Degradation of high-concentration simulated organic wastewater by DBD plasma

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ABSTRACT

In this study, a high-concentration simulated organic wastewater, made by dissolving methyl violet in water, was degraded using dielectric barrier discharge (DBD) plasma generated in air and O₂ respectively. The decoloration rate and chemical oxygen demand (COD) of wastewater were evaluated during plasma treatments with the initial concentration of methyl violet of 300 mg L⁻¹. Results showed that the highest decoloration rate of around 100% within 10 min and the highest COD decrease of 33% within 60 min could be achieved with the O₂ plasma treatment at the discharge voltage of 10 kV, while air plasma treatment showed lower efficiency in decolorizing the methyl violet solution and lower COD decrease (24%) after 60 min treatment. UV-Vis spectroscopy and chemical analysis of generated by-products during the plasma-enabled degradation process revealed that the methyl violet molecules could be completely decomposed into some refractory organics in the solution. Based on the experimental results and literature review, a pathway of methyl violet degradation attributed to energetic electrons and highly reactive species generated by DBD was proposed.

Key words | chemical oxygen demand (COD), decoloration, dielectric barrier discharge (DBD) plasma, methyl violet, organic wastewater

INTRODUCTION

In recent years, much toxic wastewater containing various pollutants has been poured into the rivers without any treatment, with the accelerating pace of industrialization, which poses a devastating effect on the entire regional ecosystem, especially for water systems (Garcia-Segura & Brillas 2017; Abargues et al. 2018; Kaur et al. 2018; Madureira et al. 2018; Zhu et al. 2018). A number of pollutants have been found in natural environments, mainly from domestic industries, such as plastic manufacturing industry, pharmaceutical industry and printing and dyeing industry. Moreover, different pollutants generated from different fields display different contamination degree. Especially, the wastewaters from washing, printing and dyeing processes in the paper industry (Li et al. 2016) and from chemical synthesis in the pharmaceutical industry (Gadipelly et al. 2014; Hama Aziz et al. 2017) are difficult to be degraded because of their problematic characteristics, such as high pollutant concentration, high potential toxicity and the existence of non-degradable substances.

The current methods for wastewater treatment mainly include electrolysis, sonication, anaerobic degradation, ultrafiltration, chlorination and a combination of these (Lettina et al. 1996; Xing et al. 2000; Maewa et al. 2007; Huang et al. 2011; Kamika & Momba 2013). Although the polluted degree of treated wastewater has decreased significantly, it is still higher than drinking water used in everyday life, indicating that the efficiency of wastewater treatment is too low to meet the requirements of environmental protection. Wastewater purification is still a huge problem in our society. Therefore, to find a fast, economical and green method of degrading organic pollutants in wastewater is a priority for technological breakthrough.

Plasma technology, referring to an initiator to induce a series of chain reactions that generate a certain number of active particles by the discharge excitation, is considered to be a fast, economical, green and efficient treatment technology for wastewater purification (Liu et al. 2017; Snoeckx & Bogaerts 2017; Attrid et al. 2018). Due to the high reactivity...
and low thermal effect of plasma, it has been successfully applied in wastewater treatment in laboratory-scale and a lightly polluted environment. However, the integration of plasma-induced effects into large-scale systems is far from trivial.

In recent years, there have been many studies about application of plasma technology for wastewater treatment. García et al. (2017) treated methylene blue as a model dye wastewater using microwave plasma jet. They suggested that treatment efficiency of methylene blue dye could be improved with low concentrations, and higher degradation rates could be obtained by increasing the argon flow rate, due to the fact that the excited argon can contribute to the formation of active species. Tichonovas and colleagues suggested that the advanced oxidation process showed a strong ability of degradation with low consumed energy, while the toxicity and pH values of wastewater met the discharging standard at the end of processing (Tichonovas et al. 2017). Yang et al. (2017) studied the degradation mechanism of pyridine in drinking water using dielectric barrier discharge (DBD), suggesting that OH radicals and O3 were the main active species responsible for wastewater degradation in the DBD system, especially for the decomposition of nitrogen-based pollutants. Zhang and co-workers studied the degradation of phenol in wastewater by using cathodic microarc plasma electrolysis, and the results showed that the phenol degradation efficacy was strongly dependent on the applied voltage, initial pH value and supporting electrolyte (Zhang et al. 2017). Syakur et al. (2017) operated a plasma reactor in a batch system with a variation of applied voltage and treatment time to reduce the amount of chemical oxygen demand (COD) in wastewater generated from natural rubber processing (Syakur et al. 2017).

