Influence of admixing oxygen on Ar plasma discharge for organic pollutant degradation in wastewater treatment

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Abstract. In previous study, non-thermal plasma system with addition of O_2 gas was proven to accelerate the decolorization process of dye solution, resulting in faster treatment of the synthetic wastewater. The present study deals with the influence of variation of O_2 gas admixing to the Ar plasma discharge to examine the decolorization of methylene blue solution underwater through measurement of absorbance value of the plasma-treated solution by UV/VIS measurement. From the experiments it was found that the best result of methylene blue solution decomposition was obtained from the application of Ar 0.3 lpm with the admixing of O_2 gas 0.3 lpm in an underwater plasma system generated at 1.56 kV. Modelling the decomposition process of methylene blue by using Ar+O_2 plasma with variation of O_2 flow rate, it was found that the system was confirmed to follow the first order kinetics equation. From this study it could be said that the plasma-based oxidation process is promising for the application in the decomposition of textile wastewater to support sustainable industry with environmentally friendly orientation.

Keywords: non-thermal plasma, wastewater treatment, advanced oxidation processes, organic pollutant degradation

1. INTRODUCTION

The most complicated and difficult variable that determines the demand of fashion goods is color [1]. Color is a tool to form product's differentiation resulting advantages, such as increased sales [2] which explain the use of synthetic dyes in textile industries. One of the greatest advantages of using synthetic dyes is the good reproducibility of color shades or hue, while natural dyes are vary depending on seasons [3]. In mass production of textile, having the same shade for the finished goods is an important quality measurement for big textile companies. In addition to that reason, other equally important reasons are the economical price and wide variety of colors [4].

Over million tons of dyes produced per year (50% are textile dyes) [5] where there is a known type of synthetic dyes that represents 70% of more than 100.000 chemical classes of dyes available commercially, named azo dyes [6]. In producing dyes, the quality parameters are the depth of the color, chromophoric strength and the brightness of hue. Those criteria exist due to the targets that are set by textile industries such as degree of color permanency, consistent with the stringent requirements of fastness to various agencies (washing, rubbing, heat, light, perspiration, etc.) with the result of fixation on selecting the appropriate dye class [7]. In achieving these targets, typical azo dyes which giving many beneficial among other dyes are chosen as the best synthetic dye to be used. Therefore, immense efforts are given to design and manufacture novel chromophores to meet the endless development of the highly competitive world market [8].

During the coloring process, a non-effective process generates a large amount of dyes residues, which are directly released after passing the conventional treatment systems of the companies [9]. Conventional wastewater treatment could no longer treat azo dyes efficiently due to their high stability to light, temperature, water, detergents, chemicals, soap and other parameters such as bleach and perspiration [10] thus discharging a large amount of azo dyes into the water [9] and resulting an environmental pollution. Azo dyes belong to a group of organic compounds [11] and contain one or more azo group (-N=N-) that could resist the breakdown and accumulate in the environment at high levels with degree of persistence [12]. This concern has led researchers to develop new technologies that could efficiently eliminate organic compounds.

In recent years, the development of advanced oxidation process has received great attention for its fast removal rate and environmental compatibility and considered as a promising technology [13]. There are several conventional oxidation methods (thermal-based and catalysis-based) that face many challenges such as counter reaction when the temperature is too high (thermal method) [14] and catalysts that come at high cost (catalysis-based method). In order to overcome the aforementioned limitations of the conventional oxidation methods, the advance oxidation processes (AOPs) are emerging. One of the promising AOPs is non-thermal plasma process. It is known for its ability to generate hydroxyl when it interacts with water [15] with no addition of catalyst. Non-thermal plasma is being utilized by many researchers due to its excellent performance of attacking organic pollutant and having no secondary pollution [16].

In previous study, non-thermal plasma system with addition of O_2 gas was proven to accelerate the decolorization process of dye solution, resulting in faster treatment of the synthetic wastewater. The present study deals with the influence of O_2 gas admixing to the Ar plasma discharge to examine the decolorization of methylene blue solution through measurement of absorbance value of the plasma-treated solution by UV/VIS measurement. Moreover, The decomposition of methylene blue solution by using $Ar+O_2$ plasma with the variation of O_2 flow rate was tried to be modelled by using first-order kinetics equation.

2. Experimental

2.1 Non Thermal Plasma System for Wastewater Treatment

The utilization of plasma systems that have been developed was performed on a process treatment of wastewater model containing organic pollutants [17]. 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 that was connected to 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. An aluminium electrode was placed by 2 mm apart from the edge of silicone, and 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 239 μS/cm measured by conductivity meter Mettler Toledo S47-K SevenMulti. The

absorbance values of the solution were obtained from Thermo Scientific Genesis 105 UV/Vis. All experiments were conducted with a submerged plasma system that generated by a high voltage power supply at 1.56 kV.

