Microwave Plasma Torch Generated in Argon for Small Berries Surface Treatment

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Featured Application: A cold gaseous plasma torch operating at low powers at atmospheric pressure, applicable in food treatment, could significantly decrease food surface microbial contamination without the use of harmful chemicals.

Abstract: Demand for food quality and extended freshness without the use of harmful chemicals has become a major topic over the last decade. New technologies are using UV light, strong electric field, ozone and other reactive agents to decontaminate food surfaces. The low-power non-equilibrium (cold) atmospheric pressure operating plasmas effectively combines all the qualities mentioned above and thus, due to their synergetic influence, promising results in fruit surface decontamination can be obtained. The present paper focuses on the applicability of the recently developed microwave surface wave sustained plasma torch for the treatment of selected small fruit. Optical emission spectroscopy is used for the determination of plasma active particles (radicals, UV light) and plasma parameters during the fruit treatment. The infrared camera images confirm low and fully applicable heating of the treated surface that ensures no fruit quality changes. The detailed study shows that the efficiency of the microbial decontamination of selected fruits naturally contaminated by microorganisms is strongly dependent on the fruit surface shape. The decontamination of the rough strawberry surface seems inefficient using the current configuration, but for smooth berries promising results were obtained. Finally, antioxidant activity measurements demonstrate no changes due to plasma treatment. The results confirm that the MW surface wave sustained discharge is applicable to fruit surface decontamination.

Keywords: microwave discharge; surface wave sustained discharge; atmospheric pressure plasma torch; low-temperature plasma; plasma diagnostics; active particles’ distribution; biomedical plasma applications; food treatment and sterilization
1. Introduction

During the last decade, consumers have been seeking more nutritious, less chemically processed foods. They are expecting “bacteria-free” products with high quality and long shelf life. These rather contradictory demands lead to a new interdisciplinary field of study that combines physics, biology and chemistry in food safety investigations, focused on guaranteeing and improving nutritional qualities. That is why plasma technologies and their applications in the food industry have become one of the newest trends in scientific research. The number of interdisciplinary scientific papers focused on cold atmospheric plasma (CAP) sources for food treatment and sterilization has increased significantly, mainly in the last decade [1–6]. The plasma applied for the food exposure must be a non-equilibrium one with a gas temperature around 20–50 °C to avoid the degradation of vitamins, proteins and other biological and biologically active compounds. On the other hand, the treating gas must be well activated, i.e., it must contain a high concentration of agents initiating bacterial inactivation. These conditions can be very effectively fulfilled by Atmospheric Pressure Non-Thermal Plasmas (APNTPs), where the neutral gas temperature (i.e., the temperature related to the kinetic motion of heavy particles—atoms, molecules and ions) remains close to the ambient one but the free-electrons temperature typically reaches thousands of Kelvin. Thus, APNTPs generate ionized gases at conditions far from the thermodynamic equilibrium. Using common gases such as air or argon, one can produce reactive oxygen and nitrogen species (ROS and RNS) [7,8] as well as ozone [9], oxides, peroxides and monoxides [10], even in a short treatment time of a few seconds. Additionally, the electrical discharge plasmas also produce effectively ultraviolet (UV) radiation in UVC range and vacuum ultraviolet radiation (VUV) that have strong bactericidal effects [11–13]. Such devices [14] could be built on the base of the corona discharge [15], the dielectric barrier discharge [16], the glow discharge [17], the plasma jet or the nanosecond pulsed discharge [18]. To achieve good bactericidal results without any harm to the food quality during the non-equilibrium plasma treatment requires low power, low temperature and short treatment times. Additionally, the technological simplicity and robustness (including a long operation lifetime without any service) of devices are required.

There is plenty of evidence for the potential of CAP in spoilage prevention of various food products and extension of their fresh state. Recent studies showed that cold plasma is efficient in the inhibition of food-borne bacteria such as Escherichia coli [19], Salmonella typhimurium [20], Staphylococcus aureus [21] and Listeria monocytogenes [22]. It is also effective against yeasts and molds [23]. Although the detailed mechanisms of cold plasma interaction with food are still not fully understood [24], the cold plasma (DBD, plasma jet) effect has been studied in surface decontamination of perishable fruits such as strawberries [25,26], blueberries [27,28] or food model systems [29].

