

Dyes degradation using atmospheric pressure dielectric barrier discharge pencil plasma jet

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Research Article

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DOI: <https://doi.org/10.21203/rs.3.rs-2606871/v1>

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Abstract

The dye degradation efficacy of the cold plasma pencil jet is presented in the present investigation. Air plasma is produced in the cylindrical coaxial dielectric barrier discharge configuration. Electrical characterization of plasma is performed and the plasma species are identified using optical emission spectroscopy. For the dye degradation study using air plasma, six different types of dyes (erythrosine, metanil yellow, sudan I, crystal violet, rhodamine B, and Indigo) are chosen. The degradation of dyes is analyzed using UV visible spectroscopy, total organic carbon, and chemical oxygen demand. The results showed complete degradation of all the dyes in UV visible analysis with minimum time for indigo (3 minutes) and maximum time for erythrosine (45 minutes). Moreover, erythrosine ($k = 1.08 \text{ mg L}^{-1} \text{ min}^{-1}$) and sudan I ($k = 3.46 \text{ mg L}^{-1} \text{ min}^{-1}$) follows zero-order degradation kinetic and metanil yellow ($k = 0.094 \text{ min}^{-1}$), crystal violet ($k = 0.25 \text{ min}^{-1}$), rhodamine B ($k = 0.17 \text{ min}^{-1}$), Indigo ($k = 0.81 \text{ min}^{-1}$) follows first-order degradation kinetics. Also, substantial enhancement in mineralization and reduction in chemical oxygen demand of all the dyes occurs after plasma treatment. The toxicity of plasma degraded dye solution toward freshwater algae species (*Chlorella Sorokiniana* and *Chlorella Pyrenoidosa*) are significantly low compared to virgin dyes solutions. The study reveals that pencil plasma jet substantially degrade dyes as well as converts the dyes solutions non-toxic.

Keywords: plasma treatment, plasma diagnosis, dye degradation, TOC and COD, toxicity analysis

Introduction

The increasing dyes demand in industries like pharmaceuticals, food, textile, etc. also increases the dyes effluents in wastewater. These dye effluents have the potential to cause serious damage to aquatic plants, animals as well as humans in an indirect manner (consumption of infected food grown in dyes contaminated water). Moreover, due to the complex organic structures of dyes, the conventional methods such as physical, chemical, and biological methods (ultrasound, cavitation, UV irradiation, oxidizing agents like chlorine and ozone, microbes, etc.) are either ineffective, economically not viable, or can create secondary toxic pollutants (1-3). Therefore, to overcome these challenges researchers explore other promising methods. Among them advanced oxidation processes (AOPs) gaining significant attention throughout the world. In which, the generation of hydroxyl ($\text{HO}\cdot$) radical occurs through various means. This generated $\text{HO}\cdot$ radical oxidized the dissolved organic waste to simpler non-toxic compounds in wastewater. Along with $\text{HO}\cdot$ radical other oxidizing species such as ozone (O_3), ultraviolet (UV) radiation, hydrogen peroxide (H_2O_2), etc. also play a significant role in the advanced oxidation process (3-9).

The cold atmospheric pressure plasma (CAPP) technology is a part of AOPs. It is recommended over other AOPs due to its eco-friendly, ease of production, and economic

advantages. It does not require expensive catalysts, chemicals, radiation uses, etc. that are needed in other AOPs. The efficacy of CAPP in dye degradation was previously explored by various researchers (1-8, 10-19). Some of the researchers that reported indigo carmine, crystal violet, and rhodamine B degradation using cold plasma are given as Crema et al.(1), Lee et al.(2), Wang et al.(3), Gao et al.(10), Ruo-bing et al.(8), Ferreyra et al.(11), Schönekerl et al.(7), Zhou et al.(6), Chen et al.(14), Chen et al.(15), Rahimpour et al.(12), Abdelmalek et al.(4), and Njiki et al.(13), Fang et al.(18), Butman et al.(17), Chen et al.(5), and Meiyazhagan et al.(16), etc.

The present work also studied the dye degradation efficacy of a device named pencil plasma jet (PPJ) based on the principle of CAPP. The PPJ uses dielectric barrier discharge (DBD) assembly to produce plasma. To study the dye degradation efficacy of PPJ, six different types of dyes are chosen. These dyes include erythrosine, metanil yellow, sudan I, crystal violet, rhodamine B, and Indigo.

Erythrosine (first dye) is an organoiodine compound and a derivative of fluorone and is pink in color. It is normally used for food coloring in various food industries. Apart from that, it is also used in printing, biological staining, radiopaque medium, etc.(20-22). The second dye is metanil yellow which is an azo dye and normally used as a pH indicator. Due to its bright yellow color, some reports say that it is used as an adulterant in turmeric powder. The studied conduct on animals suggested that it is a neurotoxic and hepatotoxic agent(23-25). Sudan I (third dye) is also an azo dye like metanil yellow, it is orange red in color. It is used as a coloring agent in food (like chilli powder, curry powder, etc.), oils, waxes, solvents, etc. As per the international agency for research on cancer, sudan I is carcinogenic in nature. Therefore, it is banned in many countries (26). The fourth dye used in the present study is crystal violet. It is a triarylmethane dye. It is used for the classification of bacteria using gram staining, histological staining, textile, and paper dye (ball-point pens and inkjet printers), etc.(27-29).

The Rhodamine B (fifth dye) has applications in biology (biomarker, fluorescent microscopy, flow cytometry, etc.), tracer dye in fluid flow, and coloring agent in food, etc. Some places (like California) in the world consider rhodamine B carcinogenic. Hence, food products containing rhodamine B are marked with warning labels. (30-33) The last dye used in the present study is an indigo dye (sixth dye). It is mainly used to dye cotton yarn for the production of denim clothes (34). As discussed, all the dyes have various applications in different sectors. Hence, the degradation of effluent waste created due to the use of these dyes becomes significantly important. Moreover, the degradation of erythrosine, metanil yellow, and sudan I using cold plasma is yet to be explored as per the authors' literature survey. Also, the use of dielectric barrier discharge pencil plasma jet configuration for degradation of dyes (erythrosine, metanil yellow, sudan I, crystal violet, rhodamine B, and Indigo) have not been reported yet as per the best of the authors' knowledge.

