), the reduction in the peak absorption of the samples at around 200 nm ($\Delta_{\text{abs}}^{\text{max}}$ (%)) was examined versus time at constant peak-to-peak voltage and current of 14.4 kV and 114 mA, respectively. The running frequency was 9.5 kHz for both pesticides endosulfan and diazinon.
The value of $\Delta_{\text{abs}}^{\text{max}}$ (%) was studied for both pesticides and various times ($5-30$ min) in 5-minute steps. It was seen that, the value of $\Delta_{\text{abs}}^{\text{max}}$ (%) showed no significant increment after 15 min, thus, the optimal treatment time was set at 15 min. Table 2 shows the influence of treatment time on the reduction of the pesticides by applying $Ar/H_2O/H_2O_2$ SDBD.

3.3 Voltage and dielectric thickness effect

In Figures 6 (a) and (b), the value of $\Delta_{\text{abs}}^{\text{max}}$ (%) is examined in terms of applied voltage and different dielectric thicknesses for the pesticides in the presence of H_2O_2 at the excitation frequency of 9.5 kHz for diazinon and endosulfan, respectively. As shown in Figures 6 (a) and (b), the maximum reduction in the absorption curve of the samples at about $\lambda = 200$ nm occurred for the dielectric of a 2 mm thickness. With the increase of the dielectric thickness from 2 mm to 6 mm, the applied voltage should also be increased to achieve a discharge, requiring a high-power supply. The pesticide reduction increases with the rise of applied voltage, as higher voltages induce a higher concentration of reactive plasma species and thus create a higher reaction rate. Tables 3 and 4 provide specific data on how varying applied voltage and dielectric thickness affect the efficiency of reducing diazinon and endosulfan concentrations in a 60 mL solution of 0.005% pesticide.

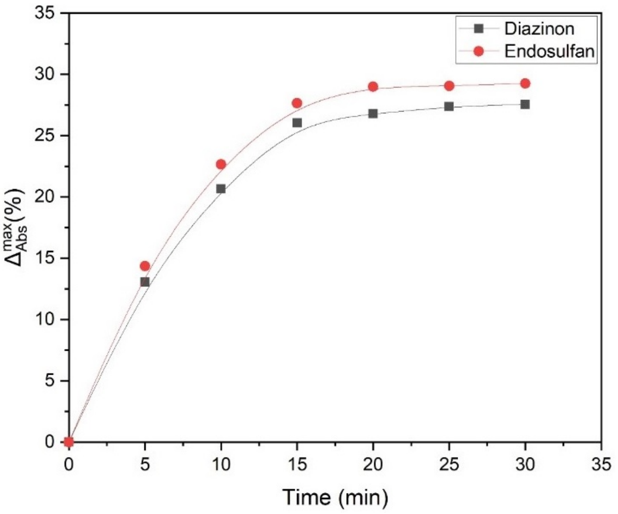

Figure 5. The change in absorption $\Delta_{\text{abs}}^{\text{max}}$ (%) at about $\lambda = 200$ nm versus treatment time from 5 to 30 minutes for reduction of diazinon (black color) and endosulfan (red color) employing $Ar/H_2O/H_2O_2$ SDBD, with a dielectric thickness of 2 mm and an initial concentration of 0.005% by volume (2.86 mg/L for diazinon and 2.97 mg/L for endosulfan) at 14 kV and 9.5 kHz.

Table 1. The effect of hydrogen peroxide oxidant and $Ar/H_2O/H_2O_2$ SDBD discharge frequency in the degradation of pesticides.

Pesticide	H_2O/H_2O_2	Frequency (kHz)	Time (min)	Voltage (kV)	The distance of the electrode from the sample surface (mm)	Dielectric thickness (mm)	c_0 (mg/Lit)	c (mg/Lit)	η (%)
Diazinon	-	-	-	-	-	-	2.84	2.84	0
	+	-	-	-	-	-	2.84	2.34	17
	-	9.5	15	14	5	2	2.84	1.98	30
	+	9.5	15	14	5	2	2.84	1.11	60
	+	6	15	14	5	2	2.84	2.21	22
	+	14	15	14	5	2	2.84	2.19	22
Endosulfan	-	-	-	-	-	-	2.95	2.95	0
	+	-	-	-	-	-	2.95	2.40	18
	-	9.5	15	14	5	2	2.95	1.83	37
	+	9.5	15	14	5	2	2.95	1.03	65
	+	6	15	14	5	2	2.95	2.29	22
	+	14	15	14	5	2	2.95	2.18	26

Table 2. The effect of treatment time in degradation of the pesticides.

