

DISCHARGE DUTY CYCLES EFFECTS OF 20 KHZ AIR ATMOSPHERIC PRESSURE PLASMA JET ON METHYLENE BLUE SOLUTION DEGRADATION

Chakkaphan Wattanawikkam^{1,2}, Atipong Bootchanont^{1,2}, Naris Barnthip^{1,2}, Sorapong Pavasupree³, Pinit Jitjing⁴, Dheerawan Boonyawan⁵, Keandtisak Kachayut⁶ and Porramain Porjai^{1,2,*}

Received: December 20, 2021; Revised: April 21, 2022; Accepted: April 24, 2022

Abstract

The degradation of methylene blue (MB) using air atmospheric pressure plasma jet (air APPJ) in contact with liquid was proposed. In this study, an AC-driven air APPJ using three discharge duty cycles (30%, 50%, and 80%) of a neon transformer was investigated. In each discharge duty cycle, the ignition and extinguishment phases were characterized. The constituent particles of the air APPJ in the gas phase were observed by an optical emission spectrophotometer (OES). The OES results of all discharge duty cycles found the NO (A-X) bands, $\cdot\text{OH}$ radical, N_2 second positive system, N_2 first negative system, N^+ , N , and O . The emission spectra produced by the discharge duty cycle of 80% were the highest relative intensity. The effects of the different discharge duty cycles on the acidity and conductivity of water with and without MB were also determined. The complete dye degradation within 30 min was obtained in the discharge duty cycle 80%, which played an essential role in carrying reactive species from the gas phase to the liquid phase, thus promoting the degradation of MB. The best reaction kinetic rate k is 0.1692 min^{-1} , which is six times compared to discharge duty cycle 50%.

Keywords: Air atmospheric pressure plasma jet, duty cycle, Methylene blue, reactive oxygen/nitrogen species, wastewater treatment

¹ Division of Physics, Faculty of Science and Technology, Rajamangala University of Technology Thanyaburi, Pathum Thani, Thailand. E-mail: porramain_p@rmutt.ac.th

² Smart Materials Research Unit, Rajamangala University of Technology Thanyaburi 12110, Pathum Thani, Thailand.

³ Department of Materials and Metallurgical Engineering, Faculty of Engineering, Rajamangala University of Technology Thanyaburi, Pathum Thani, Thailand.

⁴ Electrical Engineering Department, Rajamangala University of Technology Thanyaburi, Pathum Thani, Thailand.

⁵ Plasma and Beam Physics Research Facility, Chiang Mai University, 239 Huay Kaew Rd., Chiang Mai 50200, Thailand.

⁶ Genetron Technology (Thailand) Co., Ltd 51/3 Vibhavadi Tower Room 4 Floor 14 Ngamwongwan Road Ladyao Chathuchak Bangkok 10900, Thailand.

* Corresponding author

Introduction

Nowadays, dye in wastewater is one of the serious problems in the environment. The dye in wastewater is found in application areas, such as solar cells, microbiological pollutants, and nanomaterials. An increase of dye in wastewater has occurred from the high demand for those applications. The occurrence of dye in water damages the environment because the stable molecular structure, such as physical (color), and chemical (toxicity) properties, cannot be efficiently degraded by conventional procedures. Therefore, the natural environment does not easily remove the color and toxicity (Dutta *et al.*, 2001).

The new water treatment method is advanced oxidation processes (AOPs). Various AOPs have been developed to eliminate persistent residual pollutants efficiently in water. Ozonation, due to its high reactivity, is one of the AOPs. Because of the oxidative species produced by adding ozone (O_3) molecules, ozonation was applied to degrade the dye in wastewater (Zhang *et al.*, 2009). Ultraviolet (UV) radiation, known as photo-catalysis (Houas *et al.*, 2001), can also generate oxidative species to reduce the dye in wastewater. Another AOPs is the reaction of ferrous iron (Fe^{2+}) with hydrogen peroxide (H_2O_2), which produces the oxidative species for removing the residual pollutants in water (Dutta *et al.*, 2001). However, the cost of these AOPs in the above mentioned is expensive and difficult to combine with the other process.

Atmospheric pressure plasma (APP) or non-thermal plasma, one of the wastewater treatments, is the appearance of a low-pressure glow discharge with low gas temperature ranging from 50 to 400°C), the density of charged species about 10^{10} - 10^{13} cm⁻³, and several electron volts in order of high electron temperature (Schütze *et al.*, 1998). This plasma source can be easily operated at atmospheric pressure and room temperature without a vacuum system, causing it to be inexpensive. A vital feature of the APP is the generation of reactive oxygen/nitrogen species (RONS), especially hydroxyl radicals ($\cdot OH$), atomic oxygen (O), (O_3), H_2O_2 , and nitric oxide (NO) during plasma processing (Graves, 2012).

Due to the reactive species generated by plasma, the APP in contact with liquid has attracted the interest of scientists in several fields, such as the decomposition of harmful dissolved substances, decontamination of bacteria for the synthesis of chemical reactions (Ching *et al.*, 2001; Sano *et al.*, 2002; Locke *et al.*, 2006; Yuan *et al.*, 2010), and wastewater treatment (Peng and Lee, 2013; Jamróz *et al.*, 2014). Indeed, the APP generation in contact with water dissociated the water molecules, leading

to highly RONS production, especially $\cdot OH$, NO, NH, N, N^{2+} , and HNO_3 (Brisset *et al.*, 2011). Moreover, UV radiation, strong electrical field, and shock waves generated by APP in contact with water can promote the degradation of pollutants in water (Ionita *et al.*, 2016). Besides, many APP configurations have been investigated to degrade the dye wastewater (Huang *et al.*, 2010; Magureanu *et al.*, 2013; Yehia *et al.*, 2020). However, the source for generating the APP is expensive (i.e., radio frequency generator, ac or dc high voltage power supply).

In this article, an air atmospheric pressure plasma jet (air APPJ) generated in the gas phase in contact with water was presented. The APPJ system was controlled by a neon transformer (high voltage power supply) with an output of 12 kV, 30 mA, and 20 kHz, and its cost is inexpensive (~20 dollars). In this study, the experiment was divided into three parts. In the first part, to investigate the characteristics of the air APPJ, the experimental parameters were varied discharge duty circles (30-80%) that were the minimum and maximum values of the neon transformer. Although the APP intensity increased with the discharge duty cycle (Shi *et al.*, 2008; 2009), the influence of different discharge duty cycles on water has never been reported. The constituent particles of the air APPJ in the gas phase were revealed using an optical emission spectrophotometer (OES). Second step, water properties (acidification, conductivity, and temperature) treated by the various discharge duty cycles in contact with water were measured. The final step was to determine the optimum operating conditions of various discharge duty cycles in decolorizing a standard pollutant (methylene blue, MB).

