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The effects of nonthermal plasma on chemical quality of strawberries

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ABSTRACT

While a considerable body of research has reported the effective inactivation of food-borne pathogens with nonthermal plasma treatments, studies to unravel the plasma-food interactions are sparse. In this work, the effects of in-package plasma treatments on the chemical quality of strawberries were evaluated. Specifically, the effects on FTIR spectra, ascorbic acid, and anthocyanin content of strawberries were studied. Results indicated that nonthermal plasma treatments in sealed packages at 80 kV applied voltage can cause a minor degradation of ascorbic acid and anthocyanin content. Both voltage and treatment time were found to cause changes in the infrared absorption spectrum of strawberries.

1. Introduction

Given the diverse nature of the food industry, it is continually seeking to adopt new technologies for safety assurance, shelf-life extension and sustainability. The technology of nonthermal plasma, widely used in semiconductor and material processing, has been demonstrated to be of significant potential for the biological and food processing sectors. Often referred to as the fourth state of matter, gaseous plasma is comprised of several excited atomic, molecular, ionic, and radical species, co-existing with numerous reactive species, including electrons, positive and negative ions, free radicals, gas atoms, molecules in the ground or excited state, quanta of electromagnetic radiation (UV photons and visible light).

Recent advancements in plasma source development have enabled generation of nonthermal plasma at atmospheric pressure. The design and control of plasma sources operating at or near atmospheric pressure is of interest, both technically and commercially to the food industry because it does not require extreme processing conditions, such as high temperature and pressure (Misra et al., 2011). Within past five years, several reviews have summarised the applications, either proven or potential, of plasma treatment of foods (Deng et al., 2007; Misra et al., 2011). The in-package plasma source developed by our group is very effective in generating a wide range of chemically active species, including ozone, singlet oxygen, excited nitrogen species and other ions, besides neutrals and radicals within di- and tri-atomic gas mixtures (including air) and noble gases (Misra et al., 2013; Moiseev et al., 2014). This plasma source operates in a filamentary regime of electrical discharge and is effective in reducing bacteria on strawberries (Misra et al., 2014a), bacterial spores on paper strips (Patil et al., 2014), moulds on strawberries (Misra et al., 2014a,c), besides other model systems, combined with dissipating pesticide residues on strawberries (Misra et al., 2014b). The prime advantage of in-package cold plasma treatment is that the bactericidal molecules are generated and contained in the package, allowing extended exposure to pathogenic microbes while reverting back to the original gas within few hours of storage.

Strawberries are rich in bioactives such as phenolic compounds, including their abundant anthocyanins, which impart the bright red colour to the fruits (Hannum, 2004). Strawberries are also a good source of ascorbic acid. The pseudo fruits undergo changes in sensory attributes such as texture and colour, as well as changes in the profile of bioactive constituent over time or varying with environmental conditions. The effect of nonthermal plasma treatments on the colour, texture and respiration rate of plasma treated strawberries were described in our earlier works (Misra et al., 2014a,c). To obtain a complete insight into the changes induced by NTP treatment of strawberries, the changes in anthocyanin content, and ascorbic acid need to be assessed. It is worth noting that, providing mechanistic insights for changes in the chemical constituents of plasma treated strawberries is difficult. This is because of the inherent nature of all plasma

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states, which involves a multitude of physical and chemical phenomena occurring at various scales in time and space (Herron and Green, 2001; Sieck et al., 2000).

The specific objectives of this work are: (i) to identify if in-package plasma treatment causes changes to the chemical composition of strawberries as observed through mid-infrared spectroscopy; (ii) to quantitatively determine the ascorbic acid and anthocyanin content of plasma treated strawberries, following 24 h storage in the package. We wish to highlight that fathomable chemical changes to in-package NTP treated produce is likely to occur over the period of 24 h storage.

2. Materials and methods

2.1. Materials

All the chemicals used viz. metaphosphoric acid, acetonitrile, methanol, pelargonidin-3-glucoside standard, and acetic acid were obtained from Sigma-Aldrich, Ireland. Fresh strawberries (*Fragaria ananasa*, var. Elsanta) in passively modified atmosphere packages (MAP) were purchased from the local wholesale fruit market (Smithfield, Dublin, Ireland) and stored under refrigerated conditions for 1 h before the beginning of the experiments.

2.2. Nonthermal plasma treatments

About 100±5 g of strawberries were placed in PET (polyethylene terephthalate) trays (Holfeld Plastics, Ireland) having dimensions of 0.15 m × 0.15 m × 0.035 m and were sealed inside polymeric films of 50 μm thickness with very low gas transmission rates (oxygen transmission rate of 9.49×10^{-9} mol m^{-2} s^{-1} at 23 °C and 101,325 Pa, Cryovac BB3050, Sealed Air, Ireland). The headspace volume was estimated ca. 7.8×10^{-3} m^3. These packages were placed within the inter-electrode space of a dielectric barrier discharge set-up, further details regarding which can be obtained from our earlier publications (Misra et al., 2015, 2014b). The atmospheric air conditions at the time of packaging and treatment were 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 treatments in duplicate for 1 (60 s) and 5 min (300 s) durations at two discrete voltages of 60 and 80 kV and subsequently stored for 24 h at 10 °C and 90% RH. A maximum temperature rise of 13 ± 2 °C was observed after 60 s of treatment at 80 kV measured using a handheld infrared thermometer (Maplin Electronics, UK). For the bioactive and volatile profiling experiments, the nonthermal plasma treated strawberry samples were frozen in a cryogenic freezer and stored at −80 °C before subsequent analysis. All analyses were carried out within five days following experiments.