Pesticide	H_2O/H_2O_2	Frequency	Time	Voltage	The distance of the electrode from the sample surface	Dielectric thickness	c_0	c	η
		(kHz)	(min)	(kV)	(mm)	(mm)	(mg/Lit)	(mg/Lit)	(%)
Diazinon	-	-	-	-	-	-	2.84	2.84	0
	+	9.5	5	14	5	2	2.84	2.21	22
	+	9.5	15	14	5	2	2.84	1.11	60
	+	9.5	30	14	5	2	2.84	1.08	61
Endosulfan	-	-	-	-	-	-	2.95	2.95	0
	+	9.5	5	14	5	2	2.95	2.22	24
	+	9.5	15	14	5	2	2.95	1.03	65
	+	9.5	30	14	5	2	2.95	0.95	67

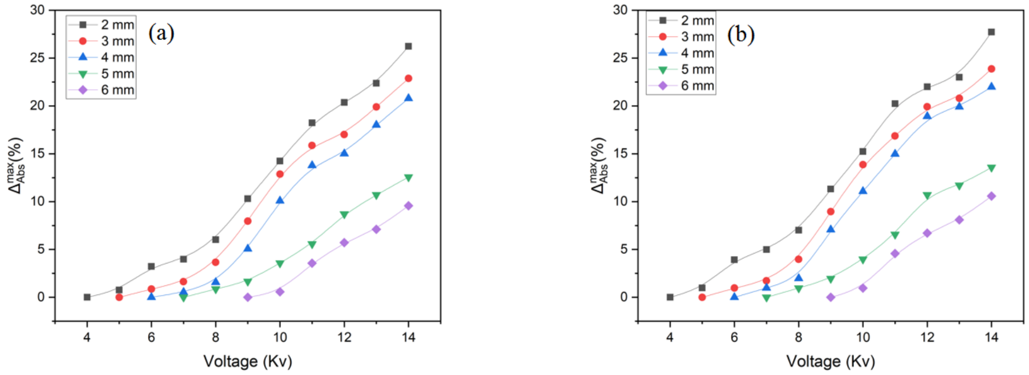

Figure 6. Effect of dielectric thickness and discharge voltage in absorption curve at about $\lambda = 200$ nm corresponding to the degradation of (a) diazinon and (b) endosulfan from water solution employing $Ar/H_2O/H_2O_2$ SDBD, with a dielectric thickness of 2 mm and an initial concentration of 0.005% by volume (2.86 mg/L for diazinon and 2.97 mg/L for endosulfan) at 14 kV and 9.5 kHz.

3.4 Distance of the electrode from the sample surface

Figure 7 shows the value of $\Delta_{\text{abs}}^{\text{max}}$ (%) of the treated samples at different distances of the SDBD from the sample surface.

The experiments were repeated for running frequencies of kHz. The maximum reduction $\Delta_{\text{abs}}^{\text{max}}$ (%) for all three frequencies was observed at a distance of 5 mm. A decline in the distance between the electrode and the sample increases the electric field between the electrode and the sample surface, however, this distance should not be too small because the shock waves created during the imaging process may disturb the surface of the solution and lead to oxidation and adhesion of the solution to the surface of the lower electrode, affecting the discharge process. Therefore, the tailored distance between the electrode and the sample surface was selected to be 5 mm.

Table 5 represents the efficiencies of pesticide reduction based on the effective distance of the sample surface from the SDBD. In this table, the treatment characteristics were also given.

