

# Removal efficiency of Rhodamine B dye by atmospheric plasma

# Josefina Vergara Sánchez<sup>a</sup>, César Torres Segundo<sup>a,\*</sup>, Esteban Montiel Palacios<sup>a</sup>, Aarón Gómez Díaz<sup>b</sup>, Pedro Guillermo Reyes Romero<sup>b</sup>, Horacio Martínez Valencia<sup>c</sup>

*a Laboratorio de Análisis y Sustentabilidad Ambiental, Escuela de Estudios Superiores de Xalostoc, Universidad Autónoma del Estado de Morelos, Xalostoc, Ayala, Morelos, C.P. 62715, México, emails: cesar.torres@uaem.mx (C.T. Segundo), vergara@uaem.mx (J.V. Sánchez), esteban.montiel@uaem.mx (E.M. Palacios)*

*b Laboratorio de Física Avanzada, Facultad de Ciencias, Universidad Autónoma del Estado de México, Instituto Literario No. 100 Col. Centro, Toluca, Estado de México, C.P. 50000, México, emails: agomezd@uaemex.mx (A.G. Díaz), pgrr@uaemex.mx (P.G. Reyes Romero)*

*c Laboratorio de Espectroscopia, Instituto de Ciencias Físicas, Universidad Nacional Autónoma de México, A.P. 48-3, Cuernavaca, Morelos, C.P. 62251, México, email: hm@icf.unam.mx (H.M. Valencia)*

Received 29 November 2021; Accepted 16 March 2022

## **ABSTRACT**

The inefficient treatment of industrial water with organic contaminants is a worldwide problem. The study of treatment alternatives for this water continues to be of great interest. A study of degradation and mineralization process were carried out of the Rhodamine B (RhB) dye in water, applying an atmospheric plasma; the RhB is a pollutant identify in the effluents of the textile industry. Aqueous solutions of the RhB dye were treated at an initial concentration of 1.0 mM, in a volume of  $250$  mL, using iron filing (Fe<sup>2+</sup>) as a catalyst. The absorption spectra in the UV/Vis range, total organic carbon and chemical oxygen demand were monitoring. In addition, the physicochemical properties such as pH, electrical conductivity, emission of  $CO<sub>2</sub>$  and temperature were measured, and concentrations of nitrates and nitrites were determined. The results show a process efficiency greater than 90% in 45 minutes of exposure to plasma. The approximate electrical cost of 1  $m<sup>3</sup>$  of aqueous solution of the RhB dye treated with plasma would be of a few dollars.

*Keywords:* Plasma; Textile dye; Total organic carbon; Chemical oxygen demand; Optical emission spectroscopy

# **1. Introduction**

Currently, synthetic dyes are widely used in various manufacturing industries, such as textile, paper, cosmetics, leather, and printing. The wide variety of colors that originate in them allows various products to be more attractive to the market, in addition to improving their design and function. However, due to the presence of toxic aromatic rings in them, wastewater from these industries without effective treatment contains synthetic dyes from industrial processes and has become a serious human health and environmental problem locally and in general worldwide [1].

Rhodamine B (RhB) dye, belonging to the xanthene class, is used in industry as a colorant in textiles and food, without effective treatment, it can cause skin irritation, eye and respiratory tract infection, toxicity chronic and neurological in both humans and animals [2]. Furthermore, due to its carcinogenicity, the European Union and China have banned its use, making it of utmost importance to efficiently manage wastewater containing RhB [3]. Therefore, its elimination from effluents is a priority and has been carried out using different methods (physical, chemical and biological). Conventional biological treatments are not efficient (or are not an option) in the degradation of

<sup>\*</sup> Corresponding author.

<sup>1944-3994/1944-3986 © 2022</sup> Desalination Publications. All rights reserved.

dyes that have a large number of aromatic rings in their chemical structure [4].

Advanced oxidation processes (AOP's) produce hydroxyl radicals (•OH) in the treatment system; however, its efficiency is limited depending on several factors, such as: the type of hydroxyl radical precursor, the catalyst used, the turbidity of the solution, the complexity of the system and the limitations of mass transfer of the reactants. For these reasons, having a highly efficient oxidation technology remains a difficult problem to solve [5].