2.3. FTIR spectroscopy

The control and treated group of strawberries were chopped and frozen for 24 h at -80 °C in a cryogenic fridge (Model 906, Thermo Scientific Forma, −86 Ultralow Freezer). Subsequently, they were freeze-dried for a period of 24 h and then manually ground into fine powder using a mortar and pestle. A 3% w/w dilution of the ground samples was prepared by mixing 9 mg of the sample with 281 mg of dry potassium bromide (KBr, Sigma–Aldrich, Ireland). Pellets were prepared by exerting a pressure of 10^6 kg/m^2 for approximately 60 s in a pellet press (Specac, United Kingdom).

The IR spectra were recorded in absorbance mode at 2 cm^{-1} resolution, using a Nicolet Avatar 360 FTIR E.S.P. (Thermo Scientific, Waltham, MA, USA) over the frequency range 4000–400 cm^{-1} by co-adding 64 interferograms. To account for variations that could result from pellet thickness and uniformity, two different pellets were prepared from the same sample (spectra were nearly identical). The sample measurements were replicated for four individual samples of each treatment class, resulting in eight spectra for each sample. Before every scan, a new reference air background spectrum was taken using the OMNIC software (version ESP 5.2) software.

The spectral data was corrected for artefacts and undesirable scatter effect by multiplicative scatter correction (MSC), a data transformation method (Rinnan et al., 2009) (see Supplementary information, SI 1). The spectral features of the freeze-dried strawberry samples were conserved, while background offsets and slopes were largely removed after the MSC. The MSC facilitated the removal of physical effects like particle size and surface blaze from the spectra, which do not carry any chemical or physical information (Maleki et al., 2007). Only the fingerprint region of the data was selected for analysis, including MSC, rescaling between 0 and 1, and subsequent multivariate analysis. Raw spectra were normalised and averaged.

2.4. Ascorbic acid

The ascorbic acid content of the strawberry samples was analysed by HPLC with a slight modification of the method described by Uckoo et al. (2013). Briefly, the strawberry samples were homogenised at 24,000 rpm using an UltraTurrax T-25 Tissue homogeniser. 1 *g* of the homogenate was diluted with 1 mL of 3% metaphosphoric acid, in a centrifuge tube and mixed for 900 s. The diluted sample was centrifuged at 10,000 rpm for 10 min and the clear supernatant was filtered through 0.45 μm membrane filter. 10 μL was injected into the HPLC for analysis.

The HPLC system consisted of a Waters 600 Satellite connected to a Waters UV-tuneable absorbance detector and Waters autosampler (Waters, Ireland). The mobile phase consisted of isocratic 3 mM phosphoric acid in water maintained at a flow rate of 16.67 μL/s. Ascorbic acid was separated on a C-18, Phenomenex Gemini-Nx series column (Phenomenex, U.K.), 5 μm particle size, 11 nm pore size (250 mm × 4.6 mm). Peak separation of ascorbic acid was monitored at 254 nm wavelength. Five concentrations of ascorbic acid standard in 6% metaphosphoric acid in the range 10–100 μg/mL were injected, and the peak area was determined (see Supplementary Material SI 2). Chromatographic data was collected and processed using Empower2 software (Waters, Ireland).

2.5. Anthocyanin content

For extraction, the strawberry samples were homogenised at 24,000 rpm using an UltraTurrax T-25 tissue homogeniser. 5 g of the homogenised strawberry puree was mixed with 10 mL of 7:3 acetone: water mixture (with 0.1% Acetic acid) and sonicated for 600 s. Following sonication, the mixture was centrifuged for 600 s at 1500 *g*, 4 °C and the supernatant collected. 10 mL of acidified methanol (0.1% acetic acid) was added to the residue, sonicated for 600 s, followed by centrifugation for 600 s at 1500 *g* (4 °C) and the supernatant was collected. The supernatants obtained were pooled and dried under a constant nitrogen flow of ∼1 mL. The volume was made up to 10 mL using water and methanol mixture (1:1 with 0.1% acetic acid). The extract was injected after filtration through 0.45 μm PTFE syringe filter (Phenomenex, U.K) and placed in an auto-sampler vial.

The HPLC system consisted of a Waters 600 Satellite connected to a Waters UV-tuneable absorbance detector and Waters auto-sampler (Waters, Ireland). Separation was carried out on a C-18 Phenomenex Gemini-Nx column (Phenomenex, U.K.), 5 μm