## Discoloration of Congo Red by Rod-Plate Dielectric Barrier Discharge Processes at Atmospheric Pressure*

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### Abstract

A dielectric barrier discharge (DBD) reactor with a rod-plate electrode configuration was used for the oxidative decomposition of Congo red dye in an aqueous solution. Plasma was generated in the gas space above the water interface under atmospheric pressure. Discharge characteristics were analyzed by voltage-current waveforms. Effects of applied voltage, initial conductivity, and initial concentration were also analyzed. Congo red discoloration increased with increased applied voltage and decreased conductivity. The initial conductivity significantly influenced the Congo red discoloration. Under the same conditions, the highest discoloration rate was obtained at 25 mg/L. The presence of ferrous ions in the solutions had a substantial positive effect on Fenton dye degradation and flocculation. At an applied voltage of 20 kV, about 100% of dye was degraded after 4 min of Fe$^{2+}$/DBD treatment. Results showed that adding a certain dosage of hydrogen peroxide to the wastewater could enhance the discoloration rate. Possible pathways of Congo red discoloration by DBD plasma were proposed based on GC/MS, FTIR, and UV-vis spectroscopy analyses.

### Keywords:
dielectric barrier discharge (DBD), Congo red (CR), discoloration, wastewater treatment

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(Some figures may appear in colour only in the online journal)

## 1 Introduction

In China, textile dye wastewater is often considered as a major water pollutant and is the second most prevalent industrial wastewater. Various traditional technologies such as adsorption, coagulation, filtration, sedimentation, and biological treatments are used to treat textile dye wastewater. However, most of these treatments are unsatisfactory because effluents usually have a high degree of polarity and a complex molecular structure [1]. In recent years, advanced oxidation processes (AOPs) have been demonstrated to be an efficient wastewater treatment technology. Among AOPs, the nonthermal plasma (NTP) process, which generates a substantial amount of activated species and ultraviolet radiation through ionization, excitation, and dissociation [2], has become a research hotspot. The NTP is widely applied to treat wastewater contaminated with all kinds of organic dyes [3−7].

Various ways such as corona discharge, glow discharge, gliding arc discharge, and dielectric barrier discharge (DBD) can generate NTP. The applications of NTP for wastewater treatment, such as direct current glow discharge plasma in and in contact with liquids [8], and gliding arc discharge under different working gases [9], have been investigated and reported [9]. DBD is considered as a highly effective discharge source for generating NTP because of its easy operation, stability, microdischarge, and large treatment area [10]. Many different DBD reactors have been reported in many recent studies. Li et al. used a plate-plate DBD reactor to degrade acetamiprid solution [11]. Manoj Kumar et al. reported a rod-cylinder coaxial DBD reactor to degrade methylene blue and crystal violet in water [12,13]. Ognier et al. used a coaxial thin-falling-water-film reactor to treat mesotriione [14]. Young et al. reported a gas phase DBD reactor submerged in water that can degrade Orange II from wastewater; the treated water is used as a grounded electrode [15]. Ghezzar et al. designed a cylinder-plate DBD reactor...
to treat yellow tartrazine azo dye solutions [6]. Wang et al. designed a multi-tube parallel surface discharge plasma reactor for wastewater treatment [16]. These studies demonstrate that different DBD reactors could satisfactorily oxidize organic compounds in wastewater, and most of them focus on plate-plate or coaxial DBD reactors. However, few studies have concentrated on the discoloration of textile-dye wastewater by using a rod-plate DBD reactor, which can easily be operated and is similar to a needle-plate corona discharge reactor. As a kind of discharge in the non-uniform electric field, the rod-plate electrode DBD combined both characteristics of a corona discharge and a DBD [17]. It can significantly reduce the discharge breakdown voltage compared with a plate-plate DBD, and has much more discharge area than a needle-plate DBD.

This study aimed to examine the possibility of applying a rod-plate DBD reactor under atmospheric pressure for Congo red (CR) dye discoloration in water solutions. DBD reactor characteristics were also studied. Effects of various parameters including applied voltage, initial concentration, initial conductivity, and catalyst addition on discoloration effects using the designed DBD reactor were investigated. Possible mechanisms of CR discoloration by the plasma process were also proposed.