In this study, the Energy yield (G_{50}) for the removal of the pesticides was evaluated. Energy yields of plasma reac-

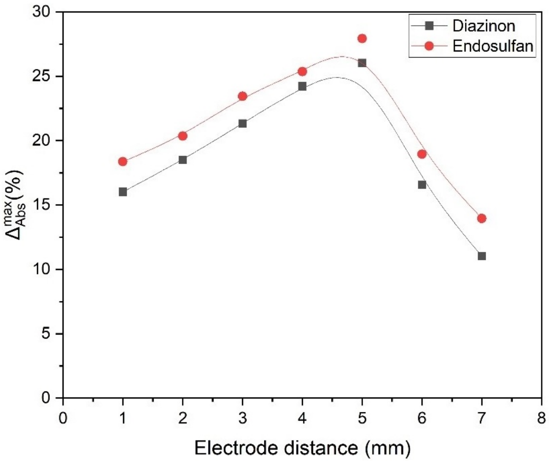

Figure 7. The effect of distance of the electrode from the sample surface in degradation of (a) diazinon and (b) endosulfan. Dielectric thickness and frequency were 2 mm, and 9.5 kHz, respectively.

Table 3. The efficiency of the pesticide degradation versus applied voltage with 5 mm thickness of the dielectric.

Pesticide	H_2O/H_2O_2	Frequency	Time	Voltage	The distance of the electrode from the sample surface	Dielectric thickness	c_0	c	η
		(kHz)	(min)	(kV)	(mm)	(mm)	(mg/Lit)	(mg/Lit)	(%)
Diazinon	-	-	-	-	-	-	2.84	2.84	0
	+	9.5	15	5	5	2	2.84	2.76	2
	+	9.5	15	10	5	2	2.84	2.11	25
	+	9.5	15	14	5	2	2.84	1.11	60
Endosulfan	-	-	-	-	-	-	2.95	2.95	0
	+	9.5	15	5	5	2	2.95	2.87	2
	+	9.5	15	10	5	2	2.95	2.08	29
	+	9.5	15	14	5	2	2.95	1.03	65

Table 4. The effect of dielectric thickness in degradation of pesticides.

Pesticide	H_2O/H_2O_2	Frequency	Time	Voltage	The distance of the electrode from the sample surface	Dielectric thickness	c_0	c	η
		(kHz)	(min)	(kV)	(mm)	(mm)	(mg/Lit)	(mg/Lit)	(%)
Diazinon	-	-	-	-	-	-	2.84	2.84	0
	+	9.5	15	14	5	2	2.84	1.11	60
	+	9.5	15	14	5	4	2.84	1.87	34
	+	9.5	15	14	5	6	2.84	2.32	18
Endosulfan	-	-	-	-	-	-	2.95	2.95	0
	+	9.5	15	14	5	2	2.95	1.03	65
	+	9.5	15	14	5	4	2.95	1.79	39
	+	9.5	15	14	5	6	2.95	2.46	16

tors vary over a wide range that depends not only on the types of plasma reactors but also on a variety of other factors, such as chemical structure, concentration, degree of conversion and by-products of the compounds, pH, added catalysts and additives, nature of gas phase and ambient pressure at which plasma is generated [16]. The energy yield (G_{50}) (mg/kWh) for the reactor investigated in this study is defined as the quantity of pollutant decomposed per kilowatt-hour of energy consumed to achieve 50% conversion, serving to illustrate energy efficiency throughout the pollutant degradation process. This parameter is calculated using Equation (2) and is represented in Figure 8.

$$G_{50} = \frac{30 \times [C]_0 \times V}{P \times t_{50}} \tag{2}$$

where $[C]_0$ represents the initial concentration of the pollutant (mg/L), V denotes the volume of the treated solution (L), P is the average discharge power(kW), and t_{50} is defined as the time (min) required for the degradation of 50% of the pollutants. It is important to note that the value of t_{50} was determined from degradation curves, considering that the SDBD experiments were conducted in a burst mode [16–18].

The results illustrate the relationship between these parameters and their impact on energy performance, providing valuable insights for optimizing reactor conditions. As can be seen from Figure 8, the reactor under study exhibited good performance for the removal of diazinon and endosulfan at an average discharge power of 1.5 kW and a frequency of 9.5 kHz, achieving removal rates of 225 mg/kWh and 220 mg/kWh, respectively.