The aim of this paper is the investigation of how a surface wave sustained plasma torch operating in argon at a 2.45 GHz wave frequency [30] interacts with strawberries, cherries and blueberries. Resistance of a fruit-borne population of microorganisms after the plasma treatment at various conditions is studied. Optical emission spectroscopy is used for reactive species determination. Thermal imaging during the treatment gives information about the fruit surface temperature. The effect of CAP on the antioxidant properties of the treated fruits is examined, too.

2. Materials and Methods

2.1. Experimental Setup

A simplified scheme of the experimental setup is presented in Figure 1. The solid state microwave generator operating at 2.45 GHz (Sairem, Neyron, France, GMS 200 W) was connected by a coaxial cable to a commercial electromagnetic surface wave resonator (Sairem, SURFATRON 80). Microwave (MW) power supplied from the generator was adjustable in order to optimize discharge conditions; the powers of 5 W, 7 W and 9 W were used in the present study for the fruit surface treatment. The surfatron resonator was continuously cooled by the ambient air flow of 4 L/min at room temperature without any resonator water cooling. Argon (purity of 99.999%) flow of 7 L/min was controlled by Omega
FMA-A2408 or Voegtlin Red-y compact mass flow controllers. The discharge was created inside a quartz tube (with the real dielectric permittivity \( \varepsilon_r = 3.2541 \) and imaginary one \( \varepsilon_i = 0.0062 \)) with 8 mm outer diameter and 3 mm inner diameter. The ambient air (temperature of 25 °C at a relative humidity of (35 ± 2)% was surrounding the plasma effluent just behind the resonator. The system axis was installed vertically with the gas flow from top to bottom (see Figure 1).

Visual observations of the plasma torch and its dependence on the MW power were made using a SONY (Sony Corporation, Minato, Tokyo) DSC-H7 camera with an exposure time of 1/10 s. An FLIR (FLIR Systems, Wilsonville, OR, USA) E30 Infrared Camera was used for thermal imaging during the fruit plasma treatment.

Optical emission spectrometry was used for the plasma diagnostics during the fruit treatment. The light emitted by the discharge was focused by a quartz lens (diameter of 25 mm, focal length of 35 mm) to the entrance (positioned at the lens focus) of a multimode optical cable connected to the spectrometer. This setting allowed proper measurement of emitted light in case the discharge channel was moving across the capillary diameter. Such an effect is well known from the literature [31]. A rectangular nonreflecting light guide made of black paper (wide of 25 mm, high of 0.4 mm) was installed at the optical axis horizontally in front of the lens to obtain a good axial resolution. A Jobin Yvon TRIAX 550 spectrometer (Horiba, France) with a LN2 cooled back illuminated CCD (1025 × 256, pixel size of 26 × 26 μm²) was used for the spectra acquisition. The whole spectra acquisition system was calibrated with respect to its spectral response using the standard Ocean Optics (Largo, FL, USA) DT-MINI-2-GS source and measured spectra were corrected with respect to the system spectral response for the plasma parameters’ calculation. Bands of NO-gamma, OH (\( A \rightarrow X \)) and \( N_2 \) first negative and second positive systems and argon and oxygen atomic lines were determined in recorded spectra. Rotational temperatures were calculated using the Boltzmann plot methods from the OH (\( A \rightarrow X \)) 0–0 transition and the nitrogen second positive 0–2 band. Vibrational temperature was calculated by the same method, using the band head intensities of the nitrogen second positive +2 sequence. The excitation temperature of argon atoms was calculated from integral intensities of selected argon lines. All technical details of these calculations as well as spectra identification were published recently [32] and thus are not repeated here.

![Figure 1. Scheme of the experimental set-up.](image-url)
2.2. Plant Material and CAP Treatment

Fresh strawberries, cherries and Canadian blueberries with uniform size and free from surface defects were purchased from the market and stored at +4 °C prior to the experiment. After individual storage in 15-mL sterile plastic containers, fruits were treated with the CAP, allowing the plasma torch tip to get in contact with the fruit’s surface.

Cherries, strawberries and blueberries were divided into four groups of 10 pieces and treated for 15, 30, and 60 s; one group was left as the control sample. MW power for this set of experiments was fixed to 9 W, argon flow to 7 L/min and cooling air flow to 4 L/min. The end of the quartz discharge tube was 2 mm outside the surfatron resonator and the plasma jet length was 9 mm. All fruits were treated individually at the torch tip without any movement.

