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In-package nonthermal plasma degradation of pesticides on fresh produce

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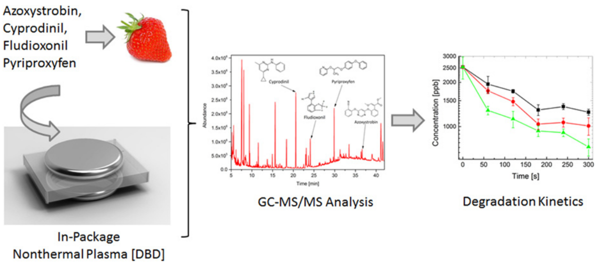
HIGHLIGHTS

- In-package nonthermal plasma treatment of strawberries with pesticide residues.
- Mixture of azoxystrobin, cyprodinil, fludioxonil and pyriproxyfen employed.
- Electrical and optical characterisation of plasma.
- GC-MS/MS reveals successful degradation of pesticides in strawberries.

GRAPHICAL ABSTRACT



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ABSTRACT

In-package nonthermal plasma (NTP) technology is a novel technology for the decontamination of foods and biological materials. This study presents the first report on the potential of the technology for the degradation of pesticide residues on fresh produce. A cocktail of pesticides, namely azoxystrobin, cyprodinil, fludioxonil and pyriproxyfen was tested on strawberries. The concentrations of these pesticides were monitored *in priori* and post-plasma treatment using GC-MS/MS. An applied voltage and time dependent degradation of the pesticides was observed for treatment voltages of 60, 70 and 80 kV and treatment durations ranging from 1 to 5 min, followed by 24 h in-pack storage. The electrical characterisation revealed the operation of the discharge in a stable filamentary regime. The discharge was found to generate reactive oxygen and excited nitrogen species as observed by optical emission spectroscopy.

1. Introduction

The use of pesticides in modern agricultural practices has enabled the stabilisation of crop production patterns globally. Nevertheless, the environmental and health problems associated with the use of pesticides at such a global scale cannot be overlooked. A constant search for new pesticides is on-going to combat the resistance developed by pests against traditional pesticides. For example, fungicides, such as azoxystrobin, cyprodinil, fludioxonil and pyriproxyfen are relatively new pesticides that have been introduced into the marketplace [1]. However, the fact that agricultural products cannot be sold if they contain pesticides exceeding the residual limit implicates the need for development of methods to effectively eliminate residual pesticides in harvested crops [2,3].

For the past two decades, research in food science has largely focused on nonthermal technologies such as high pressure, pulsed electric field, ultrasound, pulsed light, and ozone processing technologies. Nonthermal plasma (NTP) is a relatively novel technology

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for the decontamination of fresh foods and food processing surfaces. NTP is widely used at an industrial scale for material processing [4,5]. The fundamentals of NTP and its applications to decontamination of foods were reviewed by Misra et al. [6] and Niemira [7]. Unlike microbiological decontamination, only a limited number of studies have demonstrated the successful degradation of pesticides by NTP. The degradation of dichlorvos and omethoate organophosphorus pesticides sprayed onto maize samples when treated with an inductively coupled radio-frequency NTP source operating in oxygen was studied by Bai et al. [8]. Recently, Bai et al. [9] also demonstrated the successful degradation of dichlorvos pesticides coated on glass slides using the same inductively coupled plasma (ICP) source. In an earlier study, Kim et al. [10] reported the decomposition of paraoxon and parathion with an atmospheric pressure, radio-frequency plasma generated in Ar and Ar/O_2 mixture. However, to the best of our knowledge there have been no studies regarding NTP aided pesticide degradation on fruits and vegetables, in general, and strawberries in particular.