Materials and Methods

Cold Atmospheric Pressure Plasma Jet Setup

Figure 1 shows the experimental setup of the air APPJ system to treat MB solution. The air APPJ was driven by a neon transformer (output of 12 kV, 30 mA, and 25 kHz) with a pulse repetition frequency of 100 Hz. The neon transformer input was connected to a voltage controller (input of 50-220 V, 12 A). A quartz glass tube, which length, inner, and outer diameters are 100 mm, 3 mm, and 4 mm, respectively, was used to generate the air APPJ. The high voltage electrode made from a copper wire with 150 mm in length and 0.5 mm in diameter was placed in the middle of the quartz tube.

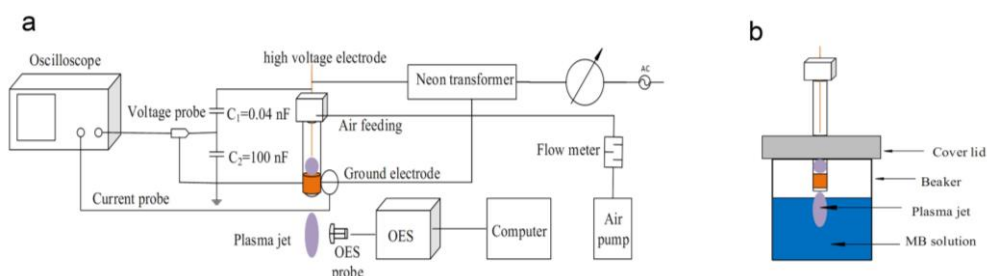


Figure 1. (a)Schematic diagram of the air APPJ system, (b) the air APPJ treated on MB solution

A copper plate with dimensions of $50 \times 10 \times 0.5 \text{ mm}^3$ was wrapped around the nozzle end for use as a ground electrode. The high and ground electrodes had a distance of approximately 10 mm for each other. When the neon power supply was turned on, the pulse- modulation air APPJ was operated between electrodes and ejected at the end of the nozzle.

The measurements of discharge voltage and current with different duty cycles of the neon transformer signal were performed using a voltage divider and a CP5030 SIGLENT current probe. The divider ratio was 2501 nF for this experiment. The calculation of voltage by the divider ratio was described in (Pavasupree *et al.*, 2021). The waveforms and frequency were recorded by a digital oscilloscope (SIGLENT T3DSO1104). The OES obtained the emission spectra with a broadband CCD spectrometer (Exemplar LS; BWTEK Inc., United States), using Grating at 600 grooves/mm and 25 μm slit width to resolve the measured spectrum ranging from 200-850 nm, as illustrated in Figure 1(a).

Plasma Treatment on Distilled Water And MB Solution

In order to investigate the efficiency of the air APPJ with the various duty cycles in eliminating organic pollutants from water, MB solution was prepared with an initial concentration of 10 mg/L and a volume of 50 mL. Water acidity was measured by pH meter (Exstik water proof), and conductivity and temperature in water were measured by conductivity meter kit (SPER SCIENTIFIC 850049). In this experiment, the distance between the ground electrode and MB solution was approximately 5 mm.

Determination of Decolorization of Mb Solution

The performance of the air APPJ for organics pollutant degradation was evaluated by using degradation of MB dye as a test reaction. In typical, 10 mg/L of MB powders was stirred in deionized water for 15 min to ensure the homogeneous dye solution, and then the air APPJ was irradiated. During the degradation reaction, 4 ml of dye solution

was taken every 5 min. The concentration of MB solution in an aqueous solution was measured by a nanodrop spectrometer at the wavelength of 664 nm. The percentage of degradation (%D) for MB solution was calculated by using the following Equation (1);

$$D = \frac{[C_0 - C_t]}{C_0} \times 100\% \quad (1)$$

Where C_0 is an absorbance value of the initial MB solution, C_t is an absorbance value of degraded MB solution at the reaction time t .

Reaction kinetics gives information about the reaction rates and mechanism of adsorption. The pseudo-first-order kinetics is given by Langmuir-Hinshelwood model at low initial concentration was tested (Ollis, 2018) as using Equation (2);

$$-\ln(C_t / C_0) = kt \quad (2)$$

where C_t and C_0 are the final and initial concentrations of MB, k is the apparent reaction rate constant (min^{-1}), and t is the irradiation time (min).

In order to quantify the efficiency of decolorization of MB solution by the air APPJ, the yield of MB removal (Y) was determined using Equation (3).

$$Y(g/kWh) = \frac{V_0(L)C_0(mg/L) \cdot [\text{Degrad}(\%)/100]}{P(kW)t(h)} \quad (3)$$

where V_0 is the initial volume (0.05 L), P is power, and t is the treatment time.

Results and Discussion

Discharge Voltage and Current of the Air APPJ with Different Duty Cycles

Figure 2 illustrates the waveform of the air APPJ modulated by pulses with a repetition frequency of 100 Hz and duty cycles of 30%, 50%, and 80%, respectively. When the neon power was

turned on, the highest peak of discharge voltage was approximately 10 kV for a duty cycle of 30% and 50% (Figures 2(a-b)), and 5 kV for duty cycles of 80% (Figure 2(c)). The highest peaks of discharge current were around 25, 28, and 25 mA for duty cycles of 30%, 50%, and 80% (Figures 2(d-f)), respectively.

In order to characterize the behavior of the air APPJ, the discharge ignition phases of voltage-current with different duty cycles at a fixed airflow

rate of 10 L/min are shown in Figure 3. For a duty cycle of 30%, the voltage ignition phase suddenly started at the peak of 10 kV and dropped to 5.6 kV at ~ 0.075 ms. Then it took ~ 0.4 ms to a stable state. However, the current ignition phase began slower than voltage, and it took ~ 0.33 ms to start the ignition phase. The ignition phase got to the stable state (from 0-25 mA) at ~ 0.4 ms, as shown in Figure 3(a). For a duty cycle of 50% Figure 3(b), voltage ignited at ~ 0.1 ms for the highest peak at 10 kV before

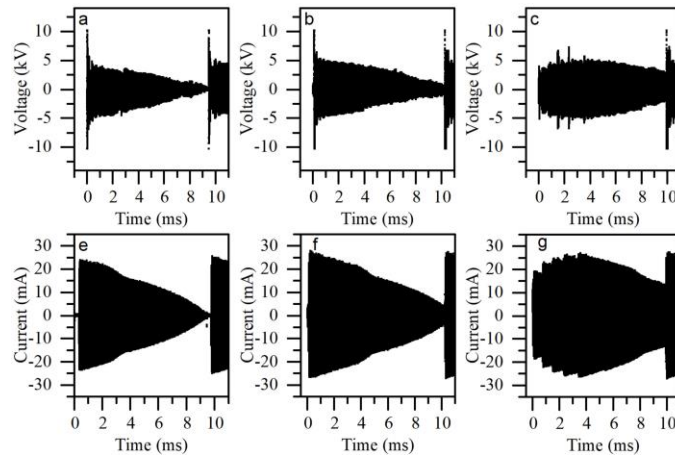


Figure 2. Pulse-modulated discharge voltage at a fixed airflow rated of 10 L/min with duty cycles of (a) 30%, (b) 50%, and (c) 80%, respectively, and discharge current at a fixed airflow rated of 10 L/min with duty cycles of (d) 30%, (e) 50%, and (f) 80%