The second set of experiments was done with blueberries only. Each sample contained 10 blueberries. Nine samples were treated according to the conditions given at the end of this paragraph. Additionally, one sample was exposed to argon flow without plasma and one sample was used as a control. Argon and cooling air flows were fixed again to 7 L/min and 4 L/min, respectively. The end of the quartz discharge tube was 2 mm outside the surfatron resonator and the plasma jet length was 9 mm, 7 mm, and 4 mm, respectively to powers of 9 W, 7 W, and 5 W. All fruits were treated individually with the plasma torch tip without any movement for times of 15, 30, and 60 s.

2.3. Sterilizing Effect of CAP Treatment

After the plasma treatment, the surface of all fruits was washed by adding of 5 mL sterile deionized water and 0.5 mL solution of 25 mM NaCl and 0.05% NONIDET™ P40 to each container. The containers were shaken for 30 min at 160 rpm. One milliliter of the liquid sample from each container was centrifuged in a tube for 4 min at 13,000 rpm using the Sigma (Sigma Laborzentrifugen GmbH, Osterode am Harz, Germany) 1-15PK centrifuge. After discarding 0.85 mL of the supernatant, the sedimented microorganisms were briefly shaken in the remaining solution (0.15 mL). The obtained suspension containing the microorganisms was spread on plates with the Lysogeny broth (LB) agar medium and incubated at 37 °C for 72 h. The total number of colony-forming units (CFU) on each plate was counted after the incubation time. The average CFU number was calculated for each group in order to estimate the sterilizing effect of the CAP treatment.

2.4. Antioxidant Activity of Methanolic Fruit Extracts

All treated fruits and control samples were frozen in liquid nitrogen and homogenized using the TissueLyser (QIAGEN, Hilden, Germany). One hundred milligrams (fresh weight) of the obtained powder, placed in a tube, were extracted with 50% aqueous methanol in the weight/volume ratio of 1/3. The extraction was conducted on a multi vortexer (VWR) at 1000 rpm for 1 h at room temperature. After the extraction, the samples were centrifuged at 12,000 rpm for 15 min and the supernatants were further analyzed by a DPPH scavenging assay.

The DPPH scavenging assay is based on discoloration of the DPPH (2,2-Diphenyl-1-picrylhydrazyl) radical solution and was conducted by the method described by Brandwilliams et al. in 1995 [33], modified for a microplate reader. Ninety-five microliters of each sample extract or methanol (as a control) were mixed with 0.65 mL of 0.1 mM DPPH (Sigma) methanolic solution in a 96 Nunc® DeepWell™ plate (Sigma) and incubated in the dark for 30 min at room temperature. The absorption was measured at 492 nm on a Biochrom EZ Read Microplate Reader (Biochrom Ltd., Cambourne, Cambridge, UK). DPPH inhibition percent was calculated according to the following formula:

\[
\text{% inhibition} = \left[\frac{\text{Abs control} - \text{Abs sample}}{\text{Abs control}}\right] \times 100,
\]

L-ascorbic acid (Sigma) was used for the construction of the standard curve. The data were presented as L-ascorbic acid equivalents (µg) in 1 mg of fresh weight according to the standard curve.
3. Results

3.1. Visual and Thermal Imaging

The plasma torch length is proportional to the applied MW power, as demonstrated by Figure 2.

![Visual plasma torch length as a function of MW power](image)

**Figure 2.** Visual plasma torch length as a function of MW power ((a) 5 W, (b) 7 W and (c) 9 W) for the fixed argon flow of 7 L/min with 4 L/min of air cooling. The torch length dependence on MW power in region of 4–12 W (d). The end of the quartz discharge tube is 2 mm outside the surfatron resonator and the presented length is measured with respect to its end.

The total length of the plasma torch is an important parameter with respect to the treatment because of active particles’ distribution [32]. The low limit of power convenient for the plasma treatment is the plasma torch length: plasma outside the discharge tube should be at least 4–5 mm long in order to be in contact with the sample. The increase of MW power leads to the extension of the torch and the dependence on the torch length is directly proportional to the applied power (see Figure 2). However, the wave power increase also influences the gas temperature of the plasma torch, which increases accordingly. The upper limit of power is determined by the maximum temperature achieved at the sample surface. To determine this parameter, infrared camera measurements were carried out. In this way, the minimum wave power for the fruit treatment is set to 5 W and the maximum power is 9 W. (In some cases 5 W is not enough power for good contact between the plasma torch and the sample; 7 W is the lower power limit in these experiments.)

