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Removal of Cochineal Dye Color through Atmospheric Pressure Plasma Discharge Jet

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Abstract: The extensive utilization of dyes across diverse industries has resulted in environmental pollution, leading to the degradation of water bodies. To prevent environmental contamination, the use of eco-friendly dyes and innovative processes for dye degradation is crucial. This study aimed to investigate the color removal process of cochineal dye (Dactylopius coccus Costa) using the atmospheric pressure plasma jet (APPJ: Atmospheric Pressure Plasma Jet) technique. The dye extracted from the cochineal insect was treated with APPJ and the resulting color removal process was analyzed. Optical emission spectroscopy (OES) was used to investigate the plasma emission lines, and UV-Vis spectroscopy was used to monitor the color removal process. The results revealed that the decolorization of cochineal dye was a result of an oxidative degradation process caused by the interaction of the reactive species (NO_3^- and NO_2^-) generated by the APPJ plasma discharge with the dye molecules. This color removal process occurs in an acidic medium, leading to a pH change from 5.4 to 2.7. These pH changes can be attributed to fluctuations in the concentrations of reactive species such as nitrates and nitrites in the liquid phase. UV-Vis spectroscopy measurements showed that 90% of the cochineal color was removed within the first 10 min of treatment. This study enhances our understanding of natural color removal and provides insights into its mechanism, opening up possibilities for controlled modification and applications in various fields.

Keywords: oxidative degradation; cochineal dye; APPJ technique

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1. Introduction

The application of synthetic dyes in textile and painting industries is increasing [1,2]. However, these chemical compounds produce highly polluting effluents in water bodies [3–5], which poses a significant environmental concern. The scientific community is exploring new methods for degrading and bleaching effluents. An alternative approach involves the use of organic dyes; however, it is important to note that the dyeing process with natural dyes also generates pollutants and textile effluents that come from the chemical compounds used in their processing and the coloring itself [6–10]. The removal of textile effluent dyes using conventional methods is challenging and adversely impacts the flora and fauna of aquatic environments [4,5].

Cochineal dyes, derived from the adult female cochineal insect (Dactylopius coccus Costa), are widely utilized in various industries, including textiles, food, and cosmetics [10]. The primary component of cochineal dye is carminic acid, an anthraquinone-7-glucopyranosyl-3,5,6,8-tetrahydroxy-1-methyl-2-carboxylic acid, which is classified as an anthraquinone. The chemical formula of cochineal dye is $C_{22}H_{20}O_{13}$ [9,11–13]. In Peru, cochineal dye is readily available and cost-effective, making it highly valued in the artisanal textile industry for coloring natural fibers in the production of crafts such as blankets and ponchos. Its vibrant color intensity and resistance to wear are among the reasons why it is the preferred choice for fabric production [11].

Among the various techniques for removing environmental contaminants, those that generate reactive species through advanced oxidation processes (POA) are particularly noteworthy [14,15]. One such technique that has received attention is the use of atmospheric-pressure plasma jets (APPJ) to generate reactive species [15,16]. This method is cost-effective, versatile, and scalable. Plasmas can be classified into two categories based on the temperature reached during generation: high- and low-temperature plasma [17]. The APPJ technique falls under the latter category, where ionized gas is maintained at room temperature [18–22]. The APPJ technique produces a variety of reactive species, including positive and negative ions, meta-stable atoms, free radicals, electrons, electric field, and photons [17,18]. The reactive species generated by APPJ discharge can be characterized by analyzing the spectral lines of the emitted light using optical emission spectroscopy [23–25]. The transport and interaction of these reactive species with different media, such as air, liquid, and solid, result in the formation of three types of species: primary, secondary, and tertiary [18].