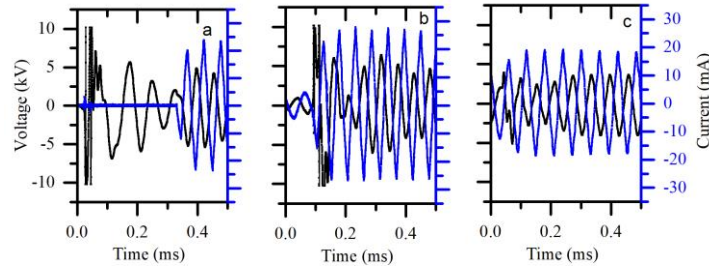


Figure 3. Voltage-current characteristics of discharge ignition phases at a fixed airflow rated of 10 L/min with duty cycles of (a) 30%, (b) 50%, and (c) 80%

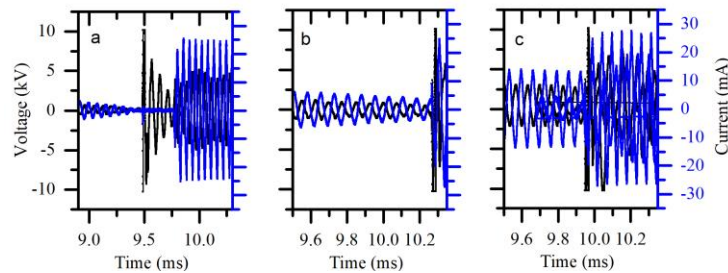


Figure 4. Voltage-current characteristics of discharge extinguishment phase at a fixed airflow rate of 10 L/min with duty cycles of (a) 30%, (b) 50%, and (c) 80%

dropped to 5.6 kV at ~ 0.2 ms. It took ~ 0.28 ms to the stable state. The current ignition phase took ~ 0.2 ms to the stable state. The voltage and current ignition phases for a duty cycle of 80% (Figure 3(c)) quickly started at ~ 0.12 and ~ 0.1 ms to the stable state, respectively.

Figure 4 demonstrates voltage-current characteristics during the discharge extinguishment phase with different duty cycles at the airflow rate of 10 L/min. The discharge voltage and current simultaneously dropped to zero at a time instant of ~ 9.3 ms for the discharge duty cycle of 30% (Figure 4(a)). However, the discharge voltage and current extinguishment phases of duty cycles of 50% and 80% were not zero before getting to the subsequent ignition phases. The discharge voltage extinguishment phase with 50% and 80% duty cycles dropped to 1 and 2.5 kV (Figures 4(b-c)), respectively, before getting to the ignition phase. Similarly, the discharge current extinguishment phase dropped to 5 and 13 mA for 50% and 80% duty cycles, respectively.

The power dissipated, and the energy per pulse with different discharge duty cycles were also summarized. The power dissipated was 8.20, 10.17, and 32.31 W for 30%, 50%, and 80% discharge duty cycles, respectively. Likewise, the energy per pulse was 80.20, 10.17, and 323.14 mJ for 30%, 50%, and 80% discharge duty cycles, respectively. It was important to note that the power dissipated and the energy per pulse of the 80% discharge duty cycle were much higher than the 30% and 50% discharge duty cycles for 74.6% and 68.5%, respectively. In addition, the length of the air APPJ was 1.46, 1.87, and 2.58 cm for discharge duty cycles of 30%, 50%, and 80%, respectively. The images of jet length with different duty cycles are presented in Figure 5.

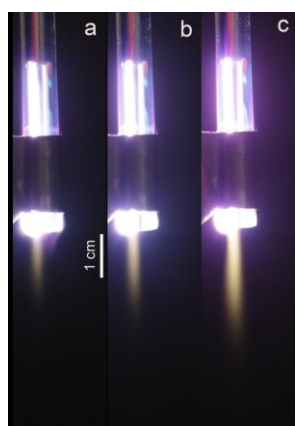


Figure 5. Images of the air APPJ at a flow rate of 10 L/min with discharge duty cycles of (a) 30%, (b) 50%, and (c) 80%, respectively

Optical Emission Spectrum of the Air APPJ in Ambient Air

In order to determine the effect of different duty cycles on the air APPJ spectra with a fixed flow rate of 10 min/L, the OES revealed constituent particles, as can be seen in Figure 6. The emission spectra for all discharge duty cycles demonstrated the presence of N_2 second positive system ($C\Pi_u \rightarrow B\Pi_g$ at 268-546 nm) and N_2 first negative system ($B\Sigma_u^+ \rightarrow X\Sigma_g^+$ at 286-587 nm), which was commonly established in several experiments (Thana *et al.*, 2019; Pavasupree *et al.*, 2021). However, the relative intensity for the nitrogen system of the air APPJ driven by a discharge duty cycle of 80% was much higher than 30% and 50%. Interestingly, the nitrogen ion (N^+) was detected at the peak of 500.6 nm because the generation of this ion required the highest energetic electrons (Parvulescu *et al.*, 2012; Thiry *et al.*, 2016). In addition, a small peak of the nitrogen atom (N) was also observed at 747.3 nm. Atomic oxygen (O) line at 777.4 nm was seen. The relative intensities of N^+ and O were no significant difference between 30-80% discharge duty cycles.

Figure 7 shows the influence of various discharge duty cycles on $\cdot OH$ and NO (A-X) bands. The $\cdot OH$ bands at 306.6 and 309.4 nm were observed (Figure 7(a)). It was obviously seen that the intensity of the $\cdot OH$ line at 306.6 nm generated by the 80% discharge duty cycle was much higher than the 30% and 50% discharge duty cycles, about 72.2% and 64.9%, respectively. Similarly, the intensity of the $\cdot OH$ line at 306.6 nm for the 80% discharge duty cycle was greater than the 30 and 50 duty cycles for 76.8% and 62.4%, respectively. The mechanism to generate the $\cdot OH$ radicals in the ambient air was described in previous work (Pavasupree *et al.*, 2021).