In this study, high-concentration methyl violet solution as a mimicked organic wastewater was treated by DBD plasma to investigate the effects of types of feeding gases, applied discharge voltage and treatment time on the decoloration rate and COD of this wastewater. Moreover, ancillary analysis was performed using an ultraviolet-visible (UV-Vis) spectrophotometer to unravel the degradation pathway of methyl violet molecules in solution.

EXPERIMENTAL MATERIALS AND METHODS

A methyl violet solution with the high concentration of 300 mg L⁻¹ was prepared using methyl violet solid powder (obtained from Tianjin Dingshengxin Chemical Co., Ltd. Formula: C₂₄H₂₈ClN₃; molecular mass: 393.95). The ultrapure water required for preparing the solution was obtained from Eco-Lab’s ultra-pure water machine KL-UP-200. Experimental analysis was performed using a UV-Vis spectrophotometer (Model No. UV-2700) with the wavelength range from 185 to 1,400 nm (with the accuracy of ±0.1 nm) from Shimadzu Corporation, Japan. A multiparameter water quality detector (5B-3B, Beijing Lianhua Science and Technology Co., Ltd) was used for COD measurements. The multi-parameter digestion device is 5B-1 (V8) obtained from Beijing Lianhua Science and Technology Co., Ltd. The digested temperature range was from 45 °C to 190 °C with the accuracy of ± 0.5 °C.

The schematic of the DBD plasma device is shown in Figure 1(a). This device consisted of the intake system, plasma discharge system and wastewater pool. The intake system was used to control the gases crossing the plasma discharge area. The working gases used to generate plasma were air and O₂ respectively. The gas flow was controlled.
by a flow meter with a flow range of 0–12 L min\(^{-1}\). The plasma discharge system consisted of a coaxial quartz tube and internal and external electrodes. The outer diameter of the inner quartz tube was 20 mm, and the outer diameter of the outer quartz tube was 38 mm. The inner quartz tube was used as a barrier dielectric. A copper rod with a diameter of 5.8 mm was used as the internal electrode by inserting it into the inner quartz tube. The external electrode formed by feeding tap water into the coaxial quartz tube helped to lower the temperature of the device. The plasma discharges could be generated between the inner quartz tube and the inner electrode. A power supply source (AC, peak voltages up to 30 kV, frequency variable from 6 kHz to 25 kHz) was selected for the DBD plasma device. The power supply source was made by inverting DC to form an AC square wave. Then the square wave was loaded into a high-frequency step-up transformer to get high voltages.

A digital oscilloscope (Tektronix TDS2012) with two channels was used to measure the discharge voltage with a 1:1000 voltage probe (Tektronix P6015A) and discharge current with an AC current probe (Tektronix P6021). The typical waveform of discharge voltage and current in O\(_2\) gas discharge (input voltage: 50 V) is shown in Figure 1(b). It can be clearly seen that the discharge peak output voltage is about 10 kV and the pulse peak current is 584 mA.

During the DBD plasma treatment of methyl violet solution, eight groups of treated samples were extracted at 0, 2, 4, 6, 10, 15, 30 and 60 min respectively, and each extract was measured to get COD content and UV-Vis spectra. The types of feeding gases and applied voltages were further selected as the experimental variables to investigate the degradation efficiency. Air and O\(_2\) were respectively used in this study as working gas with flow rate of 3 L min\(^{-1}\). The input voltages of the power source were set at 40, 50, 60 and 70 V with the output voltages measured at 8.4, 10, 12.2 and 13.8 kV respectively.