4. Discussion

The chemistry of plasma involves the generation of reactive species, which play a crucial role in the degradation of pesticides during plasma treatment. Understanding the specific reactive species produced and their degradation

Table 5. The effect of distance of the electrode from the sample surface in degradation of pesticides.

Pesticide	H_2O_2	Frequency	Time	Voltage	The distance of the electrode from the sample surface	Dielectric thickness	c_0	c	η
		(kHz)	(min)	(kV)	(mm)	(mm)	(mg/Lit)	(mg/Lit)	(%)
Diazinon	-	-	-	-	-	-	2.84	2.84	0
	+	9.5	15	14	1	2	2.84	2.31	18
	+	9.5	15	14	5	2	2.84	1.11	60
	+	9.5	15	14	7	2	2.84	2.47	13
Endosulfan	-	-	-	-	-	-	2.95	2.95	0
	+	9.5	15	14	1	2	2.95	2.25	23
	+	9.5	15	14	5	2	2.95	1.03	65
	+	9.5	15	14	7	2	2.95	2.39	18

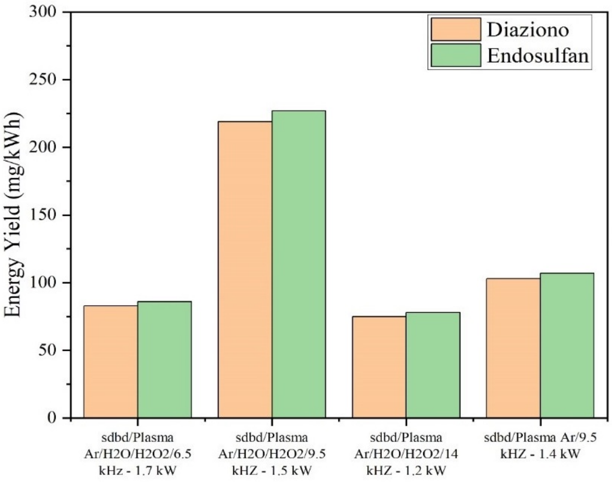

Figure 8. The energy yield (G_{50}) for the fourth group for the frequency and the average discharge power of (6.5 kHz, 1.7kW), (9.5 kHz, 1.5 kW), (14 kHz, 1.2 kW), and (9.5 kHz, 1.4 kW).

products is essential for optimizing the treatment process. This knowledge helps in elucidating the mechanisms of pesticide decomposition and the efficiency of plasma technologies. Some studies have indicated that the components of the reactive species [4] and electron energy have the potential for pesticide degradation. Plasma treatment can generate various reactive species with high oxidation potential such as ozone, hydroxyl radical, hydrogen peroxide, and UV light [23]. The presence of these active species seems to play a decisive role in the degradation mechanism [24]. Direct oxidation or a chain of several reactions that produce H_2O_2 and OH radicals are the main mechanisms of ROS in the degradation of pesticides [25]. Regarding the influence of plasma treatment on the pesticide residues, RONS directly attacked the pesticide molecules and reacted with them. Breaking the chemical bonds, results in various chemical reactions that convert the pesticides into less harmful or even harmless compounds [26]. Based on Chamberlain et al. [27], the mechanism of pesticide degradation can be assigned to the photolysis by hydroxyl radicals and oxidation-reduction reactions by ozone and oxygen. Small-molecule compounds such as acids, alcohols, amines, and carbonyls are among the byproducts of ozone oxidation [28]. Therefore, the degradation mechanism may differ depending on the pesticide type added to a specific product, matrix, and plasma discharge system. Hence, each pesticide should be explored specifically [29].

