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School of Food Science and Environmental Health

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Recommended Citation

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ABSTRACT

A high voltage dielectric barrier discharge plasma reactor using atmospheric air as the inducer gas was studied for the degradation of pesticides (dichlorvos, malathion, endosulfan) in water. The degradation kinetics of the pesticides were studied using GC–MS as a function of plasma control parameters. Electrical characterisation of the plasma revealed that the plasma discharge consisted of filamentary streamers. Excited nitrogen, reactive oxygen species and OH radicals generated in the dielectric barrier discharge (DBD) plasma reactor were identified using optical emission spectroscopy. Ozone, used as an indicator for metastable oxygen species, was quantified within the reactor at concentrations of 1600, 2200, 2800 ppm after 8 min of plasma treatment for applied voltages of 60, 70, and 80 kV respectively. The degradation efficacy of pesticides after 80 kV and 8 min of plasma treatment were found to be $78.98 \pm 0.81\%$ for dichlorvos, $69.62 \pm 0.14\%$ for malathion and $57.71 \pm 0.58\%$ for endosulfan. Degradation was found to follow first order kinetics. GC–MS analyses showed that the degraded compounds and intermediates formed were less toxic than the parent pesticide. A proposed mechanism of degradation of these pesticides is suggested.

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1. Introduction

Pesticides are widely used in modern agriculture to control crop infestation [1]. The benefits of pesticide usage include reduced crop losses and increased production per unit area of land. However, use of pesticides are often associated with risks to human and animal health along with detrimental effects to the environment [2]. Pesticides enter surface and ground water primarily as runoff from crops. Pesticide pollution has been recognized as an important global issue with scientists and environmental agencies tackling the problem with the development of more biocompatible pesticides which aim to minimise the side effects on the non-target species. However, even low levels of pesticides in drinking water may result in toxicity, with increased risk due to bio-accumulation and potential long term chronic effects [3,4]. In many cases, the environmental fate of pesticides is poorly understood, which is further complicated with the introduction of new ingredients

in pesticide formulations [5]. The potential hazards and damage caused by pesticides have been outlined by Walker et al. [6]. In order to minimise the potential health risks, various treatment processes have been investigated to remove pesticides from water, including photo catalysis [7–9], electrochemical degradation [10,11], Fenton oxidation [10], hydrogen peroxide oxidation [12], and ultrasound [13]. Physico-chemical techniques which have demonstrated treatment efficacy include adsorption [14], membrane technology [15], ozone, UV photolysis, ozone/ultraviolet (UV) photolysis [16,17], and ultrasonication [18]. Misra [19] reviewed the potential opportunities and challenges associated with various advanced oxidation processes for pesticide dissipation.

Recently, researchers have explored the potential of plasma discharges for pesticide degradation for food and water. Plasma is a partially or wholly ionised state of a gas consisting of positively and negatively charged ions, free electrons, free radicals and intermediate reactive atoms, molecules and UV photons with a net neutral charge [20]. Based on their thermodynamic energy levels, plasmas are broadly classified into thermal (hot) and non-thermal (cold) plasma. Until recently, industrial applications of plasma were mostly confined to material processing and electronics, including etching and deposition, bonding of plastics, and textile dying [21–23]. Due to technological developments it is now feasible to

induce plasmas at near ambient temperatures and under atmospheric conditions. This approach has demonstrated significant antimicrobial effects for biological applications [24–26]. Process efficacy of cold plasma for microbial inactivation, packaging modification, pesticide dissipation and wastewater treatment has been recently reviewed [19,27–30]. As a novel treatment technology, plasma oxidation offers several advantages in the production of oxidising species such as radicals (e.g., H, O, OH•, etc.), molecules (e.g., H_2O_2, O_3, etc.) and UV light [27]. The unique 'one pot' generation of multiple reactive species for the degradation of contaminants makes the approach attractive as an advanced oxidation process (AOP). Several studies have demonstrated the successful degradation of pesticides in waste waters by plasma, including; endosulfan [31] and organophosphorus pesticides [1] using oxygen containing inducer gases. Some other studies of relevance include, cold plasma degradation of pesticides on fresh produce [32], maize films [1], and solid surface [33]. Recent work by our group with plasma discharges from dielectric barrier discharges (DBDs), operating at significantly higher voltage levels (of the order of 100 kV) than previously reported in the literature, point to significantly improved efficacy in terms of pesticide degradation and antimicrobial efficacy [34] when combined with retention of the plasma afterglow (generated reactive species). A particular advantage of the use of higher voltage is that atmospheric air can be used for generating plasma, instead of the commonly used noble or mixed gases, which combined with the low energy input (<150 W) makes the approach attractive for large volume treatments and scale-up.

