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DEVELOPMENT OF INDUSTRIAL PROTOTYPE FOR ACTIVATING WATER BY PLASMA JET

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Abstract. Plasma-activated water (PAW) is increasingly used as an antimicrobial washing agent in biomedical and agricultural industries. In this study, an industrial prototype plasma jet utilizing an adjustable 500 W radio frequency (RF) power supply was developed for generating reactive species in water. A laboratory-scale plasma jet was firstly set up to test the effect of plasma on water. After activating 100 mL tap water by air plasma for 60 min, over 500 mg/l nitrate (NO_3^-) and 5 mg/l nitrite NO_2^- were obtained consistent with the increased electrical conductance and the pH reduction. For the industrial prototype, 60 ppm of hydrogen peroxide (H_2O_2) was obtained from the activation of 300 ml water for 120 min. Substituting air by argon drastically increased the H_2O_2 concentration. Although the water substantially evaporated during the plasma activation in vacuum, the low-pressure chamber is advantageous in enhancing H_2O_2 generation. With the water circulation, the PAW can continuously be produced with sufficient reactive species using a shorter activation time. The pressure and the type of gas, as well as the frequency and power in plasma generation, are all adjustable. Cost-effective PAW for industrial sanitization and other research purposes, including stimulation of seed germination and plant growth, can be generated by this flexible system.

Key words: non-thermal plasma, plasma jet, plasma-activated water, reactive species, microbial decontamination.

1. INTRODUCTION

Non-thermal atmospheric plasma is increasingly implemented in biomedical and agricultural sectors [1, 2], because it generates reactive oxygen-nitrogen species (RONS). Essential intermediate and long-live species are hydrogen peroxide (H_2O_2), ozone (O_3), nitrate (NO_3^-), and nitrite (NO_2^-). Electrons, ions, ultraviolet radiation, and electric field in the plasmas also affect biological cells. Before the 2010s, plasma treatments on fruits were primarily aimed at microbial decontamination. Subsequently, the effects of oxidations and induced metabolic pathways on shelf life, sensory, and nutritional qualities of fruits and fruit products have been explored [3]. Non-thermal plasmas were also used to treat meat and dairy products [4].

In non-thermal plasmas, the electron temperature may be as high as 10,000 K, but the ions remain at around the ambient temperature. Their applications are predominantly in the forms of dielectric barrier discharge and plasma jet [1, 4, 5]. The former deploys ceramic materials as high-voltage electrodes for short-pulse or high-frequency power supply to produce a large volume of plasma and ozone. On the other hand, the plasma jet is directed as a plume with a high velocity. These plasma packets propagate through the air and interact with targeted solids and liquids. Improved properties by such interactions lead to extensive use of plasma jets in material processing.

Plasma-activated water (PAW) has become a versatile antimicrobial washing agent for disinfection, wound healing [5], and food decontamination [6]. Reactive species with disinfecting effects on biological tissues are generated in water upon discharging plasma either above or below water surface as described in the literature [7–11]. The effect of PAW on biofilms made it a helpful alternative to the direct plasma exposure in medical treatments and food processing [5, 11]. Applying plasma directly may damage food colors and bioactive compounds during surface sterilization and sanitation [7, 12]. The oxidative effect in lipids by the plasma exposure tends to degrade meat products [4]. Thawing frozen chicken by PAW, Qian et al. found a reduction in microbial contamination and improved protein characteristics [13]. Chaijan et al. used PAW to extend the shelf life of Asian sea bass steaks [14], and its storage ability was further improved by combining PAW soaking with appropriate coating [15]. PAW applications on vegetables and fruits range from decontaminating rocket leafy salads [16] and broccoli sprouts [12], to prolonging goji berries storage [17].

The non-thermal plasma versatility is extended to seed germination stimulation because traditional processes use substantial chemicals for eliminating bacteria on the seed surface. Non-thermal plasma treatments on cereal seeds were carried out by Brasoveanu et al. [18], whereas Mosovska et al. used PAW to treat soybean seeds [19]. Effects of PAW on plant growth were also reported, as exemplified in lettuce [20]. Regarding the safety of PAW, recent investigations have ruled out short-term toxic effects [5, 21].