RESULTS AND DISCUSSION

Effect of different gas discharges on degradation of methyl violet

To explore the effect of different gas discharge on the decoloration efficiency and decline radio of COD content of the methyl violet solution, a series of experiments of different gas discharge with varying treatment time ranging from 0 to 60 min were carried out.

For the methyl violet solution treated by the plasma generated in O\(_2\) gas discharge, the effect on decoloration of solution at a discharge voltage of 10 kV was investigated. Figure 2(a) shows the effect of treatment time on UV-Vis absorption spectra of the treated solution. The UV-Vis absorption spectra have two strong absorption peaks at 301 and 584 nm. The strongest absorption peak at 584 nm reflects the color of the solution. With increasing treatment time, the absorption peak at 584 nm decreased significantly, and disappeared after the O\(_2\) plasma treatment time of 6 min. For the absorption peak at 301 nm, the height of the absorption peak decreased slightly, and increased briefly during 2–4 min treatment. During this process, the methyl violet molecules were degraded, leading to the reduction of the peak height at 584 nm. Furthermore, a large number of small organic molecules were formed, and these small organic molecules cannot be fully degraded.

For the methyl violet solution treated by the plasma generated in air gas discharge, the effect on decoloration of solution at a discharge voltage of 10 kV was investigated.

![Figure 2](https://www.wst.com/wst080081413.pdf)
Figure 2(b) shows the effect of treatment time on UV-Vis absorption spectra of the solution. After discharge treatment, the absorption peak decreased at 584 nm and the peak disappeared at the treatment time of 10 min. For the absorption peak at 301 nm, the absorption peak was reduced but the change was not obvious.

Figure 3 shows the decoloration rate of methyl violet solution treated by 50 V input voltages as a function of different gas discharge. It can be seen that the decoloration rate of the O2 gas discharge treatment was higher than that of air gas discharge treatment. The decoloration rate of solution could reach 80.88% with O2 gas discharge at the treatment time of 2 min, and then increased to 100% at 10 min. This means the methyl violet molecules were destroyed completely after 6 min. The decoloration rate could only reach 48.15% when using air gas discharge at the treatment time of 2 min, and the solution could not be decolorized entirely after 10 min.

Figure 4 shows the decline ratio curve of COD content as a function of treatment time in different gas discharge treatments. The decline ratio ($\eta$) was calculated as:

$$\eta = \frac{\text{COD}(0) - \text{COD}(t)}{\text{COD}(0)} \times 100\%$$

where COD(0) is the COD content of the solution before treatment, and COD(t) is the COD content of the solution after treatment for time t.

For O2 discharge treatment, the decline ratio of COD content increased to 30% at the first 10 min. With increasing treatment time, the COD content decreased at a slightly lower rate, and the decline ratio reached 33% at the treatment time of 60 min. For air discharge treatment, the COD content in solution using air gas discharge treatment decreased to 24% after treatment of 60 min. The downward trend of COD content was the same as that treated by O2 discharge at the first 6 min, and the COD content of the solution treated by air discharge decreased more slowly than that of O2 discharge treatment. But the downward trend in COD content was reversed when the treatment time increased from 6 to 15 min, and the COD content increased about 13% compared with the original solution at the treatment of 15 min. An explanation is that, when active particles from plasma interacted with the methyl violet molecules, a large number of short-chain small molecules were formed because the long-chain of methyl violet molecules was destroyed. The small organic molecules, such as benzene ring, C=C double bond and N=N double bond, could be decomposed to smaller organic molecules which resulted in an increase of COD content (Wang et al. 2015). With the treatment time further increased, the smaller organic molecules were degraded, reversing the upward trend in COD content. The negative values show that the COD content increased compared with the original solution, and the COD content increased about 13% at the treatment time of 15 min.