The infrared camera images of cherries’ and blueberries’ surface temperatures during the plasma treatment and a short period after it are presented in Figures 3 and 4, respectively. The treated surface was positioned at the tip of the plasma torch (i.e., 9 mm away from the quartz capillary end), perpendicular to the torch axis. The maximum temperatures for both fruits investigated during the plasma treatment are presented in Figure 5, where the average value of 10 pieces treatment is shown. It is clearly visible in both cases that the temperature of the treated fruit at the contact point with the plasma torch increases and the affected area with the elevated temperature increases with the treatment time duration. The total thermally affected area is comparable for both fruits, but due to the smaller volume of the blueberries in comparison with the cherries it is bigger with respect to the total fruit surface. The maximum temperature of the treated area achieved on the cherries’ surfaces is lower than the temperature on the blueberries’ surfaces (10 to 15 °C), while the initial temperature was more or less the same. This can be expected, keeping in mind that the blueberries’ mass is smaller than the cherries’ mass, while the thermal energy transferred from the plasma to each fruit is almost the same for a fixed treatment time and power. The orientation of the fruits and their sizes do not play a role in heating generally, while a reflection of the gas flow from the Petri dish can be much higher and thus is a potential reason for the temperature increase. Additional measurements should be done to confirm this hypothesis. The surface temperature relaxes quite fast when the plasma treatment is finished. The highest temperature obtained is still low (obtained for a short time) to initiate any
visually remarkable changes at the fruit surface. The fast surface cooling reflects the fact that there is little heating of the fruit volume.

**Figure 3.** Thermal images of cherries’ treatment at different times with MW power of 9 W, the argon flow of 7 L/min and the cooling air flow of 4 L/min. Treatment is realized by the edge of the discharge. Red triangle—maximal temperature; blue triangle—minimal temperature.

**Figure 4.** Thermal images of blueberries’ treatment at different times with MW power of 9 W, the argon flow of 7 L/min and the cooling air flow of 4 L/min. Treatment is realized by the edge of the discharge. Red triangle—maximal temperature; blue triangle—minimal temperature.
The intensity profiles of selected active species are shown in Figure 6. The presented intensities were not corrected to the device spectral sensitivity, so all values are relative. The NO radiation increases along the torch axis up to its end (i.e., the highest intensity is observed at the treated surface). Intensities are higher during the fruit treatment. We suppose that this is due to the more turbulent flow along the torch because of flow reflection by the fruit and mainly by the Petri dish used as the fruit holder. Thus, better mixing of the plasma argon flow with the surrounding gas is obtained. This effect is higher during the treatment of smaller fruits because of the shorter distance between the discharge and the Petri dish. The OH radical intensity follows the profile of argon lines intensity (see recently published data in [32]), which is a result of the slow quenching of the surface electromagnetic wave propagating along the plasma torch (for the detailed theory of the surface wave sustained MW discharge, see [34] and the Supplementary Materials of [32]). The enhancement of intensities during the fruit treatment with respect to the free jet can be explained by the combination of two effects. The first is the change in the gas flow (more turbulent, especially during the treatment of small fruits) and, additionally, by the humidity increase due to the presence of fruit and water evaporation. The intensities of the nitrogen molecular ion (and also excited molecular nitrogen, which is not presented graphically here) and atomic oxygen show an increase at distances closer to the quartz capillary end and later follow the general intensity decrease of all other species (except NO). The stronger increase in nitrogen molecular ion intensities during the fruit treatment is rather surprising and its explanation will be a subject of further experimental as well as theoretical studies. The atomic oxygen intensity decrease during the fruit treatment is a result of atomic oxygen consumption by the OH radical formation. A small O intensity enhancement under the fruit treatment point is due to the reflection of the torch radiation by the humidity increase due to the presence of fruit and water evaporation. The intensities of the nitrogen molecular ion (and also excited molecular nitrogen, which is not presented graphically here) and atomic oxygen show an increase at distances closer to the quartz capillary end and later follow the general intensity decrease of all other species (except NO). 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the fruit surface that is more efficient in the near-infrared spectral region than in the ultraviolet and visible regions.

