Development of non-thermal plasma jet and its potential application for color degradation of organic pollutant in wastewater treatment

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Abstract. This paper presents the development of non-thermal plasma-based AOPs for color degradation in wastewater treatment. The plasma itself was generated by an in-house high voltage power supply (HVPS). Instead of gas-phase plasma system, we applied plasma jet system underwater during wastewater treatment without additional any chemicals (chemical-free processing). The method is thought to maximize the energy transfer and increase the efficient interaction between plasma and solution during the process. Our plasma jet system could proceed either by using helium (He), argon (Ar) and air as the medium in an open air atmosphere. Exploring the developed plasma to be applied in organic wastewater treatment, we demonstrated that the plasma jet could be generated underwater and yields in color degradation of methylene blue (MB) wastewater model. When using Ar gas as a medium, the color degradation of MB could be achieved within 90 minutes. Whereas, by using Ar with an admixing of oxygen (O₂) gas, the similar result could be accomplished within 60 minutes. Additional O₂ gas in the latter might produce more hydroxyl radicals and oxygen-based species which speed up the oxidative reaction with organic pollutants, and hence accelerate the process of color degradation.

Keywords: non-thermal plasma, wastewater treatment, organic pollutant, color degradation

1. Introduction
The textile industry is one of the largest and most complex industrial chains in the manufacturing industry. The stages of a mechanical processing in a production are spinning, knitting, weaving, and garment production. Furthermore, the wet treatment processes like sizing, de-sizing, scouring, bleaching, mercerizing, dyeing, printing and finishing operations. The textile industry emits a wide variety of pollutants from all stages in the processing of fibers, fabrics and garment production [1]. Environmental pollution by organic dyes contribute a severe ecological matter that is elevated by the fact that most of these dyes are difficult to degrade by traditional techniques [2]. Chemical materials or dyestuffs such as acids, alkalis, surface active substances and salts [3] are the components of organic pollutants in the textile industry's liquid waste that must be treated before being discharged from the factory to the environment. Therefore, wastewater treatment technology in textile industries is a must to be accomplished before the water is discharged into the environment.
Typical textile dyes which more often contain azo group and generally used in textile industries could no longer be properly decomposed by the conventional biological wastewater treatment. In addition, the treatment requires more period of time to complete the processing. Another process of chemical treatment is more costly due to large amount of chemicals and also the possible further treatment needed for any by-products sludge problem [4].

Recently, the Advanced Oxidation Processes (AOPs) has taken great attention from many researchers due to its performance to eliminate organic pollutant more effectively compared to those processes mentioned above. As it is known that the hydroxyl radicals (OH*) as the basis of AOPs oxidative reactions has a potential oxidation of 2.80 V over the oxidation potential of ozone of 2.07 V and becomes the only radical whose oxidation capacity exceeds ozone with nontoxic property [5]. This causes the hydroxyl radicals to easily react with almost all chemical compounds, even those of more complex organic compounds. The hydroxyl radicals which are an important reactive species could also be generated by plasma-liquid interactions [6]. Scientific and technological utilization of atmospheric non-thermal plasma can be recognized by the multiplied of its application in a large number of fields such as in environmental engineering, aeronautics and aerospace engineering, biomedical field, textile technology, analytical chemistry, and several other areas. The enormous promise of atmospheric non-thermal technology stems from its remarkable potential for being environmental friendly & energy-saving, its flexibility & capability to create new products and its clear ecological advantages [7].

The results of waste treatment are not produce sludge that formed when chemical is used during the process. Designing high voltage power supply (HVPS) as an electrical energy for non-thermal plasma plant in water and effective plasma reactor design as a plasma treatment medium for wastewater one type of synthetic dye often used in the textile industry is azo dye type. Associated with their interaction with wastewater, there are two types of plasma capable of being used for this purpose, the first being the typical plasma in the form of gas-phase, in which the plasma is generated in the gas phase, above the water surface. Plasma interaction with water under these conditions results in the generation of reactive species such as OH*, \( \text{H}_2\text{O}_2 \), \( \text{O}_2 \) radicals, and other radical species responsible for oxidative reactions with organic pollutants in wastewater. A second type of plasma is the formation of plasma in water (submerged or underwater). In this condition, the oxidative efficiency of species is usually larger than the first type because plasma energy, UV light and shockwaves caused by high voltage from electrical energy are all capable of generating more radical species when in contact with direct water. In this study, we developed non-thermal plasma jet and explored the application of the plasma jet system to degrade the color of wastewater model containing organic pollutants from MB.