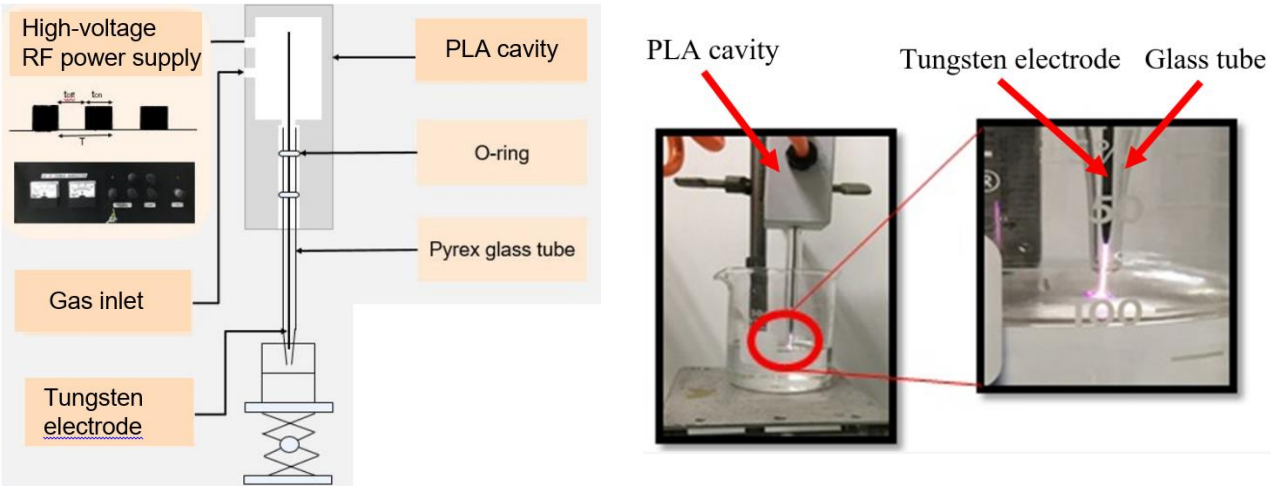
With increasing PAW applications, the plasma jet system for activating water is growing in demand. Most systems used in the literature were on laboratory scale [3, 6]. The effects of the system's geometry have been investigated [22, 23]. For dielectric barrier discharge, the PAW production can be enhanced using a bipolar pulse modulator [24]. The dielectric barrier discharge is generally recommended for O_3 enhancement, whereas the plasma jet gives rise to high concentrations of NO_3^- and NO_2^- [25]. This work demonstrates the development of plasma jet systems for generating NO_3^-/NO_2^- and H_2O_2 in water. The laboratory setup firstly assessed the influence of plasma on water characteristics. The system was then enlarged for industrial use, and reactive species were then measured in water treated by the industrial prototype plasma jet.