Dichlorvos, malathion and endosulfan are frequently used in agricultural production. As these pesticides exhibit excellent efficacy against a number of difficult-to-control pests which can cause substantial loss of crops. However, these pesticides enter surface and ground water primarily as runoff from crops and may cause a threat to ecosystems. Dichlorvos is generally preferred because of its cost-effectiveness and wide range of bioactivity. Dichlorvos is a mutagen and a suspected carcinogen for human beings [35]. It has been reported that human exposure to dichlorvos leads to the disorder of glucose metabolism and causes hyperglycaemia [36]. The use of malathion is also of concern as apart from its own neurotoxic effects the associated products contain other cholinesterase inhibitors [37]. Endosulfan poses an environmental concern because of its high toxicity to fish (e.g., 96 h LC_{50} 1.2 µg/L) [38]. A recent report form the European Union (EU) on water quality and pesticide pollution stated that the Environmental Quality Standards (EQS) for endosulfan was exceeded in 35% of monitored rivers [39]. Excessive discharges of these pesticide may significantly affect the ecosystem. The EU drinking water standards regulate a maximum contaminant level (MCL) of 0.1 µg/L for both dichlorvos and malathion, 0.2 µg/L for endosulfan and the sum of all pesticides at 0.5 µg/L, including any degradation by-products [40]. Consequently, these three test pesticides were selected to study the degradation behavior and degradation kinetics by DBD plasma. This study employs a high voltage large gap dielectric barrier discharge (DBD) in conjunction with a sealed reactor to examine the degradation of common pesticides. The work aims to quantify the efficacy of high voltage atmospheric air cold plasma for the degradation of test pesticides; dichlorvos, malathion, and endosulfan in water.

2. Materials and methods

2.1. Materials

Hexane, methanol (≥99.9% capillary GC-grade), high purity (>99.5%) dichlorvos, malathion and endosulfan standards were obtained from Sigma–Aldrich, Ireland. A cocktail of the three pesticide standards was prepared in methanol at 0.5 mg/mL. Samples for treatment were diluted in 1 L distilled water to achieve a treatment concentration of 2 mg/L.

2.2. Plasma treatment

A schematic of the experimental set-up employed is presented in Fig. 1. The experimental apparatus consists of two aluminum plate electrodes of circular geometry (outer diameter = 158 mm), one of which was placed under a 2 mm thick dielectric for grounding and the other, over a 10 mm thick Perspex for the high voltage input. Within the inter-dielectric space a rigid polypropylene container of dimensions 310 mm × 230 mm × 22 mm was placed. Each removable container contained a petri-plate with 20 mL of the pesticide cocktail placed between the electrode spaces. The container acted as a closed chamber as well as an additional dielectric. In order to prevent escape of the reactive species generated during and after treatment, the containers were sealed inside a high barrier Cryovac BB3050 film. No attempt was made to optimise the infusion of the generated species into the sample. Atmospheric air was used as the working gas. The electrodes were connected to a high voltage step-up transformer (Phenix Technologies, Inc., USA) whose primary winding receives input at 230 V, 50 Hz and delivers a high voltage output in the range 0–120 kV_{RMS}.

Treatment times of 0 (control), 2, 4, 6 and 8 min, at 60, 70 and 80 kV_{RMS} were tested. Following treatment, the containers were stored at 16 °C for 24 h storage to ensure that the reactive species generated reacted with the samples. Treatment of all samples was carried out in duplicate at ambient temperature (25 ± 2 °C).

2.3. Electrical measurements

The voltage applied across the electrodes was monitored using a high voltage probe (North Star PVM-6) coupled to a voltage divider to allow recording of the full voltage waveforms with an oscilloscope (Agilent InfiniVision 2000 X-Series, Agilent Technologies Inc., USA). A current transformer probe (Bergoz CT-E1.0S) was used to record the current waveforms.

2.4. Ozone measurement

Ozone concentrations within the reactor were measured immediately after plasma treatment (for the maximum treatment times only), using Gastec ozone detection tubes (Product No. 18M, Gastec, Japan). These tubes contain a chemical reagent, which changes color after reaction with the specified gas. 10 mL of the gas was drawn from the container into the tube using a hypodermic needle gas and sampling pump (Gastec, Japan). To avoid leakage of the gas, a silicone septum with an adhesive was used at the point of gas sampling.

2.5. Optical emission spectroscopy

Optical emission spectroscopy of the plasma discharge was carried out using a Stellarnet EPP 2000C-25 spectrometer at a resolution of 1.5 nm. The light from the plasma was coupled via an optical fibre. The spectrometer operated in a wavelength window of 190–850 nm. The integration time was 5000 ms and 5 samples were averaged for the collection of spectra. The emission spectra were qualitatively analysed to assign chemical species to the peaks. The spectra were noise canceled, averaged and analysed using National Institute of Standards and Technology [41] atomic spectra database and published works [42,43] for the identification of active chemical species.

Fig. 1. Schematic of the experimental setup with electrical and optical diagnostics.