**Effect of different discharge voltages on degradation of methyl violet**

Figure 5 shows the UV-Vis absorption spectra of methyl violet solution by the plasma treatment with different input voltages. Clearly, the strong absorption peak at 584 nm decreased significantly in all groups, then disappeared at last. For the absorption peak at 301 nm, the
height of the absorption peak reduced but the change was not obvious. Figure 6 shows the decoloration rate of methyl violet solution treated by O₂ discharge as a function of different input voltages. It can be seen that the decoloration rate decreased rapidly, and reached 100% after treatment for 10 min for all discharge voltages.

Figure 7 shows the decline ratio curve of COD content as a function of discharge voltage in O₂ gas discharge. The COD content of methyl violet solution decreased dramatically after treatment by plasma generated in input voltage of 40–70 V. At the treatment time of 5 min, it can be observed that the decline ratio of COD content increased quickly to about

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**Figure 5** | UV-Vis absorption spectra of methyl violet solution by (a) 40 V, (b) 50 V, (c) 60 V and (d) 70 V input voltage treatment.

**Figure 6** | Decolorization rate of methyl violet solution as a function of input voltage treatment.

**Figure 7** | The decline ratio curve of COD content of methyl violet solution treated by different discharge voltages in O₂ gas discharge.
20%, and reached the maximum of 33% at treatment of 60 min at discharge voltage of 50 V. An explanation is that, when active particles from plasma interacted with the methyl violet molecules, a large number of short-chain small molecules were formed because the long-chain of methyl violet molecules was destroyed. The small organic molecules, such as benzene ring, C=C double bond and N=N double bond, could be decomposed to smaller organic molecules. These smaller organic molecules contain a lot of non-degradable molecules, therefore resulting in small changes in the COD content.

Degradation pathway of methyl violet solution by DBD plasma

During plasma treatment, the gas passed through the discharge areas from the intake system. The electrons in the discharge areas obtained high energy from the external electric field. These highly reactive energetic electrons caused gas molecules to be ionized. In this process, a large number of active particles, such as high-energy electrons, O atoms, OH radicals and O3, were generated. The main mechanism for the degradation was plasma-induced chain reactions, leading to the decomposition of methyl violet molecules.

Based on the above experimental results, the degradation pathway of methyl violet solution during plasma treatment is proposed in Figure 8. The active particles attacked and oxidized the organic molecules and therefore methyl violet solution was degraded by the DBD plasma. Here, C=C or C=N bonds were firstly attacked by active particles, resulting in the formation of the benzene ring and CH3 radicals. The scission of organic molecules attacked by OH radicals indicated that the molecules of methyl violet were opened to form oxidized intermediate products. These products were mainly organic small molecules with the structure of benzene ring. Then the products were eventually oxidized and decomposed into CO2, H2O and so on (Wang et al. 2015). The formulas for generation of reactive species in O2 discharge are shown below (Bai et al. 2014a, 2014b):

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\begin{align*}
O_2 & \rightarrow O + O \\
O_2 + O & \rightarrow O_3 \\
O_2 + e & \rightarrow O_2^+ + 2e \\
O_2^+ + H_2O(aq) + M & \rightarrow O_2^\cdot H_2O + M \\
O_2^\cdot H_2O + H_2O & \rightarrow H_3O^+ + \cdotOH + O_2 \\
H_2O_2 & \leftrightarrow HO_2^\cdot + H^+ \\
HO_2^\cdot & \leftrightarrow O_2^\cdot + H^+ \\
HO_2^\cdot + O(3P) + O_2 + M & \rightarrow HO_2^\cdot + O_3^\cdot + M \\
HO_3^\cdot & \rightarrow \cdotOH + O_2
\end{align*}
\]

In this case, the excited oxygen atom, O3 and HO2 generated by the discharge can react with organic substances. These organic substances will be decomposed into small molecules and then degraded. In addition, the O3 and ozone are powerful oxidants that react with various organic substances dissolved in water.

