ORGANIC POLLUTANT MODEL OF METHYLENE BLUE DYE DECOLORATION BY NON-THERMAL PLASMA ADVANCED OXIDATION PROCESSES (AOPs) WITH PIN TO SURFACE CONFIGURATION

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ABSTRACT

The dye decoloration of methylene blue (MB) solution treated by nonthermal plasma advanced oxidation processes (AOPs) has been investigated using a pin to surface configuration plasma system at atmospheric pressure. A homemade flyback transformer was utilized to power up this gas-phase plasma system and its electrical characteristics were presented in the form of voltage amperage waveforms. UV/Vis analysis was employed to monitor the influence of plasma treatment time on the decreasing of MB concentration as well as to measure the decoloration efficiency. It was found that the decoloration efficiency of MB solution can reach 93% after 120 minutes of plasma treatment to result in transparent water. Furthermore, FTIR analysis was performed to recognize the differences in MB organic functional groups before and after plasma treatment and to confirm the mineralization process that was occurred during plasma irradiation. During plasma irradiation, the interaction between hydroxyl radicals and other various reactive species transforms the organic pollutants into the harmless sediments through complex chemistry reactions. Due to all of the plasma treatments were carried out without the addition even a single chemical; it can be conclude that nonthermal plasma system may potentially become one of the competitive environmentally friendly techniques in destruction and decoloration of an organic polluted solution such as textile wastewater.

Keywords: Dye Decoloration, Methylene Blue, Organic Pollutant, Pin to surface configuration, Plasma AOPs, FTIR

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INTRODUCTION

Textile industry can produce hazardous wastewater and it will possibly become a serious problem to the environment if it is not treated properly. That effluent contains not only the unsafe chemical pollutants but also has potentially included the toxic organic contaminants which would be very harmful to the aquatic ecosystem in rivers, lakes, and seas if it directly discharges without treatment^{1,2}. In addition, the wastewater has also an undesirable color which could inhibit the photosynthesis process in water ecosystem and possibly cause the death of flora and fauna³. The main contaminants in polluted textile effluent are mostly due to the usage of reactive synthetic organic dyes during textile colorization processes⁴. Recently, those strongly organic dyes utilized in the textile industry are dominated by typical azo dyes (up to 60%) which generally known in exhibiting superior performance among the commercial various type of organic dyes material^{5,6}.

Conventional treatment of textile wastewater using a biological process such as bacteria (bacterial consortium alkaliphilic) does not seem to be effective⁷ because the process may take up to 5 days for 50 ml of mineral salt medium⁸. On the other hand, the chemical treatment method requires a large number of

chemicals and must consider the further treatment for the by-product sludge, which will need more expensive costs⁹. The use of the two methods mentioned above is commonly applied in textile wastewater treatment, unfortunately, due to their high stability to light, temperature, water, detergents, chemicals, soap and other parameters such as bleach and perspiration, those conventional wastewater treatments could no longer treat the synthetic azo dyes in an efficient manner¹⁰. Therefore, the researchers, as well as the industry practitioners, keep trying to develop the novel technology to combat the harmful organic contaminants in textile wastewater efficiently and environmentally friendly.

Advanced Oxidation Processes (AOPs) is currently known as a new solution for textile wastewater and has received great attention from many researchers¹¹⁻¹³. AOPs is a technique of the removal process of organic contaminants from wastewater through oxidation reaction with hydroxyl radical (*OH)¹⁴⁻¹⁶. The reaction may take place because hydroxyl radicals are one of the typical highly reactive chemical compound, having a relatively high oxidation potential of 2.8 V¹⁷, thus as a consequence, it can react easily to convert any organic pollutants into harmless compounds^{18,19}. It is generally known that hydroxyl radicals in a solution can be produced through various processes, like ozonation, hydrogen peroxide addition, UV irradiation, electrochemical oxidation, and by the combination of one of them²⁰, as well as through irradiation by non-thermal plasma that can be applied either on the surface of the water or through the direct irradiation underwater, to oxidize the organic contaminant molecules²¹. When non-thermal plasma interacts with water, a variety of reactive species could be produced including excited species, excited neutral molecules, free radical, and positive and negative ions²². In the gas-liquid interface, the reactive species created are H₂O, O₃, and *OH without the addition of chemical and UV costs²³. Due to its capability in producing those of many types of reactive species above which needed to attack the organic pollutants with having no production of secondary pollution, the technology of nonthermal plasma is being highly considered to be utilized for wastewater treatment.

The present study aims to reduce and to eliminate pollutants from organic dyes solution through AOPs method using non-thermal plasma with a pin to surface configurations. Methylene blue was chosen as the azo dye model and the process of its solution decoloration was investigated. The effects of some parameters such as electrode distances and treatment time were examined to assess the prospect feature of non-thermal plasma surface treatment on the wastewater treatment. Moreover, the percentage decoloration at various plasma treatment time via UV/Vis data and the difference of molecular structure of dried methylene blue before and after plasma treatment through FTIR analysis were also investigated.

