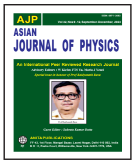

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Analysis of non-thermal atmospheric pressure plasma-source based plasma-activated water for agricultural application

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Dedicated to Prof B N Basu

Design, development, and characterization of cold atmospheric pressure plasma (CAP) source have been carried out to meet the requirements for agricultural applications. The developed source is used to treat water sample at various time intervals to generate nutrient-rich plasma-activated water (PAW). The PAW has been tested at different operating and geometrical conditions to analyze the presence of reactive oxygen and nitrogen species (RONS) such as nitrate (NO_3^-), nitrite (NO_2^-), and hydrogen peroxide (H_2O_2). The concentration of NO_3^-, NO_2^- and H_2O_2 increases linearly in PAW with the increase in plasma treatment time. The developed PAW was also used for the irrigation of wheat grains to observe the effect on plants. The plants that were irrigated with PAW have shown higher germination rate, moisture content, vigour index, growth rate, etc., compared to those with the tap water. Also, there was no sign of microbial infection in the PAW-irrigated seeds. The generated PAW shows high potential to replace use of artificial urea in plants.

Keywords: Cold plasma, Plasma-activated water, Nitrate, Nitrite, Seed germination.

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1 Introduction

The food demand is increasing day-by-day with the rise in population. However, around 40% of food produced in India is wasted each year because of fragmentation and poor storage facilities, and this loss occurs even before the food reaches the consumer [1]. Therefore, there is an urgent necessity for technology that offers high crop production, provides safety and long life to the food grains. Hence, the researchers are seeking an environment- friendly solution that offers a continuous disinfection process, and high crop production within the processing environment. In order to fulfil this requirement, cold plasma technology has been identified as one of the best solutions that overcomes the limitation caused by chemical fertilizers and pesticides such as infertility and poor-quality grains [2-4]. Cold plasma is an environment-friendly technology that has a huge potential application in heat-sensitive applications such as wound healing, agricultural practices, food processing, surface decontamination, and sterilization [3,5]. There are different methods for cold plasma generation such as corona discharge, dielectric barrier discharge (DBD), and atmospheric pressure plasma jets [6,7]. DBD-based atmospheric pressure plasma jets are majorly used in the laboratory because of their ease in design and applications. Cold plasma technology is a single-step process for nitrogen fixation without inducing any external chemical reagent [7].

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The present study focuses on non-thermal/ cold plasma technology in which the design and development of cold plasma source excited by electrical energy have been carried out to meet the upcoming and growing demand for biomedical and food applications. Cold plasma can be applied to the sample directly or by using some media known as indirect method of plasma treatment. Here, water is used as the media.The cold plasma treated water is known as plasma-activated water (PAW). The plasma activated water is found to be rich in various reactive nitrogen and oxygen species (RONS) such as nitrate (NO_3^-), nitrite (NO_2^-), hydrogen peroxide (H_2O_2), ozone (O_3), peroxide (OH), etc., which are necessary for the enhancement of plant growth, production, inactivation of microbes and for many other biomedical applications [8,9]. The presence of hydrogen peroxide (H_2O_2) in PAW makes it feasible for the inactivation of the bacteria, increasing the immunity power of the plants to fight against fungi and viruses. The electrical and optical characterization of the designed cold plasma jet along with the analysis of the PAW parameters at different time intervals have been carried out. The spectrophotometric method is used to measure the absorbance of wavelength by RONS of PAW followed by the calibration curve. The concentration of nitrate and nitrite in water is tested after cold plasma treatment at different time intervals. Also, the effect of the distance of the cold plasma jet from the water surface on the PAW parameter has been investigated. The plasma-activated water (PAW) has been applied to wheat grains in three repetitions to observe plant growth parameters and water absorption. The wheat grains are kept for germination for 15 days which have been irrigated with the produced PAW.

2 Experimental set-up

The typical experimental setup shown in Fig 1 is used for PAW generation. The setup consists of a straight quartz tube with 7 mm and 10 mm inner and outer diameters, respectively. The quartz tube is implanted with a 4 mm diameter electrode whose one end is connected to high voltage. A metallic (aluminum) ring electrode is attached at the open end of the quartz tube for the ground connection. The high-voltage electrode is coupled to a pulsed high-voltage DC supply (10 kV pulse power supply). The gas input nozzle is connected on a side of quartz tube in which the gas is filled through a gas cylinder. The gas flow is controlled by a flow meter (Matheson) that ranges from 1 to 5 SLM.

