Comparing Acid Red B Dye Decolorization by Glow and Spark Discharge Plasma in Atmospheric Pressure Air

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Abstract. We examined the decolorization of Acid Red B (ARB) in glow/spark discharge plasma (GDP/SDP). It is found that the decolorization of ARB was observably higher in GDP than in SDP. After 16 min treatment, ARB decolorization rate reached 97.16% with the energy efficiency of 7.16 kg/kW·h in GDP, and 92.76% with 0.84 kg/kW·h energy efficiency in SDP. The average yield of plasma oxidants were 1.73 kg/kW·h in GDP, and 0.14 kg/kW·h in SDP. Some factors, which probably affect the decolorization of ARB aqueous solution, such as hydroxyl radical and ultraviolet radiation etc. were investigated. The results showed that plasma oxidation, especially hydroxyl radical might be main factors accounting for ARB decolorization.

1. Introduction
The industrial dye-wastewater, which usually contains a variety of refractory organic dyes molecules, can’t be effectively decomposed by conventional water treatment techniques [1]. Therefore, the decolorization of dye-wastewater has become a research focus. In recent decades, a lot of articles which reported the dye-wastewater was treated using gas discharge plasma have been published [2-3]; and different types of discharge plasma techniques such as contact glow discharge electrolysis [4], dielectric barrier discharge [5], and streamer discharge [6] have been demonstrated to have good decolorization effect. Most of articles discussed decolorization mechanism and influence factors for a given discharge plasma. Fewer papers, which compare the decolorization effect of dye-wastewater by using two kinds of discharge plasma, were published. In this paper, we experimentally studied the decolorization of acid red B in glow and spark discharge plasma. The decolorization effects of ARB were compared in the two discharge electrolysis type; the reasons that caused the decolorization rate difference were discussed.

2. Experiment

2.1. Experimental Setup and Instruments
The schematic of experimental apparatus is shown in figure 1. The device consisted of a high-voltage (HV) dc power supply which can provide 0–13kV voltage and a reactor system. The reactor included a glass dish (height: 2 cm, diameter: 10 cm) and a pair of electrodes. The tungsten anode with a tip (diameter ~1 mm and length ~5 cm) was suspended in air above the treated solution surface; the copper wire cathode was submersed in the ARB aqueous solution, i.e. ARB aqueous solution was used...
as the cathode. The distance between the anode tip and the solution surface, i.e. so-called discharge gap was fixed to 5 mm. When a HV dc voltage was applied to the two electrodes, an air discharge in atmospheric pressure was initiated in the discharge gap and corresponding discharge plasma was generated. The discharge current and voltage were measured by an amperemeter with the range of 0-30mA and an electrostatic voltmeter, respectively. In the current work, the discharge current and voltage were repeatedly recorded three data every 30 seconds. Optical emission spectroscopy of the discharge channel were recorded using a monochromator (JOBIN YVON, 750M with resolution: 0.1 nm at a 0.2 mm slit width) with a fiber probe in the range of 200 nm-700 nm. The discharge channel snapshots during the discharge process were captured by a CCD camera (FUJIFILM FinePix S8000fd). A conductivity meter (JingKe, DDS-11D) and a PH meter (JingKe, PHS-25) were used to measure the conductivity and PH of the solution, respectively.

![Figure 1. Schematic of experimental apparatus.](image)

2.2. Dye-Wastewater
In our experiment, acid red B (CAS Number: 3567-69-9) was used as a simulated pollutant in dye-wastewater. The sample solution was prepared by dissolving analytical ARB powder (HGCJ distribution plant, TianJin) into distilled water. The conductivity of the solution was adjusted by adding sodium chloride into the sample solution. The initial concentration of the treated solution was 100 mg/L, the volume 100mL and PH value 6.4.