It was shown that the electrical and geometrical parameters of the SDBD apparatus such as running frequency, applied voltage, dielectric thickness, and the distance of the sample surface to the plasma reactor play essential roles in the degradation efficiency. As shown in Table 1, besides the impact of the H_2O/H_2O_2 presence on the degradation processes, the frequency could be tailored to increase the degradation efficiency. In our setup, 9.5 kHz has the largest efficiency as shown in Figure 6 and Table 1. Notably, voltage and treatment duration emerged as significant parameters in enhancing the degradation of water-soluble pesticides, as substantiated by prior research investigations [30–32]. As shown In Table 2 and Figure 7, the treatment time is a key factor in our scheme for degradation efficiency and energy cost. It was seen that the degradation processes did not enhance beyond 15 minutes noticeably. In a study conducted by Sarangapani et al. [4], the degradation of three pesticides (dichlorvos, malathion, and endosulfan) in aqueous media was investigated utilizing a DBD plasma reactor equipped with a novel dual circular plate electrode configuration. The experimental results revealed that the removal efficiencies achieved for dichlorvos, malathion, and endosulfan were $78.98 \pm 0.81\%$, $69.62 \pm 0.14\%$, and $57.71 \pm 0.58\%$, respectively, following exposure to plasma treatment at 80 kV for 8 minutes.

Accordingly, in Table 3 and Figure 8, the trend of the degradation versus voltage is monotonically increased which agrees well with the results of Moutiq et al. [30] and

Sarangapani et al. 2017 [32]. This increase in voltage, in turn, increases the amount of active species produced, and it can be concluded that the rate of degradation increases with an increase in voltage.

Another effective parameter in our scheme was the dielectric thickness. It was shown that among the 2, 4, and 6 mm thicknesses of the glass dielectric in the SDBD, the 2 mm one has the largest efficiency compared to the 4 and 6 mm. According to the degradation efficiencies versus the dielectric thickness, as mentioned in Table 4, the smaller the thickness, the higher the degradation efficiency. This could be understood that in a fixed voltage and fixed gap distance between the electrodes, the larger thickness produces a weaker plasma with low energy electrons and a low concentration of the reactive species. Therefore, the dielectric with a smaller thickness produces a denser plasma having higher electron energy and reactive species. As a result, the smaller thickness led to larger efficiencies.

The distance of the SDBD electrodes to the sample surface is another parameter that should be tailored to have better efficiency in this scheme. It was shown in Table 5 and Figure 7, that among distances of 1, 5, and 7 mm, a 5 mm distance led to the largest degradation efficiency. This result interprets the downstream diffusion of the plasma species that produces the RONS via collision during their journey toward the sample. Therefore, there is an optimum distance for generating needed RONS for degradation and oxidation of the pesticides when the plasma species travels downstream.

The ability of plasma to rapidly produce highly reactive species is well documented. This process is mainly initiated by the collision of high-energy electrons with the gas molecule or atoms. Upon discharge, the reactive species can be formed by reaction with newly-generated radicals or de-excitation of unstable species. Hydroxyl radicals, ozone, and hydrogen peroxide are the most abundant and studied primary and secondary species that are formed during the discharge in liquid or liquid-gas media. Nevertheless, many other ROS and RNS such as atomic oxygen, superoxide, hydroperoxyl radicals, nitrogen oxides, nitrites, nitrates, and proxy nitrites are produced in plasma which can help in the degradation of pollutants.

The generation of hydroxyl ($OH^\cdot$), hydrogen peroxide (H_2O_2) and ozone (O_3) are significantly influenced by the gas atmosphere composition, as noted by Aziz et al. in their research [15–17]. Variations in temperature, pH, additives, pressure, and the presence of other gases can all play crucial roles in determining how H_2O_2 and O_3 are formed.

It can occur through different pathways and the dominant formation mechanism can change even in the same discharge over time [33]. OH, production strongly depends on plasma parameters, such as gas temperature (T_g), electron temperature (T_e), ionization degree, electron and ion density, as well as gas composition. The formation of OH by electron dissociation of water molecules (Reaction (R1) at the following) and decomposition binding (Reaction (R2)) is dominant for plasma with $T_v > 2$ eV. For $1 < T_e < 2$ eV, however, electron-ion decomposition recombination (Reactions (R3) and (R4)) and ion-ion decomposition recombination (Reactions (R5) and (R6)) have an important contribution and can even be the dominant path in the formation of OH at sufficiently high ionization degree.