1. Petridish with pesticide samples
2. Polypropylene box
3. Dielectric Barrier
4. High Voltage source
5. High voltage probe
6. Optical fibre
7. Current probe

2.6. Analysis of pesticides

The standard curve for pesticides was established using pesticide standard solutions ranging between 0.05 mg/L and 10 mg/L. The linear correlation coefficients (r^2) were 0.997, 0.998 and 0.997 for dichlorvos, malathion and endosulfan respectively. Each sample was extracted by 50 mL hexane for two times.

Gas chromatography coupled to mass spectrometry (GC–MS) is widely used in the analysis of pesticides that are highly volatile [44]. An Agilent 7890N GC (Agilent, Dublin, Ireland) coupled with Agilent 7000A triple quadrupole MS (Agilent, Dublin, Ireland) was employed for the analysis of the pesticide samples, with ionization achieved by electron impact at 70 eV in 'multiple reaction' monitoring (MRM) mode. The capillary column used was an Agilent 190915-433 capillary column (30 m × 0.25 mm I.D. × 0.25 μm thickness) with HP-5MSI (5% phenyl methylpolysiloxane) stationary phase. The operating conditions were: injection port temperature, 250 °C; interface temperature, 280 °C; column oven temperature, 100 °C for 5 min, ramped at 20 °C/min to 180 °C, followed by 5 °C/min to 280 °C for 10 min; helium carrier gas (flow rate of 1.0 mL/min); 2 μL injection volume. The split/split less injector was operated in the split-less mode. Sample injection was automated with the use of an Agilent 7693 auto sampler.

2.7. Data analysis

GC–MS data were acquired with Agilent MassHunter Workstation acquisition software and analysed using Agilent MassHunter Workstation Qual software (MassHunter Workstation, ver. B.05.000 SP02/Build 5.0.291.4, Agilent Technologies). The significance of differences among treatments was evaluated using the Tukey multiple comparison test at a significance level of $p \leq 0.05$ (SPSS ver. 19, SPSS Inc., Chicago, IL).

2.8. Degradation kinetic modeling study

The removal efficiencies (η) of pesticides were calculated according to the following equation:

$$\eta = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

where η is removal efficiency of each pesticide, C is the concentration of pesticide at time 't', C_0 the initial concentration of the
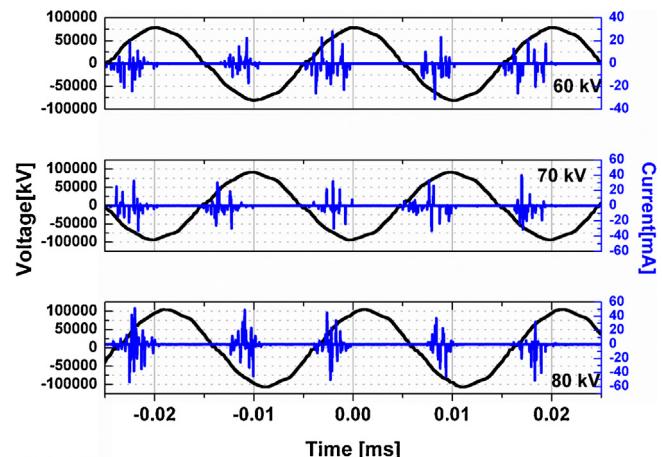

Fig. 2. Representative I–V waveforms of the discharge in packages.

pesticide. The pesticide degradation data were fitted to a pseudo-first order kinetics model using nonlinear least squares regression with Levenberg-Marquardt algorithm available from MATLAB 7.5 (The Math Works, MA, USA). The first-order kinetics is given by

$$\ln(C/C_0) = -kt \tag{2}$$

where k is the rate constant (1/s) of the reaction and t is the treatment time (s). The model fitting was evaluated based on the coefficient of regression [R^2]. The values of k was calculated based on these data.

3. Results and discussion

3.1. Current–voltage characteristic of plasma source

Typical current–voltage waveforms for the discharges within the containers for the various voltage levels are shown in Fig. 2, where the applied voltage is sinusoidal. The total current is the combination of the displacement current and several current pulses associated with filamentary micro-discharges which may trigger photo ionisation. These waveforms indicate operation in the filamentary regime, with an increasing number of current pulses at the higher voltages. Electrical characteristics of a discharge depends on the operating parameters including voltage, discharge gap width
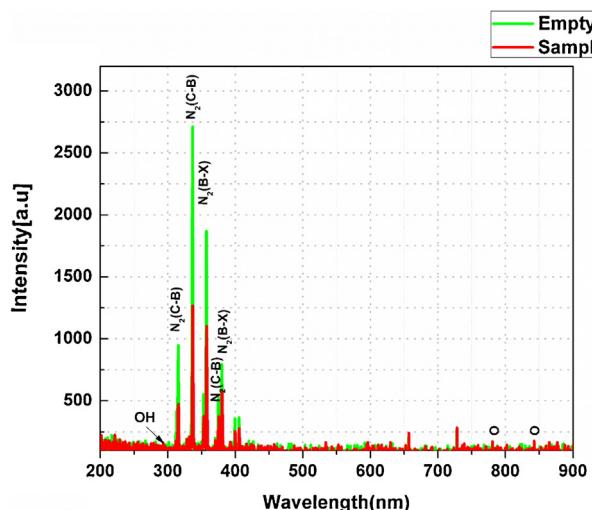
Fig. 3. Typical Optical Emission Spectrum (OES) of the dielectric barrier discharge in air. Operating voltage 80 kV.