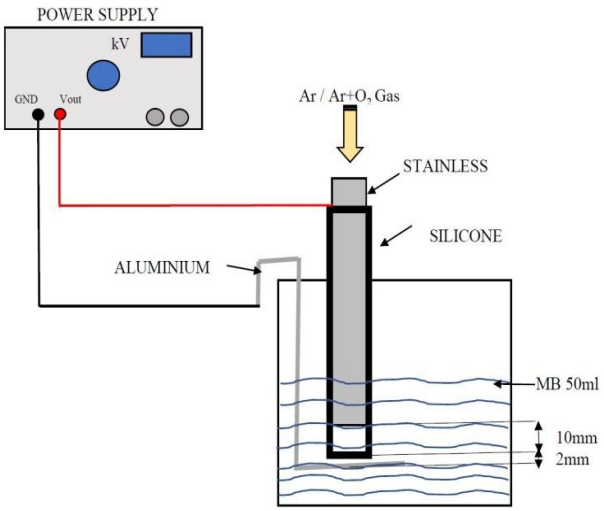

Figure 1. Schematic diagram of non-thermal plasma experiment for degradation of methylene blue solution

3. Results and Discussion

3.1 Effect of Admixing O_2 and Ar to the Absorbance Value

In this study we compared the absorbance value of the non treated MB solution to the Ar plasma with admixing of oxygen gas at the predetermined period of time. The flow rate of argon was set to 0.3 liter per minute (lpm) while the flow oxygen was set to 0.2 lpm. The absorbance value was measured by a UV/Vis spectrophotometer as a representative to the corresponding concentration of MB solution. The wavelength of light used in the spectrophotometer for MB solution was at 665 nm [18]. The following Table 1 shows the absorbance values of plasma treated MB solution with and without the admixing of 0.2 lpm oxygen gas to the Ar plasma as a response to th plasma treated time.

Table 1. The Influence of plasma treatment time on absorbance value of methylene blue solution

Time (minutes)	Ar 0.3 lpm + O_2 0 lpm	Ar 0.3 lpm + O_2 0.2 lpm
0	0.693	0.693
15	0.605	0.591
30	0.557	0.483
45	0.496	0.439
60	0.450	0.390

As it could be seen in Table 1 above, the treated solutions give a similar result in decreasing of the absorbance values as a response to plasma treatment time. The Ar plasma that was generated by admixing O_2 gives a greater result of the decreasing of UV/Vis absorbance value. The corresponding figure of the decreasing of absorbance value between the two could be observed in Figure 2.

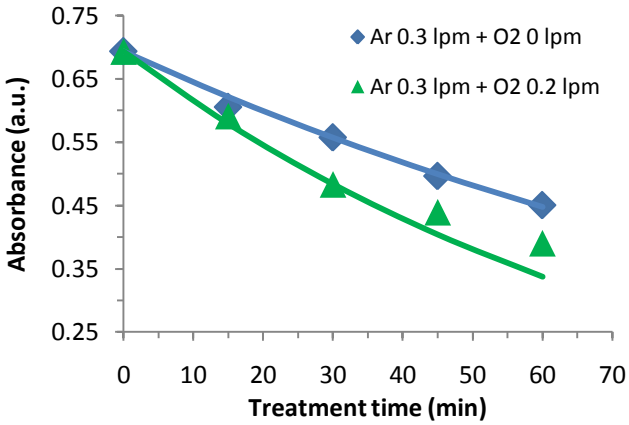

Figure 2. The influence of plasma treatment time on absorbance value of methylene blue solution

Figure 2 shows that by admixing O_2 to Ar plasma in treating MB solution, the decreasing graphic of absorbance value found to be steeper than the decreasing condition by treating with Ar plasma only, at the same plasma treatment time. By using Ar the absorbance value decreased to 0.45 at 60 minutes, while by adding oxygen to the system, it could decrease the value to 0.39 at the same time. According to Beer-Lambert law, the higher the absorbance value signifies a higher concentration of a solution. Based on the result, we could conclude that the concentration of the methylene blue solution decreases by the increasing of the treatment time; on the other hand addition of O_2 generates more oxygen-based free radical as strong oxidizers to consume more organic MB dye, resulting in the rapid decreasing of solution concentration, observed by their corresponding absorbance value.

Table 2 and its corresponding Figure 3 show the effect of O_2 flow rate variation to the absorbance value of methylene blue solution for predetermined plasma treatment period of time. From the Figure 3, it can be showed that the greater the flow rate of oxygen added to Ar plasma, the faster of the decrease in the concentration of methylene blue solution obtained. In this experiment, the addition of oxygen gas up to 0.3 lpm still keeps Ar plasma sustained and makes the largest number of radical species formed among other conditions in consuming organic MB. Adding the flow rate of oxygen to 0.4 lpm makes the discharge of the plasma underwater becomes smaller, and increasing it into 0.5 lpm will make the discharge underwater very hard to be generated.