2 Experimental setup and methods

2.1 Experimental setup

The experimental system mainly consisted of an alternating-current, high-voltage power supply and a DBD reactor, as described in Ref. [10]. Four stainless-steel rods connected in parallel were used as high-voltage electrodes. Each rod was covered by a ceramic tube serving as a dielectric barrier. The treated water was held by a transparent quartz glass vessel with 200 mm inner length and 50 mm in height. A stainless-steel plate was attached onto the outside wall of the quartz glass vessel as a grounded electrode. In a typical procedure, plasma was generated by applying a high voltage between the high-voltage electrodes and the grounded one. Discharge occurred above the water surface. The applied voltage adjustable to 0-24 kV was measured by using a voltage probe (Tektronix P6015A) and recorded using a digital oscilloscope (Tektronix TDS3014, 100 MHz, 1.25 GS/s). Discharge current was measured by placing a 100 Ω non-inductance resistor (r) between the bottom electrodes and the grounded one.

2.2 Materials

All of the chemicals were commercial samples of analytical grade and were used without further purification. CR (C_{32}H_{22}N_{6}O_{7}S_{2}, formula weight: 696.68) was purchased from Shanghai Hongguang Chemical Reagent Co., Ltd., and its molecular structure is given in Fig. 1. Pure water was obtained by filtration of tap water with a pure water machine.

![Chemical structure of a CR molecule](image)

2.3 Experimental procedures

Aqueous dye solutions were prepared by dissolving the brownish red solid CR in pure water. About 250 mL of the test solution with a 50 mg/L initial concentration of CR was used for each DBD treatment at a frequency of 17 kHz. The discharge distance from the tip of the high electrodes to the water surface was 4 mm. The pH and conductivity of the 50 mg/L solution were measured as 6.38 and 30 μS/cm, respectively. Samples were withdrawn with a syringe from the quartz glass vessel at desired times and measured immediately by using a UV/visible spectrophotometer (Shimadzu) at the maximum absorbance of 497 nm wavelength. The pH was measured using a pH meter (Model pHS-3C, Shanghai Precision & Scientific Instrument Co., Ltd.). The conductivity was measured using a conductivity meter (Model DDS-11D, Shanghai Precision & Scientific Instrument Co., Ltd.). The ozone (O_{3}) concentration in an aqueous solution was determined by the indigo method [18]. The aqueous hydrogen peroxide (H_{2}O_{2}) concentration was spectrophotometrically determined using the potassium titanium (IV) oxalate method [19]. The total organic carbon (TOC) was measured by using a TOC-VCPH (Shimadzu, Japan) analyzer. Intermediates and final products were detected by FTIR (NEXUS-870) and LC/MS (Agilent260-6430).

The discoloration percentage was calculated by using the following formula:

\[ \eta \% = \frac{Abs_0 - Abs}{Abs_0} \times 100\% \]

where Abs_0 and Abs are the initial and final CR solution absorbance at 497 nm, respectively.

3 Results and discussion

3.1 Characteristics of the DBD reactor

To understand the discharge characteristics in the rod-plate DBD reactor, typical voltage-current waveforms were obtained during the discharge, as shown in Fig. 2. Many fine- and narrow-pulsed current spikes that corresponded with microdischarges were present in each half-cycle of the applied voltage, demonstrating the occurrence of a filamentary discharge. In a discharge period, current waveforms were asymmetrical to the X-axis because of the asymmetric electrodes. However, the discharge current varied periodically with...
the discharge voltage, and its position was unchanged, indicating that discharges were macroscopically stable. The abovementioned characteristics were similar to the discharge in a coaxial thin-falling-water-film or plate-plate DBD reactor described in the literature [6,20,21].

Under the same conditions, the peak current of the discharge above the CR solution surface was greater than that of the discharge above pure water, whose conductivity was about 10 µS/cm. The resistance between high and grounded electrodes decreased with the increased solution conductivity. Therefore, the breakdown voltage of the working gas in the discharge region declined, and the migration and diffusion of charged particles in the discharge gap accelerated [22].

In the experiment, the species O₃, OH⁺, N₂O⁺, O, NO, and H₂O⁺ were produced in the gas phase and subsequently dissolved in the aqueous phase [22]. The major active species O₃ and H₂O₂ in the aqueous solution were then generated during DBD, as shown in the following reactions [23−25]:

\[
e + O_2 \rightarrow O + O(¹D) + e \quad (2)
\]
\[
e + O_2 \rightarrow O_2^+ + 2e \quad (3)
\]
\[
O(¹D) + O_2 \rightarrow O_3 \quad (4)
\]
\[
O(¹D) + H_2O \rightarrow 2 · OH \quad (5)
\]
\[
2 · OH + O_2 \rightarrow H_2O_2 + O_2 \quad (6)
\]
\[
e + H_2O \rightarrow H_· + ·OH + e \quad (7)
\]
\[
e + 2H_2O \rightarrow H_2O_2 + H_2 + e \quad (8)
\]
\[
·OH + ·OH \rightarrow H_2O_2 \quad (9)
\]