2.3. Analytical Methods
A dual-channel UV-VIS spectrophotometer (PuXi, TU-1901) was employed to test the decolorization effect. According to Beer-Lambert law, the absorbance of substance at its character wavelength is proportional to the concentration of substance in solution. The UV-VIS absorption spectra of aqueous ARB solution over the treatment time were also recorded every 2 min in the range of 200-700 nm during discharge. The relationship between the absorbance of the ARB solution at 516 nm and its concentration is linear [7]. The decolorization rate of the ARB solution, which is denoted as $\eta$, can be calculated as follows:

$$\eta = \frac{A_0 - A_t}{A_0} \times 100\%$$  \hspace{1cm} (1)

where $A_0$ and $A_t$ are the absorbance of the solution at 516 nm before and after treatment, respectively. To determine the energy efficiency of this system, a parameter $\omega$ is introduced based on the following equation:

$$\omega (kg/kW\cdot h) = \frac{m_0 (kg) \times \eta}{P(kW) \times t(h)}$$  \hspace{1cm} (2)
where $m_0$ : mass of ARB initial solution of 100 mL, $P$ : electric power, $t$ : treatment time, $\eta$ : decolorization rate. $\omega$ : decomposition amount of ARB consuming unit energy. Iodimetry was used to determine the content of oxidant in solution produced after discharge treatment.

3. Results and Discussion

3.1. Glow Discharge and Spark Discharge

For the ARB initial solution (concentration 100 mg/L, volume 100 mL and PH 6.4.), the conductivity was 160 $\mu$S/cm. When a high-voltage (HV) dc voltage was applied to the two electrodes of the reactor, a gas-liquid glow discharge was formed in the discharge gap (figure 2a). When the initial conductivity of ARB solution was adjusted to be 4010 $\mu$S/cm by adding sodium chloride into the solution, the discharge type formed in the discharge gap was gas-liquid spark discharge under the same other experimental conditions (figure 2b). For the two discharge type, the current and voltage via the discharge treatment time were also different (figure 3). Of course, optical emission spectra should be also different (figure 4).

![Figure 2](image1)

*Figure 2. Photograph of discharge channel (a) in GDP and (b) in SDP.*

![Figure 3](image2)

*Figure 3. Discharge current and voltage via the treatment time in GDP (left) and in SDP (right).*

As shown in figures 2-4, there are obviously differences between glow discharge and spark discharge. First, the discharge channel of GDP is one bright, stable and large beam; but in SDP, the discharge channel presents many bright dazzling, zigzag small beams. Then, the current ($\sim$21.0mA) and voltage of GDP after breakdown are both very stable, the discharge voltage is very low ($\sim$300V), and the breakdown voltage ($\sim$5000V) is very high. But for spark discharge, the case is just the opposite. The discharge current ($\sim$17.3mA) and voltage after breakdown are both very unstable, there are a very high discharge voltage ($\sim$3100V) and a lower breakdown voltage ($\sim$4500V) comparing with glow discharge. Finally, the emission spectra intensity of spark discharge, especially in the near ultraviolet band and low wavelength region of visible light, is obviously greater than that of glow discharge. The fact reveals that the temperatures of those tiny light channels of spark discharge are
higher than these of glow discharge. So, during the spark discharge the energy consumed in gas phase plasma channel is much greater than that in the glow discharge. From the result it can be speculated that the current density in those tiny channels of spark discharge is very big, because the channel temperature depends on the current density. All these characteristics mentioned above are consistent with corresponding characteristics of glow/spark discharge.

![Figure 4.](image1.png)

**Figure 4.** Optical emission spectra of the discharge channel in GDP (left) and in SDP (right).

Figure 4 shows the optical emission spectrum of the discharge channel in GDP (left) and in SDP (right) in 200 - 700 nm. As seen in figure 4, there are both optical emission spectra in the ultraviolet region during GDP and SDP, but the spectral line intensity in SDP is significantly larger than that in GDP. For example, the intensity of the spectral line at 385 nm is 72.834 mV in GDP, and 223.119 mV in SDP. If ultraviolet radiation plays a major role in the ARB degradation, the ARB degradation rate in SDP should be greater than in GDP. Nevertheless, the fact is that the ARB degradation rate in SDP is lower than in GDP, showing ultraviolet radiation is not the main factor for ARB decolorization.

