

Original Research

**SELF-MADE PULSATING ATMOSPHERIC PRESSURE CORONA PLASMA
REACTOR FOR DEGRADATION OF A TEXTILE DYE IN SYNTHETIC TEXTILE
EFFLUENT**

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Abstract

A self-made pulsating atmospheric-pressure corona plasma reactor was tested for the degradation of textile dye Reactive Blue 4. The reactor generated a corona-type discharge in air with low-intensity streamers, without sparks. The effect of the initial dye concentration, input reactor voltage, and pH was examined using model dye water solutions. A 50 mg dm⁻³ dye solution was completely decolorized at 18 kV and its native pH of 6.8 in less than 40 minutes. The chemical oxygen demand (COD) was reduced by 82% and 85% after 120 and 180 minutes of treatment, respectively. Decolorization rate and efficiency decreased with increasing initial dye concentration and with decreasing input voltage. Decolorization proceeded slightly faster in acid-neutral media than in alkaline media. The major degrading agent was determined to be the hydroxyl radical, generated by plasma. Textile effluent, containing 56 mg dm⁻³ RB 4, sulphates and carbonates, with pH 11.8, after removing the dyed fabric, was completely decolorized in 85 minutes, and the COD was reduced by about 76% and 78% after 120 and 180 minutes of treatment, respectively, which demonstrated the high potential of the reactor.

Keywords: corona discharge, textile effluent, RB 4, degradation.

INTRODUCTION

Textile dyeing effluents containing dyes and additives used in dyeing processes pose an environmental problem due to the high chemical stability of textile dyes and their resistance to conventional wastewater treatments. Advanced oxidation processes (AOPs) are based on the degradation of hazardous organic compounds by the highly reactive oxidative species, such as hydroxyl radical, ·OH, produced by powerful energy sources. AOPs showed high efficiency in dye degradation and mineralization, but many of them are expensive and difficult for large-scale work [1]. Plasma processes are based on electrical discharge at high voltage in air and/or water, which causes their ionization and the generation of oxidative

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species that attack and degrade the dye molecule, often leading to its mineralization. There are several types of plasma sources [2–5]. Atmospheric-pressure corona plasma exhibited many advantages, such as high efficiency, low cost, simple equipment, and relatively low energy consumption [6], which made it a choice for the removal of Reactive Blue 4 (RB 4), a representative of a large group of reactive textile dyes. In this paper, RB 4 was removed from a synthetic textile dyeing effluent by the self-made pulsating atmospheric pressure corona plasma reactor. The degrading reactive species were identified, and the process was optimized using model solutions before applying it to the effluent.

MATERIALS AND METHODS

Self-made plasma reactor

Dye degradation was done using a self-made corona plasma reactor, consisting of a power supply, a DC pulse generator, a high-voltage output stage, and an open cell. The positive corona discharge was created in the air over the water phase, on the tips of the multipoint anode, made of Ti needles, while the cathode was the dye solution's surface. The reactor cell was a PVC cylinder. The electrical contact was centered at the bottom of the cell and connected to the ground potential. The discharge current was controlled by the electronic circuitry of a device, adjusting the voltage at the multipoint anode. Gases produced by the discharge were removed through the exhaust system. The current and voltage signals were recorded using a digital oscilloscope TDS 2024C. The working frequency was 40 kHz. Corona discharge was without sparks and with the appearance of low-intensity streamers. The experimental setup is shown in Figure 1.

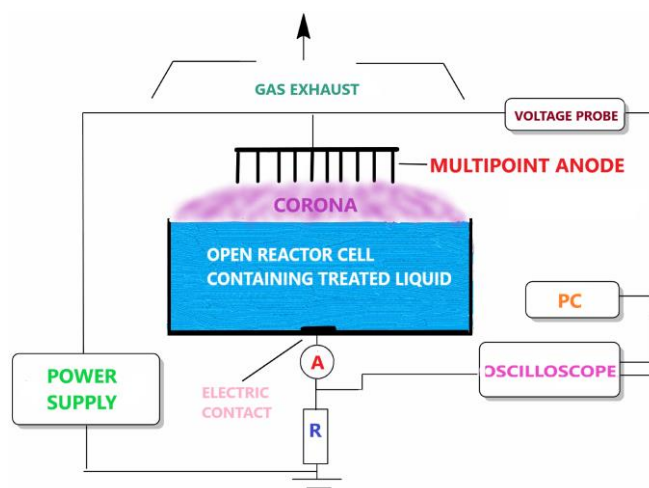


Figure 1 Scheme of a self-made pulsating atmospheric-pressure corona plasma reactor

Dye degradation experiments

RB 4 was purchased from Sigma Aldrich and used without purification. The working model dye solutions were prepared using deionized water by dissolving the required amount of dye in deionized water (stock solutions) and by diluting those solutions to the required concentrations. Solutions were then transferred to the plasma reactor cell and treated with cold plasma in open air at fixed time intervals. For the synthetic effluent experiment, a dyebath was prepared according to the references [7,8]. It contained 500 mg dm^{-3} RB 4,