In the research conducted, the APPJ discharge technique was employed with air as the working gas to generate reactive oxygen (ROS) and nitrogen (RNS) species [18,26,27]. The primary reactive species are generated when the working gas ionizes, and accelerated electrons collide with neutral particles, producing electrons (e^-), ionized gases (M^+), excited gases (M^*), such as atomic N, O, and H [18,26]. When the primary reactive species interact with the air, they give rise to secondary reactive species like NO, NO_2, and 0_3 [18,26]. The interaction of these secondary reactive species with the dye solution results in the generation of tertiary reactive species, such as long-lived O_3, H_2O_2, $NO_3{}^-$, and $NO_2{}^-$ [18]. Some of these reactive species like NO_2, and NO_3 are soluble in water, immediately transforming into $NO_3{}^-$ and $NO_2{}^-$, potentially lowering the pH of the liquid through dissolution. These radicals play a crucial role in the degradation process of organic compounds [18–20,27]. The presence of reactive nitrogen species creates an acid environment that promotes the bleaching process through oxidative color removal mechanisms [18,28–31].

According to Gürses et al. [32], pigments exhibit coloration due to the absorption of light in the visible spectrum (400–700 nm) as a result of the presence of at least one chromophore group and a structure with alternating double and single bonds in their chemical composition. In the case of cochineal dye, the acid medium generated by reactive species causes oxidative color removal through the rupture of the anthraquinone chromophore group bond and auxochromes of carminic acid (-OH, -CH_3) [31–33]. This results in the anthraquinone compound losing its ability to absorb radiation in the visible range, leading to the loss of its coloration.

In recent years, there has been an increase in the number of research studies focusing on the removal and discoloration of pigments and industrial dyes using non-thermal plasma discharge. Chouchene et al. [34], reported on the degradation of cochineal red using birnesite thin films that were treated with moist air plasma. Cream et al. [35] compared the degradation of indigo carmine in water using different methods, such as non-thermal plasma (NTP), ozone (O_3), and hydrogen peroxide (H_2O_2). NTP was found to induce physicochemical changes in water that facilitated degradation. Abdel-Fattah [36] documented the properties of helium (He) plasma at atmospheric pressure and its effect on methylene blue (MB) dye. The study showed that contact between the plasma and the MB solution generated reactive species such as OH, He*, and O, which led to the degradation of the dye. Given this background, the main objective of this study was to evaluate the effect of the reactive species produced by atmospheric pressure plasma discharge (APPJ) on the degradation of the natural dye extracted from cochineal.

2. Materials and Methods

2.1. Materials

The cochineal, a parasitic insect that infests the prickly pear cactus Opuntia ficus, was sourced from the community of Huayllabamba, situated in the province of Abancay, Apurímac region, Peru, at an elevation of 2500 m above sea level. Following collection, the cochineals underwent a process of drying, after which they were subsequently ground into a fine powder. This ground cochineal was employed directly in plasma treatment, without undergoing any prior chemical treatment.

2.2. Cochineal Dye Preparation

Cochineal dye was obtained through the use of a procedure described by Figueroa et al. [37], utilizing dried cochineal tissue. The process entailed the dissolution of 100 mg of powdered cochineal in 1000 mL of distilled water, followed by homogenization through heat treatment at 80 °C for a period of 2 h.

2.3. Mealybug Dye Treatment by APPJ Discharge

The treatment of cochineal dye using plasma discharge was performed using the PLASMA CLEAN-PL-5050 equipment from Keylink Technology Co. (Wenzhou, China). The plasma equipment was operated with an electrical voltage of 130 V and an air flow of 105 psi. The assays for cochineal color removal were conducted on 150 mL samples, with exposure to various plasma discharge times, up to a maximum of 10 m. The distance between the plasma outlet and the sample surface was maintained at 0.3 cm.

2.4. Analysis of Plasma Composition Using Optical Emission Spectroscopy

Optical emission spectroscopy was employed to investigate the spectral lines of the primary and secondary reactive species generated during the discharge of an atmospheric-pressure plasma jet (APPJ) [25,38]. The emission spectrum of the plasma discharge was measured across a broad range of wavelengths, from 200 to 1100 nm, using the ULS4096CL-RS spectrometer (Avantes, Apeldoorn, The Netherlands). To obtain a higher resolution in the ultraviolet region, the spectral range of 200–550 nm was analyzed using the ULS4096CL-RS-EVO high-resolution spectrometer (Avantes). Furthermore, a detector with a collimator connected to the spectrometer via an optical fiber was utilized to enhance information collection during the analysis of the spectral lines of the reactive species generated by the APPJ discharge.