The present work showed the electrical characterization of air plasma during dye degradation. The species/radicals generated during air gas discharge are identified using optical emission spectroscopy. The degradation of dyes after plasma treatment is monitored by using UV visible spectroscopy, total organic carbon, and chemical oxygen demand. The toxicity of degraded dyes is analyzed using freshwater algae species. At last, the species responsible for the degradation of dyes are identified.

Materials and Methods

The schematic of dye degradation using a pencil plasma jet is shown in figure 1 (a). The pencil plasma jet (PPJ) produced air plasma using dielectric barrier discharge. More details about PPJ can be found in our previous publications(35, 36). The flow rate of air through the PPJ set was fixed at 5 l min⁻¹. The voltage across the PPJ set was measured using a 1000x probe (Tektronix P6015A) and an oscilloscope (Tektronix TDS2014C). The current and transported

accumulated charge was measured by measuring the voltage drop across a resistor ($R = 30\ \Omega$) and non-inductive capacitor ($100\ \mu\text{F}$) in series with the ground. The air plasma emission spectrum in the afterglow region was measured by using optical fiber and a spectrometer (StellarNet Inc. Model EPP2000-UV) in the range of 200 to 600 nm as shown in figure 1 (a).

The dyes (analytical grade erythrosine, metanil yellow, crystal violet, sudan I, rhodamine B, and indigo procure from Sigma-Aldrich) solution was prepared by dissolving 50 mg of each dye in 1 liter of ultrapure mill-Q water each. So, the initial concentration of the freshly prepared dye solution was $50\ \text{mg L}^{-1}$. A 50 ml of each solution was treated with air plasma produced in the PPJ setup as shown in figure 1 (a). During plasma-dye solution interaction continuous stirring of the solution was performed so the produced reactive species due to plasma-solution interaction was uniformly distributed.

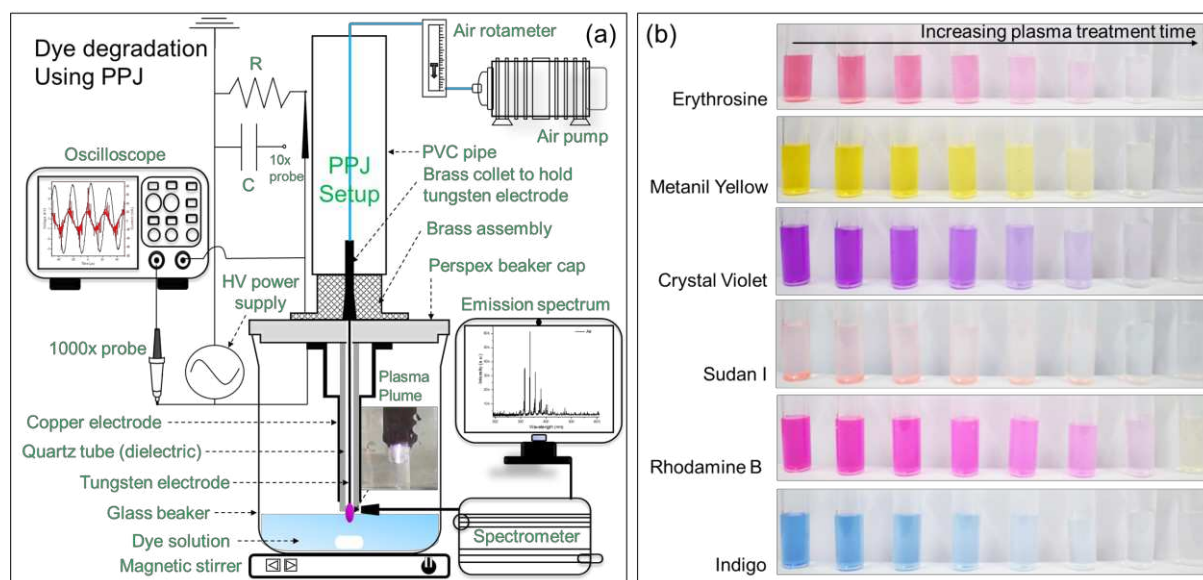


Figure 1. (a) Schematic of plasma degradation of dye, (b) Pictures of variation in dye color with increasing plasma treatment time with dye

The degradation of dyes was measured using UV-visible spectroscopy. The standard curve of all the dyes solutions was prepared using dyes of solutions of different concentrations in the range of 0 to $50\ \text{mg L}^{-1}$. If the absorbance of dyes solutions were high, dilution was

performed till the solution followed Beer's-Lambert's law. The erythrosine, metanil yellow, crystal violet, sudan I, rhodamine B, and indigo showed maximum absorbance at 527 nm, 436 nm, 590 nm, 494 nm, 553 nm, and 600 nm, respectively (1, 6, 16, 37-39). The molar attenuation coefficient from standard curve of erythrosine, metanil yellow, crystal violet, sudan I, rhodamine B, and indigo were given as $0.0477 \text{ (mg L}^{-1}\text{)}^{-1} \text{ cm}^{-1}$, $0.0376 \text{ (mg L}^{-1}\text{)}^{-1} \text{ cm}^{-1}$, $0.0014 \text{ (mg L}^{-1}\text{)}^{-1} \text{ cm}^{-1}$, $0.0308 \text{ (mg L}^{-1}\text{)}^{-1} \text{ cm}^{-1}$, $0.1149 \text{ (mg L}^{-1}\text{)}^{-1} \text{ cm}^{-1}$, and $0.0147 \text{ (mg L}^{-1}\text{)}^{-1} \text{ cm}^{-1}$, respectively. A rate kinetic model (zeroth order or first order) was fitted in the experimental data of dye degradation with increasing plasma treatment time to determine the reaction rates.

Zeroth order model

$$C = C_0 - kt$$

First order model

$$C = C_0 e^{-kt}$$

Where ' C_0 ' (50 mg L^{-1}) is the initial concentration of dye in solution, ' C ' is the concentration of dye in solution at the time ' t ' in minutes, ' k ' is the rate constant.

The mineralization of dyes in solution was analyzed using an O-I-Analytical Aurora model 1030 total organic carbon (TOC) analyzer with an autosampler (Aurora model 1088). The determination of chemical oxygen demand (COD) in dye solution of control and plasma treatment was evaluated using the method given by JOINT A.B.C.N. - S.A.C. COMMITTEE (40).