EXPERIMENTAL

Figure-1 shows the schematic diagram of the nonthermal plasma system at atmospheric pressure used to treat methylene blue solution with a pin to the surface configuration used in this study. A homemade flyback transformer was used as a source of high voltage for plasma discharge generation. A transformer driver circuit was used as a connector from the mains 220 V to power up the output of the flyback up to 6.5 kV. A cone-shaped copper rod with 3 mm in diameter as the pin electrode was connected to the positive pole of the transformer and the distance of the pin to the conductive water surface could be adjusted. On the other side, the negative pole of the transformer was connected to the conductive water surface using a stainless steel electrode. The concentration of methylene blue (C₁₈H₁₈ClN₃S) (MB) solution was made by mixing 6 ml MB indicator to the 450 ml mineral water. The conductivity of the used mineral water was 248 µS/cm measured by conductivity meter Mettler Toledo S47-K Seven Multi. 50 ml MB solution sample was poured into a glass container and was used as a solution sample to be treated by plasma discharge.

Voltage measurement was performed by using a PD-28 high voltage probe with a 1000:1 attenuation ratio. Current measurement was recorded using the Hantek clamp ampere, CC-65. The signals from both probes were viewed with a DSO 5072P Hantek digital oscilloscope. The decoloration of methylene blue solution as a result of plasma treatment on discharge period of time was studied through measurement of absorbance value by means of UV/Vis spectrophotometer (Thermo Scientific Genesys 10S). The maximum wavelength observed in the spectrophotometer was the absorbance at the peak of 665 nm.

The percent decoloration (%) was calculated by the following Eq.(1) formula:

$$\text{Percent decoloration} = \frac{(\text{Abs}_0 - \text{Abs}_n) \times 100\%}{\text{Abs}_0} \quad (1)$$

Fig.-1: Schematic Diagram of Non-thermal Plasma AOP System Based on Pin-surface Configuration for Removal of Organic Contaminants in Organic Dye Solution

Abs₀ is absorbance value with no treatment; Abs_n is absorbance value with plasma treatment. Furthermore, the investigation of the molecular structure of the methylene blue solution sample before treatment and some samples after plasma treatment were studied to understand the influence of nonthermal plasma treatment on MB chemical structure. The examination of dried MB solution sample was spectroscopically performed by means of FTIR analysis and was carried out by Thermo-Fischer Scientific Nicolet iN10 FTIR machine with condition of 64 scans/12 sec and the wavelength measurement range 675 to 4000 cm⁻¹.

RESULTS AND DISCUSSION

Determination of Electrode Distance and Electrical Diagnostic

For the plasma system that is studied, the distance between the pin electrode to the water surface can be adjusted to determine the desired plasma discharge with the highest stability. The thermal effect of the plasma irradiation can be avoided since the temperature of a plasma and the solution never exceeded 40°C during the treatment process, as measured by thermal imaging camera FLIR TG-165. This is also a confirmation that the generated plasma at one atmospheric pressure in this study was typical nonthermal plasma discharge.

Before carrying out the testing of the effect of plasma treatment on the decoloration of the MB solution, the primary thing to do was to find out what was the optimum distance between the pin electrode and conductive water in sustaining the most stable plasma utilized for treatment. From the experiment, it was found that when the distance between pin to the water surface was adjusted to 2 mm, the discharge seems to have a white arc due to the very close distance. The strong energy of the arc discharge will produce high intense local heating around the electrodes, thus it may affect the rapid evaporation of the water due to the highly localized thermal effect during the water treatment process. Increasing the distance to the 4 mm made the plasma becomes stable since the glow-like discharge appears in a good mode. Increasing the distance between electrodes to 6 mm, the condition was almost similar to the distance of 4 mm, except the diameter of discharge was thinner. In addition, it was observed that sometimes it was found that the discharge starts into an unstable mode. When the gap between electrodes was escalated to 8 mm, the occurrence of plasma instability becomes very frequent, thus it was considered not suitable to be used to treat the MB solution.

Through this experiment, we have come into the decision to use the condition of the 4 mm distance mm in between the electrodes to be used for the wastewater plasma treatment. For the electrical diagnosis of the plasma, the graphic of the voltage and amperage waveforms of that condition was exhibited at Fig.-2 and the corresponding photograph of the plasma discharge during interaction with MB surface can be seen at Fig.-3. Both of output voltage and amperage waveforms show the typical damping oscillation to sustain the glow-like plasma discharge.