2. EXPERIMENTAL

2.1. Development of Plasma Jet Systems

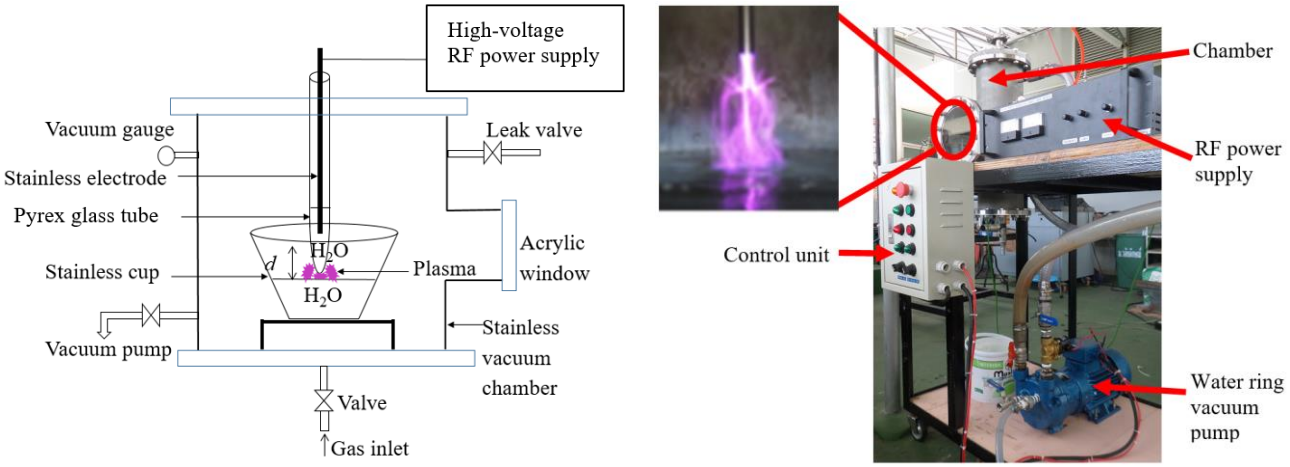
The laboratory-scale setup, schematically shown in Fig. 1a, released a plasma jet through a hollow Pyrex glass tube of 6 mm diameter with a 2 mm inner diameter (Fig. 1b). The tube was 10 cm in length with one taper end. The other end of the tube is fixed in a 3D-printed polylactic (PLA) cavity. Either argon or air was fed into this cavity, sealed by o-rings. Tungsten rod electrode was placed through the middle of the tube's cross-section. This 1.6 mm-diameter rod was connected to a high-voltage radio frequency (RF) power supply. This lab-made power supply was developed based on the system designed for generating dielectric barrier discharge [26]. An impedance matching with around 7.5 pF plasma was needed. The plasma jet was generated using the voltage from 1 to 10 kV with a 50–500 kHz frequency range.

The industrial prototype generated plasma jet at the low pressure, reducing electron collisions with air, to increase the water activation. The system in Fig. 2 incorporated a 5 l vacuum chamber, a water ring vacuum pump (Joto 2BV2060), and a RF power supply adjustable up to 500 W. A stainless steel rod electrode inside a hollow glass tube was used to discharge the plasma jet. Air, oxygen, or inert gas could be selected as feeding gases. A gas flow control system regulated the pressure in the plasma generation. This prototype costed only around 2,500 USD. This budget was predominantly on the vacuum system, i.e., vacuum chamber and flanges (~800 USD), gauge (~100 USD), and water ring vacuum pump (~460 USD). The high-voltage, RF power supply was assembled in the laboratory costing around 1000 USD. The remaining expenses were on pipes and valves (~80 USD) as well as electrode and glass (~60 USD). The electricity consumption was approximately 0.06 USD/h.



(a) (b)

Fig. 1 – (a) schematic diagram and (b) photographic images of the laboratory plasma jet.



(a) (b)

Fig. 2 – a) Schematic diagram; b) photographic images of the industrial prototype plasma jet system.