To identify the species formed during plasma-dye solution interaction, the air plasma was treated with ultrapure milli-Q water. The change in physicochemical properties (pH, oxidation-reduction potential (ORP), total dissolved solids (TDS), and electrical conductivity (EC)) and formation of reactive species (nitrate ions (NO_3^-), nitrite ions (NO_2^-), hydrogen

peroxide (H₂O₂), and dissolved ozone (O₃) in water were measured periodically by following the procedure mentioned in our earlier reported work (35, 41, 42).

For toxicity analysis, 0.1 ml of dye solution (control and plasma treated) was mixed with 0.9 ml of freshwater algae strains. The freshwater algae species *Chlorella Pyrenoidosa* (NCIM Accession No. 2738) and *Chlorella Sorokiniana* (NCIM Accession No. 5673) were procured from National Chemical Laboratory, Pune, India. The procured algae species were grown in sterile Bold's Basal Medium. The toxicity of dyes towards algae was monitored at regular intervals by measuring absorbance at 680 nm using UV visible spectroscopy (SHIMADZU UV-2600).

All experiments were performed at least three times ($n \geq 3$). The data obtained from the experiments were expressed as mean $\pm$ standard deviation ($\mu \pm \sigma$). The statistically significant difference among the obtained results was analyzed using analysis of variance (ANOVA) with a 95% significance level (p-value 0.05) methodology followed by a post-hoc test (Fisher's Least Significant Difference test).

Results

Voltage-current waveform and voltage-charge Lissajous figure of PPJ

The voltage-current waveform of air plasma produced during dye degradation of plasma dye solution interaction is shown in figure 2 (a). The observed discharge current peaks showed the produced plasma was dielectric barrier filamentary micro-discharge in nature. The micro-discharges are the collection of nanosecond current filaments that are observed during each rising and falling current half-cycle (9). The voltage-transported charge Lissajous figure is shown in figure 2 (b). It was used to calculate the energy and power consumed during plasma production (35). The calculated energy and power were given as 0.13 mJ and 5.2 W respectively.

Emission spectra of air plasma

The optical emission spectra of air plasma in the afterglow region during dye degradation are shown in figure 2 (c). The emission spectrum of air plasma in afterglow regions showed N^+ , NO, N_2 , N_2^+ , O^+ , and, O, etc. species/radicals. Among them, N_2 second positive system ($\text{C} \rightarrow \text{B}$) emission band peaks were the strongest with the strongest intensity of line was 336.5 nm ($v' \rightarrow v''$ ($0 \rightarrow 0$)) (complete list of lines were shown in support information Table S1). In addition, lines of the N_2^+ first negative system ($\text{B} \rightarrow \text{X}$) were substantially weaker compared to the N_2 second positive system. The observed N_2^+ lines were 390.5 ($0 \rightarrow 0$) and 418.5 ($2 \rightarrow 3$) respectively. Furthermore, a weak intensity of N^+ , NO, O, and O^+ was also observed in the air plasma afterglow region (see supplementary material Table S1 for further details) (43-45). These generated plasma radicals and species when interacting with dye solution results in dye degradation as shown in upcoming sections.

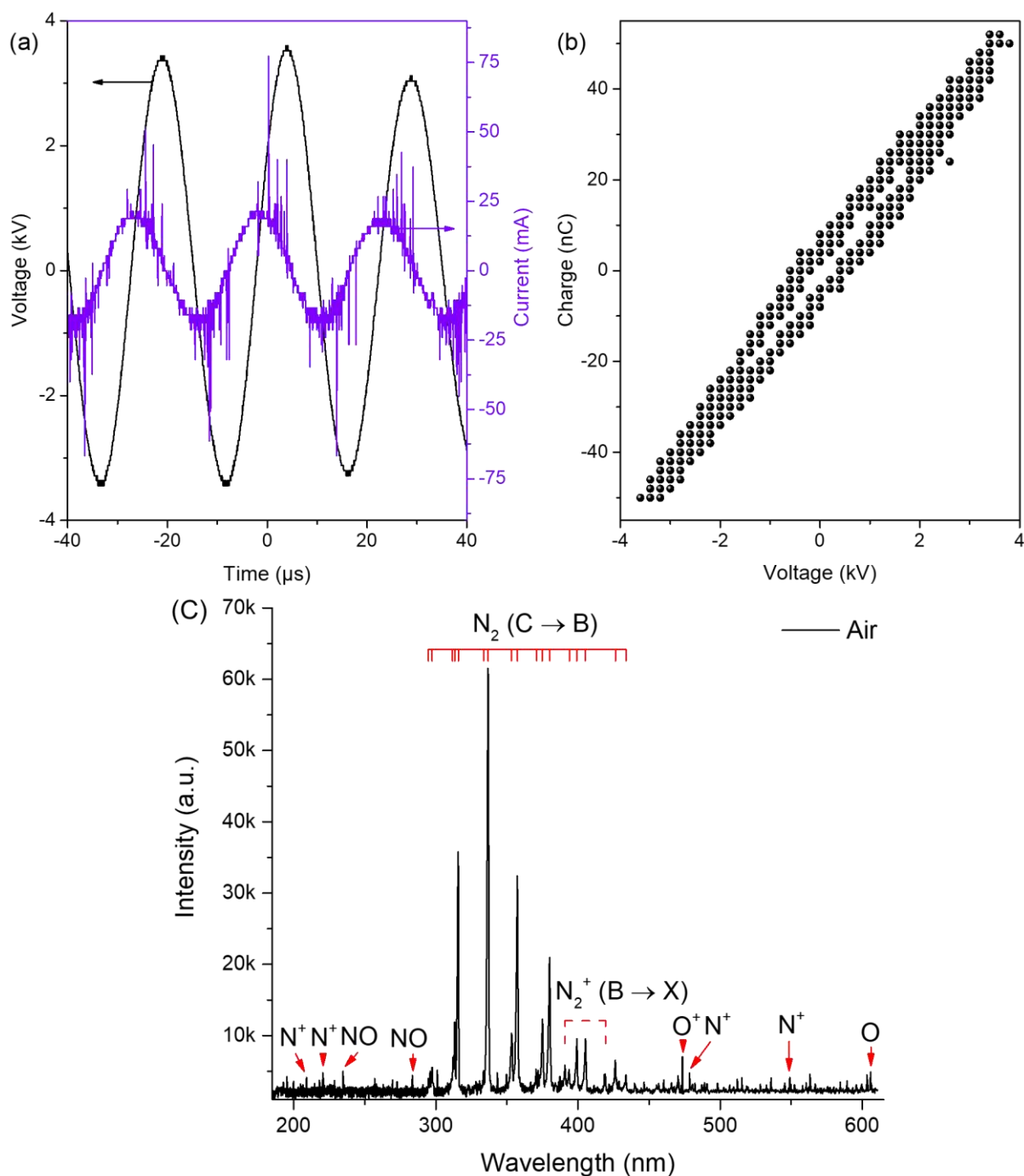


Figure 2. (a) Voltage-current waveform, (b) Charge-voltage Lissajous figure, and (c) optical emission spectra of air plasma produced in pencil plasma jet during dye degradation