2.5. The Kinetics and Efficiency of the Decolorization of Cochineal Dye through the Use of Absorption Spectroscopy

UV-visible spectroscopy was employed to identify the absorption spectra of the dye solution using a Libra S22 UV-visible spectrophotometer (Biochrom US, Holliston, MA, USA) in the spectral range of 200–1100 nm. To assess the color removal efficiency of cochineal dye during interaction with APPJ plasma, samples were taken between 0 and 10 min for analysis via absorption spectroscopy. The kinetic decoloration behavior was modeled utilizing expression (1), which is consistent with a first-order kinetic model.

$$C_t = C_0 e^{-kt} \tag{1}$$

Here, C_t (ppm) is the concentration of the dye after plasma treatment for t min, C_0 (ppm) is the concentration of the untreated sample, and k (min^{-1}) is the rate constant.

The percentage degradation of the cochineal dye was also defined from the absorption measurements using the following equation:

$$D_{degradation}[\%] = \frac{A_0 - A}{A_0} * 100 \tag{2}$$

Here, A_0 is the absorbance of the dye solution without plasma treatment and A is the absorbance after plasma treatment at the wavelength of maximum absorption. For cochineal dye, the absorption peak at 496 nm is the visible range [39,40].

2.6. pH and Electrical Conductivity Measurements

A PL-700AL multiparameter meter (LabTech, Inc., Northvale, NJ, USA) was employed to measure changes in pH and electrical conductivity during the color removal process of the cochineal dye. Sample measurements were taken every half minute during the first two min and then at 5 and 10 min of plasma treatment. The pH measurements were conducted on both samples with and without plasma treatment to ascertain the acidity or basicity of the dye [25].

2.7. Concentration of Reactive Nitrogen Species (RNS)

The concentration of nitrites and nitrates in the dye solution before and after plasma treatment was measured using a Libra S22 UV-visible spectrophotometer (Biochrom US). The procedure used to determine these reactive species, which are crucial for studying the color removal or color removal of cochineal dye, followed the methodology proposed by Vogel [41].

3. Results and Discussion

3.1. Analysis of Plasma Composition

The results of the spectral analysis of the APPJ discharge measured using OES revealed that reactive oxygen (ROS) and nitrogen (RNS) species were responsible for the spectral emission lines (Figure 1). The majority of the peaks were located in the near-UV region, ranging from 200 to 400 nm. Reactive nitrogen species (RNS), specifically the second positive system N_2(C-B), were formed in the wavelength range of 315–356 nm, and the first negative system N_2+ was observed in the wavelength range of 375–391 nm (see inset Figure 1). Additionally, two excited atomic oxygen peaks were identified at 777 and 844 nm [42], and the emission of OH was observed at 309 nm. Similar results were reported by Sarangapani [27], who used a dielectric barrier discharge (DBD) plasma source and identified singlet emission. These results highlight that APPJ plasma utilizing air as the working gas is an efficient source of reactive oxygen and nitrogen species (RONS) N_2, N_2+, OH, and O.

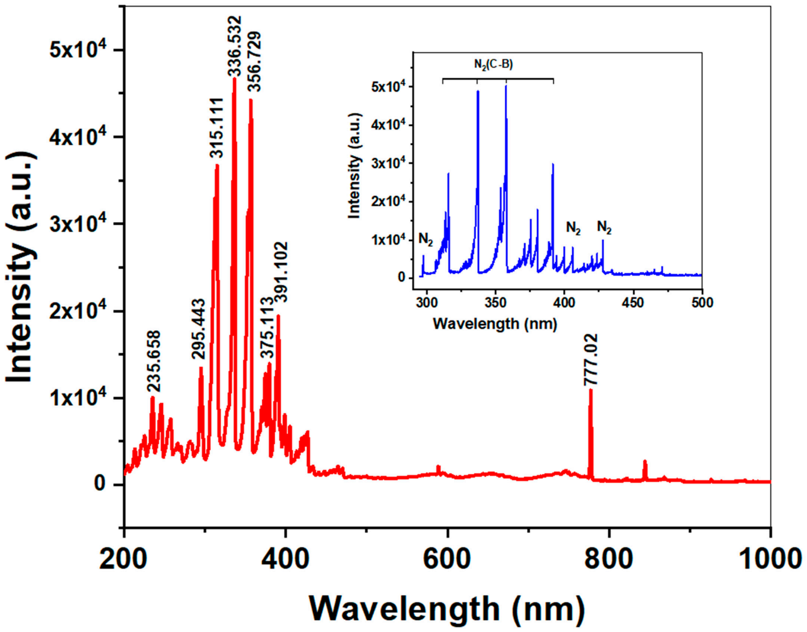

Figure 1. Air plasma emission line spectrum (OES). Inset graph shows RONS.