$e^- + H_2O \rightarrow OH^\cdot + H + e^-$ (R1)
$e^- + H_2O \rightarrow OH^\cdot + H^-$ (R2)
$e^- + H_2O \rightarrow OH^\cdot + H^\cdot$ (R3)
$e^- + H_2O \rightarrow OH^\cdot + H_2 + e^-$ (R4)
$H^- + H_2O \rightarrow OH^\cdot + H_2$ (R5)
$H^- + H_3O+ \rightarrow OH^\cdot + H_2 + H^\cdot$ (R6)

The formation of $OH^\cdot$ was confirmed through spectroscopic techniques: optical emission spectroscopy [34, 35], broad-band UV absorption spectroscopy [36, 37], and laser-induced fluorescence [38–40]. The density of $OH^\cdot$ in the gas phase was reported to be in the order of $10^{21} - 10^{23}$ $1/m^3$. Part of the hydroxyl radicals diffuses from the gas to the liquid surface and dissolves in the liquid as evidenced by chemical probe measurements, for example with terephthalic acid [41] or coumarin-3-carboxylic acid. The formation of ozone in non-thermal plasma in air or oxygen has been also well documented [42]. The electrons produced in the electrical discharge excite and dissociate diatomic oxygen (Reaction (R7)). The resulting atomic oxygen reacts with another oxygen molecule in the presence of a third object (an M-a N_2 or O_2 molecules that eliminate excess energy), giving rise to ozone formation (Reaction (R8)). In the presence of water vapor, ozone production is much less than dry gas due to the consumption of atomic oxygen in the reaction with water molecules or with radicals resulting from the decomposition of H_2O. In the electric discharge of water, the concentration of O_3 is reported to be several thousand parts per million [43–45].

$O_2 + e^- \rightarrow 2O^\cdot + e^-$ (R7)
$O^\cdot + O_2 + M \rightarrow O_3 + M$ (R8)

Several researchers proposed that a part of the ozone formed in the gas phase is transferred to the liquid and is involved in the destruction of organic compounds [41, 46, 47]. It is generally accepted that in discharge in contact with water, hydrogen peroxide is mainly formed by dimerization of $OH^\cdot$ radicals (Reaction (R9)).

$OH^\cdot + OH^\cdot \rightarrow H_2O_2$ (R9)

H_2O_2 is a relatively stable secondary oxidizing agent which accumulates in the liquid phase during plasma processing. A review by Locke and Shih [48] summarizes data on the formation of H_2O_2 in water using a wide range of discharges and experimental conditions. Their results showed that the production of H_2O_2 is highly dependent on the experimental setup, and the energy efficiency is about three orders of magnitude (4×10^{-2}–80 g kW/h). The concentration of hydrogen peroxide has been reported up to several mmol/L depending on several factors, including the nature of the gas and aqueous phases and discharge polarity [44, 45, 49, 50]. The researchers proposed that organic molecules diffuse into the plasma channels and react with OH radicals, thus, preventing the formation of H_2O_2. The situation is more complicated in gas phase discharges in contact with liquid. There are two opposing actions, from one hand, the decomposition of H_2O_2 by $OH^\cdot$ or O_3 is suppressed by the presence of an organic substrate that consumes these oxidizing species. On the other hand, fewer $OH^\cdot$ radicals are available for its formation [45]. Therefore, the concentration of H_2O_2 in the liquid can be increased or decreased depending on the concentration of organic compounds [51]. In addition to the direct production of hydroxyl radicals in plasma, excess OH may be generated from the interaction of dissolved O_3 with H_2O_2 (Reaction (R10)) [52].