The study of real samples of water contaminated with dye from the textile industry, for example, is very interesting; However, its study turns out to be very complex and it is for this reason that the analysis of model samples treated by means of the interaction with a plasma at atmospheric pressure turns out to be novel and important because there is no complete knowledge of the formation of intermediate products, which should be controlled to avoid the production of unwanted elements. To have a more complete understanding of the problem, it is important that in the study of the models not only the relevant chemistry is considered, but also the dynamic effects of the fluids and the physical characteristics of the plasma used.

In general, this work aims to examine the degradation process of the RhB dye with the application of a plasma produced under atmospheric pressure. Corona-type plasma is generated by applying an electric potential difference on the liquid–air interface, inside the batch-type reactor that is used to treat water samples with textile dye [6]. This study combined the physical treatment (atmospheric plasma) with the chemical effects generated by using a catalyst ( $Fe<sup>2+</sup>$ ), which provides a similarity to the well-known Fenton process. During the treatment, the following physical and chemical parameters were measured in real time: potential difference, electrical current, solution temperature, volume, pH, electrical conductivity, absorbance, concentration of nitrates and nitrites, the behavior of total organic carbon (TOC) and chemical oxygen demand (COD) and the optical emission spectrum of plasma. In addition to this, the dye concentration, the discoloration factor, the mineralization percentage,  $G_{50}$  and the electrical cost were determined. This experiment was performed in the Environmental Analysis and Sustainability Laboratory of the Autonomous University of the State of Morelos.

# **2. Methodology**

#### *2.1. Experimental system*

Fig. 1 shows the diagram of the plasma reactor used for the study of the degradation of the RhB dye, the reactor is manufactured in acrylic, and the solution container is made of Pyrex glass with a volumetric capacity of 400 mL. Plasma is generated by applying an electric potential difference of 2,000 V between two tungsten electrodes, the electrodes have a diameter of 3.0 mm and are aligned to the center of the reactor, the cathode is submerged in the solution 1.0 cm and the anode was placed on the surface of the solution 3.0 mm apart. Plasma is produced between the anode and the surface of the water, using air particles from the atmosphere to generate the ionized gas. The container was fitted with an optical fiber, which allowed it to connect to a spectrometer (StellarNet EPP2000, wavelength range of 200–1,100 nm) to obtain the optical emission spectroscopy (OES) in real time. The plasma was generated on the surface of the solution with a DC power supply (HP Mod. 6525A, 4.0 kV–50 mA) at a constant power of 80 W. The plasma treatment time was between 15 and 60 min.

The sample to be treated comprised 1.0 mM of RhB and 1.0 mM of Fe<sup> $2+$ </sup>. The initial volume of the sample was 250 mL. A Hach HQ40d potentiometer (United States) was used to perform the pH and electrical conductivity measurements, and a Hach DR3900 Spectrophotometer (United States) was used to measure the absorbance in the range of 320−800 nm. COD and TOC were determined using Hach's low-ranking reagents (HACH). The mineralization was monitoring as a function of treatment time with the plasma. Iron filings  $(Fe<sup>2+</sup> salt, Analytical grade)$  are used as catalyst. These particles are removed from the solution, after treatment, by filtration and subsequently the measurements of color, COD and TOC are made. Sampling was performed every 15 min. Nitrates and nitrites were determined using HACH Nitrate TNT835 Vial Test and HACH Nitrite TNT839 Vial Test.

## *2.2. Preparation of the RhB solution*

The RhB dye (analytical reagent grade) has a molecular weight of 479.02 g/mol, CAS number of 81-88-9, color index of 45170, and chemical formula of  $C_{28}H_{31}N_2O_3Cl$  (Table 1).