As for DBD discharge, O3 is the dominant radical to decompose the chromogenic bond owing to its faster reaction speed than ·OH and H2O2 (Zhang et al. 2004). The decomposition of ozone dissolved in water produces OH radicals that can take part in the degradation of the organic contaminant (Staehelin et al. 1984). The O3 molecules attack the N=N double bond, followed by the reactions of OH radicals with the intermediate benzenic and naphthalenic products. The intermediate products can be further oxidized to inorganic compounds such as CO2, CO3^2\^- , HCO3\^- and NO3\^- by ozone (Mok et al. 2008).

However, in air discharge, the plasma induced reactions between N2 and O2, and this decreases the O2 concentration (Chen et al. 2006). On the other hand, the produced nitrogen oxides (e.g. N2O) in the air plasma destroyed the ozone (O3), which is one of the main products in the air or O2 discharge (Busca et al. 2005). Therefore, O3 and other active species...
(e.g. O atoms) in the air plasma are far less than those in O2 plasma under the same treating dosage. Moreover, NO2 in the air plasma might further react with the aromatic ring structure and form more stable molecules that cannot be degraded by oxygen radicals (Busca et al. 2005). This agrees with the results that the COD content of the solution treated by air discharge decreased slower than by O2 discharge, shown in Figure 4.

To further investigate the degradation mechanism of the methyl violet solution, the decline ratio curve of COD content and the UV-Vis absorption spectra of the solution were applied to identify the degraded pathway. Due to the fact that methyl violet molecules are mostly attacked by the oxidizing substances in the initial stage to cause the long chain to be broken, the number of small organic molecules rose rapidly. Therefore, the COD content in solution increased. Following this process, the small organic molecules were oxidized by reactive oxygen species, and the benzene ring structures in these by-products were opened to form CO2, H2O and other non-degradable organics.

According to the UV-Vis absorption spectra, the absorption peaks at 200–300 nm indicated the formation of a large number of small organic molecules due to the fact that chromophores were destroyed. It also means that benzene rings were formed after the C=C bond and the C=N bond were broken when treated. With the increase of the treatment time, the absorption peaks of chromophores were going down largely, and meanwhile some new absorption peaks at 200–300 nm appeared and had an increase in peak value. It was considered that the chromophores could be easily destroyed to smaller molecules but the products and also the high-concentration benzene organics were difficult to be degraded. This also happened in some studies. For example, Shu (2006) found that degradation of high-concentration benzene organic is difficult, and degradation capacity can be improved with the treatment time; Zhou et al. (2012) investigated the conversion of benzene with the increase of gas residence time and the discharge voltages. This could also be the reason why the content of COD in the solution was difficult to decrease dramatically.

CONCLUSION

In this study, we have found that the highest decoloration rate of 100% after the treatment time of 10 min and the highest COD decline ratio of 33% after the treatment time of 60 min were achieved in the O2 gas discharge processing at the discharge voltage of 10 kV. While the methyl violet solution was slightly less decolorized when being treated by air discharge rather than by O2 gas discharge, the higher COD decline ratio of 24% after the plasma treatment time of 60 min was achieved in air gas discharge.

Based on the experimental results, a pathway of methyl violet degradation attributed to energetic electrons and highly reactive species generated by DBD plasma was proposed. In the discharge process, a large number of active particles were produced, such as high-energy electrons, O atoms, OH radicals and O3. These active particles are regarded as the main participants for the degradation of the methyl violet molecules in solution. UV-Vis and chemical analysis of end-product treated by DBD plasma revealed that the methyl violet molecules could be decolorized, and formed refractory organics in the solution. It was considered that the chromophores could be easily degraded into smaller molecules but the by-products including the high-concentration benzene organics were difficult to be degraded. This could also be the reason why the content of COD in the solution was difficult to decrease dramatically.

For further work, the effects of concentration of wastewater and gas flow on the degradation of organic wastewater, and how it can meet the practical industry application better, need to be investigated.

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