Plasma Activated Water Generation and its Application in Agriculture

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Abstract

Use of fossil fuels to produce nitrogenous fertilizer contributes to global warming and climate change. The plasma activated water (PAW) provides an alternative option for nitrogen supply to plant by fixing the nitrogen available in the air into the water using plasma. The PAW is a mixture of nitrate, nitrite, and hydrogen peroxide as its major constituents. In this work, an attempt was made to generate PAW using an efficient and scalable PAW generator. Then plasma is characterized by measuring the power, and OES spectrum. This is a study in which for the first-time arc plasma has been used to demonstrate enhanced plant growth on tomato plant. The results indicate that compared to control, the plants fed with PAW activated for 30 minutes (PAW-30) have 1.5 times higher shoot length, 4 times higher leaf count and more than twice the chlorophyll content in the leaves. The wet weight of the plants fed with PAW-30 was 61% higher than that of the control. Copyright © VBRI Press.

Keywords: Plasma activated water, direct discharge plasma, energy density, tomato, chlorophyll.

Introduction

Global food demand is expected to increase between 60% to 98% by 2050 due to the rising population, diet shifts coming from rising incomes in developing countries, and increasing use of agricultural products for production of biofuels [**1**]. To meet this demand, increasing the agricultural yield is necessary, which needs additional plant nutrients which facilitate higher crop yield. Nitrogen is a vital plant nutrient which plays a major role in the development of dark green leaves, promotes growth of roots, steam, and leaves of the crop eventually leading to increased yield [**2**]. Conventional nitrogen fertilizer production needs fossil fuels. A recent study estimates that almost 1.8% of the global fossil fuel consumption is used for ammonia production [**3**].Use of fossil fuels to produce nitrogenous fertilizer is a contributor to global warming and climate change. At the farmland, the nitrogen fertilizer which is typically available in the granular form is applied (typically sprinkled) to the soil as a shot dose. Urea and Ammonium nitrate are the most common forms of nitrogen fertilizers which in contact with the bacteria in the soil gets converted into plant consumable nitrates. It has been well established that at most 50% of the added nitrogen is converted into this plant consumable nutrient [**4**]. Given all these consequences conventional nitrogen fertilizers, it is imperative to find alternate sources of nitrogen. Use of plasma activated water (PAW) which is rich in nitrogen content can be an alternative to conventional nitrogen fertilizers. This study focuses on generation of nitrogen rich PAW and its application in agriculture.

When air plasma is created above a water column, the nitrogen and oxygen molecules present in the air gets converted predominantly into nitrogen oxides. This eventually dissolve into the water column leading to the formation of PAW, which contains nitrate and nitrite as a major reactive nitrogen species. A small amount of hydrogen peroxide is also generated. The PAW can be generated using different varieties of plasma sources namely dielectric barrier discharge [**11, 12, 13**],spark discharge [**14, 15**], glow discharge [**16, 17**], Gliding arc discharge [**12**] and hot arc plasma [**19**]. The PAW, which is rich in nitrogen species can be generated in-situ, at the point of consumption i.e., at the farmland and can be supplied to the plant in a controlled way either through drip irrigation or sprinkling systems. Nowadays, Plasma was applied to different applications namely agriculture [**5**], waste water treatment [**6**], gas reforming [**7, 8, 9**], material application [**10**] etc.

During recent years researchers have focused on the PAW generation using different methods [**20**]. In this work, the focus was on the PAW generation and its application for plant growth. L. Sivachandiran *et al.* [**12**] have used DBD plasma source for PAW generation. In their study, the PAW was generated using DM water and they report a maximum of 16.22 mg/l of Nitrate and 0 mg/l of nitrite. The PAW generated was used for studying seed germination and plant growth of tomato, pepper and radish seeds. They have observed that, at the end of 5 days, when PAW-30 min was used, the radish plant growth was 45% higher compared with their control. Pepper seeds also showed enhanced growth compared to control. However, they report that there was no significant difference in the growth of tomato seeds between PAW and control. S. Zhang *et al.* [**21**] have generated PAW starting from tap water using atmospheric pressure plasma jet. In their study, they report a maximum of 37 mg/l of nitrate in PAW. They report a comparative study on lentil seeds growth between PAW and chemical-nitrogen fertilizer fed plants. In their 15 days long study, they show that PAW can result in four times higher shoot length vs the control (tap water). F. Jud *et al.* [**22**] used DBD plasma for PAW generation using tap water. They report a maximum nitrate and nitrite concentration of 220.1 mg/l and 5.78 mg/l in PAW respectively. They have observed 38% higher mean length of lentil seeds fed by PAW versus their control which was tap water. Dayonna *et al.* [**18**] have generated PAW starting from tap water, using spark discharge plasma and transferred gliding arc plasma. They report that, they have achieved a maximum of 56 mg/l and 12 mg/l of nitrate and nitrite respectively. In their study, using PAW, growth studies on watermelon, radish, tomato, and pole bean plants were studied. They report that there was no difference in the effect of PAW for plant growth.