The RhB dye was weighed on an analytical balance and dissolved in distilled water in a beaker. The solution was placed in a volumetric flask. Iron filings  $(Fe^{2+})$  were added, and the volume was adjusted to 250 mL. The initial solution contained 1.0 mM of RhB and 1.0 mM of iron filings. A Hach HQ40d multi-parameter meter was used to measure the pH, electrical conductivity, and temperature. The initial temperature was 25°C, the initial pH was 7.42, and initial electrical conductivity was 86 µS/cm. A Hach DR3900 spectrophotometer was used to measure the initial absorbance of the RhB dye solution. Specifically, 1.0 mL of the dye solution was obtained, diluted with 2.0 mL of distilled



Fig. 1. Atmospheric plasma reactor.

Structure	Characteristic	Reference
$H_3C_$ CH3	Color index name	Basic Violet 10
CI-	Chemical formula	$C_{28}H_{31}N_{2}O_{3}Cl$
$H_3C_$ $\mathcal{L}$ CH <sub>3</sub>	Chemical class	Xanthene
	Color index number	45170
COOH	$\lambda_{\max}$ (nm)	554
	Molecular weight (g/mol)	479.02
	CAS number	81-88-9

Table 1 Chemical information of the Direct Orange 39 azo dye [7,8]

water, and placed in a quartz cell. The sample was measured using a spectrophotometer. In this case, the characteristic absorbance peak was at 554 nm. To employ spectrophotometry as an analytical technique using the Beer–Lambert law, the dye calibration curve was obtained. This allowed the adjustment equation that related absorbance and solution concentration to be obtained. The analysis was performed every 15 min for 60 min. All solutions were made from analytical-grade chemicals, and the experiment was performed five times under the same initial conditions.

## *2.3. Analysis methods*

# *2.3.1. Removal efficiency of RhB*

The removal efficiency of Rhodamine B can be calculated by Eq. (1):

$$
\eta = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}
$$

where  $\eta$  (%) is RhB removal efficiency,  $C_0$  (mM) is the initial concentration of RhB, and  $C_t$  (mM) is the concentration of RhB after of plasma treatment [9]. Removal efficiency determines the performance of the plasma treatment, in terms of the relationship of the initial concentration of the dye and the concentration at different study times.

## *2.3.2. Percentage of mineralization*

The mineralization of RhB in the aqueous solution during the atmospheric plasma treatment was monitored by determining the TOC by the Hach Method using low-range vials. The TOC concentration includes the carbon content of the organic dye and other organic intermediate compounds, which were generated during the plasma treatment. A UV-Vis spectrophotometer (Hach, DR3900) was used to determine the TOC. The percentage of mineralization was calculated using the following equation [10]:

% of mineralization = 
$$
\frac{\text{TOC}_{0} - \text{TOC}_{F}}{\text{TOC}_{0}} \times 100\%
$$
 (2)

The percentage of mineralization determines the amount of the organic compound that is converted into  $CO<sub>2</sub>$  and water, in terms of the ratio of the initial TOC value and the TOC value at different study times.

# 2.3.3. Energy efficiency  $(G_{50})$

The energy efficiency of the degradation process was calculated in terms of the  $G_{50}$  constant. This constant expresses the amount of energy required to eliminate 50% of the contaminant. Its equation is as follows [11]:

$$
G_{50} = 1.8 \times 10^6 \frac{C_0 V_0 M}{P t_{50}}
$$
\n(3)

where  $C_0$  denotes the initial molar concentration of the pollutant at  $t = 0$ ,  $V_0$  is the initial volume of the solution treated in liters, *M* is the molecular weight of the pollutant, *P* is the electrical power in *W*, and  $t_{50}$  is the time in seconds required to eliminate 50% of the contaminant. The  $G_{50}$  factor is expressed in g/kWh.