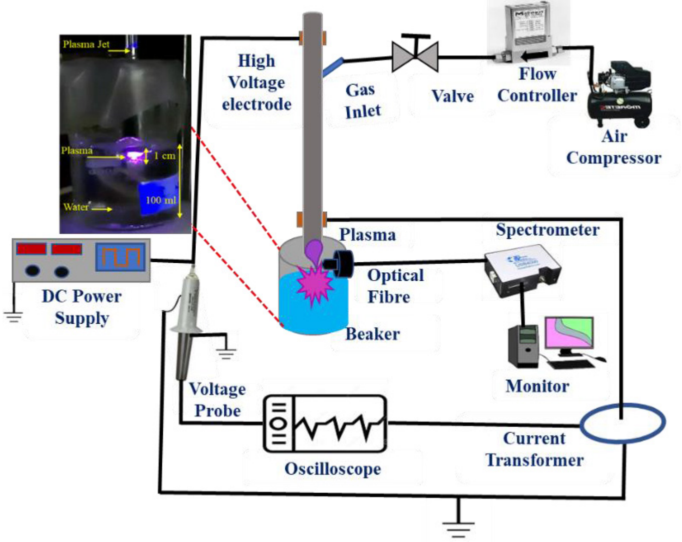


Fig 1. Typical experimental setup of cold plasma jet for water treatment.

For electrical characterization of the PAW, the voltage and current are measured using a high voltage probe (Tektronix P6015 A) and a current transformer (CT) (Pearson Model 110; 0.1VA–1) which are connected to the oscilloscope. A digital oscilloscope is used to record the voltage and the current waveforms (Tektronix DPO 4054, bandwidth: 500MHz) at the operating conditions. For optical characterization, a spectrometer is used to detect the spectrum of the plasma plume and is connected to an optical fiber (Ocean Optics 400 USB) to capture the light rays emitted by the plasma. The spectrometer is connected to the personal computer in which the Spectrasuit software is used for extracting the optical data.

The water sample has been collected from the tap water of CSIR-CEERI, Pilani Rajasthan, India. 100 ml of this water was taken in a glass beaker and kept under the plasma source for the treatment. The cold plasma treatment was carried out on several samples of water maintaining different distances between the jet end-nozzle and the water surface. Also, the plasma treatment of the water sample was done for different time intervals of 0, 1, 3, 6, 9 min (0 min is for the untreated sample) at a supply voltage of 5 kV with a pulse repetition rate of 25 kHz and Argon gas flow rate of 3 SLM. Local wheat seeds were collected for germination and irrigated with PAW and tap water. The results were compared for PAW assisted performance against those for normal tap water.

3 Results

A. Electrical characterization

The typical voltage-current (V-I) characteristics of the designed cold plasma source is shown in Fig 2. The cold plasma jet was operated at the applied voltage of 5 kV with the pulse repetition rate of 25 kHz and Argon gas flow of 3 SLM. The actual voltage was measured through the high voltage probe (Tektronix P6015 A) and current through the current transformer (Pearson Model 110; 0.1VA–1) connected to the oscilloscope (Tektronix DPO 4054, bandwidth: 500MHz).

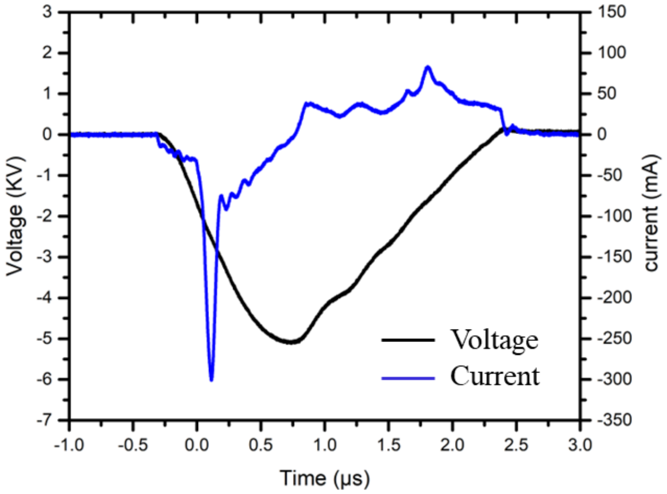


Fig 2. Voltage- Current plot of cold plasma jet at applied voltage of 5 kV with the pulse repetition rate of 25 kHz and Argon gas flow of 3 SLM.