Understanding the reactive species present and their potential formation mechanisms can be valuable for optimizing the dye removal process. However, it is important to note that the characterization of the spectral lines generated by the APPJ discharge using optical emission spectroscopy has limitations concerning the spectral resolution and sensitivity of the equipment used. Additionally, it is possible that not all reactive species present in the discharge were identified. Further research should be conducted to delve deeper into the formation mechanisms of reactive species and their relationship with the properties of APPJ discharges. Moreover, exploring other potential applications of this technology in fields such as disinfection, medicine, and agriculture could be worthwhile [17].

3.2. Effects of Plasma Treatment on pH and Electrical Conductivity during Dye Degradation

The blue curve in Figure 2 shows that the pH of the dye solution exponentially decreased with the interaction time between the dye and the reactive species (RONS) generated by the APPJ discharge. A significant decrease in pH was observed during the first two min, while it tended to stabilize between 2 and 10 min. The pH value change from 5.4 to 2.7, indicating a transformation from an acid dye to an extremely acidic state. These findings are consistent with those reported by Zhou et al. [42], where a decrease in pH (<5) was associated with the following chemical reactions:

$$\mathrm{NO_2} + \mathrm{NO_3} + \mathrm{HO_2} \rightarrow \mathrm{NO_2^-} + \mathrm{NO_3^-} + 2\mathrm{H^+}$$

$$\mathrm{NO} + \mathrm{NO_2} + \mathrm{H}O_2 \rightarrow 2\mathrm{NO_2^-} + 2\mathrm{H^+}$$

$$\mathrm{HO_2} + \mathrm{e^-} \rightarrow \mathrm{HO_2} + 2\mathrm{e^-}$$

$$\mathrm{O} + \mathrm{HO_2} \rightarrow \mathrm{H_2O_2}$$

$$\bullet\mathrm{OH} + \bullet\mathrm{OH} \rightarrow \mathrm{H_2O_2}$$

The results obtained from the conductivity measurements (red curve in Figure 2) indicate a variation between 10 and 650 μS cm^{-1} during the first 10 min of irradiation with APPJ plasma. Similar findings were reported by Zhou et al. [42], who showed a substantial increase in the electrical conductivity of water from 24 to 724 μS cm^{-1} after 30 min of plasma irradiation. This significant conductivity variation is associated with the formation of free radicals, such as O_3, H_2O_2, NO_3^-, and NO_2^-, which contribute to the formation of the acid dye and induce changes in the conductivity [16].