## *2.4. Plasma characterization*

# *2.4.1. Optical emission spectroscopy*

Optical emission spectroscopy was analyzed when the atmospheric plasma was generated on the surface of the solution. This analysis was conducted using an optical fiber, which passed through the sample container and was located in front of the place where the luminescence was produced. This configuration allowed the direct measurement of the entire luminescence in real time using a StellarNet EPP2000 spectrometer. The spectrometer was operated in the wavelength range of 200–1,100 nm with an integration time of 1,000 ms and five samples were averaged to collect the spectra. The emission spectra were qualitatively analyzed to assign chemical species to the peaks. To describe the atmospheric plasma used for the treatment, the electron temperature and electron density can be calculated using the intensities of several spectral lines, assuming that the population of the emitting levels follows the Boltzmann distribution [12] and considering that the system has a local thermodynamic equilibrium in some small fraction of this. The following expression was used to calculate the electron temperature:

$$
T_e = \frac{E_m(2) - E_m(1)}{k} \left[ \ln \left( \frac{I_1 \lambda_1 g_m(2) A_m(2)}{I_2 \lambda_2 g_m(1) A_m(1)} \right) \right]^{-1} \tag{4}
$$

where  $E_m(i)$  denotes the energy of the upper levels of the lines, *k* is the Boltzmann constant,  $g_m(i)$  represents the statistical weights of the upper levels, and  $A_m(i)$  represents their corresponding transition probabilities. These values were obtained from the NIST Atomic Spectra Database Lines [13].  $I_1$  and  $I_2$  denote the relative line intensities in questions, and  $\lambda_1$  and  $\lambda_2$  denote the wavelengths of the lines, which were experimentally measured. Using the value of  $T_{e}$ , the value of the electron density of the plasma used during the treatment could also be obtained. Electrons are responsible for most processes in the corona discharge (i.e., ionization, dissociation, and recombination processes) with water molecules. In this study, the following Saha–Boltzmann equation was used to calculate the electron density:

$$
n_e = 6 \times 10^{21} \left( T_e \right)^{\frac{3}{2}} \left( \exp \left[ -\frac{E_i}{kT_e} \right] \right) \tag{5}
$$

where  $T_e$  denotes the electron temperature,  $E_i$  is the ionization energy of the species, and *k* is the Boltzmann constant [14–16].

## **3. Results**

Fig. 2 shows the absorption spectrum which was obtained during the treatment of the RhB dye with the plasma. When the wavelength of 554 nm (maximum absorption peak of the RhB dye) is used as a reference, it is observed that the absorbance decreases as the treatment time elapses. The discoloration of the solution serves as a primary measure to evaluate the degradation efficiency of the chemical compounds used as dyes. In Fig. 2, it is possible to observe the discoloration of the water by the effect of the plasma treatment as a function of the exposure time for the solution of the RhB. This discoloration process is due to the interaction of the free radicals generated by the plasma, which are highly oxidizing, being able to break the chromophore bonds of the dye.

In Fig. 3 to observe the value of removal efficiency, this value was calculate using the Eq. (1); in 15 min was 47.98%,

> 0 min 15 min 30 min 45 min 60 min **350 400 450 500 550 600 650 700 750 800 0 1 2 3 4 5 6 7 8 Absorbance (arb. units)** λ **(nm)**  $(A)$  8  $\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 &$

after in 30 min was 79.46%, later in 45 min was 96.09% and finally in 60 min an efficiency percentage of 99.81% was obtained. The increase in the magnitude of this parameter is effect of the interaction of OH• radicals with the dye (R2, R3 and R5).

Fig. 4 shows how the pH and electrical conductivity (EC) values varied during the interaction of the Rhodamine B dye with the non-thermal plasma.

When the plasma interacts with the solution, chemical variables of the solution, such as pH and EC, are affected, because of the system is supplied with high energy electrons, causing ionization, dissociation, and recombination processes with water molecules, generating OH<sup>·</sup> and H<sup>·</sup> radicals, as described in reaction R1 [17,18]:

H<sub>2</sub>O + e<sup>-</sup> → OH<sup>•</sup> + H<sup>•</sup> + e<sup>-</sup> rate constant  
\n
$$
k = 2.3 \times 10^{-12} - 1.8 \times 10^{-10} \frac{\text{cm}^3}{\text{s}} (T_e = 1 - 2 \text{ eV})
$$
\n(R1)



Fig. 3. Removal efficiency of RhB vs. treatment plasma time.