2. Experimental

2.1. Electrical Characteristics
The measurement of the electrical characteristics of the non-thermal plasma was performed by connecting the positive to the 6 mm (ext.) cylinder stainless steel and the other electrode of the aluminum was grounded. Both sides of the electrodes are connected to High Probe PD-28 which has a 1000:1 attenuation for the measurement of voltage waveform. Hantek CC-65 current meter was clamped to the negative charge cable for measurement of plasma electric current from plasma. Both meters and the probe are attached to the Hantek DSO5072P oscilloscope for amplitude signal readings.

2.2. Plasma Length Characteristic
In these experiments, we used helium (He), argon (Ar) and air to test the performance of our developed in-house HVPS. The characteristic length of the plasma will be gained as a response to the flow rate of the selected operating gas. The length of plasma measurement was carried out by adjusting the distance of the grounded aluminum electrode towards the positive charge of stainless cylinder at a predetermined applied voltage.
2.3. Exploring the Developed Plasma Source for Wastewater Treatment

The utilization of plasma systems that have been developed was performed on a process treatment of wastewater model containing organic pollutants. The organic pollutant model was MB. Figure 1 shows a schematic diagram of a non-thermal plasma system, prepared for color degradation of organic wastewater model. The stainless cylinder with outer diameter 6 mm and inner diameter 3 mm of the positive electrode was wrapped with a 3 mm in thick of silicone hose. The distance of the edge of silicone hose to the nozzle of cylinder was adjusted at 10 mm. This side of electrode was immersed in 50 ml MB solution in a glass container, while the other side as a place for a flow of gas medium. 2 mm apart from the edge of silicone an aluminum electrode was placed and it connected to the ground. The concentration of MB solution was made by diluting the MB indicator solution as much as 6 ml into 450 ml of mineral water. The measured conductivity of mineral water was 257 μS/cm measured by conductivity meter Mettler Toledo S47-K SevenMulti.

3. Result and Discussion

3.1. Electrical Diagnostic

Figure 2 displays the waveform of voltage and electric current of the Ar plasma sustained by the developed in-house HVPS, measured by the oscilloscope at a distance of 30 mm between the electrodes using 2 liter per minute (lpm) of Ar gas as medium.

![Figure 2](image_url)  
**Figure 2.** The waveform of the voltage and the current signals of the non-thermal plasma that was measured against the time.
From the figure above it is clear that the voltage and signal of electric current oscillate in one phase. The measured voltage amplitude was 3.56 kV peak-to-peak (p-p) and an electric current of 1.74 A peak-to-peak (p-p). The measured frequency was 346 Hz or the wave period was 2890 µs.

3.2. Plasma in Action

The developed plasma jet system with in-house HVPS can generate non-thermal discharge either by using He, Ar or air as the medium in an open air atmosphere source. The operation temperature of both He plasma and Ar plasma could reach not more than 28°C, whereas the air plasma produce higher operation temperature up to 38°C during 2 minutes measurement by using a digital thermal imaging camera FLIR-TG 165. The picture of He plasma, Ar plasma and air plasma in real condition can be seen at the Figure 3-5.

![Figure 3. Helium plasma in action, with flow of He: 2 lpm and applied voltage 3.5 kV](image)

![Figure 4. Argon plasma in action, with flow of Ar: 2 lpm and applied voltage 3.5 kV](image)

![Figure 5. Air plasma in action, with flow of air: 2 lpm and applied voltage 3.5 kV](image)
As shown on those figures, He plasma reveals a typical glow-like discharge with luminous light. On the other hand, the Ar plasma and air plasma have typical filamentary plasma, in which many micro discharges in the form of light filaments occurred during the sustainable plasma between those two electrodes.

3.3. Plasma Length Characteristics
From the length characteristic of the plasma, we can determine how far a material or object can be placed to be treated with non-thermal plasma by using developed HVPS. Table 1 shows the length of plasma as a response to the various flow rate of the gas medium.

| Gas   | Flow (liter per minute) | Plasma length (mm) |
|-------|-------------------------|---------------------|
| Argon | 1                       | 35                  |
|       | 2                       | 30                  |
|       | 3                       | 25                  |
|       | 4                       | 22                  |
|       | 5                       | 20                  |
|       | 6                       | 18                  |
|       | 1                       | 30                  |
|       | 2                       | 35                  |
|       | 3                       | 42                  |
|       | 4                       | 32                  |
|       | 5                       | 28                  |
|       | 6                       | 26                  |
| Helium| 1                       | 15                  |
|       | 2                       | 10                  |
|       | 3                       | 5                   |
| Air   | 1                       |                     |
|       | 2                       |                     |
|       | 3                       |                     |