![Intensity profiles of the selected active species along the plasma torch during the fruit treatment. Zero position is the end of the quartz capillary, the fruit surface was positioned at 9 mm (the tip of the plasma torch). MW power of 9 W, the argon flow of 7 L/min and the cooling air flow of 4 L/min were maintained in all cases.](image)

Based on the selected band intensities, the plasma parameters were calculated according to the Boltzmann plot methods (for details of calculation, see [32]). The excitation temperature of argon atoms was about \((4400 \pm 200)\) K regardless of the fruit treated. The vibrational temperature calculated from the nitrogen second positive system was \((3200 \pm 100)\) K at the end of the quartz capillary and decreased linearly to \((2800 \pm 100)\) K at the treated surface regardless of the fruit type. The rotational temperature obtained from the nitrogen second positive system was \((2400 \pm 150)\) K at the end of the quartz capillary and decreased linearly to \((1800 \pm 150)\) K at the treated surface. The rotational temperature obtained from the OH radical was \((650 \pm 50)\) K at the end of the quartz capillary and decreased linearly to \((600 \pm 50)\) K at the treated surface. Also, the rotational temperature was independent of the type of fruit treated. All these results are in good agreement with our recently published detailed torch characterization [32], and they fully confirm the fact that such plasma is strongly non-equilibrium.

3.3. Plasma Inactivation of Microorganisms at Fruit Surface

The results of the weighted average number of the total colony-forming microorganism units (no microorganism specified) are presented in Figure 7. There is no significant variation in the number of colony-forming microorganism units between the groups for strawberries, as is shown in Figure 7 on the left. This means that no bacteria inactivation is achieved.
In contrast to strawberries, for both cherries (Figure 7, middle) and blueberries (Figure 7, right) a decrease in the number of colonies is observed. For cherries, the treatment duration of 15 s has a negligible effect, but a longer treatment of 30 or 60 s has a positive effect, as shown in Figure 7 (middle). The most pronounced antimicrobial effect of the plasma torch treatment is detected for blueberries, where 30 and 60 s treatment durations cause a reduction in the CFU number (Figure 7, right).

The inhibiting impact of the plasma torch is determined by the surface characteristics of the tested fruits and the kind of microbial contamination. Strawberries often grow in contact with the soil microbiota and their rough surface covered with seeds would requires prolonged plasma exposure. In contrast, smooth fruits as cherries and blueberries would be easier to disinfect. Bearing in mind the smaller size of the blueberries, one can assume that the most pronounced antimicrobial effect obtained after their treatment is due to the larger relative surface area in contact with the plasma jet. Because of the higher temperature of the blueberries’ surface, one can assume that thermal effects play an important role in this case.

Comparing the results in Figure 7 with those in Figure 6, one can assume that there is a correlation between the NO intensity (i.e., the NO density) and a decrease in the number of colonies in the different types of fruits. The NO intensity strongly increases close to the plasma torch end where the cherries and blueberries are. The NO intensity at this axial position is lower when the strawberries are treated and there is no effect on the microorganisms in this case. Similar behavior, but with less significant a difference for the strawberries, can also be seen for the OH intensity. The obtained results suggest the need for specific CAP adjustment for the treatment conditions depending on the particular object.

Optimization of the gas discharge conditions may result in a change in the total number of vital microorganisms (i.e., microorganisms able to replicate). Results for blueberries treated at different discharge power are presented in Figure 8.

The most investigated variation of the treatment conditions is directed to decrease the average number of CFU per group compared to the control group. The results obtained show two interesting features that are in contradiction with the expectations and results obtained for other plasma sources.
The better results in microorganism deactivation are obtained at lower wave power (5 W, Figure 8 left). At low power (5 W and 7 W) the treatment time of 30 s gives the best results. Increasing the treatment time to 60 s does not lead to a decrease in the colonies; a slight increase can even be noticed, but it is within the error range. The assumption of the importance of the thermal effect does not correlate with the obtained results. The worst results in microorganism deactivation are obtained at the highest power used in this experiment (9 W) when the surface temperature of the fruits is the highest. However, in this case the longer treatment time is more effective (see Figure 8 right). The standard deviation of the results for all investigated groups is without any significant change compared to the single result deviation.

That is why we can conclude that the bigger amount of fruits in the single group is necessary for precise statistical analysis or additional investigation of the discharge conditions in order to optimize the sterilizing effect of the plasma torch.