From these literatures, it is clear that, increased plant growth from PAW was restricted to few types of seeds namely radish, pepper and lentils. It is also clear that the plasma source used also affects the seed germination and plant growth rates. When direct discharge arc plasma was used as a source of plasma to generate PAW, the reported literature shows no enhanced plant growth. From these studies, there is still scope to enhance the understanding on the effects of PAW for enhanced plant growth. Also, in studies reported, no enhanced growth was observed for tomato seeds fed with PAW.

This study reports for the first-time enhanced growth of tomato seeds with PAW generated from arc plasma discharge. An attempt has been made to develop efficient and scalable PAW generator. PAW was generated using commercially available neon lighting power supply staring from tap water. Arc plasma was generated on the surface of the water. The PAW generated was characterized for its pH, nitrate, nitrite and hydrogen peroxide species using standard techniques. The PAW generated with different activation time was used to study the effect of plant growth on tomato seeds. The details are presented below.

Experimental setup and procedure

Plasma activated water generator and Plasma characterization

Fig. 1 shows a picture of the PAW generation setup used in this study. The setup consisted of a 5 L glass container with a closing lid, a commercially available off the shelf 10 kV, 20 kHz AC neon power supply and a recirculating pump-spray system. The spray nozzle was fixed onto the lid of the 5 L jar. Metal electrodes were used in this study. One electrode was submerged inside the water column, and the other electrode was placed about 18 mm above the water surface.

To generate PAW, 2 L of tap water to be activated was taken in the glass jar. A plasma arc was created between the free surface of the water and the hanging electrode. To ensure proper mixing of the plasma species generated into the water a recirculation pump-spray mechanism was used, with which the water was drawn from the jar using a pump and sprayed from the lid of the glass jar which ensured that the plasma species formed are well mixed in water. The tap water was activated for different lengths of time. The power consumption was measured using a power meter. For all the experiments, the average power consumption was 37±1W. During operation, the plasma operating rms voltage was 10 ± 0.5 kV and the operating frequency was 19 ± 1 kHz. At fixed time intervals, representative PAW samples were drawn from the bottle and was characterized for its parameters. A minimum of three repeats were performed and the average values and standard deviations were incorporated in all the plots.

Optical emission spectroscopy (OES) of the plasma discharge in the air was measured using M/s Ocean optics HR4000 equipment with fiber optic sensor. This spectrometric system had an optical resolution 0.02-8.4 nm full width half maximum (FWHM), wavelength range 190-1100 nm, 300 lines per mm grating density blazed and 5µm slit width. The spectrometric parameters namely integration time and boxcar width were 5s and 0s, respectively.

Plasma activated water characterization

Nitrite concentration in PAW was measured using standard USEPA diazotization method [**23**] using spectrophotometer at 507 nm. Nitrate concentration in PAW was measured using Metrohm-861 advanced compact ion chromatography. H_2O_2 was measured using H_2O_2 Quantofix strips. pH was measured using Thermo Fisher-8172BNWP Ross Sure-Flow Glass pH probe.

Fig. 1. Arc discharge plasma activated water generation setup.