Table 2. The effect of variation admixing oxygen flow rate to Ar plasma on the absorbance value of methylene blue solution at different time of tretment

Time (minutes)	Ar 0.3 lpm	Ar 0.3 lpm + O_2 0.1 lpm	Ar 0.3 lpm + O_2 0.2 lpm	Ar 0.3 lpm + O_2 0.3 lpm
0	0.693	0.693	0.693	0.693
15	0.605	0.597	0.591	0.481
30	0.557	0.543	0.483	0.439
45	0.496	0.479	0.439	0.354
60	0.450	0.412	0.390	0.323

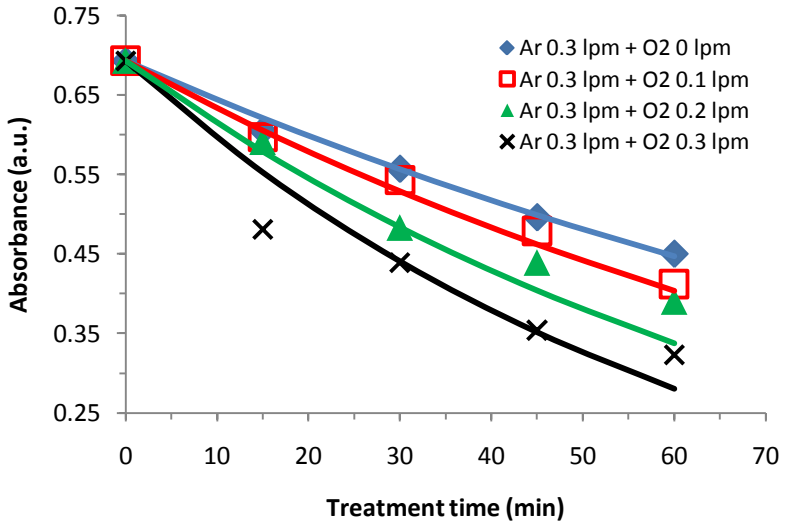

Figure 3. The influence of variation admixing O_2 ratio to Ar plasma on absorbance value of methylene blue solution at different plasma treatment time.

The decomposition of MB by using Ar+O_2 plasma with variation of O_2 flow rate could be modelled by using first-order kinetics equation, as follows:

$$\frac{dC}{dt} = -k\,C \tag{1}$$

With C= concentration (or in this case the absorbance intensity), t = treatment time (min), and k = first-order kinetics parameter. The above formula could be rearranged to:

$$\frac{dC}{C} = -k\,dt \tag{2}$$

And when we integrated those sides, it would become:

$$\int \frac{1}{C}\,dC = \int -k\,dt \tag{3}$$

With initial conditions of t = 0, and C = C_0, Equation 3 could be integrated as follows:

$$\int_{C_0}^{C} \frac{1}{C}\,dC = \int_{0}^{t} -k\,dt \tag{4}$$

and rearranged into:

$$\ln C - \ln C_0 = -k\,t \tag{5}$$

$$\ln \frac{C}{C_0} = -k\,t \tag{6}$$

By converting the logarithmic form in the left-hand side,

$$\frac{C}{C_0} = \exp\,(-k\,t) \tag{7}$$

It would be resulting in the exponential-based model equation of:

$$C = C_0 \exp\,(-k\,t) \tag{8}$$

By employing Equation 8 into the results in Table 2, the decomposition of MB by using Ar+O_2 plasma in this study could be modelled by applying the kinetics parameter in tabulated Table 3, with the goodness of fit (R^2) is >0.9 (or >90%). Furthermore, it could be confirmed from Table 3 that the plasma-assisted oxidation process follows the first-order reaction. Moreover, the kinetic parameters are obviously increasing as function of O_2 flow rate, suggesting the strong relationship of O_2 for aquatic plasma-based decomposition of MB as the model dye. Based on this result, it could be estimated that the plasma-based oxidation process is promising for the application in the decomposition of textile dyes, directly in the liquid form.

Table 3. First-Order Kinetics Modelling Parameter for MB Decomposition by Using Ar+O_2Plasma in This Study

Treatment	k	R^2
Ar 0.3 lpm + O_2 0 lpm	0.0073	0.995
Ar 0.3 lpm + O_2 0.1 lpm	0.0090	0.991
Ar 0.3 lpm + O_2 0.2 lpm	0.0120	0.984
Ar 0.3 lpm + O_2 0.3 lpm	0.0151	0.933

Note: Initial concentration of MB solution was correlated with absorbance value of 0.693.

4. Conclusion

In this study, an apparatus of plasma for advanced oxidation process have been successfully developed and applied to degrade the methylene blue dye solution directly in the form of aquatic phase. The best result is from application of Ar plasma 0.3 lpm, combined with O_2 plasma 0.3 lpm. The plasma-assisted decomposition was confirmed to follow the first-order kinetics, owing to the application of modeling in this study. This method would be very promising to be applied for the large-scale use of textile wastewater treatment to support sustainable ecological environment.

5. Acknowledgement

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6. References

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