Dye degradation using cold pencil plasma jet

The degradation and mineralization of different dyes solution with increasing plasma treatment time is shown in figures 3 and 4. The degradation of these dyes was occurring due to the

formation of various reactive oxygen-nitrogen species (RONS) in water as shown in figure 5. The reactive species formed in dye solution due to air plasma-dye solution, degraded the dye solution as shown in figures 3 and 4. Moreover, the formation of these RONS also physicochemical modified the water properties such as pH, ORP, TDS, and EC are shown in figure 5.

Erythrosine

The degradation and mineralization of erythrosine with increasing plasma treatment time with dye solution are shown in figures 3 (a) and 4 (a). A 45-minute plasma treatment with dye solution gave complete degradation of initial concentration of erythrosine. Moreover, erythrosine degradation followed zero order reaction with a rate constant of $1.08 \text{ mg L}^{-1} \text{ min}^{-1}$.

The mineralization of erythrosine with increasing plasma treatment time further supported the results of erythrosine degradation. In which, 92.16% removal of total organic carbon (TOC) occurs after a plasma treatment time of 45 minutes. However, the mineralization of erythrosine did not follow zeroth order kinetics. Initially, rapid mineralization of erythrosine occurs, a 5 minutes plasma treatment given 52.73% mineralization. However, after 25 minutes no significant ($p < 0.05$) decrease in TOC concentration was observed till 45 minutes. Also, the reduction in chemical oxygen demand (COD) was reduced to 68.33% after 45 minutes of plasma treatment. The degradation of erythrosine using tin oxide (TiO_2) and zinc oxide (ZnO) photocatalysts previously reported by Uddin et al. (37). In which they fitted a first-order kinetic rate model and observed the rate constant of erythrosine was 0.00385 min^{-1} when using TiO_2 and 0.00323 min^{-1} when using ZnO for the initial concentration of erythrosine was $9 \text{ }\mu\text{M}$. Therefore, air plasma degradation of erythrosine has a significant edge over conventional degradation processes.

Metanil Yellow

The degradation of metanil yellow with air plasma follows first-order kinetics as shown in figure 3 (b) with a rate constant of 0.09356 min^{-1} . Increasing plasma treatment time with metanil yellow solution showed continuous degradation in its concentration. A plasma treatment of 30 minutes with methanil yellow solution gave complete degradation. The metanil yellow degradation in solution after plasma treatment is also shown in TOC analysis (figure 4 (b)). A continuous increase in mineralization of metanil yellow solution occurs with increasing plasma treatment time. A maximum mineralization of 97.33% was achieved after 30 minutes of mineralization. However, after 15 minutes of plasma treatment, the increase in mineralization of metanil yellow solution becomes non-significant with a p-value of 0.5. The change in COD of metanil yellow after plasma treatment of 30 minutes was given as 75.89%. The degradation of metanil yellow using the electrochemical Fenton process was previously reported by Matyszczyk et al. (38) using different catalysts (Fe^{2+} , Co^{2+} , and Mn^{2+} , etc.). After 120 minutes of the electron-Fenton process, the maximum degradation efficacy of metanil yellow (initial concentration $30 \mu\text{mol L}^{-1}$) was 67.11% when using nickel (Ni^{2+}) catalyst with a rate constant of 0.07 min^{-1} . Hence, the present work showed better metanil yellow degradation efficacy compared to the conventional electrochemical Fenton process.

Sudan I

The degradation of sudan I solution using plasma treatment showed similar behavior as erythrosine solution as shown in figure 3 (c). Since, it also followed zero-order degradation reaction with a rate constant of $3.4643 \text{ mg L}^{-1} \text{ min}^{-1}$. A 15 minutes of plasma treatment time gave complete degradation of sudan I in solution. Moreover, 76.58% mineralization and 84.61% reduction in COD of sudan I in solution occurs after 15 minutes of plasma treatment. The work reported by Aarthi et al. (39) studied the degradation kinetic of sudan III and sudan IV using different catalysts. The degradation of these sudan dye groups appeared to follow both zero-order and first-order degradation kinetics.

Crystal Violet

The variation in crystal violet solution concentration when treated with the plasma of different treatment times is shown in figure 3 (d). A 11 minute plasma treatment with dye gave 99.98% degradation of initial concentration. The degradation of crystal violet dye with plasma treatment time followed first-order kinetics with a rate constant of 0.2486 min^{-1} . Moreover, 1 minute of plasma treatment gave ~90% mineralization of crystal violet solution as shown in figure 4 (d). And, the maximum mineralization and reduction of COD of crystal violet solution after 11 minutes of plasma treatment were 98.24% and 77.5%, respectively. Previously, Rahimpour et al. (12) also showed crystal violet solution followed by first-order degradation kinetics with plasma. Hence, support the finding of the present study. In addition, Rahimpour et al. (12) used Ar/O₂ as plasma forming gas for degradation study and a very low concentration (10 μM) of crystal violet solution.

Rhodamine B

The degradation and mineralization of rhodamine B, when treated with air plasma, is shown in figures 3 (e) and 4 (e). Figure 3 (e) shows the rhodamine B followed by first-order degradation kinetics with plasma treatment time. The observed rate constant for rhodamine B degradation was 0.1691 min^{-1} . A complete degradation of rhodamine B initial concentration was observed for the plasma treatment time of 15 minutes. Increasing plasma treatment time with rhodamine B showed a continuous increase in mineralization of rhodamine B as shown in figure 4 (e). Hence, supports the results of rhodamine B degradation. A 97.87% mineralization and 74.12% reduction in COD of rhodamine B occurs for a plasma treatment time of 15 minutes. Meiyazhagan et al. (16) used a microplasma reactor with different plasma-forming gases for rhodamine B dye degradation. For 10 mg L⁻¹ of rhodamine B solution, the optimum parameters for complete degradation of rhodamine B using air microplasma were given as 7.2 kV voltage,

8 minutes of treatment time, and 0.81 min^{-1} of rate constant. Hence, the substantially enhanced performance observed in their work compared to the present study. This was due to the use of a low initial concentration of rhodamine B dye and significantly higher applied voltage (or, plasma discharge power) in work reported by Meiyazhagan et al. (16).