$H_2O_2 + O_3 \rightarrow O_2 + OH^{\cdot} + HO_2$ (R10)

The formation of excess hydroxyl radicals is of interest as $OH^{\cdot}$ is a strong and nonselective oxidant that reacts with most organic compounds including short-chain carboxylic acid and mediators in the degradation of complex organic molecules. Therefore, an increase in the concentration of HO^* guarantees the decomposition/advanced mineralization of organic pollutants. When discharge occurs in the air in contact with liquid, reactive nitrogen species such as nitric oxide (NO), nitrogen dioxide (NO_2), nitrite (NO_2^-), nitrate (NO_3^-) and peroxynitrite ($ONOO^-$) are also formed in addition to ROSs as highlighted in the work of Lukes et al. [53]. Although N_2 is a highly stable molecule with high binding energy, the high-energy electrons in the discharge can detach atomic nitrogen (Reaction 11). Nitrogen oxides are then rapidly formed by the interaction of atomic nitrogen with two-atom or three-atom molecular oxygen (Reactions R12 and R13). The exchange between two nitrogen oxides can be obtained by the interaction of nitrogen monoxide with ozone and the dissociation of nitrogen dioxide under UV illumination in plasma (Reactions 14 and 15). Further dissolution and oxidation of nitrogen oxides in an aqueous medium result in the formation of nitrite, nitrates, and peroxynitrite.

$N_2 + e^- \rightarrow 2N^{\cdot} + e^-$ (R11)
$N^{\cdot} + O_2 \rightarrow NO^{\cdot} + O^{\cdot}$ (R12)
$N^{\cdot} + O_3 \rightarrow NO^{\cdot} + O_2$ (R13)
$NO^{\cdot} + O_3 \rightarrow NO_2^{\cdot} + O_2$ (R14)
$NO_2^{\cdot} + h\nu \rightarrow NO^{\cdot} + O^{\cdot}$ (R15)

The presence of these active nitrogen species in the reaction medium, in addition to hydroxylation products, is responsible for the formation of nitration and nitrosation products. Based on various studies, different reactions are involved in the formation of nitrogen-containing compounds [54–56]:

1- The attack of $NO^{\cdot}$ and $NO_2^{\cdot}$ radicals formed by electric discharge or decomposition of peroxynitric acid.
2- The reaction of the organic substrate with nitrosium ion (NO^+) is formed in acidic environments by the protonation of nitric acid or the decomposition of peroxynitric acid.
3- Direct reaction of peroxynitrite ion with organic compound in alkaline medium.
4- Or by nitration of organic substrate with soluble nitric acid.

The increase in ozone concentration at higher voltages and the production of higher levels of other active species explain the degradation kinetics that attack the functional groups of the target pesticides. At minimum voltage levels, dissociation of pesticide molecules occurs with fewer electron collisions, ionization, and ultimately a lower reaction rate. Conversely, with increasing voltage, higher energy electrons may lead to increased dissociation reactions to form free radicals, reactive species, and unstable compounds. Ozone and hydroxyl radicals are considered to be the main active species in pesticide degradation, in addition to countless other species produced by the plasma. The pesticide degradation mechanism by ozone can be through direct oxidation or several other chain reactions to produce peroxide and hydroxyl radicals, which subsequently oxidize the pesticide. Ozone breaks double bonds and leads to oxidation through direct reaction with compounds such as OH, CH_3, OCH_3, and NH_2 [57–59].

5. Conclusion

This study showed that the $Ar/H_2O/H_2O_2$ SDBD plasma system significantly improves the degradation of pesticides like diazinon and endosulfan in water compared to using individual methods. With energy yields of 225 mg/kWh for diazinon and 220 mg/kWh for endosulfan, the system achieves reductions of 60% and 65% in pesticide levels, respectively, after just 15 minutes of treatment. Factors such as running frequency, dielectric thickness, treatment time, and working voltage notably impact the efficacy of degradation, emphasizing this method's potential for sustainable water treatment.

Overall, plasma technology presents a promising alternative for sustainable and efficient pesticide removal from contaminated water sources due to enhanced degradation efficiency, environmentally friendly approach, rapid treatment, versatility, scalability, and In-Situ treatment.

Supplementary: Degradation of diazinon and endosulfan pesticides using surface dielectric barrier discharge cold plasma employing $Ar/H_2O/H_2O_2$ working gas

The photograph of the experiment is shown in Figure S1.
According to Figure S2(a) in the supplementary file, the absorption of the negative control sample and treated endosulfan samples by the Ar SDBD are 87% and 63%, respectively. The absorption for negative control and treated diazinon samples was 90% and 65%, respectively, as seen in Figure S2(b).