Fig.-2: Voltage and Current Waveforms of The Plasma with Electrodes Distance of 4 mm

Fig.-3: Non-Thermal Plasma in Action with Electrodes Distance of 4 mm

UV/Vis Analysis

The effect of plasma treatment time on the methylene blue decoloration is shown in Fig.-4. The data was taken from the absorbance value at 665 nm of each MB solution with the associated of the plasma treatment time. It was found that MB decoloration increased with the increasing of plasma treatment time and the decoloration efficiency could reach 93% when the plasma treatment was carried out in 120 min. It is generally known that the gas-phase chemistry of continuous plasma irradiation to the water surface causes the production of hydroxyl radicals and many other active species which drives the process of advanced oxidation in solution. Gas-phase species of reactive oxygen and nitrogen species, along with hydrogen peroxide diffuse into the water via Henry's law²⁴ may responsible to consume the organic compounds in the dye solution.

As a result, based on the principle of this advanced oxidation processes, the decoloration and mineralization process were occurred simultaneously during plasma irradiation to transform almost all of those MB organic compounds to the sediment mineral and change the blue color of solution into colorless water. The picture which shows the sequence of color degradation of MB solution that corresponds to the gas-phase plasma treatment time in every 20 min sample can be seen at the Fig.-5.

Fig.-4: The Effect of Plasma Treatment Time on The Percentage Decoloration of Methylene Blue

Fig.-5: Color Degradation of MB Solution as a Response to The Gas-Phase Plasma Treatment Time

FTIR Analysis

Infrared spectrophotometer that was utilized in the present study was performed to confirm the presence of methylene blue functional groups as well as to distinguish the molecular structure of methylene blue solution after plasma treatment. Fig.-6 shows the FTIR spectrum of methylene blue as a control. It can be observed from the figure that some important MB functional groups such as: the broad band with the peak at 3417 cm^{-1} which may be associated to the -NH/-OH overlapped vibration, the peak at 2889 cm^{-1} that belongs to the stretching vibration of -CH- aromatic group. The absorbance bands at 1606 cm^{-1} and the peaks ranging from 1456 cm^{-1} to 1352 cm^{-1} may indicate the stretching band of C-N from amide II and the aromatic ring structures in methylene blue, respectively. The strong peak at 1112 cm^{-1} and 852 cm^{-1} are assigned to the bending band of N-H and C-N from the amide III band functional group²⁵. Plasma treatment in methylene blue solution converts molecular structure from solution to become just water structure. This can be seen clearly on FTIR spectra of the solution after plasma treatment in Fig.-7. The sample spectrum displayed is the spectrum of MB solution after plasma treatment in 20 minutes 40 minutes and 80 minutes treatment time. The spectrum of 20 minutes plasma treatment shows the very broad band in the range from $3000 - 3700\text{ cm}^{-1}$ which represents the O-H stretching and the strong peak at 1643 cm^{-1} which is associated with O-H-O bending scissors. Extending the plasma treatment time to 40 min and 80 min exhibit no remarkable differences in the FTIR spectrum compared to the 20 min plasma treatment. From FTIR analysis, we can conclude that the destruction of the MB functional group has occurred during the plasma gas phase irradiation to the methylene blue solution. The complex chemistry of the reaction between produced hydroxyl radicals and other active species due to plasma discharge irradiation with the organic contents gave reasonable analysis to proceed the decoloration process which simultaneously transforms them into the harmless and undissolved sediments through the mineralization process.

Fig.-6: FTIR Spectrum of Dried Methylene Blue

Fig.-7: FTIR spectrum of MB after treated by nonthermal plasma for 20 min, 40 min and 80 min

In this study, the processing of wastewater containing organic pollutant seems too long to treat wastewater to become almost completed decoloration water which requires 120 minutes. However, by using nonthermal plasma technology one can assure that the organic pollutants contained in wastewater can be decomposed through mineralization processes. Thus, even though some textile wastewater containing some hazardous matter such as azo substance, nonthermal plasma system is capable enough to transform them into carbon dioxide, water and harmless material. As a result, the discharging effluents may environmentally friendly. It should be noted that the improvement of this system must continue to be made so that this system can be used in treating wastewater containing organic pollutants on a larger scale with processes that can take place faster and produce better results. For example, the necessity to design a similar plasma system with a configuration of multiple pins to enhance the interaction of the plasma volume with the water surface.

CONCLUSION

The present study deals with a development of non-thermal plasma with homemade Flyback-based power supply to be applied for the degradation of organic pollutant in model solution with a pin to water surface configuration at atmospheric pressure. Our experiment result with gas-phase plasma system shows that the distance of 4 mm between the two electrodes is the most stable condition to sustain plasma discharge. Exploring this plasma configuration in decolorizing MB solution, it was found that the decoloration efficiency will increase with the increase of plasma treatment time and it achieved as high as 93% when it was treated for 120 minutes. FTIR analysis confirms the destruction of methylene blue functional groups into water structural and the mineralization process that was occurred during gas-phase plasma irradiation

to transform all functional groups of MB solution into harmless material. Through these experiments, we can conclude that non-thermal plasma AOPs method has a great possibility for textile wastewater treatment in substituting conventional biological and chemical processes because plasma AOPs could be carried out without addition of any chemicals, which of course considered as an environmentally friendly treatment processes.

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