Effect of external axial magnetic field on a helium atmospheric pressure plasma jet and plasma-treated water

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Abstract
Potential in biomedical-related applications by atmospheric pressure plasma-treated water gradually increased recently. In order to enhance the generation of reactive species in atmospheric pressure plasma in regards to liquid treatment, this study aims to investigate the effect of external axial magnetic field on a helium atmospheric pressure plasma jet (APPJ) and plasma-irradiated water. Magnetic field strength up to 2.0 T was generated by an electromagnet in Helmholtz configuration. The dielectric barrier discharge-based APPJ is driven by 4.4 slm helium and sinusoidal 30 kHz, 10 kVpp signals. Plasma was mainly characterized by optical emission where vibrational and rotational temperature was estimated by nitrogen second positive system, and electron temperature and density by emission intensity line ratio method. Representative reactive species of nitrite, nitrate, and hydrogen peroxide concentration in the plasma-treated water were also quantified. Results of vibrational temperature and electron density showed a first drop then rise trend which partially corresponds to the reactive species in the plasma-treated water. No significant changes were found in rotational temperature, while electron temperature monotonically increased with the magnetic field.

Keywords: atmospheric pressure plasma jet, plasma-treated water, magnetic-assisted plasma, plasma-activated water

(Some figures may appear in colour only in the online journal)

1. Introduction
Since the last two decades, high potential has been shown from studies on atmospheric pressure plasma jets (APPJ) and their application in the biomedical field, for instance microbial inactivation, cancer treatment, and wound healing [1–8]. The advantage of applying APPJ are the relative high efficiency, flexibility, and low cost compared to conventional treatment. It is usually believed that the mechanism of the biological effects originates from the reactive species generated by the plasma [2]. Reactive oxygen and nitrogen species (RONS) generated by plasma induces oxidative stress on cells which leads to inactivation of bacteria or apoptosis of cancer yet also could stimulate angiogenesis for wound healing [9, 10].

A common treatment target by APPJ is liquid media [11–14]. Besides intentionally setting liquids as targets such as waste water and liquid food treatment, the contact of plasma with water is difficult to avoid in regards to wound or cancer treatments which is often covered by a liquid layer. In addition, plasma-treated water or plasma-activated water were proven to have bactericidal effects and effects on growth rate acceleration of plants which could last for days or weeks where long living reactive species such as hydrogen peroxide, nitrite, or nitrates were considered to be crucial [15, 16]. It is possible...
that additional magnetic fields could enhance the generation of reactive species. Applying magnetic fields on low pressure plasma has been shown to confine plasma and increase plasma density with relative small magnetic field (mT range) due to the Lorentz force on the electrons [17–20]. Although due to the much smaller mean free path of atmospheric pressure plasma (APP), it is usually believed that magnetic fields do not significantly effect the plasma. However, previous study using permanent axial magnets on a helium APPJ could enhance generation of reactive species and bactericidal effects, while no clear changes were found in the plasma [21]. On the other hand, it has been reported that 1.4 T of axial magnetic field could increase the confinement and electron density of plasma in an atmospheric pressure dielectric barrier discharge (DBD) [22]. It is worth knowing that the term axial magnetic field used in this study is referred to as magnetic fields parallel to the axis of symmetry of the discharge configuration.

Since the underlying mechanisms are not totally understood, in this study, we aim to understand the mechanism of magnetic-assisted plasma on water more clearly. By using an electromagnet, we were able to apply different magnetic field strength up to 2.0 T on a helium APPJ. Not only searching for a better understanding of the plasma and plasma-treated water, this study could also benefit application-wise by searching for an optimal point to enhance efficiency on generation of reactive species.

2. Materials and methods

2.1. Atmospheric pressure plasma jet and electromagnet setup

The plasma jet applied in this study is a dielectric barrier discharge (DBD)-based APPJ (figure 1). A quartz tube with 4 mm inner and 6 mm outer diameter was used as the dielectric where two thin aluminum foils with a distance of 10 mm were attached outside of the tube as the power (lower foil) and grounded electrode (upper foil). Throughout the whole study, helium (purity: 6.0) was the carrier gas whose flow rate was set to 4.4 slm, while the driving voltage was generated by a sinusoidal high voltage bipolar frequency generator and fixed at 30 kHz and 10 kVpp.