Fig. 2. (A) Absorbance vs. treatment time and image of discoloration of water with RhB obtained during treatment with plasma. (B) Photographs of discoloration process.

The recombination of OH<sup>•</sup> radicals in the solution produces hydrogen peroxide, reaction R2 [19].

$$
\text{OH}^{\bullet} + \text{OH}^{\bullet} \to \text{H}_2\text{O}_2 \text{ rate constant } k = 4 \times 10^{-9} \frac{\text{cm}^3}{\text{s}} \tag{R2}
$$

In this study iron filings were used as a catalyst, then for organic oxidation, the  $Fe^{2+}$  can directly involve in the catalytic formation of hydrogen peroxide into hydroxyl radicals in R3 [17].

$$
H_2O_2 + Fe^{2+} \rightarrow OH^* + OH^- + Fe^{3+}
$$
 (R3)

On the other hand,  $Fe^{3+}$  is transformed into  $Fe^{2+}$  consuming the hydrogen peroxide generating for the plasma.

$$
H_2O_2 + Fe^{3+} \rightarrow H^+ + Fe^{2+} + HO_2^{\bullet}
$$
 (R4)

The initial magnitudes of pH and electrical conductivity were 7.42 and 86 µS/cm, respectively. After 60 min of treatment, the pH and electrical conductivity values were, in the order mentioned, 3.70 and 417 µS/cm.

When plasma is generated on the water surface, electrons interact with the water molecules in the solution and dissociate them, leading to a series of reactions that favor the production of  $H_2O_2$ . Subsequently, these hydrogen peroxide molecules break down generating hydroxyl radicals (OH•) in the solution.

Regarding TOC and COD behaviors, Fig. 5 shows that both parameters decrease as a function of treatment time. The initial values of these parameters are 336 and 48 for TOC and COD, respectively, decreasing by 48% in the first 15 min in both parameters, having final values in 60 min of 0.64 and 0.09 for TOC and COD, respectively. These behaviors were expected in this process because the mineralization of the pollutant was achieved. Fig. 6 shows the



Fig. 4. Behavior of pH and electrical conductivity during the treatment of RhB dye with non-thermal plasma.

behavior of the percentage of mineralization calculated with Eq. (2).

Considering this type of reactions in the treatment by plasma (R1–R4), the generation of the hydroxyl radical can mineralize the initial organic compound and its by-products, as described by the reaction (5) [17].

$$
Intermediates + OH^{\bullet} \rightarrow CO_{2} + H_{2}O
$$
 (6)

The intermediate compounds, in turn, react with other  $HO<sup>+</sup>$  radicals until they transform into  $CO<sub>2</sub>$ .

The measurement of  $CO<sub>2</sub>$  is important in this type of treatment, because, this serves to verify that the organic pollutant is being mineralized by the plasma applied; using the air quality sensor MQ135 (the sensor was calibrated according to its user manual), based on the Arduino hardware platform, along with open source software resources;



Fig. 5. Behaviors of COD and TOC vs. time.



Fig. 6. Percentage of mineralization of RhB by plasma vs. time.

the concentration of carbon dioxide was measured during the plasma degradation process, obtaining in (min, ppm) (5, 83), (10, 95), (15, 104), (20, 109), (25, 106), (30, 102), (35, 95), (40, 87), (45, 79), (50, 74), (55, 68) and in (60, 63); Also, in the first 30 minutes the highest concentration (in this time 79% of the pollutant is eliminated) and then gradually decreases that value to 63 ppm in 60 min, because the concentration of the dye in the solution decreases. The values obtained for  $CO<sub>2</sub>$  are like those reported in literature in previous works related to water treatment [20].

Fig. 7 shows the behavior of the emission of  $CO<sub>2</sub>$  as a function of the time of treatment by corona discharge plasma of the solution with RhB dye and iron filings. In addition, the measurement of this gas, when the dye was only heated (the solution was heated with a laboratory hot plate heater), is presented, obtaining as a result that the solution does not emit  $CO_{2'}$  since plasma is necessary to transform the contaminants into  $CO<sub>2</sub>$ . Also shows the temperature of the solution when interacting with the plasma, reaching



Fig. 7. Graph of the  $CO_2$  emission in the degradation process of RhB vs. treatment time.