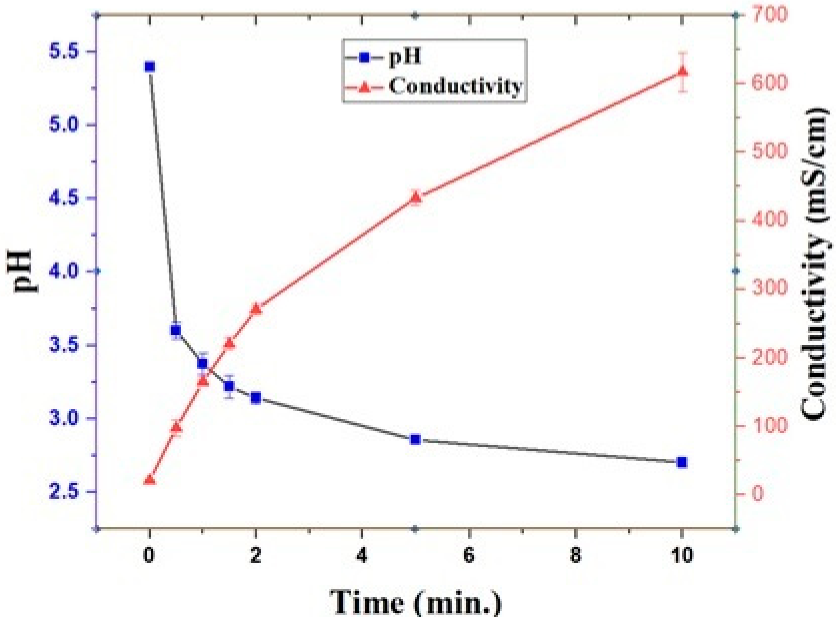

Figure 2. Changes in pH and dye conductivity owing to APPJ exposure.

Plasma treatment has been found to effectively reduce the pH of the dye solution and increase its electrical conductivity during dye removal. These changes are a result of chemical reactions involving reactive species generated by plasma discharge. However, further research is required to understand the mechanisms involved in dye degradation. Understanding the effects of APPJ plasma parameters on dye degradation can be used to tailor the degradation process for specific applications. These findings have important implications for the future research and development of plasma-based solutions for wastewater treatment and environmental remediation [13].

3.3. Measurement of the Concentration of Nitrites, Nitrates, and Their Role in the Dye Bleaching Process

Table 1 shows the quantification of nitrites and nitrates in the samples before and after treatment with the APPJ plasma. A 10 min treatment results in an approximately 200% increase in the concentration of the reactive species NO_2^- and NO_3^-. These species belong to the group of tertiary reactive species of RONS, including O_3, H_2O_2, NO_2^-, and NO_3^-, which are generated in the liquid phase because of the interaction of the secondary reactive species with the dye solution [18]. As noted by Barjasteh et al. [18], NO_2 and NO_3 are soluble in water and promptly transform into NO_2^- and NO_3^- through the following reaction patterns:

$$\mathrm{NO_2 + OH \rightarrow H^+ + NO_3^-}$$

$$\mathrm{NO_2 + NO_3^- + HO_2 \rightarrow NO_2^- + NO_3^- + 2H^+}$$

$$\mathrm{NO + NO_2 + HO_2 \rightarrow 2NO_2^- + 2H^+}$$

This mechanism could explain why a liquid solution with a strong acidic character is responsible for the oxidative color removal of the cochineal dye [13,35].

The findings indicate that subjecting cochineal dyes to an atmospheric-pressure plasma jet (APPJ) for a period of 10 min results in a significant increase in the concentration of reactive species, including NO_2^- and NO_3^-. These reactive species, including O_3, H_2O_2, and NO_2^-/NO_3^-, are produced in the liquid phase as a result of secondary reactive species interacting with the cochineal dye solution The solubility of nitrogen oxides (NO_2 and NO_3) in water facilitates their rapid conversion into nitrate and nitrite ions (NO_2^- and NO_3^-) through a variety of reactions involving the presence of hydroxyl radicals and other reactive species. This transformation results in the formation of a highly acidic liquid solution that is responsible for the oxidative degradation of the dye. By understanding the mechanisms involved in the generation of these reactive species, it is possible to control and optimize the dye degradation process and develop alternative methods for removing the dye. Future studies should investigate the effects of varying plasma treatment parameters, such as duration and intensity, as well as the utility of alternative reactive species like O_3 and H_2O_2, to gain further insights and uncover potential industrial applications. Additionally, it is crucial to perform a total organic carbon (TOC) test to evaluate the efficacy of dye degradation treatment using APPJ plasma and identify other organic pollutants [43].

Table 1. Concentration (mL) of nitrates and nitrites from spectrophotometry method.

Treatment Time	Nitrates	Nitrites
0 min	0.892	0.058
10 min	2.32	0.122

3.4. UV-Visible Spectral Analysis

The UV-visible spectrum analysis of the dye sample without plasma irradiation shows two prominent absorption peaks at 276 and 496 nm, as depicted by the dark blue curve in Figure 3. It is observed that the intensity of these peaks diminishes as the dye samples are subjected to plasma treatment for varying durations of irradiation. The data reveal that there is a substantial decrease in intensity during the initial 2 min, which then slows down between 2 and 10 min.