Indigo

The complete degradation of indigo dye solution took significantly lower plasma treatment time compared to other dye solutions as shown in figure 3. A 3-minute plasma treatment with indigo dye solution gave complete degradation of initial concentration as shown in figure 3 (f). The indigo dye degradation due to dye solution-plasma treatment followed first-order rate kinetics with a rate constant of 0.8126 min^{-1} . Moreover, the continuous increasing mineralization of indigo solution with plasma treatment also proved degradation of indigo dye as shown in figure 4 (f). A 3-minute plasma treatment with indigo dye gave 97.17% of mineralization and a 69.8% reduction in COD. In the past, Crema et al. (1) showed the degradation of indigo carmine using O_2 and N_2 as plasma-forming gas in a plasma reactor. They used an initial concentration of 20 mg L^{-1} of indigo carmine and fitted first-order rate kinetics to obtain degradation results. They reported the evaluated rate constant for N_2 and O_2 gas plasma reactor were 0.02 min^{-1} and 0.3 min^{-1} , respectively. Therefore, the performance of PPJ using air as plasma forming gas was significantly higher compared to the previously reported plasma reactor.

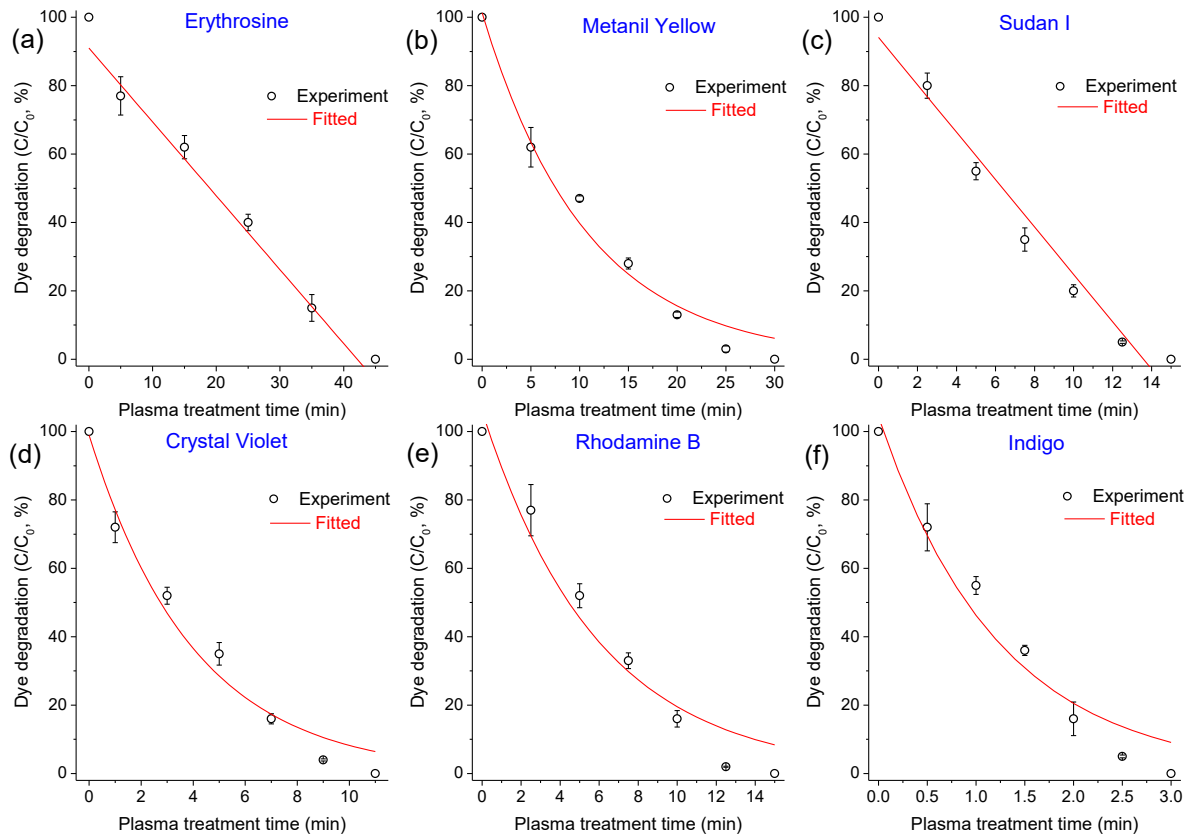


Figure 3. The effect of plasma treatment time on degradation of dye solution. (a) Erythrosine, (b) Metanil yellow, (c) Sudan – I, (d) Crystal violet, (e) Rhodamine B, (f) Indigo. The statistically significant ($p < 0.05$) difference among different plasma treatment time percentage dye degradation $\mu \pm \sigma$ is shown by a different lowercase letter