In order to examine the effect of axial magnetic field on the APPJ, the plasma jet was placed in the center of an electromagnet with the diameter of 430 mm which has a Helmholtz coil configuration and produces magnetic field strength with variation not higher than 0.65% in the central cylinder volume of 100 mm diameter and 50 mm height [23]. Measurements of optical emission and liquid reactive species were performed up to 2.0 T.

2.2. Optical emission spectroscopy

Optical emission spectroscopy (OES), which is frequently applied for atmospheric pressure plasma diagnostics, was applied to characterize and to estimate several plasma parameters including rotational temperature, vibrational temperature, electron temperature, and electron density [12]. Measurements were performed on both plasma bulk, whose emission was recorded at the midpoint between the two electrodes, and afterglow, whose emission was measured 10 mm below the lower edge of the power electrode. OES was also recorded with and without water target since the water molecules could potentially affect the emission [24]. A 0.5 m Czerny–Turner monochromator with an optical resolution of approximately 0.4 nm and an intensified-CCD camera (PI-MAX4 1024f, Princeton Instruments) were used to record the OES. The intensity measurements were done in accumulative mode over hundreds of discharge periods with an exposure time comparable to the discharge period time of 33 µs. Relative intensity was calibrated by a tungsten–halogen calibration lamp.

2.2.1. Rotational and vibrational temperature. Rotational (\(T_{\text{rot}}\)) and vibrational temperature (\(T_{\text{vib}}\)) was estimated from the relative band intensities and shapes from wavelength range of 390 nm to 407 nm which corresponds to the nitrogen second positive system (2PS) (\(N_2\), \(C^{3}Π_u - B^{3}Π_g\)) and was also presented in previous studies [12]. A fitting program Massiv-OES was used to acquire the \(T_{\text{rot}}\) and \(T_{\text{vib}}\) [25, 26]. This method provides the estimation of the \(T_{\text{rot}}\) and \(T_{\text{vib}}\) of atmospheric pressure discharges, where several different components of the air plasma could be analyzed in parallel. Therefore, the intensity \(I\), which is proportional to the ro-vibrational state population \(N_{\nu, J}\), is modeled state by state for different line intensities with an assumption of Boltzmann distribution which contains \(T_{\text{rot}}\) and \(T_{\text{vib}}\):

\[
\frac{N_{\nu, J}}{N_0} = e^{-\frac{E_{\text{vib}}(\nu)}{kT_{\text{vib}}} - (2J + 1) \cdot e^{-\frac{E_{\text{rot}}(J)}{kT_{\text{rot}}}}} \cdot e^{-\frac{E_{\text{elec}}(\nu, J)}{kT_{\text{elec}}}}.
\]

In which \(N_0\) is the total number density, \(\nu\) is the vibrational quantum number, \(J\) is the total angular momentum, \(k\) is the energy constant, \(E_{\text{vib}}\) is the vibrational energy, \(E_{\text{rot}}\) and \(E_{\text{elec}}\) are rotational, and electronic partition, respectively [27]. The modeled emission intensities are convoluted with lineshapes chosen among Gaussian and Lorentzian types which takes into account, just to name a few, the instrumental-, Doppler-, and pressure broadening to fit the measured molecular bands.

2.2.2. Electron density and electron temperature. An emission intensity line ratio method was applied for estimation of averaged electron density (\(n_e\)) and temperature (\(T_e\)) where the method was applied in previous studies on atmospheric pressure DBD under magnetic field strength of 1.4 T [22, 28]. This model uses specific nitrogen emission lines to estimate \(n_e\) and \(T_e\). The relative line intensity ratio of 371.1 nm and 380.5 nm correlates to the average electron density, while ratio of 391.4 nm and 380.5 nm of the nitrogen second positive system (2PS) to electron temperature. Calculation of \(n_e\) and \(T_e\) was performed from results of previous studies with the following expressions for the line ratios [22, 28]:

\[
\frac{I_{391.4}}{I_{380.5}} = C_1 \cdot \left(\frac{T_e}{e}\right)^{C_2} \cdot e^{\frac{E_{C_3}}{T_e}}.
\]
Figure 1. (a) Schematic design of the atmospheric pressure plasma jet, and (b) typical image of plasma jet. (1) Helium gas inflow, (2) quartz dielectric, (3) grounded electrode, (4) high voltage electrode, (5) sample solution, (6) collimators, (7) OES.