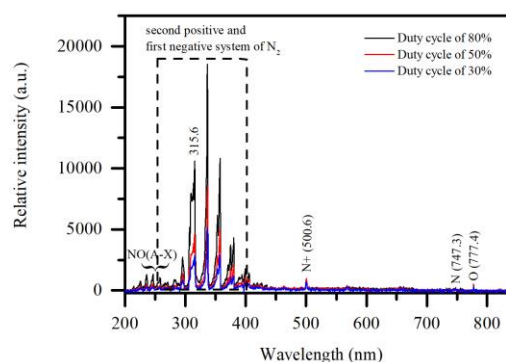


Figure 6. Optical emission spectra of the air APPJ with a flow rate of 10 L/min with various duty cycles

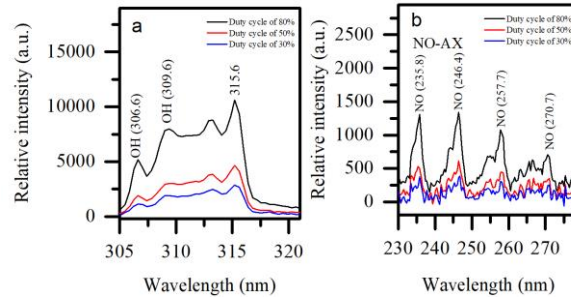


Figure 7. Emission spectra of (a) •OH bands and (b) NO (A-X) bands with different discharge duty cycles

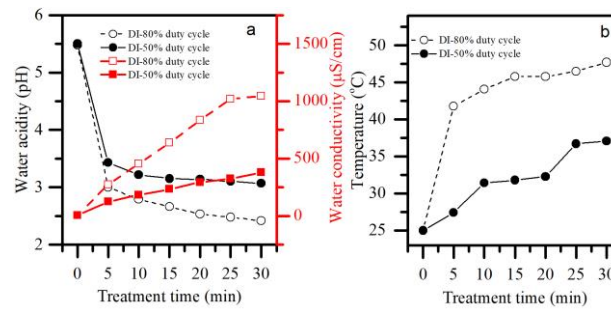


Figure 8. Time development of (a) acidity and conductivity and (b) temperature of deionized water with 50% and 80% discharge duty cycles

The detection of the NO (A-X) bands with different duty cycles are depicted in Figure 7(b). The NO (A-X) bands for every duty cycle were found at peaks of 235.8, 246.4, 257.7, and 270.7 nm, respectively. The intensity of NO driven by the 80% duty cycles at peaks of 235.8, 246.4, 257.7, and 270.7 nm was higher than the 30% discharge duty cycle for 71.9, 73.5, 72.0, and 65.2%, respectively. Also, the differences between the NO spectra at peaks of 235.8, 246.4, 257.7, and 270.7 nm of 80% and 50% discharge duty cycles were 59.1%, 54.7%, 58.7%, and 50.6%, respectively.

Due to the production of the NO bands in the air APPJ, the mechanism is proposed in Equations (4)–(6) (Burlicaa *et al.*, 2006). Firstly, energetic electrons dissociate with nitrogen (e^- : Equation (4)) and oxygen (e^- : Equation (5)) in the ambient air, which generates the nitrogen ion (Equation (4)) and the O in a ground state (Equation (5)). Then, the interaction between the O and N^+ generates NO (Equation (6)).



Our results showed that the relative intensity of RONS increased with the discharge duty cycle at a fixed flow rate. The highest relative intensity was the discharge duty cycle of 80%, while the discharge duty cycle of 30% was the lowest relative intensity. Several types of research have proposed the influence of different duty cycles on optical emission line intensity. For instance, the intensities of He (706 nm) and O (777 nm) were suddenly increased by a pulse-modulated radiofrequency dielectric barrier discharge (rf-DBD) in helium with duty cycles from 0–20%. Then the intensities slowly inclined with duty cycles from 20–100% (Shi *et al.*, 2008). Besides, the dissipated power also increased with the discharge duty cycle. Moreover, the emission intensities of •OH (309 nm), O (777 nm), and nitrogen system increased by pulse-modulated radiofrequency atmospheric pressure glow discharge with the various duty cycles (from 0 to 100%) (Shi *et al.*, 2009).

Effects of the Air APPJ on Deionized Water

The acidity, conductivity, and temperature in the deionized water during the APPJ processing with discharge duty cycles of 50% and 80% are presented in Figure 8(a). Notice that the intensities of the optical emission spectra between discharge duty

cycles 30% and 50% were not significantly different. Thus, the air APPJ treatment effects on the deionized water were performed only 50% and 80% discharge duty cycles. For all experiments, the water acidity as a function of time plotted into two phases are plotted in Figure 8(a). In phase 1, $t < 5$ min, the water acidity quickly declined from ~ 5.5 to ~ 3.0 pH for 80% discharge duty cycle and from ~ 5.5 to ~ 3.5 pH for 50% discharge duty cycle. Meanwhile, in phase 2, $t > 5$ min, the water acidity of 50% and 80% discharge duty cycles slowly decreased depending on discharge duty cycles. For instance, after 30 min of the air APPJ processing on deionized water, the water acidity value of the discharge duty cycle of 80% was ~ 2.4 pH, compared to ~ 3.0 pH in the discharge duty cycle of 50%.

However, water conductivity increased quasi-linearly with the increasing treatment time (Figure 8(a)). After 30 min of the air APPJ processing, the water conductivity increased from ~ 4 – $1,100$ $\mu\text{S}/\text{cm}$ in discharge duty cycles of 80%, and to ~ 400 $\mu\text{S}/\text{cm}$ in discharge duty cycles of 50%. The water conductivity value of the discharge duty cycles of 80% was 2.75 times higher than the value induced by the discharge duty cycle of 50%.

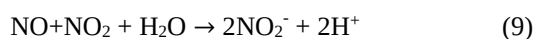
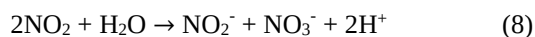
In addition, the temperature of deionized water during the air APPJ with different discharge duty cycles was observed, as shown in Figure 8(b). The initial temperature for all experiments was set at $25.0 \pm 1^\circ\text{C}$. The temperature of discharge duty cycles of 50 and 80% raised with treatment time. However, $t < 5$ min, the temperature inclined from 25.0 to $\sim 41.8^\circ\text{C}$ for the 80% discharge duty cycle and $\sim 27.4^\circ\text{C}$ for the 50% duty cycle. Then the temperature slowly increased to $t = 30$ min. The final temperatures were ~ 37.1 and $\sim 47.7^\circ\text{C}$ for 50% and 80% discharge duty cycles. In order to estimate the rate of temperature, linear fits were provided. The increased rates of water temperature were 0.398 ± 0.044 and $0.565 \pm 0.202^\circ\text{C}/\text{min}$ for discharge duty cycles of 50 and 80%, respectively.

In general, the contribution of nitrogen species, including nitrite (NO_2^-) and nitrate (NO_3^-), indicates the acidity of the water (Huang *et al.*, 2010). The mechanisms for generating NO_2^- and NO_3^- are described in Equations (4)–(6). The production of NO bands in the gas phase combines with the oxygen atom and leads to the formation of nitrogen dioxide (NO_2) (Equation (7)).



After that, the production of NO_2 in the gas phase can dissolve in water, which leads to forming the NO_2^- and NO_3^- species, as described in Equations (8)–(9) (Kanazawa *et al.*, 2016). The formation of

NO_3^- and H^+ may occur from the reaction between NO_2 and H_2O (Equation (8)). Similarly, the generation of NO_2^- and H^+ may come from NO_2 reacted with the NO and H_2O (Equation (9)).



Then, the disproportion of NO_2^- into NO_3^- and NO is indicated the decrease of water acidity along with the increasing water conductivity (Equations (9)–(10)) (Oehmigen *et al.*, 2010).