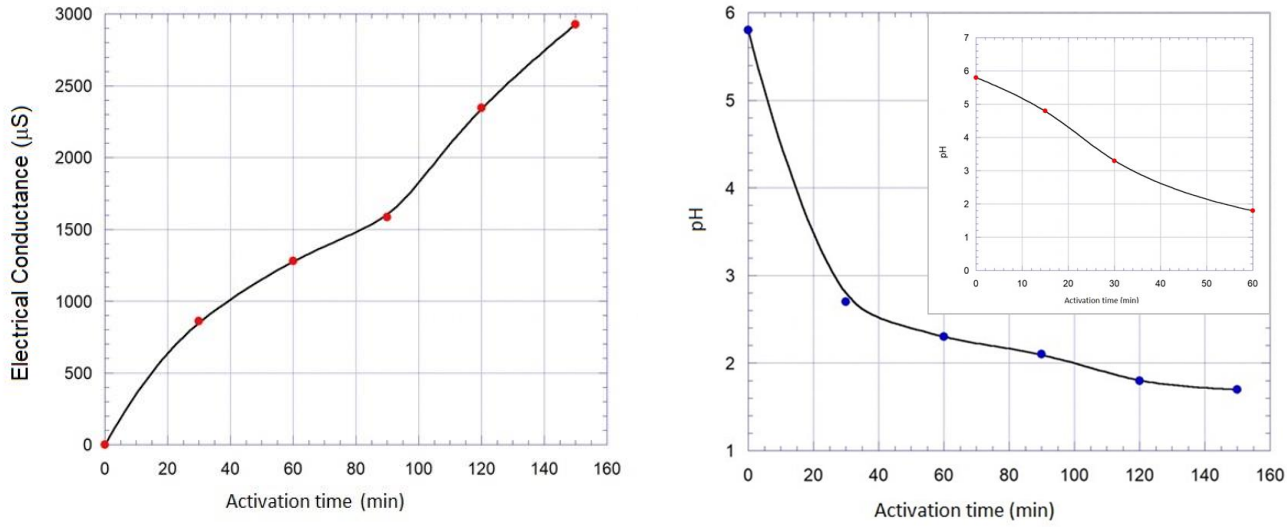
2.2. Preparation and characterization of PAW

The tip of the laboratory-scale plasma jet was placed 0.5 cm above a beaker containing 100 ml tap water. In the industrial prototype, the plasma jet treated 40–1000 ml tap water filled in a cup inside the chamber of 36–760 torr. Exposed to the plasma jet up to 150 min, the pH and electrical conductivity in activated water were monitored by Mettler Toledo Seven Compact pH/Ion meters every 30 min. PAW was also characterized using semi-quantitative "Quantofix" test strips (Macherey-Nagel), namely Nitrate/Nitrite for NO_3^-/NO_2^- and Peroxide 100 for H_2O_2.

3. RESULTS AND DISCUSSION

The plasma plume generated by the laboratory setup using 8 kV and 66 kHz is shown in Fig. 1b. At an electric current of 20 mA, the purple glow discharge is stable. By activating water with the plasma jet, water characteristics drastically change since the initial period. The electrical conductance shown in Fig. 3a is steeply increased from the minimal with an almost linear variation during the 150 min activation. Such increase is consistent with the RONS generation in water by plasma. In Fig. 3b, the pH value exhibits a rapid

reduction from 5.8 to 2.6 after 30 min. The pH then steadily decreases to 1.7 at the end of 150 min treatment. This pH reduction, corresponding to positive hydrogen ions (H^+) from dissociation processes in PAW, was consistent with the literature [17, 19, 25, 27]. When the argon gas replaced the air, the test water was reduced to 40 mL, following previous reports that the pH reduction by argon plasma was slower [25, 28]. As shown in the inset of Fig. 3b, the reduction in pH to less than 2 was obtained within 60 min.



(a) (b)

Fig. 3 – a) Electrical conductance; b) pH of 100 mL of tap water activated by air plasma from the laboratory setup up to 150 min. The pH of 40 mL of water activated by argon plasma up to 60 min is compared in the inset of (b).

Table 1

NO_3^- and NO_2^- concentrations in 100 ml tap water activated by air plasma up to 150 min

Concentration (mg/L)	Activation time (min)					
	0	30	60	90	120	150
NO_3^-	0	100	500	>500	>500	>500
NO_2^-	0	1	5	10	10	10

The negligible NO_3^- and NO_2^- concentrations in tap water before plasma treatments were recorded as a control. The detectable changes after 30 min in Table 1 confirm the generation of reactive species in water. The energy from the plasma jet dissociates N_2, O_2, and water molecules. Subsequent reactions lead to NO_3^- and NO_2^- [5, 27]. Within 60 min, the NO_3^- concentration rapidly reaches 500 mg/l, whereas the NO_2^- concentration increases to 5 mg/l. The rapid NO_3^- generation is often reported and does not follow the linear increase in the one-film theory model [9].