It is interesting to note that our developed in-house HVPS can generate plasma by using more economical gas of air as gas medium. This potential replacement of noble gases will bring the benefit of reducing the operating cost. It is generally known that normally plasma at atmospheric pressure operates on noble gases such as He and Ar as a feeding gas flow. However, in this study the developed HVPS could demonstrate good performance with plasma-generating capability in both He, Ar and air as its gas media. Both of Ar and air plasmas show the decreasing of plasma length when the flow rate increases. While the trend of the length of He plasma increases into the maximum before decreases by flowing more He volume. From Table 1, it can also be seen that the longest plasma as far as 35 mm can occur with the Ar gas medium at a flow rate of 1 lpm. For He gas, the largest plasma length was 42 mm at the flowrate of He 3 lpm. Air with a flow rate of 1 lpm was also capable of generating plasma as far as 15 mm. All of the plasma length has been achieved at the applied voltage of 3.5 kV. It should also to be noted from our trials that the plasma length can expand to 50 mm by adjusting both of gas flow rate and utilized applied voltage.

3.4 Initial Experiment of Implementation Plasma System for Color Degradation
In order to realized the possibility of the application of the non-thermal plasma powered by the developed HVPS into practical textile industry, the decoloration process of organic wastewater with a methylene blue solution model has been examined. The plasma jet system operated underwater was performed with using 0.4 lpm Ar gas as a medium. In this experiments, the plasma jet was not generated when the used of Ar flow was more than 0.8 lpm. Adjusting the gas flow rate and applied voltage were done to gain the optimal Ar discharge underwater like depicted in the Figure 6. The more intense of discharge light visually occurred will be presumed to the more formation of radical species which will oxidatively
consume the organic pollutants. The voltage and current waveforms during plasma treatment in wastewater model was inspected and the oscillograms can be seen at the Figure 7.

Figure 7. The voltage and the current waveforms which were measured against the time of the non-thermal plasma during wastewater treatment.

As seen on Figure 7, the measured voltage is 1.52 kV (p-p) and an electric current of 410 mA (p-p) was thought to be capable of generating plasma for the benefit of water treatment of organic pollutant in the form of plasma under water. The measured wave frequency was 12.82 kHz or the wave period of 78 µs. The results obtained due to non-thermal plasma treatment on methylene blue (MB) solution is shown in Figure 8, where the color of MB solution degraded from blue color in the initial solution to almost transparent after the treatment of plasma up to 90 minutes with Ar gas as a medium as well as bubbling gas in solution. It was generally known that during plasma treatment, interaction of the discharge an the water would produce the hydroxyl radicals through the decomposition of water molecules and lead to the production of the successive the longer-live hydrogen peroxide [8]. Those radical species as well as the shockwaves and UV production due to the plasma underwater are responsible to make oxidative reaction with the MB molecule and hence proceeds the process of color degradation. Figure 8 shows the decoloration trend of the MB solution which was in order of the plasma treatment time of 0, 30, 60, and 90 minutes.
Figure 8. Color degradation in wastewater treatment using Ar plasma.

Figure 9. Comparison of color degradation of MB solution using Ar plasma and Ar+O\textsubscript{2} plasmas.

The wastewater that was treated by the Ar in 90 minutes has almost the same color as the one treated with 0.4 lpm Ar and 0.2 lpm O\textsubscript{2} that only took 60 minutes. The results of these tests suggest that by using Ar plus O\textsubscript{2} as media could accelerate the process of water degradation. Additional O\textsubscript{2} gas in the latter plasma might produce more hydroxyl radicals and other oxygen-based species which speed-up the oxidative reaction with organic pollutants, and hence accelerate the process of color degradation. However, there is still much improvement to be done regarding to the implementation of non-thermal plasma system for organic wastewater treatment. Designing plasma chamber, optimization of plasma parameters are some of the tasks that must be investigated in order the non thermal plasma system can run more effectively and therefore open the possibility to be applied in the textile industry.

4. Conclusion
We are successful in developing non thermal plasma powered by an in-house HVPS which has the possibility to be applied for decoloration of organic wastewater. The plasma system can be generated by using He, Ar and air as a feeding gas and the characteristics of the non thermal plasma has been investigated. Initial exploration of this plasma system in degrading organic wastewater of MB solution gave a results that the solution can turns into almost transparent water in 90 minutes by using Ar plasma jet underwater. With using a similar system, an admixing of oxygen gas into Ar plasma makes an acceleration of the decoloration process with giving a similar result to the former in 60 minutes. Through this result we can conclude that non-thermal plasma in organic wastewater processing may provide an environmentally friendly treatment due to its potential of utilizing no chemical (chemical-free) during the processes and also have a potential application in textile industry.
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