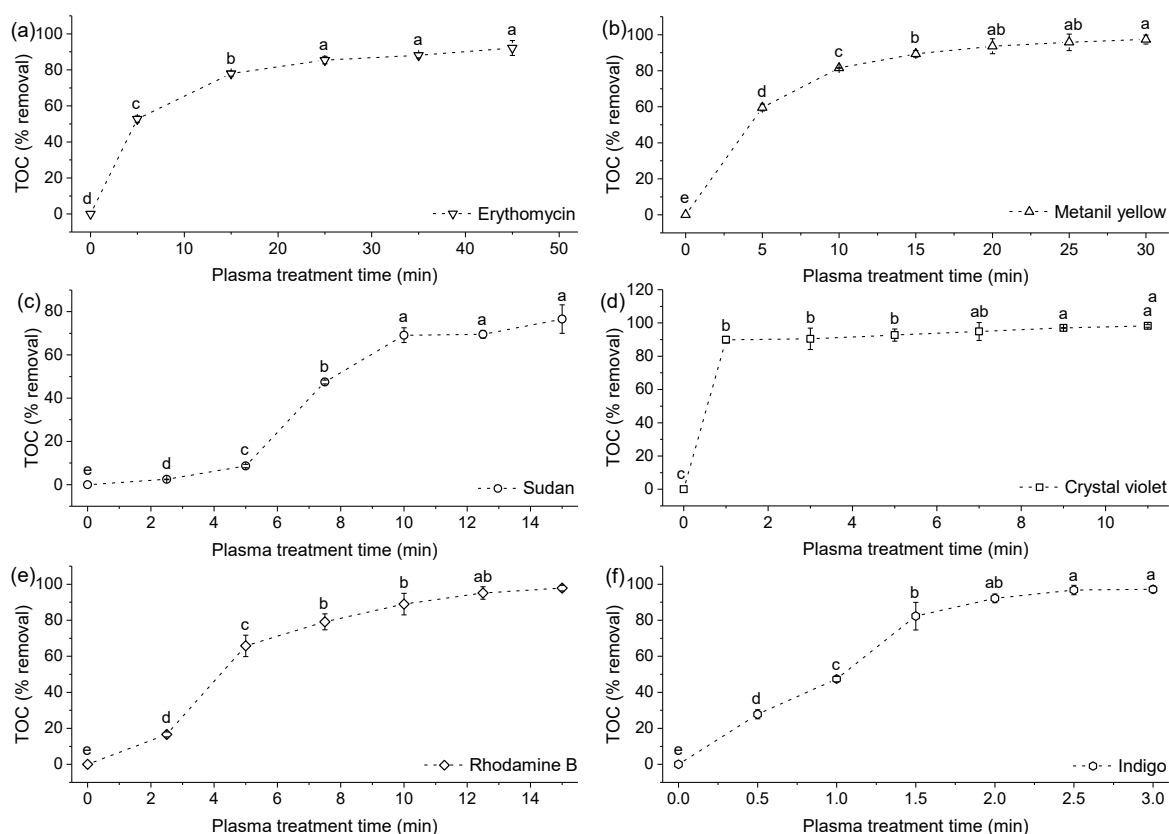


Figure 4. Mineralization (total organic carbon (TOC)) of dye solutions with increasing plasma treatment time. (a) Erythrosine, (b) Metanil yellow, (c) Sudan – I, (d) Crystal violet, (e) Rhodamine B, (f) Indigo. The statistically significant ($p < 0.05$) difference among different plasma treatment time TOC $\mu \pm \sigma$ is shown by a different lowercase letter

Physicochemical properties and reactive oxygen-nitrogen species concentration

The above degradation of dyes solution with plasma solution occurs due to the formation of various reactive species in dye solution (35, 41, 42, 46). These species were responsible for the degradation and mineralization of the above-mentioned dyes. Therefore, figure 5 showed the measurement of these reactive-oxygen nitrogen species (RONS) concentrations in ultrapure water as the initial solution. The enhancement of physicochemical properties and increasing RONS concentration of ultrapure water with increasing plasma treatment time is shown in figure 5. A continuous significant ($p < 0.05$) decrease was observed in the pH of PAW with increasing plasma treatment time. For a plasma-water treatment time of 50 minutes, the

observed pH of PAW was 1.8. Simultaneously, the continuous ($p < 0.05$) increase in oxidation reduction-potential (ORP), total dissolved solids (TDS), electrical conductivity (EC), etc. occurred with increasing plasma-treatment time with water. The maximum value of ORP, TDS, and EC were occurring at 50 minutes of plasma-water treatment time and these values were given as 653 mV, 4500 ppm, and 11.3 mS cm^{-1} , respectively.

The above-observed changes in physicochemical properties of water occur due to the formation of RONS in water due to plasma treatment (35, 47, 48). The RONS concentration variation of water with plasma treatment time is shown in figure 5 (e-h). The NO_3^- and NO_2^- ions concentration in PAW increases continuously with increasing plasma-water treatment time as shown in figure 5 (e, f). However, the H_2O_2 and dissolved O_3 concentrations initially rise and then fall continuously. The maximum concentration of NO_3^- ions, NO_2^- ions, H_2O_2 , and dissolved O_3 in water after plasma treatment were given as 635 mg L^{-1} , 11.5 mg L^{-1} , 6.5 mg L^{-1} , and 21 mg L^{-1} , etc.