B. Optical characterization

The optical characteristics of the designed source obtained using the spectrometer (HR-400 ocean optics) consisting of optical fibre is presented in Fig 3. A collimating lens is connected to one end of the optical fiber to have the spatial resolution of the plasma plume. Spectrasuit software is used to store the emission spectra of the plasma jet.

The range of wavelengths observed mainly spans from 700 to 850 nm, signifying the argon emission lines, while the wavelengths between 300 and 400 nm denote the presence of reactive oxygen and nitrogen species (RONS). The argon species are observed to be dominating the RONS because of the difference in breakdown potential of gases. Argon gas has lower breakdown potential than the molecular oxygen and nitrogen. There are various RONS forms which are summarized by the following equations:

The collision of the water molecules with an electron results in hydroxide (OH) [10].

$$e + H_2O \rightarrow OH + H + e \tag{1}$$

Also, in case of Ar gas plasma, the excited species are formed and produces OH as they collide with water molecule [10].

$$Ar + e \rightarrow Ar^{+} + e + e \tag{2}$$

$$Ar + e \rightarrow Ar^{+} + e \tag{3}$$

$$Ar^{*} + H_2O \rightarrow Ar + OH + H \tag{4}$$

In addition to the above, some reactions also take place in gaseous state as [11]:

$$e + N_2 + O_2 \rightarrow 2N + 2O + e \tag{5}$$

$$N + O \rightarrow NO + O \tag{6}$$

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

The nitrate and nitrite are formed when the ozone molecules react with the nitric oxide (NO) [12], as follows:

$$O_3 + NO \rightarrow NO_2 + O_2 \tag{8}$$

$$O_3 + NO_2 \rightarrow NO_3 + O_2 \tag{9}$$

Two molecules of the hydroxide react to form hydrogen peroxide known for its antibacterial agents [10]:

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

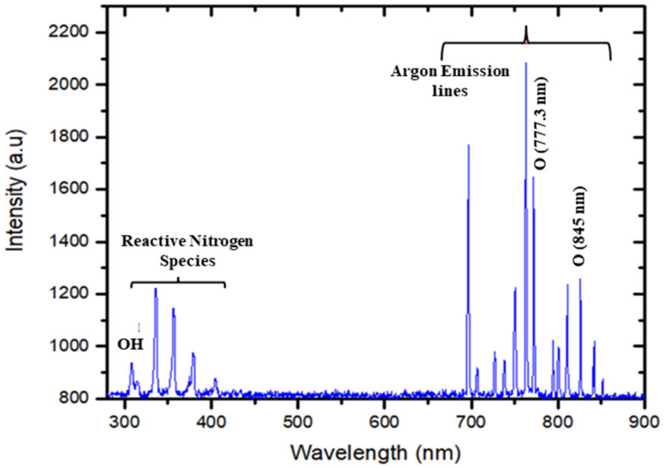


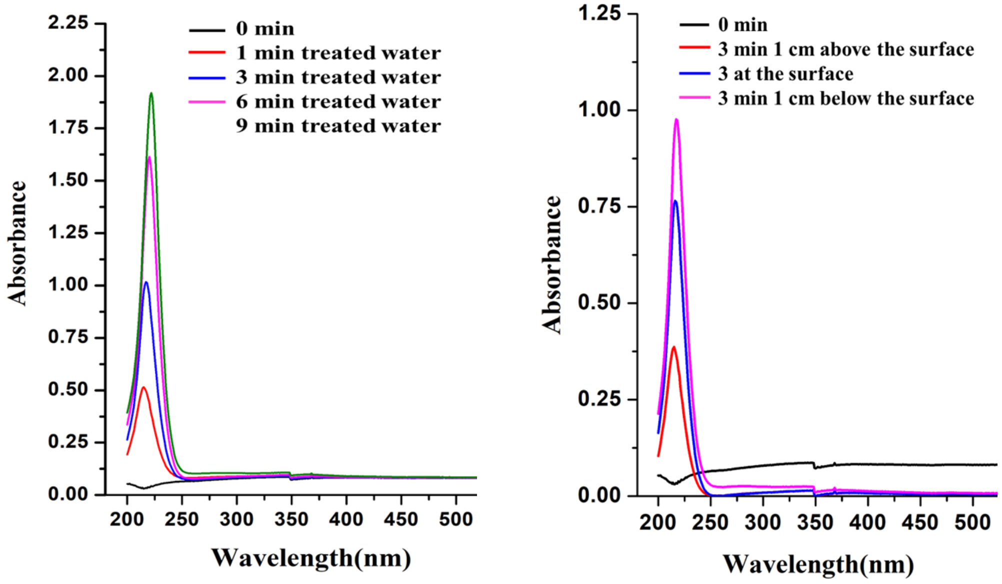
Fig 3. Optical characteristics of cold plasma jet at applied voltage of 5 kV with the pulse repetition rate of 25 kHz and Argon gas flow of 3 SLM.