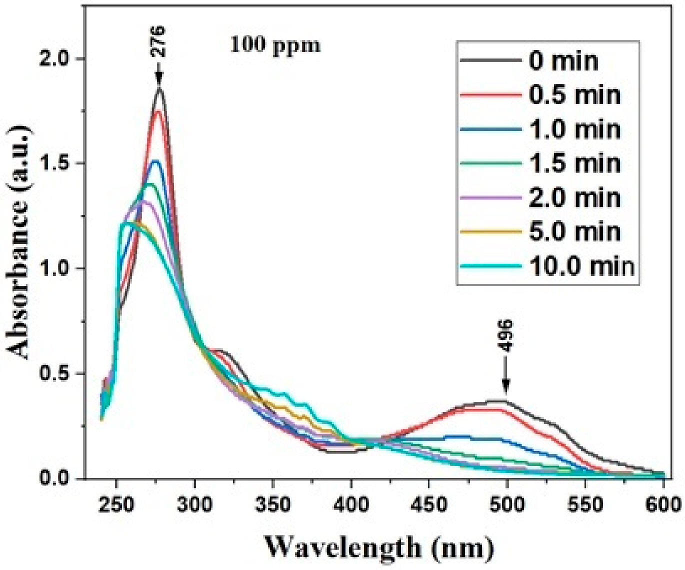

Figure 3. UV-vis spectra measured for different plasma irradiation times.

The effectiveness of atmospheric-pressure plasma discharge (APPJ) in degrading cochineal dye was evaluated using Equation (2) to measure the rate of color removal during APPJ discharge irradiation. The results demonstrated that approximately 90% of the dye was degraded after 10 min of exposure (Figure 4). This finding is consistent with a similar study reported by Chouchene et al. [34] and Crema et al. [35]. Indeed, Chouchene reported that the interaction of cochineal dye with a plasma-treated birnessite layer leads to 95% degradation after 24 h. These results support the hypothesis that plasma treatment can be an effective method for dye removal, making plasma irradiation a promising technique for eliminating dyes. However, it is important to recognize the limitations of this research, such as the specific experimental conditions used. Further research is needed to optimize the process and investigate the effects of different plasma parameters on dye removal efficiency. Additionally, future studies could explore the potential use of plasma treatment for other types of dyes and examine the long-term stability and environmental impact of plasma-treated dye samples.

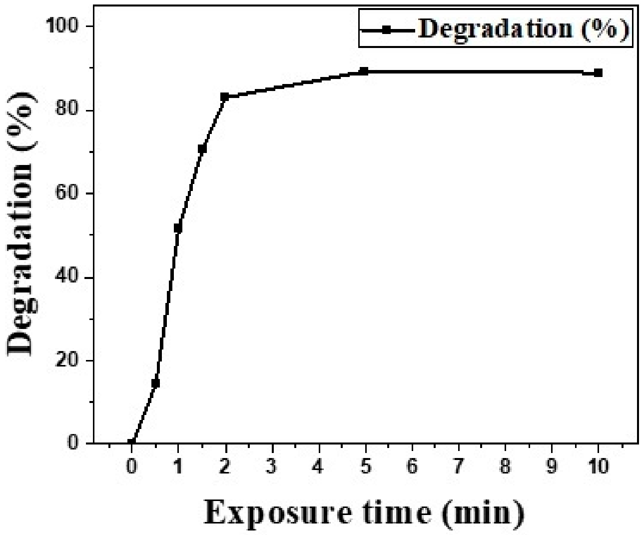

Figure 4. Percentage degradation of cochineal dye by APPJ discharge.

3.5. Kinetic of Cochineal Dye Color Remotion

The kinetic process of color removal can be divided into two distinct stages, as illustrated in Figure 5. The initial stage commences at the onset of the experiment and continues until the 2 min mark, while the subsequent phase begins at 2 min and persists until the 10 min mark. Based on the study reported by Gibaja [13], it is believed that the removal of cochineal dye occurs through an oxidative process induced by the interaction with reactive species (RONS) generated by the APPJ discharge.