\[ \frac{I_{371.4}}{I_{380.5}} = C_4 + C_5 \cdot \log_{10}(n) + C_6 \cdot (\log_{10}(n))^2 \]  

where \( C_1 \) to \( C_6 \) are constants of \( C_1 = 27280.076 \), \( C_2 = -3.235 \), \( C_3 = -18.147 \), \( C_4 = 141.730 \), \( C_1 = -9.265 \), \( C_1 = 0.152 \), and \( n \) is the ionization degree.

2.3. Reactive species in plasma treated water

Reactive species of nitrite, nitrate, and hydrogen peroxide are measured by colorimetric methods. Nitrite and nitrate are considered as end products of reactive nitrogen species (RNS) and are relatively stable, while hydrogen peroxide for reactive oxygen species (ROS) [14]. Both RNS and ROS are believed to be crucial in plasma on biomedical application [2]. For all treatments, 200 \( \mu \)L of distilled water was treated by plasma under different magnetic field strength in 200 \( \mu \)L PCR tubes (Carl Roth) for 5 min and afterwards underwent the assay protocol. The treating distance was kept 20 mm between the low edge of the power electrode and surface of water sample. All measurements were repeated at least three times.

2.3.1. Nitrite and nitrate. The nitrite and nitrate concentration was quantitatively estimated by a Griess reagent-based nitrate/nitrite colorimetric assay kit (item no. 780 001; Cayman Chemical). This method is well-established and applied in previous studies [12, 29]. Immediately after plasma treatment, the liquids were transferred into transparent 96 well plates and reagents were added according to the assay kit protocol. Absorbance at 560 nm was measured by a microplate reader (GloMax Explorer; Promega) and the nitrite and nitrate concentration were estimated by a standard curve from the assay.

2.3.2. Hydrogen peroxide. The hydrogen peroxide concentration was quantified by the titanylsulfate method [12, 14, 30]. Sodium azide and titanylsulfate was added into the plasma-treated water which reacts specifically with hydrogen peroxide. The solution is stable for 6 h and absorbance could be measured to quantify the concentration. After treatment, 100 \( \mu \)L of sample solution was transferred into 96 wells. 20 \( \mu \)L of sodium azide solution (60 mM) followed by 50 \( \mu \)L of titanylsulfate solution (2.0%) was immediately added afterwards. The optical absorption at 405 nm was measured by a microplate reader. Calibration was performed with the absorption of a series of hydrogen peroxide solution with different concentrations.

3. Results and discussion

3.1. Optical emission spectra

Results of vibrational temperature and electron density obtained from OES depicts a first drop then rise trend with the increase of magnetic field. Electron temperature gradually increased with the increase of magnetic field, while no clear changes were found in rotational temperature.

3.1.1. Rotational and vibrational temperature. Estimation of rotational temperature \( T_{rot} \) from the nitrogen 2PS were in the
Figure 2. Vibrational temperature of the plasma estimated by the N\textsubscript{2} second positive system.

Range of 360 K to 380 K in the bulk plasma and 340 K to 360 K in the afterglow. No significant changes were observed by applying magnetic field up to 2.0 T. On the other hand, vibrational temperature ($T_{\text{vib}}$) first drops then rises under different magnetic fields (figure 2). This trend was observed both in plasma bulk and in the afterglow with and without water target. Generally, bulk plasma has a higher $T_{\text{vib}}$ compared to afterglow region. Regarding plasma bulk, the lowest value of $T_{\text{vib}}$ (3340 K) was at 1.0 T while the highest (4075 K) at 1.75 T. For afterglow with and without water as target, the lowest point of $T_{\text{vib}}$ was at 0.75 T and 1.0 T while the highest both at 1.75 T.