C. PAW analysis

The analysis of plasma-activated water (PAW) parameters, including nitrate and nitrite concentrations, is conducted through UV-based spectroscopy. Using a conventional single-beam source (Carry UV-Vis 100), the content of nitrate and nitrite in PAW is analyzed, covering a wavelength measurement range from 200 nm to 800 nm. The spectrophotometer shows the diverse wavelengths absorbed by the species (such as nitrate, nitrite, H_2O_2). Initially, a standard curve is formed using standard solutions of nitrate and nitrite with varying concentrations. From this standard curve, the specific wavelengths for the species are determined.

Figure 4 displays the absorbance curve obtained from spectroscopy, indicating peaks in the 200-250 nm wavelength range, representing the nitrogen species band in PAW. Figure 4(a), a depicts the increasing nature of reactive nitrogen species (RNS) with an extended cold plasma treatment time. Figure 4 (b) illustrates the impact of the distance between the plasma jet and the water surface on RNS concentration, revealing a decrease as the distance increases. The highest absorbance is observed when the jet is submerged at a depth 10 mm in the water for a 9-minute treatment.

Furthermore, Table 1 outlines hydrogen peroxide (H_2O_2) concentrations at different intervals of plasma treatment time, with the plasma plume consistently positioned 1 cm into the water surface throughout the entire treatment duration. It has been measured by using the Mquant strips.



(a) (b)

Fig 4. Absorbance vs. wavelength curves were obtained for (a) various distances between the plasma plume and the water surface and (b) different durations of plasma treatment on water.

Table 1. H_2O_2 concentration in PAW when jet is dipped 1 cm into water surface

Treatment Time (minute)	H_2O_2 Concentration (PPM)
0	0
3	1-3
6	3
9	3-10
12	10-15
15	10-15

D. PAW for irrigation

The wheat grains are kept in a petri-dish wrapped with filter paper for germination and are irrigated with 10 ml of PAW on the first day of plantation, while 5 ml of PAW on the 3rd day to maintain the proper moisture content for germination to occur. The germination of grains is shown in Fig 5 after 2 days. On the second day, the grains irrigated with PAW initiated germination, as depicted in Fig 5(b), while the seeds irrigated with tap water did not show any signs of germination Fig 5(a). A faster growth rate in PAW irrigated grains was observed. The seeds irrigated with PAW absorb more water, resulting in a higher concentration of nitrogen species in the grains. This alteration in nitrogen concentration contributes to changes in the morphology of the grain and facilitates faster germination [7-15].

(a) (b)

Fig 5. Seed germination after two days as irrigated with (a) tap water (b) PAW

After 15 days of plantation, the grains irrigated with the tap water was found to have fungal infection while the seeds irrigated with the PAW had no sign of infection as shown in Fig 6. This represents the antimicrobial property of PAW. The PAW consists of NO, and H_2O_2 and possesses enhanced ORP (oxidation reduction potential) which helps the PAW to fight against the microbes [9,16]. All the grains irrigated with plasma-activated water (PAW) exhibited proper germination and nearly uniform, healthy growth, in contrast to the grains irrigated with tap water which have non-uniform sampling growth. Upon analysis of tap water irrigated seeds, it was observed that 2 out of 10 seeds (20% seeds) did not germinate.

(a) (b)

Fig 6. Germination of wheat grains after 15 days of plantation as irrigated with (a) tap water (b) PAW.