50 g dm⁻³ Na₂CO₃, 100 g dm⁻³ Na₂SO₄, and 100 g dm⁻³ previously washed cotton fabric. Dyeing was performed at 40°C for 30 minutes. The dyed fabric was then removed, cooled to room temperature, and the effluent was treated using a self-made plasma reactor in the same way as the model solutions. Dye concentration was measured using a UV-VIS spectrophotometer Shimadzu UV-1650 PC (Japan) at 600 nm. Chemical oxygen demand (COD) was determined using the kit consisting of thermoreactor RD125, the Lovibond® COD Vario tube test, and the Lovibond® Multidirect photometer (Lovibond). The pH was measured using a SensIon3 pH meter (Hach, USA). The dye removal efficiency was presented as the percentage (%) of the dye removed at time t . The COD decrease was expressed as a percentage (%) of the initial COD removed at the treatment time t .

RESULTS AND DISCUSSION

Effect of initial dye concentration on decolorization

A radical scavenger test was performed to identify the oxidative species participating in the degradation. The addition of isopropanol ($\cdot\text{OH}$ scavenger) reduced the decolorization rate by more than 90%, while the other tested scavengers did not notably affect it. Thus, it was assumed that the $\cdot\text{OH}$ radical was the major dye-degrading agent. It was produced by plasma decomposition of the plasma-generated H₂O₂ (which was also detected in the treated solutions) via a mechanism described elsewhere [9].

Decolorization rate and efficiency decreased with increasing initial dye concentration (C_0). (Figure 2a). Complete decolorization was achieved in less than 40 minutes for lower C_0 values, and it took significantly more time at higher C_0 values. As the initial dye concentration in the solution increased, the ratio between dye concentration and $\cdot\text{OH}$ became less favorable, which reflected the decolorization rate. The effect was more pronounced at higher concentrations, where that ratio became more significant.

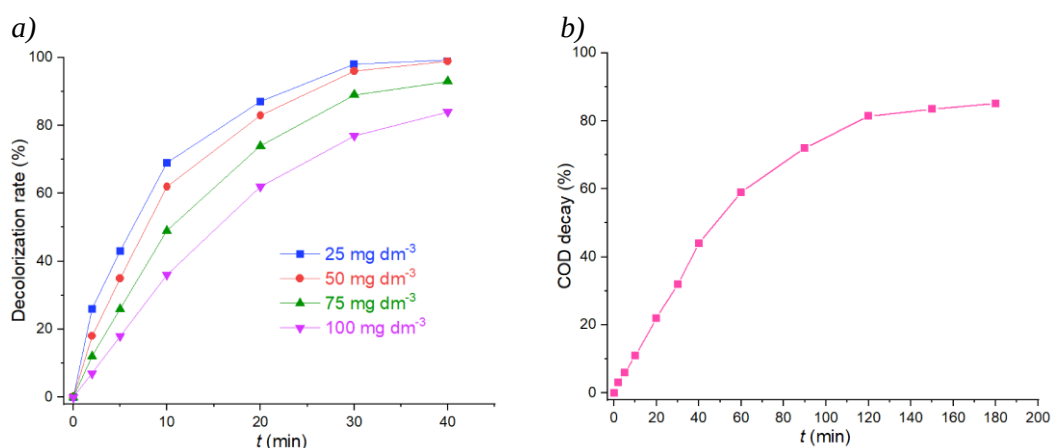


Figure 2 a) Effect of initial dye concentration on decolorization rate; b) COD decay in the RB 4 plasma degradation process (50 mg dm⁻³ dye solution, 18 kV, native pH)

Chemical oxygen demand (COD)

COD decay increased with the increase in electrolysis time, rapidly at shorter times, and slowly at longer times (Figure 2b). The increase was becoming less significant as the

electrolysis time was extended over 120 minutes. It reached about 82% after 120 minutes, and 85% after 180 minutes of the treatment, so it can be assumed that it approximately entered its equilibrium between 120th and 180th minutes of electrolysis. That value can be considered high.

Effect of operational parameters

Effect of input voltage

Decolorization rate and efficiency increased with increasing input discharge voltage (U) at a constant current density of 1.2 mA (Figure 3a). U is one of the most important factors affecting the plasma reaction rate because it is directly linked to the reactive species generation and acceleration. Higher input voltage provided more energy and intensified ionization and thus generation of dye-degrading radical oxidative species, which reflected the decolorization rate and efficiency. The input voltage was tested in the range 8V – 18V because the first value is the minimum U at which the ionization occurred in this case (the corona disappeared at lower values), and the second is the highest value of the stable corona and the selected discharge regime (Above that value sparks started to appear and the discharge became unstable).