The results obtained that the water properties were significantly changed by the air APPJ depending on discharge duty cycles. The 80% discharge duty cycle produced higher intensity of NO in the gas phase than the 50% discharge duty cycle. It was impossible to generate a high number of NO_2^- , NO_3^- , and H_3O^+ in water under the 80% discharge duty cycle, which impacted lower acidification in water and higher water conductivity than the 50% discharge duty cycle at the same treatment duration. Nevertheless, the relationship between the discharge duty cycles and acidification or conductivity in water was not direct. Our results are similar to the effect on various air plasma discharge modes in contact with water (Diamond *et al.*, 2019). This research reported that the low water acidity and high water conductivity depended on the electrical characteristics of discharge, but they were not straightforward. In addition, the effects of the APP in water on the decreased water acidity and increased water conductivity had been reported (de B Benetoli *et al.*, 2011; Ionita *et al.*, 2016;).

Effects of the Air APPJ on MB Solution

The temporal evolution profiles of acidity and conductivity in the MB solution via different discharge duty cycles are illustrated in Figure 9(a). Similar to the acidity in the deionized water, the acidity in the MB solution was separated into two phases. In phase 1, $t < 5$ min, the acidity values of MB solution rapidly dropped from ~ 5.5 to ~ 3.0 pH for the 80% discharge duty cycle and ~ 3.5 pH for the 50% discharge duty cycle. In phase 2, the acidity in the MB solution slowly changed. After 30 min of the air APPJ treatment, the final acidity values were ~ 2.8 and ~ 2.3 pH for 50% and 80% discharge duty cycles, respectively. Herein, the acidity in the MB solution treated by the 80% discharge duty cycle was lower than the 50% discharge duty cycle. On the other hand, the conductivity values in the MB solution

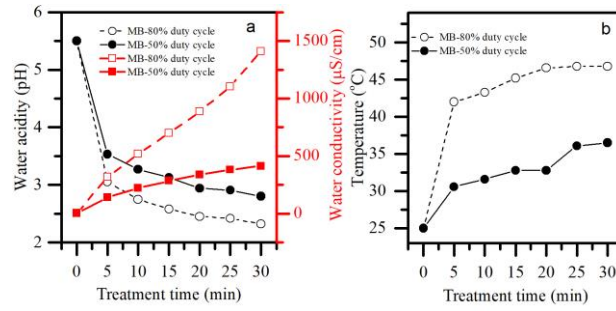


Figure 9. Temporal evolution of (a) acidity and conductivity, and (b) temperature in the MB solution treated by the air APPJ with discharge duty cycles of 50% and 80%

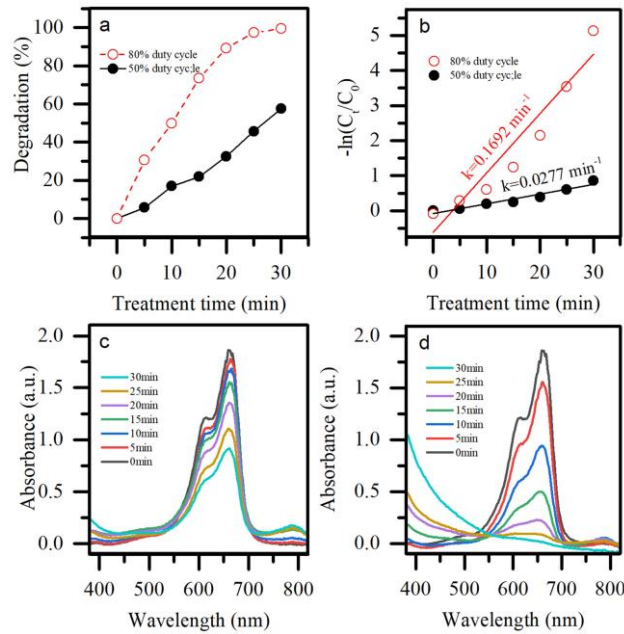


Figure 10. (a) Degradation of MB solution and (b) the corresponding rate constant k values for the air APPJ discharge duty cycles of 50% and 80%. UV-vis absorption spectra of MB solution by the air APPJ treatment with different time intervals for discharge duty cycles of (c) 50% and (d) 80%

increased from $\sim 4\text{--}400 \text{ }\mu\text{S/cm}$ and $\sim 1,400 \text{ }\mu\text{S/cm}$ for the 50% and 80% discharge duty cycles, respectively. Therefore, the conductivity value in the MB solution under the 80% discharge duty cycle was 3.5 times greater than that of the value induced by the 50% discharge duty cycle.

Besides, the temperature in the MB solution during the air APPJ processing is shown in Figure 9(b). At $t < 5 \text{ min}$, a strong temperature increment was observed in the discharge duty cycle of 80% (from 25.0 to 41.8°C). At $t > 10 \text{ min}$, the temperature slowly changed, and the final temperature was 47.7°C . The increased rate of temperature in MB solution was $0.599 \pm 0.206^\circ\text{C/min}$. However, the temperature

in discharge duty cycles of 50% slightly increased from the initial temperature of 25.0°C to the final temperature of 37.1°C with an increased rate of $0.333 \pm 0.057^\circ\text{C/min}$.

Degradation of MB solution Treated by Discharge Duty Cycles

In order to compare the efficiency of the air APPJ affected to MB solution between discharge duty cycle of 50% and 80%, the degradation percentages are presented in Figure 10(a). During the first 15 min, the degradation percentage of the discharge duty cycle of 80% increased linearly from 0 to $\sim 80\%$. Then it reached a maximum value

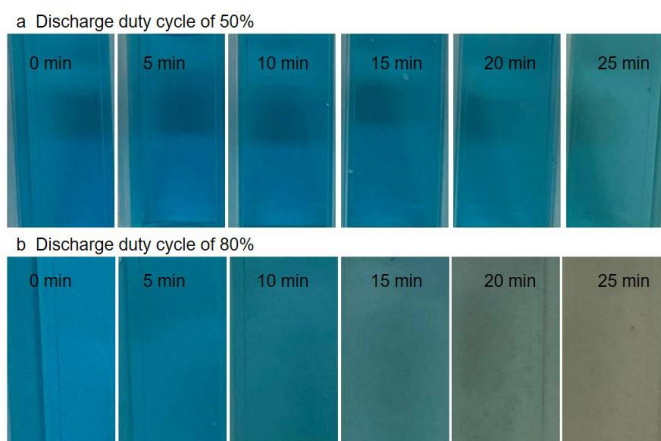


Figure 11. Images showing the degradation of MB solution via the air APPJ with different time intervals for (a) discharge duty cycles of 50% and (b) 80%

of ~100% at $t = 30$ min. However, the degradation percentage of the discharge duty cycle of 50% slightly raised from 0 to ~20% at $t < 15$ min. Moreover, the maximum value was just 60% after 30 min of the air APPJ treatment. Overall, the results showed that the degradation percentage of the discharge duty cycle of 80% was much higher than that of the discharge duty cycle of 50%, which had a different percentage between them for 50%. It was worth noting that the degradation percentage in MB solution depended on the discharge duty cycles. To further explore the dye decolorization reaction, the air APPJ degradation reaction kinetic of MB solution based on the data plotted in Figure 10(a) was investigated as presented in Figure 10(b). The graph shows that the air APPJ treated in MB solution degraded follows the first order-kinetics as a correlation constant. The results demonstrated that the discharge duty cycle of 80% exhibited a good MB dye degradation which corroborated the corresponding degradation efficiency. The discharge duty cycles of 80% illustrated the higher reaction rate constant of 0.1692 min^{-1} , which was about six times over the discharge duty cycles of 50% (0.0277 min^{-1}).