Plant growth

The same method reported by L. Sivachandiran *et al.* [**12**] was used to study the effect of PAW on plant growth for tomato seeds using coco peat as the support material. The plant growth was studied with 10, 20 and 30 min activated PAW while tap water was used as a control. The experiments were run in batch mode. A total of 80 seeds were used for each batch. 20 seeds were taken for each of PAW-10, 20,30 and control in different 100 ml cups, each containing 4 seeds. In each cup, 30 gram of coco peat was used as supporting material. Plant growth study was conducted for 46 days per batch. The plants were exposed sunlight, with 10 ml of PAW addition every alternate day for the first 14 days and 20 ml of PAW addition on alternate days for the rest of the experiment. The growth parameters like length of shoot, wet weight of shoot, leaf count, and chlorophyll were measured after 46 days. The length of root and shoot were measured using ruler scale with a precision of 1mm. The number of leaves was measured by counting them in each plant. The chlorophyll present in the leaves was measured using standard tri-chromatic method [**24**]. Three batch experiments were conducted i.e., a total of 240 seeds were studied and ANOVA analysis was done for all the plant growth parameters.

Results and discussion

Characterization of PAW and plasma

Nitrate and Nitrite concentration in PAW **Fig. 2a** and **Fig. 2b**, shows the nitrate and nitrite concentration as a function of activation time in the generated PAW. It can be seen from **Fig. 2**, that the nitrate concentration of tap water was 1.2 mg/l and the nitrite concentration was 0 mg/l. With activation time, the nitrate and nitrite concentration in PAW increased linearly indicating that the amount of RNS formed is proportional to the exposure time. At the end of 30 min activation, the nitrate and nitrite concentrations in PAW were8 mg/l and 60mg/l respectively. This increase in concentration of nitrate and nitrite in PAW is attributed to the formation of reactive nitrogen and reactive oxygen species in the air plasma. This species subsequently dissolved in water ends up as nitrate and nitrite in water.

Hydrogen peroxide concentration in PAW – The concentration of H_2O_2 was measured using Quantofix strips. The H_2O_2 was between 0-2 ppm for 30 min activation. It is hypothesized that the generation of H_2O_2 in the PAW is due to the generation of OH^- radicals when plasma interacts with water [**15, 17**].

pH of PAW- **Fig. 3** shows the change in pH with activation time. As can be seen from **Fig. 3**, the pH reduction was not very significant with activation i.e., the pH change was only from 7.8 ± 0.1 to 7.0 ± 0.03 after 30 minutes of activation. It is believed that the salts present in the tap water acts like a buffer [**22**] to stabilize the pH in PAW.

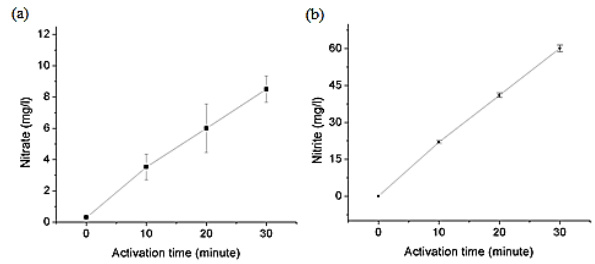

Fig. 2. (a) Nitrate (mg/l) production with different activation time. (b) Nitrite (mg/l) production with different activation time.

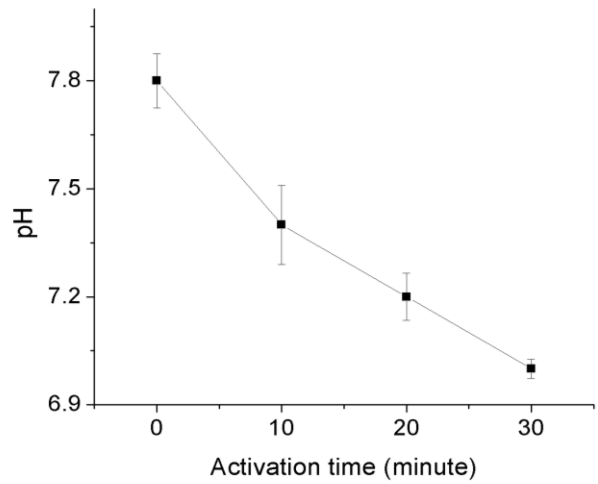

Fig. 3. pH varation with different activation time.

OES –OES is a common technique to diagnosis the plasma. **Fig. 4** shows the OES spectrum captured during activation. As can be seen from **Fig. 4**, peaks of second positive system of Nitrogen between 300-450 nm [**16, 25**] range were present in the OES spectra indicating that the nitrogen species are the major contributor in the spectra. Nitrogen oxides [**25**] generated in the air plasma eventually react with the water column below, leading to the formation of nitrate and nitrite in the water.