In-package nonthermal plasma is a novel and highly desirable technology for food and bio-decontamination [11]. It involves generation of a NTP inside a sealed package containing the food or biomaterial intended for treatment. The reactive species generated by plasma persist up to a few hours inside the packaging, during which time there is a significant anti-microbial effect. Critically the generated short life active species revert back to the original gas [12]. We have successfully demonstrated the ability of DBD based in-package NTP in air to inactivate background microflora on strawberries, without inducing significant changes in quality [13]. Recently, our group also demonstrated the inactivation of an enzyme in tomato extract using the same plasma source [14]. We have not found significant changes in the food packaging material following NTP treatments to declare hazards from this process [15,16]. Besides microbiological concerns, pesticides residues in strawberries also pose a serious health risk, for they are often consumed without washing or are minimally processed. This work investigates the potential of in-package NTP for the degradation of pesticide residues on strawberries.

The aims of the present study were to find out if in-package NTP can degrade pesticide residues on strawberries. More specifically, the study involves quantifying the degradation of fungicides, namely azoxystrobin, cyprodinil, fludioxonil, and pyriproxyfen on strawberry surface by GC-MS/MS analysis, under the influence of NTP treatment. A brief summary of these pesticides, including chemical structure, toxicity is provided in Table 1. With an aim to explain the observed effects, the electrical and optical characterisation of the plasma source has also been carried out.

2. Experimental

2.1. Produce

Fresh strawberries (*Fragaria ananasa*, var. Elsanta) were purchased from the local wholesale fruit market (Dublin, Ireland) and stored under refrigerated conditions for ~1 h before carrying out the experiments. The strawberries were screened for the presence of pesticides and those selected were found to be absent for the studied pesticides.

2.2. Chemicals

Acetone (≥99.9% capillary GC-grade), dichloromethane (≤0.0005% non-volatile matter), petroleum ether, ethyl acetate (≤0.0005% non-volatile matter) and sodium sulphate (anhydrous) were all obtained from Sigma–Aldrich, Ireland. Azoxystrobin, cyprodinil, fludioxonil and pyriproxyfen standards were also obtained from Sigma–Aldrich, Ireland.

2.3. Exposure of samples to pesticides

A cocktail of all the four pesticide standards was prepared in ethyl acetate at 100 ppm concentration each. Initial quality control runs in our laboratory have shown that the selected pesticides do not react with each other. To ensure a homogeneous distribution of pesticides on the fruit surface, we adopted the method of immersion into the pesticide solution for 15 s. The dipped pesticides were allowed to air-dry under dark, inside a laminar flow hood for 1 h, followed by a second dip for 15 s and repeated drying.

2.4. Plasma treatment

A schematic of the experimental set-up employed in the study is presented in Fig. 1. The DBD system comprises of two circular aluminium plate electrodes (outer diameter = 158 mm) over dielectric layers (10 mm thick perspex for high voltage electrode and 2 mm thick polypropylene for ground electrode) between which a PET (polyethylene terephthalate) package containing the food sample is placed. The high voltage step-up transformer (Phenix Technologies, Inc., USA) powered at 230 V, 50 Hz delivers a high voltage output in the range 0–120 kV rms. Three discreet voltages viz. 60, 70 and 80 kV (RMS) at 50 Hz frequency were applied across the electrodes for these experiments. The rigid PET package had dimensions of 150 mm × 150 mm × 35 mm and also served as a dielectric material. Boxes with strawberry samples were sealed inside polymeric film of 50 micrometre thickness (Cryovac BB3050) with very low gas transmission rates, in order to prevent leakage of the plasma-generated reactive species. This film served as an additional layer of dielectric. All treatments were conducted in air. Literature reveals that most DBD treatments for food application operate in single diatomic gases or noble gases [6]. However, for practical applications, it is attractive to use less costly molecular gases, for example air [17]. The atmospheric air conditions at the time of packaging and treatment was 42 ± 1% relative humidity (RH) and 25 ± 2 °C, as measured using a humidity-temperature probe connected to a data logger (Testo 176 T2, Testo Ltd., UK). The strawberry samples were subjected to nonthermal plasma treatment for 60, 120, 180, 240, and 300 s and subsequently stored for 24 h at 10 °C and 90% RH. These operating conditions were selected based on previous experiments conducted in our laboratory.

2.5. Electrical measurements

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

2.6. Ozone measurement

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