The changes in absorption spectra of MB solution observed at a characteristic peak of 664 nm for different periods by using air APPJ treatment are presented in Figures 10(c-d). The reduction of the characteristic peak intensity showed that the MB solution had been degraded around 55% in the 50% discharge duty cycle for 30 min, as seen in Figure 10(c). In contrast, the complete degradation of MB dye in 30 min of exposure time was obtained for the 80% discharge duty cycles (Figure 10(d)). As the MB decolorization results, the discharge duty cycle of 80% is a promising air APPJ system for the degradation of wastewater. In addition, the photos of

degradation of MB solution taken every 5 min during the air APPJ treatment are shown in Figure 11.

An essential thing for considering the MB degradation is ROS. The generation of ROS by cold plasma increased the formation of $\cdot\text{OH}$ radicals, which improved the dissociation of the water and H_2O_2 in the gas phase and gas-liquid interface (Park *et al.*, 2006; Kostyuk *et al.*, 2008). The attraction of ROS produced in the gas phase above the water surface led to the generation of $\cdot\text{OH}$ radicals at the gas/liquid surface (Park *et al.*, 2006). The occurrence of $\cdot\text{OH}$ radicals in the MB molecules resulted in the ring of the MB opening, leading to the mineralization (amines and organic acids) produced in the MB solution (de B Benetoli *et al.*, 2011). Due to our results, the ROS was detected by the OES, such as the $\cdot\text{OH}$ radicals and O generated in the gas phase. The intensity of $\cdot\text{OH}$ radicals in the air APPJ driven by the discharge duty cycle of 80% was much stronger than that of the discharge duty cycles of 30% and 50% (Figures 5 and 6). Thus, the degradation of MB solution treated by the discharge duty cycle of 80% was the fastest, which correlated to the high intensity of $\cdot\text{OH}$ radicals.

The decreased acidity value and the increased conductivity value in the MB solution treated by the air APPJ were due to the formation of nitrous acid as described in Equations (8)-(10). The generation of RNS during the plasma process is important, affecting the diminution in water acidity (Kostyuk *et al.*, 2008; Sivachandiran and Khacef, 2017). Because of the generation of RONS by the air APPJ, especially NO (A-X) bands (Figure 6(a)), the highest intensity of RNS was generated in discharge duty cycle of 80% according to the lowest acidity and the highest conductivity in the MB solution in our experiments (Figure 9(b)). Likewise, the changes

Table 1. Calculated value of energy yields (Y_{50%}) for treated MB solution with various plasma reactors

Concentration (mg/L)	Type of plasma reactor	Y _{50%} (g/kWh)	Reference
10	The air APPJ with different discharge duty cycles	0.045	This work
13	CGDE in water	0.024	Gong and Cai (2007)
5	RFD in water	0.037	Maehara <i>et al.</i> (2008)
12	Diaphragm discharge in water	0.042	Stará <i>et al.</i> (2009)
50	Microwave plasma jet in contact with water	0.033	García <i>et al.</i> (2017)

in acidity and conductivity in the MB solution treated by the effects of various plasma configurations were proposed, such as electrical discharge plasma reactor (de B Benetoli *et al.*, 2011), pulse nanosecond air discharge (Hamdan *et al.*, 2020), and pulse corona discharge (Magureanu *et al.*, 2013).

The temperature in the solution during the plasma processing also plays a vital role in removing the organic pollutants (Jiang *et al.*, 2012). Due to the joule heating and the heat released by the exothermic reaction, the temperature of the solution increased with the plasma treatment time. An increased temperature in the solution may affect the inclining degradation percentage (Chen *et al.*, 2019; Meiyazhagan *et al.*, 2020). Our results had been shown that the increase of temperature in the MB solution during the air APPJ treatment was related to the increasing degradation percentage. Especially the discharge duty cycle of 80% was found to be ~ 10°C higher than the discharge duty cycle of 50% after 30 min plasma processing. Also, the increase of temperature in MB solution during plasma treatment had been reported (Hamdan *et al.*, 2020; Yehia *et al.*, 2020).

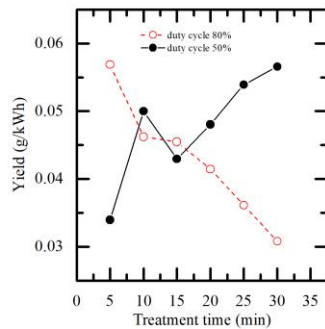
In order to measure the efficiency of the MB degradation, the energy yield was discussed, as demonstrated in Figure 12. The energy yield of the discharge duty cycle of 80% decreased with the increasing treatment time. On the other hand, the trend of the energy yield of the discharge duty cycle of 50% was growth with the increasing treatment time. Interestingly, the energy yields between

discharge duty cycles of 50% and 80% were quite different. Herein, there were two reasons to explain the phenomenon. The first reason is that the MB concentration decreased rapidly with the increasing degradation efficiency over time, causing the energy yield to decrease with the increasing treatment time (Wu *et al.*, 2019). Another reason, the MB concentration slowly declined with the growing degradation efficiency over time, which energy yield increased with the treatment time. Thus, the efficiency of the discharge duty cycle of 80% was the most useful to complete the MB degradation. In contrast, the efficiency of the air APPJ with the discharge duty cycle of 50% was not enough to remove the MB solution. The reduction of the energy yield along plasma treatment time was presented in Ref. Hamdan *et al.* (2020); Yehia *et al.* (2020).

To evaluate the efficiency of MB degradation, the Y_{50%} (the energy yield at half of the treatment time) was calculated. Herein, the Y_{50%} of the discharge duty cycle of 80% was only considered. The Y_{50%} value was 0.045 g/kWh. Comparison of the MB degradation efficiency with other plasma configurations, the literature is present in Table 1.