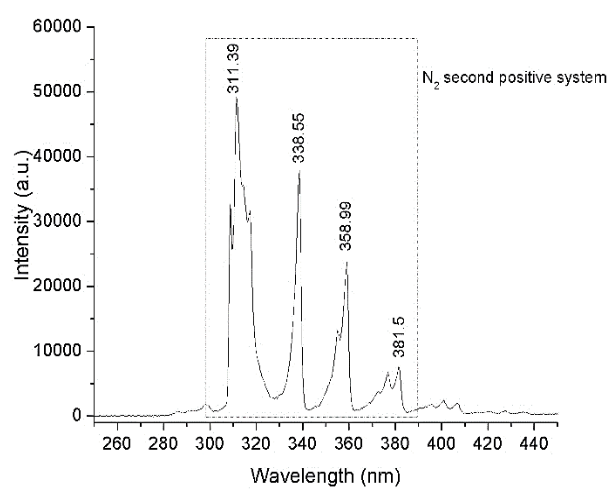

Fig. 4. Optical emission spectra of Direct discharge plasma.

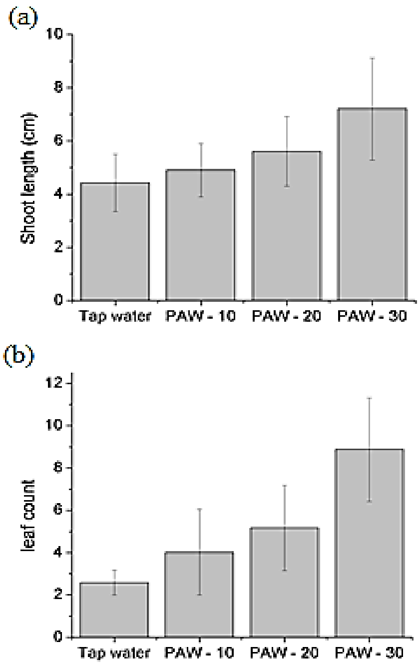

Fig. 5. (a) Shoot length of tomato with tap, PAW 10, 20, 30 min. (b) Leaf Count with different PAW and tap water.

PAW for plant growth

Shoot length of tomato seeds **Fig. 5a** shows the average shoot length measured at the end of 46 days, for different water studied. As can be seen from **Fig. 5a**, the mean shoot length of the control was 4.4 ± 1 cm whereas the mean shoot length of PAW-20 and PAW-30 was 5.6 ±1.0 cm and 7.2 ± 2 cm respectively. Anova analysis of this data also shows that the mean shoot length of PAW-30 was statistically higher than the mean shoot length of the control.

The leaf count – **Fig. 5b** shows leaf count in the tomato plant measured at the end of 46 days for different waters studied. As can be seen from **Fig. 5b**, the leaf count of the control was 3 ± 1 cm whereas the leaf count in PAW-10, PAW-20 and PAW-30 were 4 ± 2, 5 ± 2 and 9 ± 2 respectively. These results indicate that the leaf count with PAW fed plants were statistically higher than that of the control. The increase in the leaf count is attributed to be the combined effects of nitrate and nitrite present in PAW.

Chlorophyll content in the leaves– **Fig. 6a** shows chlorophyll content of the leaves in the tomato plants measured at the end of 46 days for different waters studied. As shown in **Fig. 6a**, the chlorophyll content of the tap water fed leaves was 0.27 ± 0.03 mg/g of leaves whereas that of the PAW-30 was 0.75 ± 0.07 which is more than double of the control. The chlorophyll content in the leaves depends on nitrogen uptake in plants. This result is again attributed to the increased level of RNS present in the PAW, which results in higher levels of chlorophyll content in the leaves. Moreover, as can be seen from **Fig. 7** which shows the pictures of the representative plants, the leaves of the PAW fed plants looked greener and healthier relative to the control.