Table 1
Percentage removal efficiencies (ŋ) of pesticides after plasma treatment.

Pesticide	Time(s)	%Removal efficiency (η) Voltage (kV)		
		60	70	80
Dichlorvos	120	7.93 ± 0.27	20.67 ± 0.55	32.96 ± 0.88
	240	12.31 ± 1.32	27.94 ± 3.22	45.45 ± 0.79
	360	22.49 ± 0.06	52.26 ± 0.84	63.98 ± 0.75
	480	47.60 ± 2.58	68.43 ± 1.71	78.98 ± 0.81
Malathion	120	4.15 ± 0.35	11.48 ± 0.34	33.32 ± 0.63
	240	12.78 ± 1.71	19.04 ± 1.07	43.18 ± 0.22
	360	13.69 ± 0.73	33.64 ± 0.14	54.15 ± 1.04
	480	25.64 ± 0.43	43.41 ± 2.27	69.62 ± 1.41
Endosulfan	120	8.55 ± 0.49	23.14 ± 0.95	33.03 ± 0.61
	240	11.48 ± 0.83	26.45 ± n0.90	42.26 ± 0.62
	360	19.30 ± 0.17	36.50 ± 0.99	47.86 ± 1.42
	480	26.95 ± 0.84	39.07 ± 0.51	57.71 ± 0.58

All the data are expressed as mean ± standard deviation. Means with the different superscript letters differ significantly ($p < 0.05$).

Table 2
Model parameters for pesticide degradation based on first-order kinetics.

Pesticide	Voltage (kV)	Rate constant k (s^{-1})	R^2
Dichlorvos	60	0.00103 ± 1.74E − 04	0.87
	70	0.00215 ± 1.73E − 04	0.96
	80	0.00303 ± 1.36E − 04	0.98
Malathion	60	0.00054 ± 0.49E − 04	0.96
	70	0.00113 ± 0.51E − 04	0.98
	80	0.00239 ± 1.13E − 04	0.98
Endosulfan	60	0.00062 ± 0.27E − 04	0.99
	70	0.00117 ± 1.11E − 04	0.95
	80	0.00192 ± 1.56E − 04	0.96

and frequency [45]. A stable discharge was found at the high voltages employed at the large discharge gap of 2.2 cm. As a charge trapping agent the dielectric limited the charge transported in the discharge and prevented arcing [46]. Further details regarding the electrical characteristics of the discharge using capacitance-voltage calculations can be found in a previous publication [47].

3.2. Ozone concentration

The ozone concentrations measured after 8 min of plasma treatment were found to be 1500, 2700 and 3000 ppm (within ± 10% errors) for applied voltages of 60, 70, and 80 kV respectively. Ozone is one of the most chemically stable and active species generated in DBD because of its relatively long lifetime and high oxidation potential [34]. The ozone generation reactions are shown in Eqs. ((3)–(5)) The dissociation of the oxygen molecule by energetic electron results in singlet oxygen. The ozone is formed by the combination of resulting singlet oxygen (O•) with oxygen. Ozone may react with water molecules to yield hydrogen peroxide which furthers results in formation of hydroxyl radicals (•OH). The process of generation and consumption of ozone is continuous during plasma treatment.

$$e^- + O_2 \rightarrow O + O + e^- \tag{3}$$

$$O + O_2 \rightarrow O_3 \tag{4}$$

$$3O_3 + H_2O \rightarrow 2^\circ OH + 4O_2 \tag{5}$$
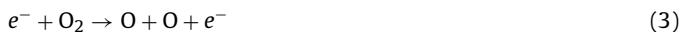
3.3. Optical emission spectroscopy (OES) of plasma discharge

Energy transferred to the plasma produces various chemical species in excited states. The generated chemical species in the gas phase were investigated by employing OES during the DBD discharge. Fig. 3 shows the emission spectrum over the wavelength range of 180–900 nm for the atmospheric air plasma reactor containing a pesticide sample operating at 80 kV (RMS). Emissions were found to be stronger in the empty containers relative to containers containing the samples, which could be due to the increased resistance caused by the presence of the sample in the discharge gap. From the emission spectrum, it is evident that the emission is in the near UV region (300–400 nm), which is similar to reported studies for DBDs operating at atmospheric pressures in air [48]. Emissions from N_2 and excited species of N_2^+ exhibited distinct peaks in the UV region [49]. Small peaks of OH are recorded near

295–300 nm. In addition, low intensity emissions from singlet O are noted at 750 nm and 780 nm [50]. Particle collisions resulting in quenching of O (^{3}P) and O (^{5}P) energy in the air plasma are responsible for the low intensities observed. As reported for plasma in air the main reactive species include; O_3, singlet oxygen and nitric oxides, while H_2O_2, •OH radicals and HNO$_x$ (x = 1, 4) are also generated with humid gases. During plasma treatment, RNS may have synergistic effects with ROS. From these results it is evident that the non-thermal plasma is source of reactive nitrogen and oxygen species (RNOS).