where O(¹D) is the excited state oxygen atom, and O₂⁺ is the dioxy radical positive ion. O₃ and H₂O₂ concentrations in pure water increased with the increased discharge time (Fig. 3). Approximately 10 min after discharge, O₃ concentration was 0.13 mg/L, whereas H₂O₂ was 0.20 mg/L at 20 kV of applied voltage.

3.2 Effect of applied voltage

CR solutions were treated at different applied voltages. The CR discoloration rate increased with the increased applied voltage (Fig. 4). The maximum discoloration rate reached 61.8% at 20 kV after 30 min of discharge. In this case, more activated species were produced and the UV intensity increased in the DBD discharge regime with increased applied voltage, and the CR effectively decomposed at 20 kV.
3.3 Effect of initial concentration

Three different initial CR concentrations were treated by DBD at a discharge voltage of 18 kV. The CR discoloration rate decreased with the increased initial concentration, as shown in Fig. 5. The initial concentration significantly affected dye degradation. The maximum discoloration efficiency of 62.8% was achieved at 25 mg/L after 30 min of plasma treatment.

![Fig. 5](image)

**Fig. 5** Effect of initial concentration on the CR discoloration rate as a function of time (applied voltage: 18 kV)

3.4 Effect of initial conductivity

Furthermore, the solution conductivity influenced the efficiency of wastewater treatment by DBD plasma. Sodium chloride was used to adjust the initial conductivity of the aqueous mixture to 60 µS/cm, 100 µS/cm, 300 µS/cm, and 500 µS/cm. Fig. 6 shows changes in the discoloration rate with treatment time for different initial conductivities at 22 kV. Dye destruction efficiency decreased with increased wastewater conductivity. This decrease in the discoloration rate gradually diminished as DBD proceeded. Although the peak current of discharge above water with a high conductivity was larger than that with low conductivity, the species -OH, -H, -O_H and O_3 collided with ions in the solution, thereby reducing the probability of collision with dye molecules.

![Fig. 6](image)

**Fig. 6** Effect of initial conductivity on the CR discoloration rate as a function of time (applied voltage: 22 kV; initial concentration: 50 mg/L)

3.5 Effect of ferrous ions addition

Metal ions could reportedly increase the degradation and mineralization rate in a DBD reactor [14]. To determine the influence of ferrous ions addition on the discoloration efficiency, different FeSO_4·7H_2O dosages were added to CR solutions just before plasma treatment. Fig. 7 illustrates the changes in the discoloration rate with treatment time for Fe^{2+} addition at 20 kV (calculated by Fe^{2+} concentration). CR discoloration can be accelerated in the presence of different Fe^{2+} dosages. All Fe^{2+}/DBD systems were more efficient than the DBD system, and treatment time sharply decreased. The dye discoloration rate dramatically increased upon adding 25-40 mg/L ferrous ions to the reactor after 4 min of treatment.

![Fig. 7](image)

**Fig. 7** Variation of discoloration rates as a function of treatment time for different concentrations of Fe^{2+} (applied voltage: 20 kV; initial concentration: 50 mg/L)

Fe^{2+} was found to have a significant enhancement effect on the dye-abatement rate. Active -OH concentration is known to increase in Fe^{2+} reaction with H_2O_2 or O_3 generated in a DBD reactor [1,14]. Meanwhile, Fe^{2+} has a flocculating effect on hydrophilic dyes. Many ionic substances can exist because of the small hydrolysis constant of Fe^{2+} in water. Fe^{2+} is the central ion when complexed with a single dye molecule. N, O, and S in the amino, azo, and sulfonic acid groups of CR can be coordinated atoms. Black sediments were generated in the solution during treatment.