3.2. Reactive species in plasma treated water
Concentration of nitrite, nitrate, and hydrogen peroxide treated by plasma under different magnetic fields all showed a trend similar to vibration temperature and electron density.

3.2.1. Nitrite and nitrate. Generally, concentration of nitrite and nitrate were lower after applying magnetic field on the APPJ compared to 0 T treatment (figure 5). Nitrite concentration was significantly lower under 1.0 T compared to 0 T yet a slight increase could be observed if higher magnetic fields were applied. Nitrate follows a similar trend while significant drop could be found after 0.5 T. In addition, the total concentration of nitrite and nitrate showed a drop then rise curve. The minimum points for nitrite, nitrate, and nitrite+nitrate were all at 1.0 T, while the maximum points were at 0.5 T, 0 T, and 0 T, respectively.

3.2.2. Hydrogen peroxide. Hydrogen peroxide concentration also showed first drop then rise trend (figure 6). An initial concentration of 150 $\mu$M decreases till around 100 $\mu$M under 1.5 T, which is the lowest point, and increases to 175 $\mu$M under 2.0 T, which is the maximum point.

3.3. Discussion
Although extensively studied on low pressure plasma conditions, the understanding of atmospheric pressure plasma under external magnetic field is relatively poor. Liu et al [21] used...
a 0.587 T permanent magnet on a helium APPJ yet only on the tip of the discharge. Their results indicated an increase in electron density and sterilization effects but only if there was a water target. The effect of water was highlighted in their study. Liu et al [22], on the other hand, used 1.4 T on a DBD reactor and showed that both $n_e$ and $T_e$ were strongly increased. Jiang et al [31] reported that under 0.42 T, enhancement of several emission lines and improvement of uniformity was observed on a DC glow discharge. Generally, improvement of plasma generation was reported in previous studies.
yet mostly under a fixed magnetic field. No studies were performed under different magnetic field strengths and estimation of reactive species in plasma-treated water which this study mainly focuses on. Regarding plasma, both $T_{\text{vib}}$ and $n_e$ in the plasma bulk were first decreasing then increasing with the increase of magnetic field. This trend was also found in the afterglow yet relatively more fluctuating due to the instability of the plasma afterglow (data not shown). $T_{\text{vib}}$ could provide information about the efficiency of energy transfer between particles in the plasma, especially between electrons and heavy particles, since the population of excited vibrational levels originates mainly through electron excitation, while $n_e$ is commonly related to ionization [32]. A drop in $T_{\text{vib}}$ and $n_e$ under lower magnetic field indicates a decrease in energy transfer efficiency. The increase of $T_{\text{vib}}$ and $n_e$ under higher magnetic field could originate from the decrease of dissipation of electrons [22]. Increase of $T_e$ was also shown in previous studies [22, 33]. It is assumed that rise of $T_e$ is rather unlikely under magnetic fields perpendicular to the axis of symmetry of the discharge configuration due to a short mean free path, while under axial magnetic field, high velocity electrons were strongly effected by confinement effect from the Lorentz force which increases the $T_e$ [31, 33].

Concentration of reactive species in plasma-treated water also showed a trend similar to $T_{\text{vib}}$ and $n_e$. Nitrite and nitrate are both important reactive species in biomedical application of plasma since it could not only inactivate microbes such as bacteria but also stimulate plant growth [34, 35]. Partial correlation could be found between vibrational temperature and nitrite/nitrate concentration. Vibrationally excited nitrogen could be a reason for the trend in nitrite and nitrate concentration according to reaction (Rate constant $= 1.0 \times 10^{-17}$ m$^3$ s$^{-1}$) [36]:

$$\text{N}_2(\nu) + \text{O} \rightarrow \text{NO} + \text{N}$$

where nitrite and nitrate are the end product of NO dissolved in water. Hydrogen peroxide is also an important reactive species since it could indicate the production of highly reactive hydroxyl radicals and could also react with nitrite to produce highly reactive peroxynitrite [12, 14]. Hydrogen peroxide is possibly produced by the reaction of two hydroxyl radicals which is generated either by collision of electron with water molecules or penning ionization of helium plasma [12, 37, 38]. Although either $T_{\text{vib}}$ and $n_e$ or nitrite, nitrate, and hydrogen peroxide showed a first drop then rise trend, which could indicate a correlation between these parameters. The axial external magnetic field is changing the charged particle dynamic that could lead to different effects:

Confinement of electrons within the discharge (Effect 1): The electron mobility perpendicular to the external magnetic field is reduced with increase of magnetic field strength. Also, the effective magnetic field strength acting in the center of the discharge tube is lower than the magnetic field strength close to the dielectric wall due to diamagnetic property of plasma [33]. Therefore, a radial-dependent confinement of electrons exists in the discharge. In general, the amount of electrons from the plasma volume which reaches the dielectric wall is lowered in
the presence of axial magnetic field due to the confinement in axial direction.

Interaction of electrons with the dielectric surface wall (Effect 2): Accumulated electrons on the dielectric surface create an electrostatic repulsion force on further incoming electrons. These repulsed electrons will be pushed back and could go to the tube center where further collision could occur. However, an axial external magnetic field confines these electrons in the vicinity of the dielectric wall (Effect 1). This effect could be critical in APPJ configurations because the volume where electrons are interacting with the neutral gas gets reduced. Most of the driving gas is flowing in the center of the tube with much smaller fraction near the dielectric surface. Hence fewer species can be produced.

It is expected that the number of accumulated electrons on the dielectric surface reduces with increase of axial magnetic field due to Effect 1 and so it lowers the impact of Effect 2. Above a certain threshold value of the magnetic field strength, Effect 2 could be neglected. The plasma dynamics depends on the axial external magnetic field strength and so on the interaction between Effect 1 and 2.

4. Conclusion

In this work, investigation of a helium APPJ under axial magnetic field was performed. Magnetic field strengths up to 2.0 T were applied. Results showed that vibrational temperature as well as electron density partially correlate with the concentration of nitrite, nitrate, and hydrogen peroxide in the plasma-treated water under different magnetic field. In general, reactive species do not necessarily increase with the rise of axial external magnetic field strength. Nevertheless, the axial magnetic field could be used as a tool to manipulate reactive species concentration.