Conclusions

In this study, the generation of the air APPJ was carried out using three discharge duty cycles with a repetition rate of 100 Hz (sinusoidal) of the neon transformer. The OES results illustrated the NO(A-X) band (235.8, 246.4, 257.7, and 270.7 nm), •OH radical (306.6 and 309.6 nm), N₂ second positive system ($C\Pi_u \rightarrow B\Pi_g$ at 268-546 nm), N₂ first negative system ($B\Sigma_u^+ \rightarrow X\Sigma_g^+$ at 286-587 nm), N⁺ (500.6 nm), N (747.3 nm), and O (777.4 nm) had peaked. Especially the air APPJ spectra under the discharge duty cycle of 80% was the highest relative intensity. The effects of each discharge duty cycle on water properties of deionized water with and without MB, water acidity, conductivity, and temperature, were discussed. Water acidity for all experiments decreased with the increasing treatment time. However, water conductivity and temperature increased with treatment time. Regarding dye degradation, the complete decolorization of MB within 30 min was found in the discharge duty cycle

**Figure 12. Energetic yield for discharge duty cycles of 50% and 80%**

of 80%, with six times of reaction rate constant compared to discharge duty cycle of 50%, which plays an essential role in conveying ROS or RNS from the gas phase to the liquid phase, thus stimulating the degradation of the MB solution.

References

- Brisset, J.L., Benstaali, B., Moussa, D., Fanmoe, J., and Njoyim-Tamungang, E. (2011). Acidity control of plasma-chemical oxidation: applications to dye removal, urban waste abatement and microbial inactivation. *Plasma Sources Science and Technology*, 20(3):034021. <https://doi.org/10.1088/0963-0252/20/3/034021>.
- Burlica, R., Kirkpatrick, M.J., and Locke, B.R. (2006) Formation of reactive species in gliding arc discharges with liquid water. *Journal of Electrostatics*, 64(1):35-43. <https://doi.org/10.1016/j.elstat.2004.12.007>.
- Chen, B., Zhu, C., Fei, J., Jiang, Y., Yin, C., Su, W., He, X., Li, Y., Chen, Q., Ren, Q., and Chen, Y. (2019). Reaction kinetics of phenols and p-nitrophenols in fowing aerated aqueous solutions generated by a discharge plasma jet. *Journal of Hazardous Materials*, 363:55-63. <https://doi.org/10.1016/j.jhazmat.2018.09.051>.
- Ching, W.K., Colussi, A.J., Sun, H.J., Neelson, K.H., and Hoffmann, M.R. (2001). *Escherichia coli* disinfection by electrohydraulic discharges. *Environmental Science & Technology*, 35(20):4139-4144. <https://doi.org/10.1021/es010643u>.
- De B. Benetoli, L.O., Brono, M., Cadorin, B.M., Da S. Postiglione, C., De Souza, I.G., and Debacher, N.A. (2011). Effect of temperature on methylene blue decolorization in aqueous medium in electrical discharge plasma reactor. *Journal of the Brazilian Chemical Society*, 22(9):1669-1678. <https://doi.org/10.1590/S0103-50532011000900008>.
- Diamond, J., Profili, J., and Hamdan, A. (2019). Characterization of Various Air Plasma Discharge Modes in Contact with Water and Their Effect on the Degradation of Reactive Dyes. *Plasma Chemistry and Plasma Processing*, 39(6):1483-1498. <https://doi.org/10.1007/s11090-019-10014-9>.
- Dutta, K., Mukhopadhyay, S., Bhattacharjee, S., and Chaudhuri, B. (2001). Chemical oxidation of methylene blue using Fenton-like reactions. *Journal of Hazardous Materials*, 84(1):57-71. [https://doi.org/10.1016/S0304-3894\(01\)00202-3](https://doi.org/10.1016/S0304-3894(01)00202-3).
- García, M.C., Mora, M., Esquivel, D., Foster, J.E., Rodero, A., Jiménez-Sanchidrián, C., and Romero-Salguero, F.J. (2017) Microwave atmospheric pressure plasma jets for wastewater treatment: degradation of methylene blue as a model dye. *Chemosphere*, 180:239-246. <https://doi.org/10.1016/j.chemosphere.2017.03.126>.
- Gong, J. and Cai, W. (2007). Degradation of methyl orange in water by contact glow discharge electrolysis. *Plasma Science and Technology*, 9(2):190-193. <https://doi.org/10.1088/1009-0630/9/2/15>.
- 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. *Journal of Physics D: Applied Physics*, 45(26):263001. <https://doi.org/10.1088/0022-3727/45/26/263001>.
- Hamdan, A., Ridani, D.A., Diamond, J., and Daghrir, R. (2020). Pulsed nanosecond air discharge in contact with water: influence of voltage polarity, amplitude, pulse width, and gap distance. *Journal of Physics D: Applied Physics*, 53(35):355202. <https://doi.org/10.1088/1361-6463/ab8fde>.
- Houas, A., Lachheb, H., Ksibi, M., Elaloui, E., Guillard, C., and Herrmann, J.M. (2001). Photocatalytic degradation pathway of methylene blue in water. *Applied Catalysis B: Environmental*, 31(2):145-157. [https://doi.org/10.1016/S0926-3373\(00\)00276-9](https://doi.org/10.1016/S0926-3373(00)00276-9).
- Huang, F., Chen, L., Wang, H., and Yan, Z. (2010). Analysis of the degradation mechanism of methylene blue by atmospheric pressure dielectric barrier discharge plasma. *Chemical Engineering Journal*, 162(1):250-256. <https://doi.org/10.1016/j.cej.2010.05.041>.
- Ionita, M.D., Vizireanu, S., Stoica, S.D., Ionita, M., Pandele, A.M., Cucu, A., Stamatina, I., Nistor, L.C., and Dinescu, G. (2016). Functionalization of carbon nanowalls by plasma jet in liquid treatment. *The European Physical Journal D*, 70(2):31. <https://doi.org/10.1140/epjd/e2016-60499-8>.
- Jamróz, P., Gręda, K., Pohl, P., and Żymnicki, W. (2014). Atmospheric pressure glow discharges generated in contact with flowing liquid cathode: production of active species and application in wastewater purification processes. *Plasma Chemistry and Plasma Processing*, 34:25-37. <https://doi.org/10.1007/s11090-013-9503-3>.
- Jiang, B., Zheng, J., Liu, Q., and Wu, M. (2012). Degradation of azo dye using non-thermal plasma advanced oxidation process in a circulatory airtight reactor system. *Chemical Engineering Journal*, 204:32-39. <https://doi.org/10.1016/j.cej.2012.07.088>.
- Kanazawa, S., Kawano, H., Watanabe, S., Furuki, T., Akamine, S., Ichiki, R., Toshikazu, O., Kocik, M., and Mizeraczyk, J. (2011) Observation of OH radicals produced by pulsed discharges on the surface of a liquid. *Plasma Sources Science and Technology*, 20(3):034010. <https://doi.org/10.1088/0963-0252/20/3/034010>.
- Kostyuk, P.V., Park, J.Y., Han, S.B., and Park, S.H. (2008). Effect of Ni and TiO₂ on hydrogen generation from aqueous solution with non-thermal plasma. *Journal of Physics D: Applied Physics*, 41(9):095202. <https://doi.org/10.1088/0022-3727/41/9/095202>.
- Locke, B.R., Sato, M., Sunka, P., Hoffmann, M.R., and Chang, J.S. (2006). Electrohydraulic discharge and nonthermal plasma for water treatment. *Industrial & Engineering Chemistry Research*, 45(3):882-905. <https://doi.org/10.1021/ie050981u>.
- Maehara, T., Miyamoto, I., Kurokawa, K., Hashimoto, Y., Iwamae, A., Kuramoto, M., Yamashita, H., Mukasa, S., Toyota, H., Nomura, S., and Kawashima, A. (2008) Degradation of methylene blue by RF plasma in water. *Plasma Chemistry and Plasma Processing*, 28(4):467-482. <https://doi.org/10.1007/s11090-008-9142-2>.
- Magureanu, M., Bradu, C., Piroi, D., Mandache, N.B., and Parvulescu, V. (2013). Pulsed corona discharge for degradation of methylene blue in water. *Plasma Chemistry and Plasma Processing*, 33(1):51-64. <https://doi.org/10.1007/s11090-012-9422-8>.
- Meiyazhagan, S., Yugeswaran, S., Ananthapadmanabhan, P.V., Sreedevi, P.R., and Suresh, K. (2020). Relative Potential of Different Plasma Forming Gases in Degradation of Rhodamine B Dye by Microplasma Treatment and Evaluation of Reuse Prospectus for Treated Water as Liquid Fertilizer. *Plasma Chemistry and Plasma Processing*, 40(5):1267-1290. <https://doi.org/10.1007/s11090-020-10085-z>.
- Oehmigen, K., Hahnel, M., Brandenburg, R., Wilke, C., and Weltmann, K.D. (2010). The role of acidification for antimicrobial activity of atmospheric pressure plasma in liquids. *Plasma Processes and Polymers*, 7(3-4):250-257. <https://doi.org/10.1002/ppap.200900077>.
- Ollis, D.F. (2018). Kinetics of photocatalyzed reactions: five lessons learned. *Frontiers in Chemistry*, 6:378. <https://doi.org/10.3389/fchem.2018.00378>.
- Park, J.Y., Kostyuk, P.V., Han, S.B., Kim, J.S., Vu, C.N., and Lee, H.W. (2006). Study on optical emission analysis of AC air-water discharges under He, Ar and N₂ environments. *Journal of Physics D: Applied Physics*, 39(17):3805-3813. <https://doi.org/10.1088/0022-3727/39/17/015>.