3.4. Quantification of pesticide residues and degradation kinetics

From Fig. 4 it is evident that the three pesticides, namely dichlorvos, malathion and endosulfan were identified at retention times of 5.76, 18.80, and 22.59 min respectively. The initial concentrations of pesticides were found to be 850 ppb, 1320 ppb, and 350 ppb for dichlorvos, malathion and endosulfan. An enhanced degradation was observed with an increase in plasma process parameters of voltage and treatment time (Fig. 5). It can be observed from Table 1 that the degradation was significant ($p \leq 0.05$) with respect to the control samples for both applied voltage and treatment time. The removal efficiencies were 78.98 ± 0.81%, 69.62 ± 0.14% and 57.71 ± 0.58% for dichlorvos, malathion and endosulfan respectively, after 80 kV for 8 min of plasma treatment.

The degradation was modeled using a first-order kinetics linear regression model. From Table 2 it can be observed that the model is in agreement with the experimental data with high correlation coefficients. It is apparent that the rate constants (k) increase with increases in voltage. It should be noted that the active species produced in the gas phase subsequently dissolves in the aqueous phase and reacts with the pesticide sample. The first-order kinetics observed can be explained by the production and consumption
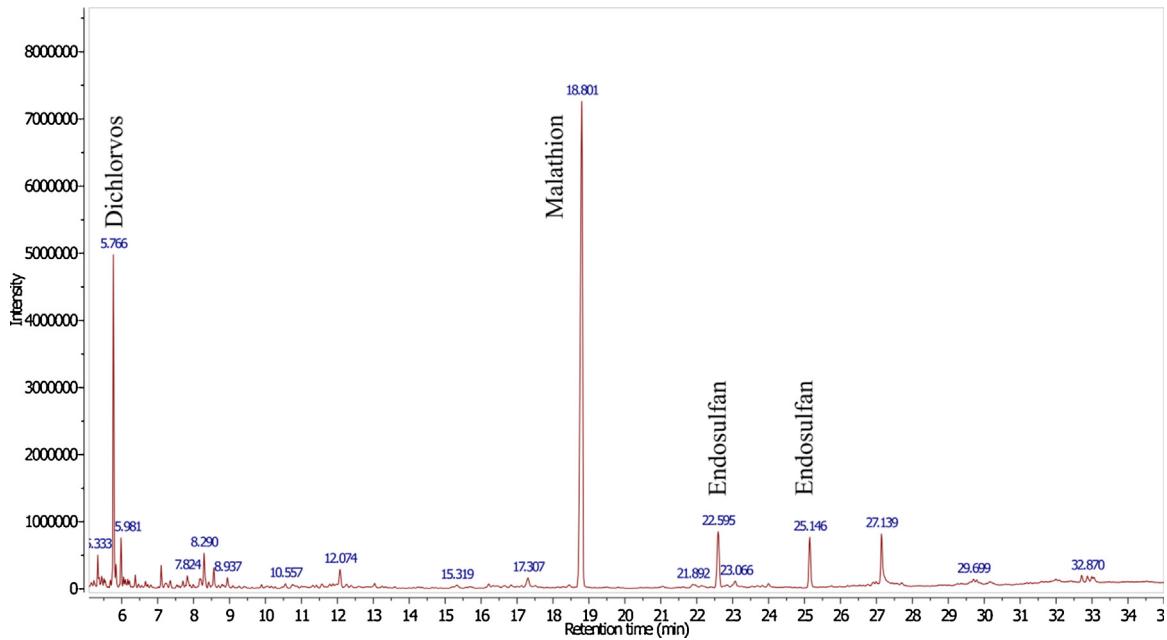
Fig. 4. Total ion chromatogram for complete ion scan.
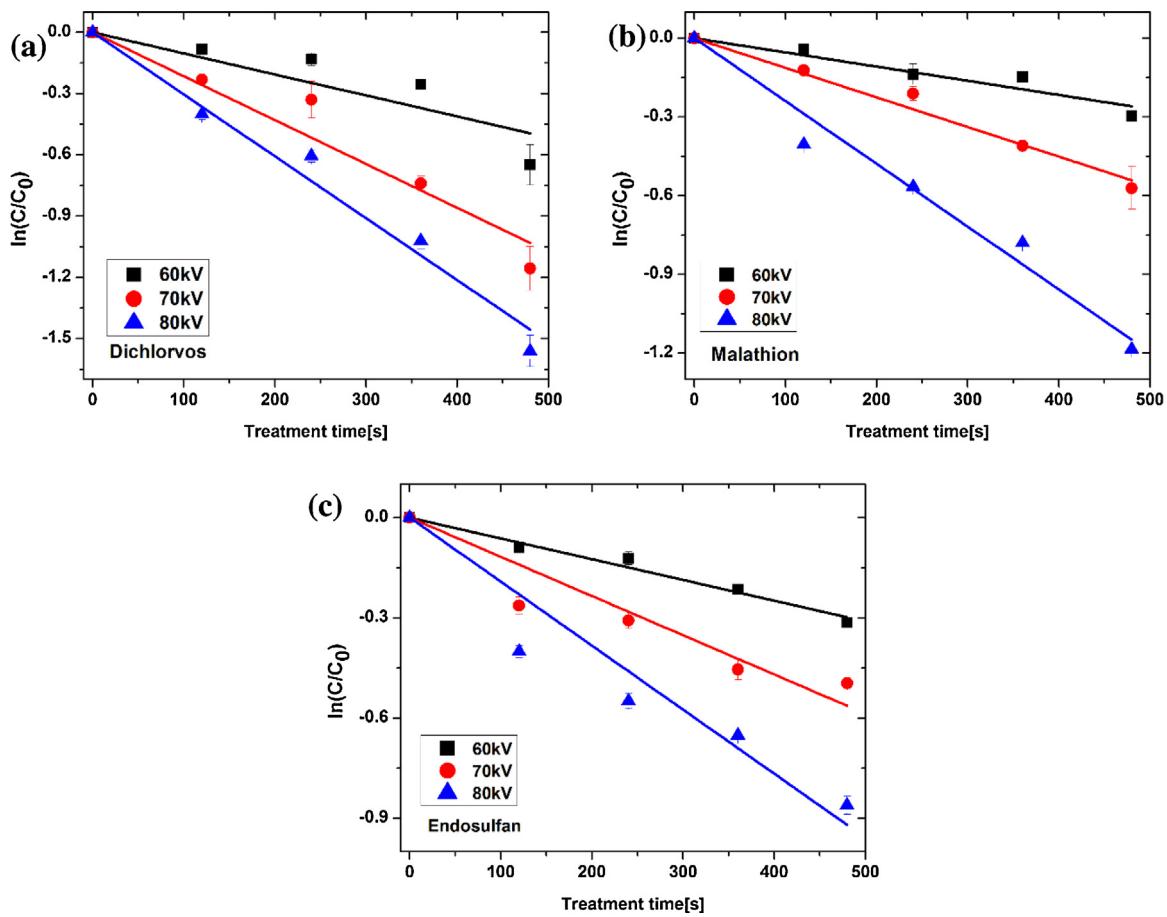
Fig. 5. Degradation of three pesticides (a) dichlorvos, (b) malathion and (c) endosulfan.