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References

[1] Gorbanev Y, O’Connell D and Chechik V 2016 Non-thermal plasma in contact with water: The origin of species Chem. Eur. J. 22 3496–505
[2] Graves D B 2012 The emerging role of reactive oxygen and nitrogen species in redox biology and some implications for plasma applications to medicine and biology J. Phys. D: Appl. Phys. 45 263001
[3] Bekeschus S, Schmidt A, Weltmann K-D and von Woedtke T 2016 The plasma jet kinpen—a powerful tool for wound healing Clin. Plasma Med. 4 19–28
nanosecond pulsed dielectric barrier discharge under different pulse repetition frequencies Phvs. Plasmas 25 033519
[23] Choudhary M, Berger R, Mitic S and Thoma M H 2019 Influence of external magnetic field on dust acoustic waves in a capacitive RF discharge Contrib. Plasma Phys. 60 e201900115
[24] Darney T, Pousseval J M, Puech V, Douat C, Dozias S and Robert E 2017 Analysis of conductive target influence in plasma jet experiments through helium metastable and electric field measurements Plasma Sources Sci. Technol. 26 045008
[25] Vorac J, Synek P, Prochazka V and Hoder T 2017 State-by-state emission spectra fitting for non-equilibrium plasmas: OH spectra of surface barrier discharge at argon/water interface J. Phys. D: Appl. Phys. 50 294002
[26] Vorac J, Synek P, Potočnáková L, Hnilica J, and Kudrle V 2017 Batch processing of overlapping molecular spectra as a tool for spatio-temporal diagnostics of power modulated microwave plasma jet Plasma Sources Sci. Technol. 26 025010
[27] Luque J and Crossley D R 1999 Lifbase: Database and spectral simulation SRI International Report MP 99 009
[28] Yun W, Yinghong Li, Jia M, Song H, Guo Z, Zhu X and Yikang P 2008 Influence of operating pressure on surface dielectric barrier discharge plasma aerodynamic actuation characteristics Appl. Phys. Lett. 93 031503
[29] Cheng K-Y, Lin Z-H, Cheng Y-P, Chiu H-Y, Yeh N-L, Tung-Kung W and Jong-Shinn W 2018 Wound healing in streptozotocin-induced diabetic rats using atmospheric-pressure argon plasma jet Sci. Rep. 8 12214
[30] Lukes P, Dolezelova E, Sisrova I and Clupek M 2014 Aqueous-phase chemistry and bactericidal effects from an air discharge plasma in contact with water: evidence for the formation of peroxynitrite through a pseudo-second-order post-discharge reaction of H2O2 and HNO2 Plasma Sources Sci. Technol. 23 015019
[31] Jiang W, Tang J, Wang Y, Zhao W and Duan Y 2014 Non-thermal atmospheric-pressure plasma possible application in wound healing Biomol. Therapeutics. 22 477
[32] Haertel B, Von Woerdke T, Weltmann K-D and Lindeque U 2014 Non-thermal atmospheric-pressure plasma possible application in wound healing Biomol. Therapeutics. 22 477
[33] Skidmore M, Sharshurin A, Volotokova O, Stepp M A, Srinivasan P, Sandler A and Trink B 2013 Cold atmospheric plasma in cancer therapy Phys. Plasmas 20 057101
[34] Bruggeman P J et al 2016 Plasma–liquid interactions: a review and roadmap Plasma Sources Sci. Technol. 25 053002
[35] Kaupe J, Tschang C-Y T, Birn F, Coenen D, Thoma M H and Mitic S 2019 Effect of cold atmospheric plasmas on bacteria in liquid: the role of gas composition Plasma Process. Polym. 16 1800196
[36] Tian W and Kushner M J 2014 Atmospheric pressure dielectric barrier discharges interacting with liquid covered tissue J. Phys. D: Appl. Phys. 47 165201
[37] Tschang C-Y T and Thoma M 2019 In vitro comparison of direct plasma treatment and plasma activated water on escherichia coli using a surface micro-discharge J. Phys. D: Appl. Phys. 53 055201
[38] Traylor M J, Pavlovich M J, Karim S, Hatt P, Sakiyama Y, Clark D S and Graves D B 2011 Long-term antibacterial efficacy of air plasma-activated water J. Phys. D: Appl. Phys. 44 472001
[39] Thirumadas R, Kothakota A, Annupure A, Siliveru K, Blundell R, Gatt R and Valdranamis V P 2018 Plasma activated water (PAW): chemistry, physico-chemical properties, applications in food and agriculture Trends in Food Sci. & Technol. 77 21–31
[40] Lee H-J, Yang I-D and Whang K-W 1996 The effects of magnetic fields on a planar inductively coupled argon plasma Plasma Sources Sci. Technol. 5 383
[41] Leung K N, Sameck T K and Lamn A 1975 Optimization of permanent magnet plasma confinement Phys. Lett. 51 490–2
[42] Charles C and Boswell R W 2007 The magnetic-field-induced transition from an expanding plasma to a double layer containing expanding plasma Appl. Phys. Lett. 91 201505
[43] Bergert R and Mitic S 2019 Optical properties of magnetized transient low-pressure plasma Plasma Sources Sci. Technol. 28 115001
[44] Liu C-T, Kumakura T, Ishikawa K, Hashizume H, Takeda K, Ito M, Hori M and Wu J-S 2016 Effects of assisted magnetic field to an atmospheric-pressure plasma jet on radical generation at the plasma-surface interface and bactericidal function Plasma Sources Sci. Technol. 25 065005
[45] Liu Y, Yan H, Guo H, Fan Z, Wang Y, Yun W and Ren C 2018 Effect of parallel magnetic field on repetitively unipolar plasma jet for liquid spray treatment J. Phys. D: Appl. Phys. 49 205202