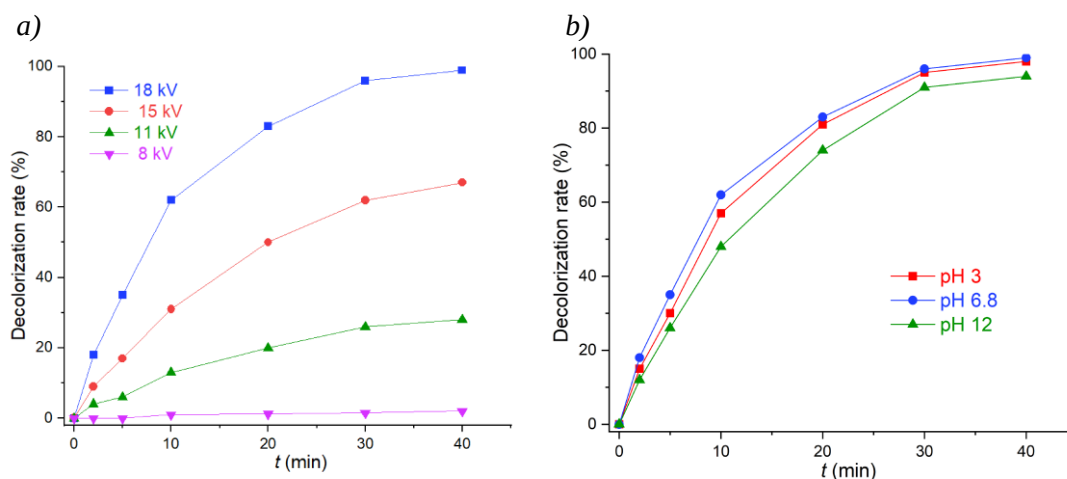


Figure 3 a) Effect of reactor input voltage; b) initial pH on RB 4 decolorization in plasma degradation process (50 mg dm^{-3} dye solution)

Effect of initial pH

The pH affects the decolorization rate because the present H^+ and OH^- ions can react with the plasma-generated oxidative species that degrade organics. In this case, pH had a relatively slight effect on the RB 4 decolorization rate and efficiency (Figure 3b). Decolorization was faster in acidic and neutral media (pH of 6.8 was the native pH of the treated model solution), with negligible differences, achieving complete decolorization in less than 40 minutes. In an alkaline medium, decolorization proceeded slightly slower, and its efficiency was slightly lower than in acidic/neutral media in the same treatment time. The reason was probably the reaction of hydroxyl radicals with hydroxyl ions, which had a quenching effect (due to the formation of a much weaker O^- radical), and thus reduced the quantity of hydroxyl radicals for dye oxidation [10]. However, the decolorization remained relatively fast and efficient in the entire examined pH range.

Plasma treatment of a textile effluent

The remaining dye concentration in the textile effluent after dyeing and removing the dyed fabric was 56 mg dm^{-3} , and its pH was 11.8. The effluent was treated with plasma at 18 kV without any previous treatment. Decolorization was completed in about 85 minutes (Figure 4).

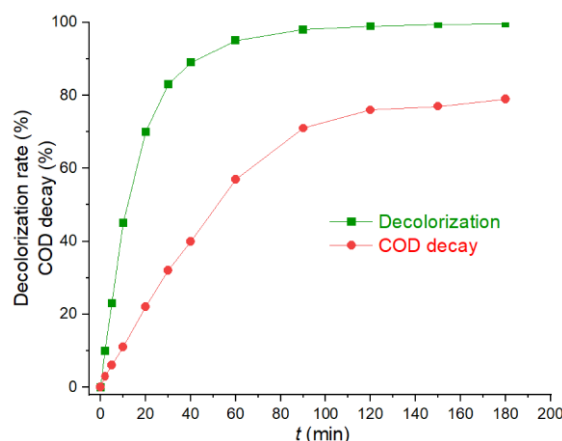


Figure 4 Decolorization rate and COD decay in the plasma treatment of a dyeing effluent

The COD removal reached its equilibrium value of 76% at about the 120th minute of the treatment and remained approximately the same in the next 60 minutes (it was 78% after 180 minutes of the treatment), and this can be considered its maximum value at given conditions, which is considered high for a typical dye bath. The decolorization process can be compared with the decolorization of the model solution containing 50 mg dm^{-3} RB 4 at pH 12. It proceeded somewhat more slowly because of the presence of SO_4^{2-} and CO_3^{2-} ions, which react with hydroxyl radicals, forming corresponding less active radicals and therefore making the decolorization process less efficient than it would be in the absence of sulphates and carbonates.

CONCLUSION

A self-made pulsating atmospheric-pressure corona plasma reactor exhibited high efficiency in the degradation of textile dye Reactive Blue 4. The corona operated with the streamers and without the sparks. It was found that the degradation proceeded mostly via plasma-generated hydroxyl radical $\cdot\text{OH}$. The effect of initial dye concentration and operational parameters on decolorization rate and efficiency was examined. Decolorization rate decreased with increasing initial dye concentration. It increased with increasing input reactor voltage due to more intensive ionization and the generation of oxidative species. It proceeded somewhat faster in the acidic-neutral media than in alkaline media because of the quenching effect of hydroxyl ions. Textile dyeing effluent, prepared according to a practical recipe, was decolorized in about 85 minutes without any previous treatment. The chemical oxygen demand decreased by about 85% for the tested model solution, and by about 78% for the textile dyeing effluent after 180 minutes of the treatment. The plasma generator showed notable potential for practical use.

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