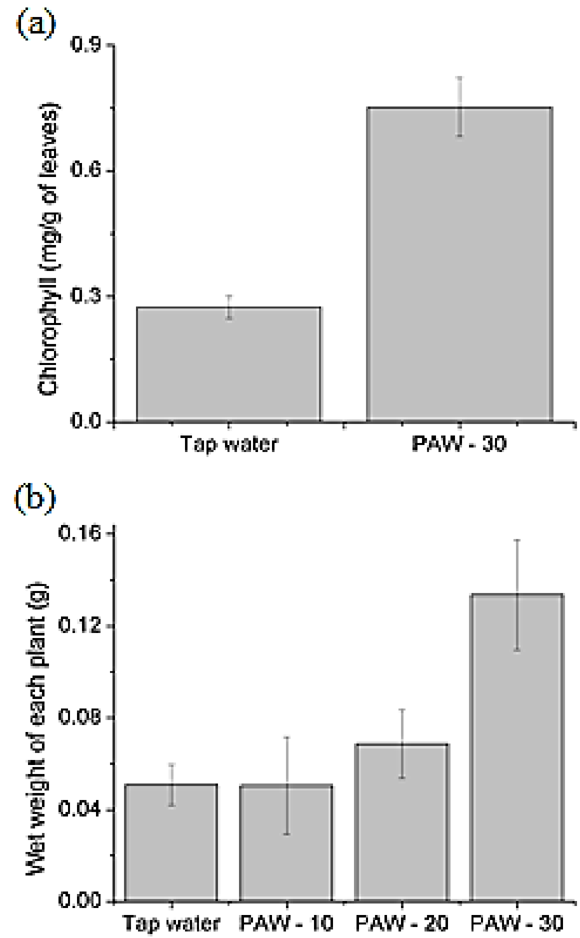

Fig. 6. (a) Chlorophyll comparison between tap water and PAW (b) Wet weight of each plant for different PAW-10, 20, 30 min and Tap water.

Wet weight of each plant shoot – **Fig. 6b** shows the wet weight of each plant shoot measured at the end of 46 days for all the waters studied. Wet weight of each plant shoot is an indication of the overall health of the plant with higher wet weight being an indication of the healthier plant. As can be seen in **Fig. 6b**, the wet weight of control was 0.05 ± 0.01 g whereas that of PAW-30 was 0.1 ± 0.02 g. This increase in wet weight for the PAW fed water can also be attributed to the higher RNS present in the PAW.

This study shows that, PAW is a good alternative for nitrogen fertilizer, due to PAW being a growth enhancer for plants. We hypothesize that, the nitrite content present in the PAW is converted to nitrate by nitrogenous bacteria which helps in the enhancement of plant growth.

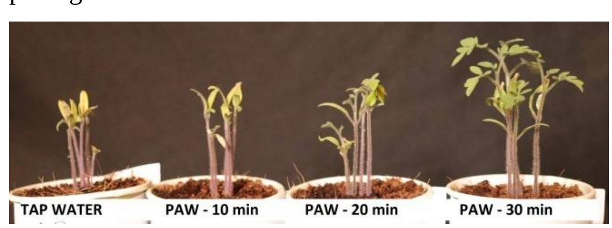

Fig. 7. Pictorial view of plants grown using PAW for different activation time and tap water.

Conclusion

In this work, experiments have demonstrated that the enhanced seed growth can be achieved with PAW generated using arc plasma discharge. For the first time the enhanced plant growth effect of PAW on tomato plants is demonstrated. The results indicate that compared to control, the PAW-30-minute fed plants have nearly 1.5 times higher shoot length, 4 times higher leaf count more than twice the chlorophyll content in the leaves. The wet weight of the plants fed with PAW-30 was 61% higher than that of the control.

Use of PAW as an alternative source of nitrogen for agricultural applications is gaining interest recently. Though this new technique is a green way of providing nitrogen to the plants, as it does not use any fossil fuels, it still has limitations. The main challenges that needs to be addressed is the scalability of PAW for agricultural applications and reduction of specific energy consumption. which is of the order of 2270 kWhr/kg of Nitrogen[26] added to the soil as against 9-14 kWhr/kg of Nitrogen added through the conventional Haber-Bosch process.

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Author's contributions

Punith N. and Lakshminarayana R. wrote the manuscript and designed the experiments. Punith N. performed the experiments and interpreted the results. Harsha R. and Hemanth M. helped with the experiments. Lakshminarayana R., Dasappa S. and Anand M.S. supervised the study, and provided the necessary experimental materials and facilities needed to conduct the experiments.

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