3.2. Decolorization of Aqueous ARB Solution in GDP and SDP

The UV-VIS absorption spectra of ARB aqueous solutions with treatment time in GDP and SDP are shown in figure 5. From figure 5 we can tell that there are two characteristic absorption peaks for aqueous ARB solution, and each of them lies in 516 nm and 292 nm, respectively. The absorption peak at 516 nm is the maximum absorption wavelength of ARB chromophoric group. The absorbance was significantly reduced with increasing treatment time due to the fact that the structure of the chromophore group was destroyed in the discharge process. The absorbance reduced to 0.3803 after 2 min in GDP, and the corresponding decolorization rate reached 54.47%, but only 20.64% in SDP. And after 16 min treatment time, the water purification reaches 97.16% in GDP and 92.76% in SDP. Obviously, the energy efficiency in GDP (7.16 kg/kW-h) is higher than that in SDP (0.84 kg/kW-h), almost an order of magnitude larger.

![Figure 5.](image2.png)

**Figure 5.** UV-VIS absorption spectra of ARB aqueous solutions in GDP (left) and in SDP (right).
3.3. Reasons Accounting for the Difference of the ARB Degradation between Using GDP and SDP

It is well known that many active species such as hydroxyl radical, hydrogen peroxide, ozone and ultraviolet radiation are produced in gas-liquid discharge process [8-10]. These species play a very important role in the organic compounds degradation, especially among which hydroxyl radical with oxidation potential of 2.80 V is regarded as one of the most powerful oxidants. Sodium carbonate is a type of free species scavenger. Since the reaction rate of sodium carbonate and hydroxyl radical is higher than that of other chemical pollutants, a set of experiments by adding sodium carbonate into the treated aqueous solution was designed to investigate whether hydroxyl radical plays a major role in ARB degradation. Figure 6 presents the residual concentration of ARB in solution as a function of treatment time treated by GDP (left) and SDP (right), respectively. As seen in figure 6, the decolorization rates of aqueous ARB solution were reduced significantly by adding sodium carbonate in both GDP and SDP. For example, after 6 min GDP treatment the concentration of aqueous ARB solution with 20 mg/L sodium carbonate and 60 mg/L sodium carbonate were 31.57 mg/L and 71.25 mg/L, respectively, which were much higher than 22.01 mg/L without sodium carbonate. In SDP treatment, the situation is similar. Of course, the concentration of ARB in solution by GDP treatment were always less than that by SDP treatment given the same other condition. The experimental results verified that hydroxyl radicals were indeed the main factor of ARB degradation in GDP and SDP treatment, and the amount of hydroxyl radicals produced in GDP process was greater than that in SDP process.

![Figure 6. The residual concentration of ARB in solution via the treatment time in GDP (left) and in SDP (right).](image-url)

As mentioned above, various active radicals, such as \( \cdot \text{OH}, \cdot \text{H}, \cdot \text{O}, \cdot \text{O}_2 \) and \( \cdot \text{HO}_2 \), and active molecules, such as \( \text{H}_2\text{O}_2 \) and \( \text{O}_3 \) are produced in gas-liquid discharge process. All of these active species have high oxidation potentials and can break the chemical bands of organic compounds [11-12]. In general, either the active radicals or the active molecules existing in solution play a very important role in the ARB degradation, i.e. the ARB degradation is dependent on the concentration of these oxidants in solution to some extent. Huang et al. [13] conducted an experiment on the degradation of the methylene blue, suggesting that the degradation rate in acidic solution was the maximal. Meanwhile, the concentration of the oxidants in acidic solution was higher than the ones in neutral and alkaline solution. Therefore, groups of experiments of iodimetry were conducted to investigate the content of oxidants in the solution generated by GDP and SDP, respectively, and the results are presented in figure 7. In addition, figure 8 shows the solution PH with treatment time using GDP and SDP, respectively. From figure 7, it can be found that the concentration of oxidants increased with the proceeding of degradation, and the concentration of the oxidants during GDP treatment was always bigger than that during SDP treatment. Meanwhile the solution PH during GDP treatment was less than that during SDP treatment. The concentration of ARB in solution decreased with increasing concentration of oxidants, indicating that the amount of oxidants in the solution is probably the key factor responsible for ARB degradation. The fact that the much more oxidants and

![Graph showing the concentration of ARB in solution versus treatment time for GDP and SDP.](image-url)
more acidic solution were produced using GDP corresponds with the higher ARB degradation rate, indicating that the difference of oxidants concentration in solution generated by GDP and SDP is a key reason accounting for the difference in degradation rate.