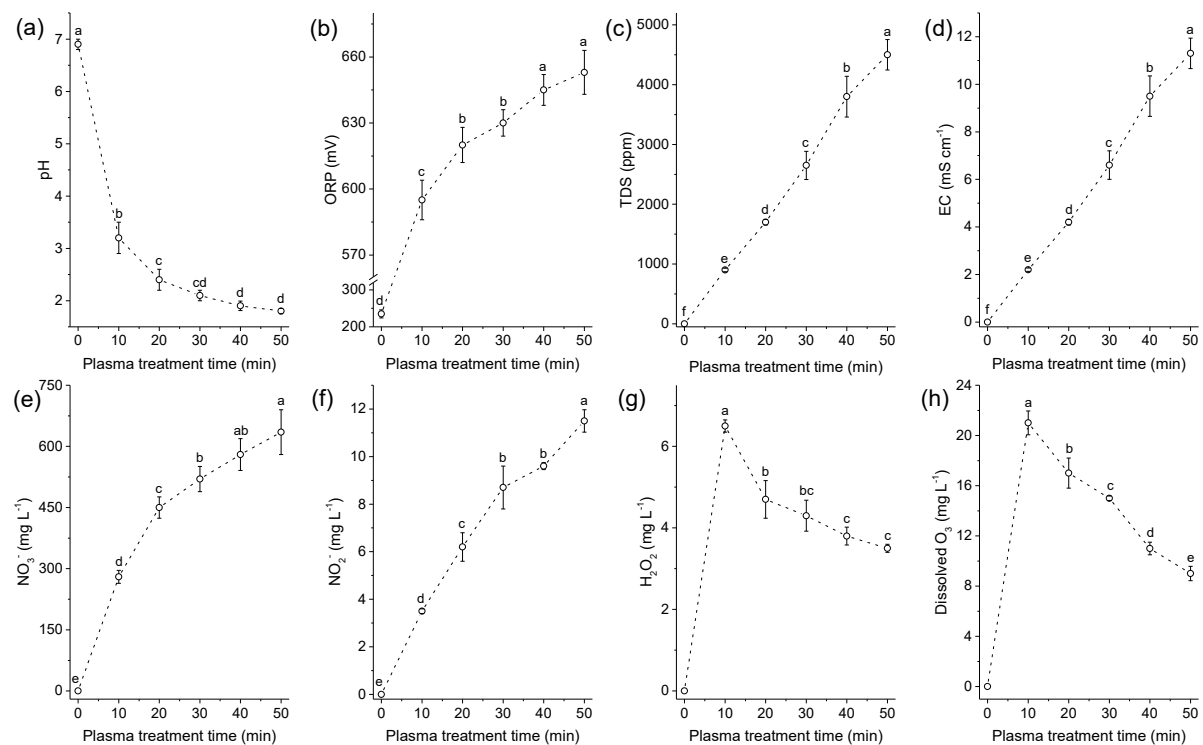


Figure 5. Change in physicochemical properties ((a) pH, (b) oxidation-reduction potential (ORP), (c) total dissolved solids (TDS), (d) electrical conductivity (EC)) and measurement of reactive oxygen-nitrogen species ((e) NO_3^- ions, (f) NO_2^- ions, (g) H_2O_2 , (h) dissolved O_3) in water due of plasma-water treatment. The statistically significant difference ($p < 0.05$) among different plasma treatment time PAW properties $\mu \pm \sigma$ is shown as different lowercase letter

Toxicity of plasma-treated dye solutions

The toxicity of virgin dye solution (control) and plasma-treated dye solution toward freshwater green algae *Chlorella Sorokiniana* (*C. Sorokiniana*) and *Chlorella Pyrenoidosa* (*C. Pyrenoidosa*) is shown in figure 6. The growth of both the algal species were monitored for 15 days. For toxicity study, plasma-treated dye solutions with maximum dye degradations (Erythrosine – 45 minutes, Metanil yellow – 30 minutes, Sudan I – 15 minutes, Crystal violet – 11 minutes, Rhodamine B – 15 minutes, Indigo – 3 minutes) were chosen, and shown in figure 6.

The growth of *C. Sorokiniana* when exposed to plasma-treated crystal violet solution, indigo solution, and sudan I solution was slightly higher (not statistically significant, $p < 0.05$) than a virgin solution of these dyes (control) after 15 days of incubation. Moreover, the growth of *C. Sorokiniana* was significantly high in plasma treated erythrosine solution, metanil yellow, and rhodamine B solution compared to control at similar incubation conditions. However, in the case of *C. Pyrenoidosa*, the observed growth of *C. Pyrenoidosa* in plasma treated crystal violet solution, indigo solution, erythrosine solution, metanil yellow, and rhodamine B solution significantly ($p < 0.05$) higher compared to control under the end of the incubation period of 15 days. Nevertheless, the growth of *C. Pyrenoidosa* in the sudan I solution was slightly higher ($p < 0.05$) compared to the control (virgin sudan I) solution. The toxicity of microplasma bubble degraded mixed dye solution containing alizarin yellow, orange II, and methylene blue towards

human cell lines was studied by Zhou et al. (6). They showed a reduction in toxicity of dye solution towards human cell lines after plasma treatment of dye solution. Hence, plasma treatment can be used to degrade the dyes present in wastewater as well as the degraded solution is non-toxic.

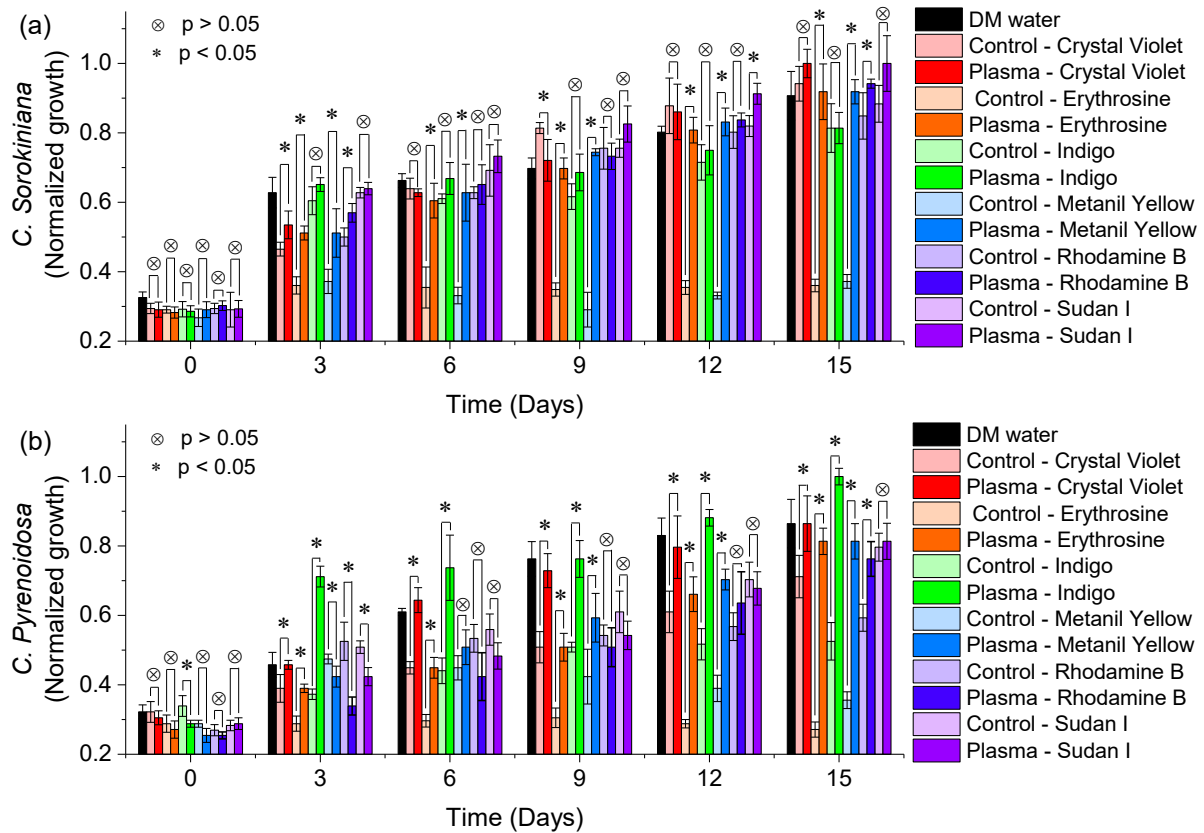


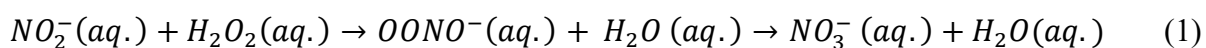
Figure 6. Toxicity of plasma degraded dye solution towards freshwater algae (*Chlorella Sorokiniana* and *Chlorella Pyrenoidosa*). The statistically significant ($p < 0.05$) difference among columns $\mu \pm \sigma$ is shown by different symbols