The industrial prototype was adjusted to obtain 105 W and 135–138 kHz for plasma generation. With the airflow rate of 4 l/min, the plasma plume is dispersive, as shown in Fig. 2. Nevertheless, the effects on the water conductivity and pH (not shown here) are comparable to those obtained from the laboratory setup. The industrial prototype was further tested with increasing water to 300 mL and H_2O_2 was measured based on peroxidase enzymatic activity. The results in Fig. 4 shows the H_2O_2 generation by the plasma activation. The increase in concentrations after 20 min is approximately linear, reaching 60 ppm at 120 min. However, such a plasma exposure inside a low-pressure chamber significantly evaporates the water, reducing the volume to 236 ml.

Figure 5 shows the results when the power supply of the industrial prototype is adjusted to 70 W. This power reduction could be advantageous in reducing the energy consumption and water loss during the plasma activation. The H_2O_2 concentration in PAW of varying volume is measured at 10–40 min and compared in Fig. 5a. By activating the 300 and 200 ml tap water for 40 min, the concentration is 30 and 60 ppm, respectively. In the case of 100 ml, the H_2O_2 steeply rises to 20 ppm within 10 min and reaches 90 ppm after 40 min of activation. The activation time could be selected for each batch based on this result. To

explore the possible increase in H_2O_2 generation, the gas and pressure inside the chamber are varied. From Fig. 5b, the use of low pressure substantially enhances the H_2O_2 concentration in PAW. By reducing the pressure from 760 torr down to 120 torr, the H_2O_2 in the 100 ml water after exposing to either air or oxygen plasma for 10 min is increased by over four times. Using the argon plasma, the higher H_2O_2 concentration of 10 ppm is obtained from the activation at the atmospheric pressure and the pressure effect is not as pronounced, saturating around 20 ppm at 250 torr and less. Argon plasmas tend to increase RONS and hence microbial inhibition. It has been reported that argon plasmas prevent radical quenching reactions and therefore increase bacteria inhibition compared to air [22, 25], whereas O_3 concentration is enhanced using oxygen plasma. However, industrial applications tend to exploit the cost-effective air plasma [7].

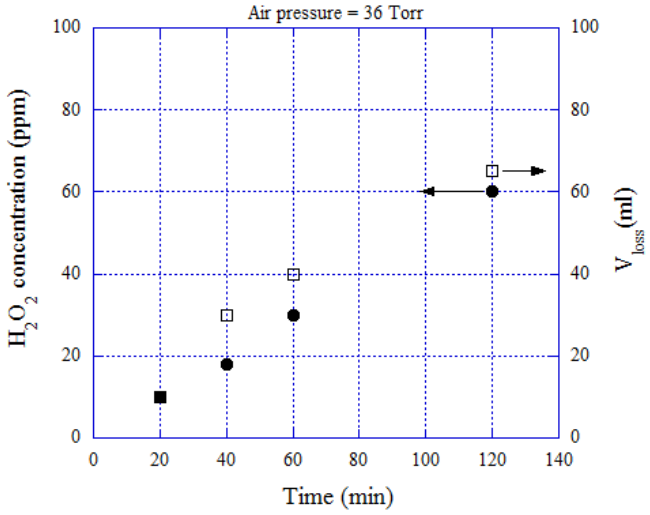
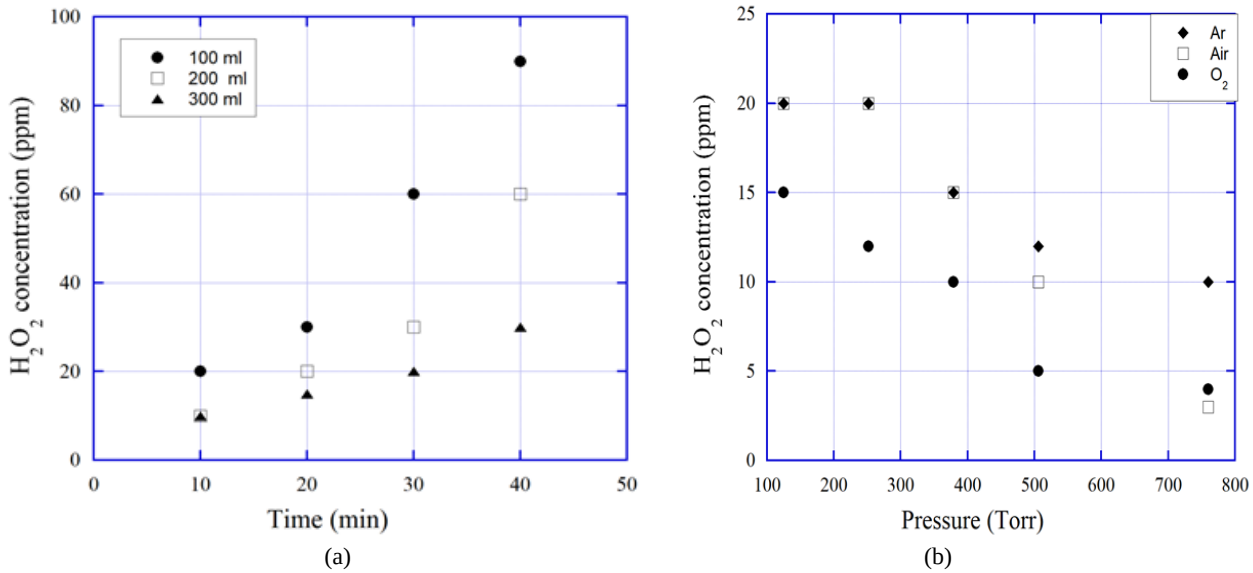