of reactive oxygen and nitrogen species which degrades the pesticide sample [51]. The intensity of the discharge increases with applied voltage which in turn increases the amount of reactive species generated. However, it is known that besides ozone, electrical discharges in humid air also produce a variety of excited and active species, such as O, $^{\bullet}OH$, $N^{\bullet}$, $HO_2^{\bullet}$, N_2^{*}, N^{*}, OH^{-}, O_2^{-}, O^{-}, O_2^{+}, N_2^{+}, N^{+}, and O^{+} [46]. The increase in measured ozone concentrations at the higher voltages and the generation of higher amounts
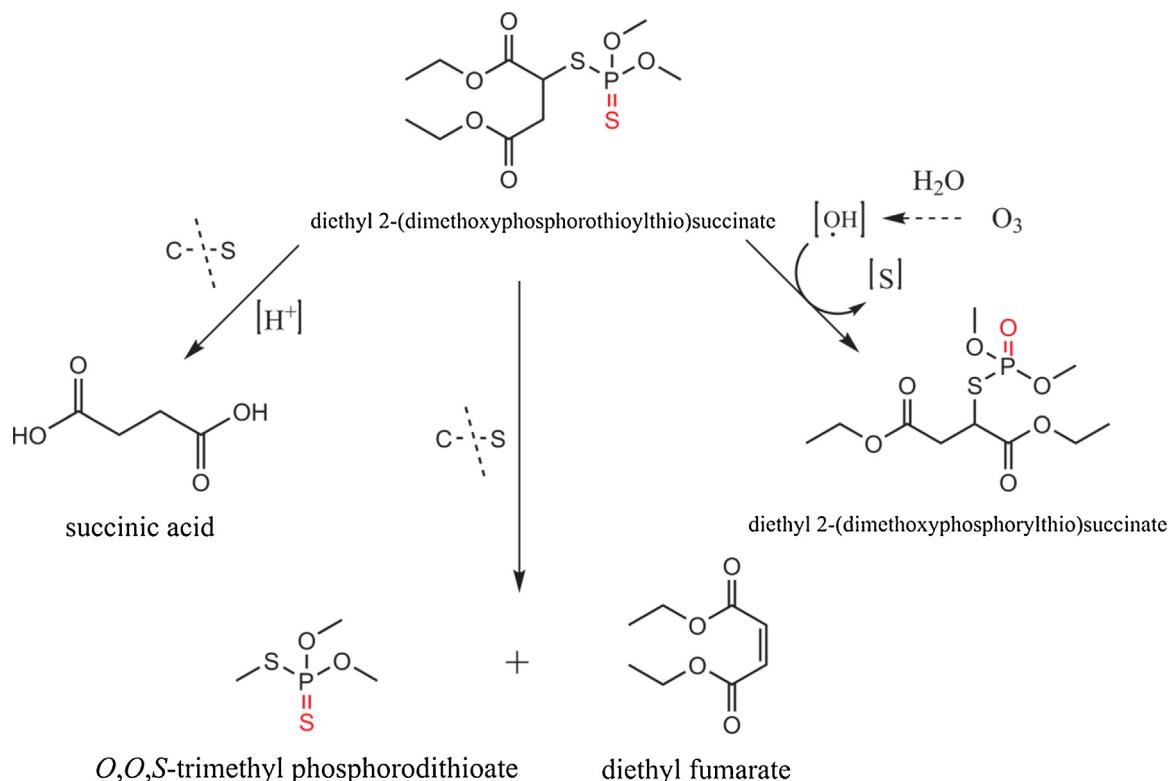
Fig. 6. Degradation mechanism of malathion in atmospheric pressure dielectric barrier plasma.