3.4. Antioxidant Activity Measurements

After the fruits were washed in the saline solution, each was homogenized and the method of the stable free radical diphenylpicrylhydrazyl (DPPH) was used to estimate the activity of antioxidants [35]. It was calculated as an equivalent µg of L-ascorbic acid (vitamin C, vitC) per mg of fresh weight, averaged for each group. Results for antioxidant activity for each group of the treated berries are presented in Figure 9.

![Figure 9.](image-url)

The antioxidant activity is not significantly affected by the fruit surface treatment by the MW plasma torch at any time duration or applied power, as shown in Figure 9. We assume that this is mainly due to the fact that the plasma-fruit interaction is limited to the fruit surface and thus all changes are below the used method resolution. We suppose that a very long treatment might lead to a decrease in antioxidant activity.

4. Discussion

The obtained optical emission spectroscopy experimental results show the presence of various active species that can play a significant role in fruit surface sterilization. The initiated processes can lead to bacteria inhibition, death or even their whole destruction by the cell wall opening. First of all, the presence of a nitrogen monoxide radical (NO) can start more bacteria deactivation processes. The UV radiation of this radical belongs to the UVC region, which is well known for its bactericide effects [13,36]. Simultaneously, the NO radical is very reactive and, in a reaction with water (present also at the fruit surface), forms nitrous acid, which decreases the surface pH. Also, this effect might
contribute to the deactivation of some kinds of bacteria. The OH radical, confirmed by optical emission spectra, is well known as one of the strongest non-selective oxidative species and is strongly indicative of bacteria present at the surface. The results obtained for the NO and OH intensities in the presence of different fruits and the deactivation of microorganisms from the fruit surface show some correlation, and these radicals can be assumed as playing the main role in the microorganisms’ deactivation in our experiments. The presence of atomic oxygen supports the same effect [37], but in our case its intensity decreases when the plasma is in contact with the fruits. All these species also form other active molecules like peroxynitrile, but their role in bacteria deactivation is still not fully understood. Additionally, the presence of atomic oxygen leads to ozone formation, which was successfully tested for food/sterilization bacterial protection [38].

The results obtained show that a shorter treatment time and lower power give better effects in microorganism deactivation. We assume that the electromagnetic field frequency in the microwave region (2.45 GHz) is one of the main reasons for this. All the other plasma sources operate up to the MHz frequencies.

An important result is that the antioxidant activity of the fruits is not significantly affected by MW plasma torch treatment. We are supposing that a very long plasma treatment will lead to its decrease, but long plasma treatment is inapplicable in practice, mainly due to the time and energy consumption.

All the processes described above are running simultaneously and thus many synergetic effects can be expected. It is well known that bacteria have different sensitivity to the separate effects described above. As was shown in the results, the active species as well as the plasma torch conditions are dependent on the position in the plasma torch. Moreover, all properties are dependent on other parameters like the quartz tube dimensions, the surrounding air (mainly its humidity), etc. Thus, the optimization of any device used for food treatment against given bacteria must be completed separately. Also, model fruit samples with selected contamination should be studied after plasma exposure by other methods to verify the mechanism of bacteria deactivation. Some standard procedures currently developed in the field of plasma medicine can be adapted for food treatment.

5. Conclusions

In this paper we have investigated the effect of a microwave-sustained plasma micro torch in argon at atmospheric pressure on small fresh fruits. The fruit’s maximum temperature during the treatment does not exceed the temperature for the biological damage of the fruit contents (like vitamins or proteins), and thus the nutritive value of the fruit is preserved. The antioxidant activity of the fruits is not significantly affected by the plasma treatment. The level of surface bacterial decontamination strongly depends on the kind of fruit. We assume that NO and OH radicals play the most important role in the decontamination process in our experiments. Although not achieving the acceptable deactivation level of microorganisms, the microwave plasma torch shows interesting non-trivial features that need further investigation. More detailed studies focused on the inactivation of selected kinds of bacteria must be completed before application at the technological scale.

Author Contributions: The experimental concept was proposed during personal discussion between all paper authors. The visual measurements (optical and infrared) were carried out by I.T., P.M. and T.B.; optical emission spectroscopy was completed by F.K. All biological experiments were done by K.R., M.R. and I.A. The manuscript writing was done by T.B. and F.K.; final revisions were done by E.B. and Z.K.

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References


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