![Figure 7. Concentration of oxidants via treatment time.](image)

![Figure 8. The solution PH via treatment time.](image)

4. Conclusion

Glow discharge plasma (GDP) and spark discharge plasma (SDP) were used in the degradation of aqueous ARB solution in atmospheric pressure air. Comparison between the water purification of aqueous ARB solution treated by the GDP and SDP were conducted. Reasons resulting in the differences between water purification were discussed. The conclusions concerning this study are presented, as follow:

1) Be treated by the GDP and SDP for 16 min, the water purification of the ARB reaches 97.16% and 92.76% with the energy utilization efficiency of 7.16 Kg/Kw-h and 0.84 Kg/Kw-h, respectively, suggesting that the discharge plasma is a very effective method for the ARB degradation, and the water purification in the GDP is always faster than in the SDP.

2) By investigating the oxidants content and the intensity of ultraviolet radiation in the GDP and SDP, it is found that there are much more oxidants produced in the solution in the GDP compared with that in the SDP. Nevertheless, stronger ultraviolet radiations are emitted from discharge region in the SDP, which is stronger than that in the GDP.

3) Through the comparison of the ARB degradation rate with and without adding of sodium carbonate which is a scavenger of hydroxyl radical, the results showed that hydroxyl radical is the key factor in the degradation process of aqueous ARB solution, and the yield rate of hydroxyl radical in the GDP is higher than that in the SDP.

Acknowledgments

This work was supported in part by the national natural science foundation of China under Grant 51872227 and in part by NWU Undergraduate Teaching Quality Improvement Funds of China under Grant JX17074.

References

[1] Nishioka H, Saito H and Watanabe T 2009 Thin Solid Films 518 (3) 924-928.
[2] John E and Foster 2017 Physics of Plasmas 24 (5) 055501.
[3] Chandana L, B Lakshminarayana and C Subrahmanyam 2015 Journal of Environmental Chemical Engineering 3 (4) S2213343715002614.
[4] Chen Y and Jin X 2018 Electrochimica Acta DOI:10.1016/j.electacta.2018.11.021.
[5] Jingwei Feng, Lin Jiang, Dan, & Zhu, et al. (2016). Environmental Science & Pollution Research. DOI:10.1007/s11356-016-6148-9.
[6] Tampieri F, Giardina A, Bosi F J, Pavanello A, Marotta E, Zaniol B, et al. 2018 Plasma Processes and Polymers 15 (6) e1700207.1-e1700207.12.
[7] Yang S-J 2012 Application of Gas Discharge Plasma in Simulated Wastewater Degradation (Master’s Thesis) (Northwestern University, China) p 26.
[8] Yang C and Jin X 2019 Electrochimica Acta 296 (1) 379-386.
[9] Zhao C, Yang H, Ju M, Zhao X, Li L, Wang S and An B 2019 Plasma Chemistry & Plasma Processing 39 751-767.
[10] Bansode A S, More S E, Siddiqui E, Satpute S, Ahmad A, Bhoraskar S V and Mathe V L 2017 Chemosphere, 167 396-405.
[11] Wang T C, Lu N, Li J and Wu Y 2010 Journal of Hazardous Materials 180 (1-3) 436-441.
[12] Magureanu M, Piroi D, Mandache N B, David V and Parvulescu V I 2010 Water Research 44 (11) 3445-3453.
[13] Huang F, Chen L and Wang H 2010 Chemical Engineering Journal -Lausanne-. 162 (1) 250-256.