4 Conclusion

Cold plasma is an environment-friendly, energy efficient nitrogen fixation process and a residual free source. It has a huge potential in agricultural applications for the germination of seed, crop growth and production. The work presented herein focuses on the design, development, and characterization of cold atmospheric plasma (CAP) sources tailored to meet the needs of heat-sensitive applications. The developed cold plasma sources were used to produce nutrient rich plasma activated water (PAW) for potential agriculture applications. The generated PAW can also be suitably used for biomedical and food processing applications. The results clearly indicate faster germination rate for the wheat grains irrigated with the generated PAW as compared to tap water. The generated PAW is full of many reactive oxygen and nitrogen species.

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References

1. FAO, The State of Food and Agriculture 2021 Making agrifood systems more resilient to shocks and stresses 2021; https://www.fao.org/documents/card/en?details=cb4476en, Rome, FAO,2021.
2. Punith N, Harsha R, Lakshminarayana R, Hemanth M, Anand M S, Dasappa S, Plasma Activated Water Generation and its Application in Agriculture, *Adv Mater Lett*, 10(2019)700–704.
3. Bermudez-Aguirre D, Advances in cold plasma applications for food safety and preservation, (Academic Press, London, U K), 2019.
4. Patil B S, Wang Q, Hessel V, Lang J, Plasma N_2-fixation: 1900–2014, *Catal Today*, 256(2015)49–66.
5. Pal U N, Dubey S K, Parab S, Alexander A, Agrawal M, Achalla V P K, Cold atmospheric plasma therapy in wound healing, *Process Biochem*,112(2022)112–123.
6. Sharma N K, Misra S, Varun, Pal U N, Experimental and simulation analysis of dielectric barrier discharge based pulsed cold atmospheric pressure plasma jet, *Phys Plasmas*, 27(2020)113502; doi: 101063/50018901.
7. Misra N N, Schlüter O, Cullen P (eds), Cold Plasma in Food and Agriculture Fundamentals and Applications, (Elsevier), 2016.
8. Chiappim W, Sampaio A D G, Miranda F, Fraga M, Petraconi G, Sobrinho A S, Kostov K, Ito C K, Pessoa R, Antimicrobial effect of plasma-activated tap water on staphylococcus aureus, escherichia coli, and Candida albicans, *Water*, 13(2021)1480; doi: 103390/w13111480.
9. Ali M, Cheng J H, Sun D W, Effect of plasma activated water and buffer solution on fungicide degradation from tomato (Solanum lycopersicum) fruit, *Food Chem*, 350(2021)129–195.
10. Bolouki N, Kuan W H, Huang Y Y, Hsieh J H, Characterizations of a plasma-water system generated by repetitive microsecond pulsed discharge with air, nitrogen, oxygen, and argon gases species, *Appl Sci*,11(2021)6158; doi. 103390/app11136158.
11. Cheng H, Li Y, Zheng K, Liu D, Lu X, Numerical analysis of nitrogen fixation by nanosecond pulse plasma, *J Phys D: Appl Phys*, 54(2021)184003; doi: 101088/1361-6463/abdf99.
12. Feizollahi E, Iqdiam B, Vasanthan T, Thilakarathna M S, Roopesh M S, Effects of atmospheric-pressure cold plasma treatment on deoxynivalenol degradation, quality parameters, and germination of barley grains, *Appl Sci*, 10(2020)3530; doi: 103390/app10103530.
13. Liu Z, Zhou C, Liu D, He T, Guo L, Kong M, Quantifying the concentration and penetration depth of long-lived RONS in plasma-activated water by UV absorption spectroscopy, *AIP Adv*, 9(2019)015014; doi: 101063/15037660.
14. Joshi H, Kumar R, Meena D, Yadav P C, Explosion of plasma technology in agriculture, *Int J Chem Stud*, 6(2018)2531–2536.
15. Karmakar S, Billah M, Hasan M, Sohan S R, Hossain M F, Hoque K M F, Kabir A H, Rashid M M, Talukder M R, Reza M A, Impact of LFGD (Ar+O2) plasma on seed surface, germination, plant growth, productivity and nutritional composition of maize (Zea mays L), *Heliyon*, 7(2021)6458; doi: 101016/jheliyon2021e06458.

16. Shaer M E, Eldaly M, Heikal G, Sharaf Y, Diab H, Mobasher M, Rousseau A, Antibiotics Degradation and Bacteria Inactivation in Water by Cold Atmospheric Plasma Discharges Above and Below Water Surface, *Plasma Chem Plasma Process*, 40(2020)971–983.

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