3.6 Effect of hydrogen peroxide

To determine the influence of H_2O_2 addition on CR discoloration, different volume concentrations of H_2O_2 (0.5%, 1%, 3%, and 5%) were added to the target solutions just before DBD treatment. DR degradation can be inhibited or accelerated in the presence of different H_2O_2 dosages, as presented in Fig. 8. The CR discoloration rate was 56.56% with the addition of 1% H_2O_2 at 20 min, which was more effective than a noncatalytic DBD treatment. The higher dye degradation efficiency can be attributed to the more efficient OH generation in the DBD reactor with the proper concentration of H_2O_2 added [26]. For high H_2O_2 concentrations (3% and 5%), dye abatement efficiencies were lower than that without H_2O_2 addition after 15 min of
treatment, thereby indicating the consumption of ·OH by H₂O₂, as expressed by Eqs. (9) and (10) [27].

\[ \cdot \text{OH} + H_2O_2 \rightarrow H_2O + HO_2 \]  \hspace{1cm} (10)

\[ \text{HO}_2 \cdot + \cdot \text{OH} \rightarrow H_2O + O_2 \]  \hspace{1cm} (11)

**Fig. 8** Variation of discoloration rates as a function of treatment time for different concentrations of H₂O₂ (applied voltage: 20 kV; initial concentration: 50 mg/L)

### 3.7 Study of the reaction mechanism

CR is a type of diazo dye with two benzene rings and two naphthalene rings in its molecular structure. Three important and distinct bands were present in untreated CR solution. A maximum absorption at 497 nm attributed to the chromophore azo bond was located in the visible part. The two other absorptions at 236 nm and 343 nm, which were attributed to the presence of unsaturated benzene and naphthalene rings, respectively, were located in the ultraviolet part. Fig. 9 shows the UV-vis spectrum of CR solutions at appropriate time intervals by DBD treatment at 20 kV. Absorption peaks decreased and disappeared after plasma treatment, suggesting that the chromophore azo group was responsible for the color and that the benzene and naphthalene rings were broken. Discoloration was due to the destruction of the chromophore azo group as characterized by the absorption band with the maximum wavelength of 497 nm [6].

**Fig. 9** UV/visible spectrum of CR discoloration process

To identify degradation products, FTIR and LC/MS analysis were carried out. Fourier transform infrared

**Table 1.** Characteristic infrared absorption peaks of a Congo red molecular

<table>
<thead>
<tr>
<th>Groups</th>
<th>Absorption peak position (cm⁻¹)</th>
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<th>Absorption peak position (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N=N</td>
<td>1447</td>
<td>S=O</td>
<td>1200-1040</td>
</tr>
<tr>
<td>C=N</td>
<td>1365</td>
<td>S–O</td>
<td>900-700</td>
</tr>
<tr>
<td>–NH₂</td>
<td>1610-1580</td>
<td>benzene ring</td>
<td>900-750</td>
</tr>
</tbody>
</table>

**Fig. 10** The infrared spectrum of CR: (a) before the reaction, (b) after 20 min reaction

According to the abovementioned data and LC/MS analysis in Fig. 11, CR was degraded to other products after DBD treatment. The possible reaction pathways are shown in Fig. 12. With the destruction of –N=N– groups were broken, CR may be first decomposed to benzidine, even phenol, 1,2-diamino -4- sulfonic acid naphthalene. The amino group was oxidized to nitro and phenol groups easily by non-thermal plasma [10]. The TOC of the solution treated for 20 min decreased by 19.7%, indicating that C–S and C–H were oxidized and complete mineralization was achieved.
4 Conclusions

A rod-plate DBD reactor was applied to degrade CR in aqueous solutions. Experimental results showed that CR discoloration using DBD treatment was feasible and effective. A filamentary discharge in the DBD reactor was observed by measuring voltage-current waveforms. The radical species $\text{O}_3$, $\text{OH}^+$, $\text{N}_2\text{O}^+$, $\text{O}$, $\text{NO}$, and $\text{H}_2\text{O}_2^+$ were produced in gas phase and transferred into wastewater to generate $\text{O}_3$ and $\text{H}_2\text{O}_2$. Discoloration rates of the CR solution were influenced by the applied voltage, and the maximum discoloration ratio was obtained at 20 kV. Discoloration efficiency also decreased with increased initial conductivity and initial concentration. The addition of ferrous ions to the wastewater significantly enhanced the degradation efficiency for oxidation and complexation effect. Adding a certain concentration of $\text{H}_2\text{O}_2$ to the solutions can accelerate the CR discoloration rate. However, more $\text{H}_2\text{O}_2$ molecules can act as free-radical scavengers, which decreased the discoloration rate. Based on UV-vis, FTIR, and GC/MS data, a possible CR discoloration mechanism by DBD was elucidated. CR was oxidized into smaller molecular weights and inorganics with $\text{N}=\text{N}$-groups broken first, and then C–S and C–H were oxidized.

References


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