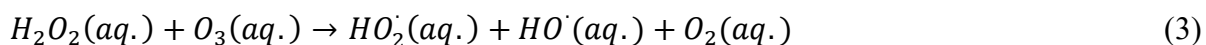
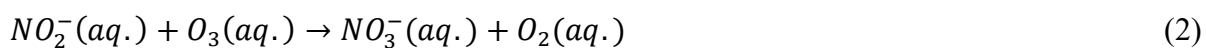
Discussion

The above results sections showed the characterization of air plasma using voltage-current characterization. The energy and power consumed during dye degradation were calculated using the charge voltage Lissajous figure. The species present in the air plasma afterglow region were identified using optical emission spectroscopy. The degradation and

mineralization of dyes (erythrosine, metanil yellow) due to plasma-dye solution interaction were analyzed using UV-visible spectroscopy and total organic carbon. The toxicity of degraded dyes solution was analyzed by exposing degraded dyes solution to freshwater green algae *Chlorella* species (*Chlorella Sorokiniana* and *Chlorella Pyrenoidosa*).

The above degradation of dyes occurs due to the interaction of highly oxidizing intermediate radicals/species such as free electrons, hydroxyl radical ($\text{HO}\cdot$), nitric oxide radical ($\text{NO}\cdot$), atomic oxygen (O), etc. and stable species like aqueous ozone (dissolved O_3) and hydrogen peroxide (H_2O_2) during plasma-dye solution interaction (3, 5, 16-18, 49, 50). Since, these species are significantly high oxidizing potential such as $\text{HO}\cdot$, dissolved O_3 , and H_2O_2 had standard oxidizing potential (E^0) of 2.85 V, 2.07 V, and 1.77 V, respectively (1, 7, 11). Moreover, the reaction of H_2O_2 with NO_2^- ions also give strong oxidizing specie ONOO^- (equation (1)) that have a standard oxidizing potential (E^0) of 2.44 V (1, 11). The presence of these oxidizing species in solution also increased the oxidizing tendency of solution/water (6, 11, 16). Therefore, we observed a significant increase in the oxidizing tendency of water with increasing plasma treatment time as shown in figure 5 (b). The reactions involved in the formation of these species in water are shown in supplementary material Table S2. Also, with these oxidizing species, nitrogen-containing species also formed in solution/water due to the interaction of post-discharge generated NO_x dissolution in solution/water. As a result, the formation of NO_2^- ions and NO_3^- ions occurred in solution/water in the form of nitrous and nitric acid. Hence, the pH of solution/water decreased after plasma treatment (1, 11). This decrease in pH with increasing plasma treatment time with water is also observed in the present study as shown in figure 5 (a). Moreover, the dissolution of these inorganic ions increased the total dissolved solid as well as the electrical conductivity of water as shown in figure 5 (c, d).





Increasing plasma treatment time with water increased the concentration of reactive nitrogen species (RNS, NO_2^- ions, NO_3^- ions). However, the reactive oxygen species (ROS, dissolved O_3 , H_2O_2) initially increase with time and then continuously decrease with time. This was due to the dissociation of dissolved O_3 and H_2O_2 occurring in high reactive water by following equations (1-3) (1, 6, 35, 42, 43). Hence, the decrease in these species' concentration is observed with treatment time. Moreover, the reaction between these species substantially increased the oxidizing tendency of solution/water such as $HO_2^\cdot$, $HO^\cdot$, and $OONO^-$, etc. helped in the degradation of dyes with complex structures (1-3, 5-8, 11, 16-18, 50).

The degradation and mineralization of different types of dye solutions used in the present investigation after plasma treatment proved the significance of oxidizing species in wastewater treatment. Also, the degraded solution after plasma treatment did not show toxicity toward freshwater algal species. The generation of oxidizing species only occurs due to plasma-solution interaction. Therefore, plasma-solution treatment technology has the potential to replace conventionally used chemicals, catalysts, and biological agents used for dyes degradation. Also, the plasma-treated solution is well known for its antimicrobial properties. Along with this, the nitrogen-rich species (NO_2^- ions and NO_3^- ions) produced during plasma-solution interaction can be used as a nitrogen source for plant growth. Hence, plasma degradation of dyes solution moving on the path of green chemistry and leading towards sustainable development.

Conclusion

The presented work reveals the dyes degradation efficacy of pencil plasma jet on six different types of dyes solution (Erythrosine, Metanil yellow, Sudan – I, Crystal violet, Rhodamine B, and Indigo). The complete degradation of all the dyes is observed in the present study. Moreover, more than 76% mineralization is observed in sudan I dye and more than 90% mineralization is observed in the remaining dyes after plasma treatment. The formation of various oxidizing species in dye solution during plasma dye solution interaction is responsible for dye degradation and mineralization. The change in physicochemical properties and reactive species concentration measurement in water confirm the formation of dye oxidizing reactive species. At last, the degraded dye solution toxicity is checked using freshwater green algal species that confirm the degraded solution is non-toxic. In conclusion, the plasma treatment of industrial (dyes production industries, textile, food industries, paint industries, etc.) wastewater technology has the potential to replace conventional wastewater management techniques. Since, it is an eco-friendly and economic alternative to conventionally used toxic oxidizing chemicals and expensive catalysts, etc. used for wastewater management.

Acknowledgments

This work was supported by the Department of Atomic Energy (Government of India) graduate fellowship scheme (DGFS).

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Conflict of interests

The authors declare that there are no conflicts of interests.

Authors' contributions

All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Vikas Rathore, Akanksha Pandey, Shruti Patel. The first draft of the manuscript was written by Vikas Rathore, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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