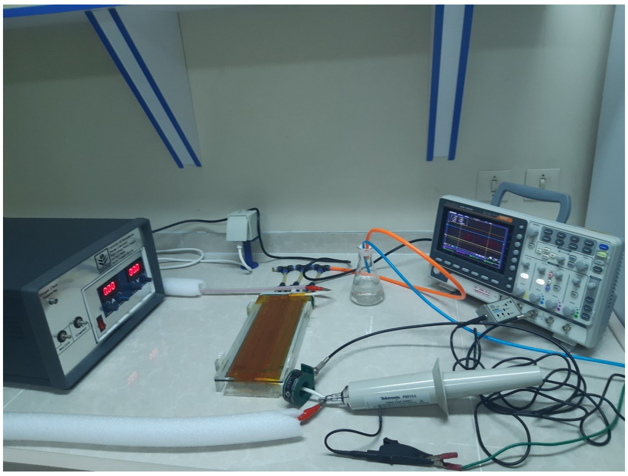

Fig. S1: A photograph of the $Ar/H_2O/H_2O_2$ SDBD approach for diazinon and endosulfan degradation.

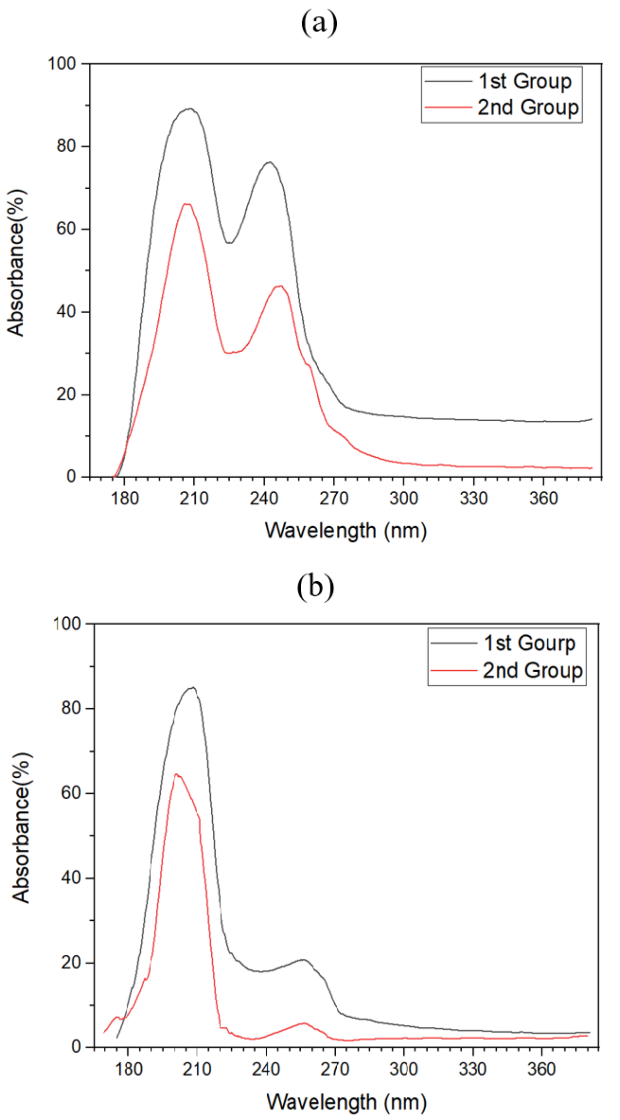

Fig. S2: Absorption spectrum of the negative control (first group) and treated samples with Ar SDBD (second group) for diazinon (a), and endosulfan (b). The treatment time, frequency, and applied voltage were 15 min., 9.5 kHz, and 14 kV, respectively.

Authors contributions

Authors have contributed equally in preparing and writing the manuscript.

Availability of data and materials

The authors confirm that the data supporting the findings of this study are available within the article.

Conflict of interests

The authors wish to confirm that there is no known conflict of interest associated with this publication.

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