of other reactive species explain the kinetics of degradation which attack the functional groups of the the target pesticides [1]. It can be seen from Table 2 that the degradation rates increase with increases in voltage. The rate constant (k) for dichlorvos was found to be 0.0009 ± 0.0001 for 60 kV and 0.0029 ± 0.0001 for 80 kV treatment. Similar trends were seen for both malathion and endosulfan. The rate constant values ranged from $0.00054 \pm 0.49E - 04$ (s^{-1}) to $0.00239 \pm 1.13E - 04$ (s^{-1}) for malathion and $0.00062 \pm 0.27E - 04$ (s^{-1}) to $0.00192 \pm 1.56E - 04$ (s^{-1}) for endosulfan. At the minimum voltage levels, the dissociation of pesticide molecules takes place with fewer electrons collisions, ionization and ultimately lower reaction rates with the generated species. Conversely, with increasing voltage the higher energy electrons may lead to increased dissociation reactions to form free radicals, reactive species and unstable compounds.

Ozone and hydroxyl radicals are considered as the principal active species responsible for the degradation of the pesticides, in addition to the other myriad of species generated by plasma. The mechanism of ozone in the degradation of pesticides can be either by direct oxidation or by several other chain reactions to yield peroxide and hydroxyl radicals which subsequently oxidized the pesticide. The indirect reaction by ozone takes place at high pH, while in acidic environments direct reaction is predominant. At low pH a slow reaction takes place between the dissolved ozone and hydrogen peroxide which result in the formation of hydroxyl radicals, but these reactions are greatly accelerated at high pH. Ozone cleaves double bonds and direct reactions with compounds such as $-OH$, $-CH_3$, $-OCH_3$, $-NH_2$ also leads to oxidation [52–54]. The following are few chemical reactions which might take place during and post plasma treatments.

$$H_2O + e^- \rightarrow H^\bullet + OH^\bullet + e^- \tag{6}$$

$$O + O_2 \rightarrow O_3 \tag{7}$$

$$H_2O + e^- \rightarrow H^\bullet + OH^\bullet + e^- \tag{8}$$

$$O_3 + {}^\bullet OH \rightarrow {}^\bullet HO_2 + O_2 \tag{9}$$

$$OH^\bullet + OH^\bullet \rightarrow H_2O_2 \tag{10}$$

$$H^\bullet + O_2 \rightarrow HO_2 \tag{11}$$

$$HO_2^\bullet + H^\bullet \rightarrow H_2O_2 \tag{12}$$

$$H_2O_2 + O_3 \rightarrow {}^\bullet OH + O_2 + {}^\bullet HO_2 \tag{13}$$
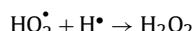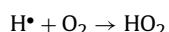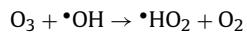
It was noticed that the pH value was decreased after plasma treatment from 6.8 ± 0.2 to 4.3 ± 0.2, whereas, there was an increase in temperature during plasma treatment from $25 \pm 2\,^\circ C$ to $35 \pm 3\,^\circ C$. This was confirmed by recording the temperature rise using a hand-held infrared thermometer (Maplin Electronics, UK), which recorded a maximum temperature rise of only $10\,^\circ C$ for all experiments. Similar observations have been reported by Pankaj et al. [55]. The raise in temperature was found to have an insignificant effect ($p > 0.05$). The shift in pH values in dye samples after plasma treatment has been reported to be due to the formation of strong acids including nitric acid (HNO_3) and nitrous acid (HNO_2) as well as hydrogen peroxide (H_2O_2) [56]. The degradation kinetics indicate that the rate constant increases with voltage and treatment time. At extended timescales the excited nitrogen species may be more effective than the oxygen species [57]. The formation of acidic environments might be due to dissolution of nitrogen oxides with the following reactions:

$$N_2 + e^- \rightarrow 2N^\bullet + e^- \tag{14}$$

$$O_2 + e^- \rightarrow 2O^\bullet + e^- \tag{15}$$

$$N^\bullet + O^\bullet \rightarrow NO \tag{16}$$

$$NO + O \rightarrow NO_2 \tag{17}$$

$$NO_2 + OH^\bullet \rightarrow HNO_3 \tag{18}$$

The increased degradation of pesticide in alkaline environments over acidic has been reported in the literature [58]. An increase in

the applied power to the plasma discharge had significant effects on the degradation efficacy for dichlorvos [1]. However, these pesticides have several functional groups, which provides several sites for attack by reactive species. It has been suggested that the photo degradation of pesticides proceeds via multiple, parallel reaction pathways including photo-isomerisation, photo-hydrolysis of the methyl ester and of the nitrile group, cleavage of the acrylate double bond, photo hydrolytic ether cleavage between the aromatic ring resulting in phenol, and oxidative cleavage of the acrylate double bond [59,60]. The degradation behavior between these three pesticides appears to differ. These differences are due to the different chemical nature of the selected pesticides. It is known that dichlorvos and malathion belongs to organophosphorus pesticides, whereas endosulfan is an organochlorine pesticide [61]. The chemical structure of pesticide is the dominant factor for the persistence because it influences the chemical stability during the degradation reaction [62]. From Table 1 it is evident that the removal efficiencies of dichlorvos and malathion was higher compared to that of endosulfan. The difference in degradation behaviour might be due to difference in electronegativity and bond energies. The lower bond energies of P—O in dichlorvos and P—S in malathion leads to maximum removal efficiencies when compared to higher bond energy for S=O in endosulfan. The availability of the chlorine group might be another reason for the lower removal efficiency of endosulfan. System parameters like sample volume, discharge gas, electrode gap, sample chemistry and viscosity may affect the degradation rates. Higher electric fields will be required to initiate the breakdown and also be influenced by the presence of material such as the petri dish or sample present in the gap. In the case of a large discharge gap, the breakdown voltage is quite high. The gap size will govern the volume of the inducer gas but also influence the electron avalanche and subsequently ionizing and the generated reactive species.

Post plasma treated samples were found to have a series of less-toxic molecules than the parent pesticide molecules. An analysis of the mass fragments of the peak at ca. 18.79 min retention time confirmed the presence of malaoxon in samples following plasma treatment. The oxidation of the P=S group of malathion to P=O due to hydroxyl radicals led to oxidative desulfuration and the formation of malaoxon [63]. Similarly the breakdown of the C—S bond by elimination is suspected to result in other degradation products such as succinate and *O,O,S*-trimethylphophorodithioate, and their presence was also confirmed through the MS analysis. Such end products were also reported by Zhu et al. [64] who employed an atmospheric pressure plasma jet using a helium/oxygen feed gas. The active species generated during plasma could be consumed not only in reactions with the target pesticide, but also in reactions with the degradation products. These reactions are summarised in Fig. 6. It may be noted the end-points of degradation are characterised by simpler chemical groups [37,65]. DBD air plasma offers a number of specific advantages as an AOP for water treatment including a 'one pot' generation source of short-lived oxidants, mineralization of pesticides without reversible reactions, use of low energy input even at pilot scale (<150 W) and use of environment friendly gases such as atmospheric air. Such features make the approach attractive for large volume treatments and scale-up. These results indicate the feasibility of atmospheric air plasma as a water or effluent treatment technology.

4. Conclusions

Atmospheric pressure dielectric barrier discharge plasma in air was successfully employed for the degradation of pesticides in water. The discharge was operated in the filamentary regime at high voltages and found to be a rapid and effective source of reactive oxygen and excited nitrogen species. The maximum degradation achieved was $78.98 \pm 0.81\%$, $69.62 \pm 0.14\%$ and $57.71 \pm 0.58\%$ for dichlorvos, malathion and endosulfan respectively. Active species such O_3, H_2O_2, $^\bullet OH$ and other plasma species are responsible for the degradation of such pesticides. The end products of degradation are characterised by simpler chemical groups. The degradation of pesticides was found to increase with voltage and treatment time, following first-order kinetics. The attractive features of the approach for water treatment include the use of atmospheric air as the inducer gas, making the technology economically viable and environmentally friendly. Also the low energy input, comparable to that of ozone generation, should allow scale up of the technology. No attempt was made in this study to optimise the infusion of the plasma species into the water samples which would facilitate scale-up and improve treatment times. These findings suggest that atmospheric cold plasma technology is an efficient and prospective method for the removal of aqueous pollutants.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jwpe.2016.01.003.

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