- Parvulescu, V.I., Magureanu, M., and Lukes, P. (2012) Plasma Chemistry and Catalysis in Gases and Liquids. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. <https://doi.org/10.1002/9783527649525>.
- Pavasupree, S., Chanchula, N., Bootchanont, A., Jitjing, P., Boonyawan, D., and Porjai, P. (2021). Enhancement propagation of protocorms in orchid (*Cymbidium tracyanum* L. Castle) by cold atmospheric pressure air plasma jet. Plasma Chemistry and Plasma Processing, 41(2):573-589. <https://doi.org/10.1007/s11090-020-10148-1>.
- Peng, J.W. and Lee, S. (2013) Atmospheric pressure plasma degradation of azo dyes in water: pH and structural effects. Plasma Chemistry and Plasma Processing, 33:1063-1072. <https://doi.org/10.1007/s11090-013-9483-3>.
- Sano, N., Kawashima, T., Fujikawa, J., Fujimoto, T., Kitai, T., Kanki, T., and Toyoda, A. (2002). Decomposition of organic compounds in water by direct contact of gas corona discharge: Influence of discharge conditions. Industrial & Engineering Chemistry Research, 41(24):5906-5911 17. <https://doi.org/10.1021/ie0203328>.
- Schütze, A., Jeong, J.Y., Babayan, S.E., Park, J., Selwyn, G.S., and Hicks, R.F. (1998). The atmospheric-pressure plasma jet: a review and comparison to other plasma sources. IEEE Transactions on Plasma Science, 26(6):1685-1694. <https://doi.org/10.1109/27.747887>.
- Shi, J.J., Cai, Y., Zhang, J., and Yang, Y. (2009). Characteristics of pulse-modulated radio-frequency atmospheric pressure glow discharge. Thin Solid Films, 518(3):962-966. <https://doi.org/10.1016/j.tsf.2009.07.166>.
- Shi, J.J., Zhang, J., Qiu, G., Walsh, J.L., and Kong, M.G. (2008). Modes in a pulse-modulated radio-frequency dielectric-barrier glow discharge. Applied Physics Letters, 93(4):041502. <https://doi.org/10.1063/1.2965453>.
- Sivachandiran, L., and Khacef, A. (2017). Enhanced seed germination and plant growth by atmospheric pressure cold air plasma: combined effect of seed and water treatment. RSC Advances, 7:1822-1832. <https://doi.org/10.1039/C6RA24762H>.
- Stará, Z., Krčma, F., Nejezchleb, M., and Skalný, J.D. (2009) Organic dye decomposition by DC diaphragm discharge in water: Effect of solution properties on dye removal. Desalination, 239(1-3):283-294. <https://doi.org/10.1016/j.desal.2008.03.025>.
- Thana, P., Wijaikhum, A., Poramapijitwat, P., Kuensaen, C., Meerak, J., Ngamjarrojana, A., Sarapirom, S., and Boonyawan, D. (2019). A compact pulse-modulation cold air plasma jet for the inactivation of chronic wound bacteria: development and characterization. Heliyon, 5(9):e02455. <https://doi.org/10.1016/j.heliyon.2019.e02455>.
- Thiry, D., Konstantinidis, S., Cornil, J., Snyders, R. (2016) Plasma diagnostics for the low-pressure plasma polymerization process: A critical review. Thin Solid Films 606:19-44. <https://doi.org/10.1016/j.tsf.2016.02.058>.
- Wu, L., Xie, Q., Lv, Y., Zhang, Z., Wu, Z., Liang, X., Lu, M., and Nie, Y. (2019). Degradation of methylene blue by dielectric barrier discharge plasma coupled with activated carbon supported on polyurethane foam. RSC Advances, 9(45):25967-25975. <https://doi.org/10.1039/C9RA05238K>.
- Yehia, S.A., Zarif, M.E., Bita, B.I., Teodorescu, M., Carpen, L.G., and Vizireanu, S. (2020). Development and Optimization of Single Filament Plasma Jets for Wastewater Decontamination. Plasma Chemistry and Plasma Processing, 40(6):1485-1505. <https://doi.org/10.1007/s11090-020-10111-0>.
- Yuan, M.H., Narengerile, Watanabe, T., and Chang, C.Y. (2010). DC water plasma at atmospheric pressure for the treatment of aqueous phenol. Environmental Science & Technology, 44(12):4710-4715. <https://doi.org/10.1021/es9038598>.
- Zhang, J., Lee, K.H., Cui, L., and Jeong, T.S. (2009). Degradation of methylene blue in aqueous solution by ozone-based processes. Journal of Industrial and Engineering Chemistry, 15(2):185-189. <https://doi.org/10.1016/j.jiec.2008.09.014>.