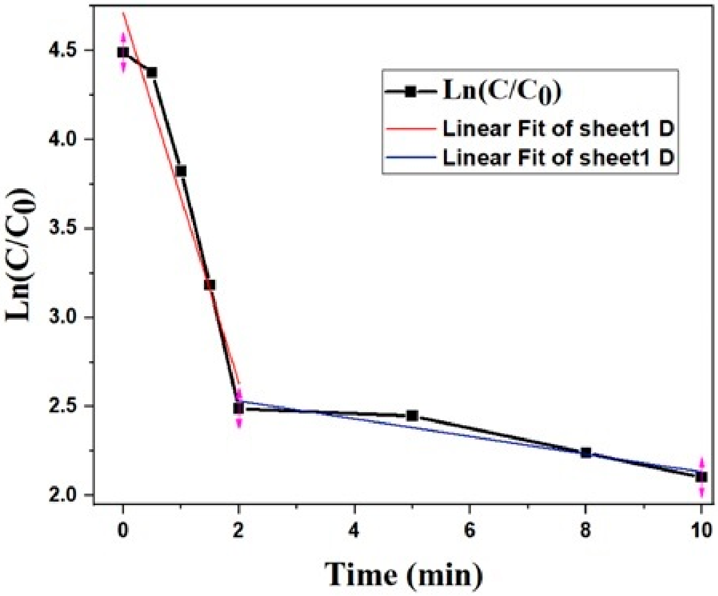

Figure 5. The color removal of cochineal dye through atmospheric pressure plasma discharge jet (APPJ) follows a kinetic process consisting of two distinct stages.

The observed kinetics parameters showed in Table 2 indicate that, in the initial stage, a rapid color removal reaction occurs until reaching a critical point of dye exhaustion within 2 min. Subsequently, in the second stage, the color removal reaction proceeds more slowly due to the reduced number of dye molecules remaining. A study conducted by Pankaj et al. [38] reported that color removal follows first-order kinetics. Accordingly, the experiment's data were fitted to the first-order color removal model using Equation (1). The model parameters obtained from the fitted equation are shown in Table 2. The kinetic parameter (k) transitions from a rapid rate (0.966) in the first stage to a slower rate (0.039) in the second stage, attributed to dye depletion and oxidative degradation induced by RONS. According to Zuo et al. [44]. (2020), the performance of FeSiBP amorphous alloys in degrading the dye Methyl Blue (MB) through a Fenton-like process was analyzed. The study found that the pH of the solution affects the degradation efficiency of the dye. It was observed that the degradation of MB was more effective in acidic conditions (pH 3), with almost 95% of the dye being degraded. However, under neutral conditions (pH 7), the degradation reaction barely occurred within the first 11 min, and only 17% of the dye was degraded.

Table 2. Parameters of first-order kinetic model for cochineal (woodlouse) dye degradation.

Exposure Time	Kinetic Parameters k (min^{-1})	R2 (adj.)
0–2 min	0.96645 ± 0.10845	0.9636
2–10 min	0.03919 ± 0.00427	0.97684

These findings have important implications in the field of textile dye wastewater treatment, as APPJ treatment shows promise as an efficient and environmentally friendly method to reduce dye pollution. However, this study has some limitations. Further research is required to explore the effects of different dye properties and experimental conditions on the removal process. Additionally, the study did not evaluate the toxicity or potential environmental impact of the oxidation products. Future research should address these limitations to provide a more comprehensive understanding of the dye removal process and its implications.

4. Conclusions

The results of this research demonstrated that the use of an atmospheric-pressure plasma jet (APPJ) on cochineal dye is effective in removing its color. The research revealed that the decoloring process occurs within the initial ten minutes of treatment and comprises two distinguishable stages characterized by first-order kinetics. Throughout the entire ten-minute treatment, almost 90% of the dye color was eliminated due to the reaction between the reactive species (O_3, H_2O_2, NO_2^-, and NO_3^-) and the dye molecules. This reaction results in the formation of a highly acidic liquid solution, which can be attributed to the oxidative degradation of the dye. These findings are significant because they demonstrate that APPJ plasma has potential for color removal in various industrial applications, particularly in the textile and paint industries. However, further research is required to investigate the effects of plasma parameters on the degradation of different types of dyes and the environmental impact of the plasma-treated dye samples.

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