Fig. 4 – H_2O_2 concentration and water loss by activating 300 ml tap water with air plasma in the industrial prototype.



(a) (b)

Fig. 5 – H_2O_2 concentration in PAW from the industrial prototype as a function of: a) activation time from 10 to 40 min by argon plasma under 125 torr with varying water volume; b) pressure of 120–760 torr with varying gas after 10 min activation of 100 ml tap water.

The results in Fig. 5 demonstrate that the proposed industrial prototype plasma jet produce PAW in a larger bath than those obtained from the laboratory setup. With this low-cost and flexible system, the pH, electrical conductance, and RONS concentrations in PAW can be regulated by adjusting gas and RF supplies [5]. However, the water loss by evaporation in vacuum and electrical consumption must be controlled in the large-scale implementation. For cost-effectiveness, the RF power of 70–105 W should be sufficient to

stabilize plasma for generating RONS and the activation time can be selected according to the desirable water volume and RONS concentration. Moreover, the pressure inside the chamber must be adjusted depending on the gas species to control the water evaporation.

Finally, the prospects of modifying and developing the industrial prototype plasma jet are discussed. The PAW production rate higher than 1 l/h can be obtained from this prototype, because the changes in water after activating for 60 min are larger than those in typical PAW applications. For example, the pH of PAW around 4 was implemented [27]. Stoleru et al. treated lettuce using PAW with NO_3^- concentrations of 3 mg/l [20], much less than 500 mg/l obtained in Table 1. PAW with sufficient RONS from a shorter plasma exposure can be continuously produced using a circulation system. The system connecting the chamber to a water reservoir for circulation and storage. The system is applicable to any supply type of water, but the effectiveness may be reduced in the presence of trace metals and organic substances [8].

4. CONCLUSION

Two non-thermal plasma jet systems were developed for generating RONS in water. The treatment of 100 ml water by air plasmas from the laboratory-scale setup for 150 min, increased the electrical conductivity and decreased the pH down to 1.8. Such changes were also obtained by argon plasmas. The concentrations of NO_3^- and NO_2^- in water respectively reached 500 and 5 mg/l within 60 min of activation. Replacing air by argon plasma in the industrial prototype increased the H_2O_2 concentration in PAW. Lower gas pressure inside the chamber down to 120 torr enhanced the H_2O_2 generation. However, the substantial water evaporation by prolonged plasma exposure in vacuum must be considered. Shorter plasma treatments with sufficient RONS could increase the PAW production in the circulation system.

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