Table 2 Comparison of  $G_{50}$  values for Rhodamine B dye degradation with different AOPs



a value of 87.4°C in 60 min, without this affecting the degradation process. The magnitude of the  $CO<sub>2</sub>$  emission is directly related to TOC, because its magnitude will decrease whereas the carbon has been eliminated by the plasma in the form of carbon dioxide. The total organic carbon was obtained to determine if the contaminant was effectively removed from the solution. Fig. 5 shows the values of TOC and COD as a function of the time of interaction with the plasma, with the catalyst and without the catalyst, observing that the presence of the catalyst in the solution favors the decomposition process of the organic compound.

The temperature increased when plasma was applied to the solution surface. The average rates of change for the intervals of 0–15, 15–30, 30–45, and 45–60 min was 2.8°C, 0.69°C, 0.42°C, and 0.11°C, respectively. The maximum temperature of 87.4°C was measured in 60 min; however, this did not affect the degradation process.

In this study, the values of the variables are:  $C_0 = 0.001$  M,  $V_0 = 0.25$  L,  $M = 479.02$  g/mol,  $P = 80$  W and  $\dot{t}_{50} = 948$  s. By substituting the data in the Eq. (3), it is calculated that  $G<sub>50</sub>$  for this process is equal to 2.84 g/kWh, which is similar to those reported in the literature (Table 2).

Table 2 shows the  $G_{50}$  values obtained for different AOPs using the Rhodamine  $\tilde{B}$  dye, it is possible to observe that in this work acceptable results were obtained compared with the different AOPs.

Secondly, with an increase in the treatment time, other RS were generated in the solution (ROS and RNS), and some organic acids (for example HNO<sub>3</sub>) were produced and contributed to a decrease in pH and an increase in conductivity (Fig. 4). Specifically,  $NO_2^-$  and  $NO_3^-$  (which are presented in Fig. 8) were formed in plasma-treated water through the dissolution of nitrogen oxides formed in the plasma *via* the gas-phase reactions of dissociated  $N_2$  and  $O_2$ or  $H_2O$ ; this behavior was also observed by Torres et al. [22] and Zhou et al. [23] in 2016.

Fig. 8 verify that nitrates were formed in water with a constant growth rate in the first 45 min, and their concentration was almost constant during the rest of the treatment; the initial value before starting the treatment was zero, which

indicated that the presence of these compounds was directly related to the plasma treatment.

Fig. 9 shows the OES spectrum of corona discharge, similar that Direct Orange 39 in [22]. The spectrum was normalized for nitrogen because the atmosphere used included air, and, in the air, the most abundant gas was nitrogen. The intensity of the OH emission bands was found to be higher in 309.5 nm that nitrogen in 337.0 nm, maybe because of the greater amount of oxygen in the solution due to the presence of the dye, which aid the generation of OH.

In this type of system, the generation of active species such as  $H_{\alpha'}$ ,  $H_{\beta'}$ , N<sub>2</sub>, OH, and Na through OES (Fig. 9) was observed  $(Tab\le 3)$  [13,22]. Furthermore, the characteristic doublet of sodium in the spectra with pollutants (D-lines), commonly present in water, was also noticed.

The generation of atmospheric plasma on the surface of water supplies the electrons in the solution. These electrons can interact with the water molecules and dissociate them.



Fig. 8. Nitrate and nitrite concentration in the solution during the plasma treatment.



Fig. 9. OES of corona discharge used for RhB mineralization.

This will produce a chain of reactions that aid the production of  $H_2O_{2'}$  which will, in turn, aid the production of  $\text{ }^{\bullet}$ OH radical in the mixture.

In some studies, it is mentioned that hydrogen atoms, hydroxyl radicals and hydrogen peroxide (which are the main oxidative species in the system) are generated at the plasma-liquid interface due to the interaction of the corona discharge with the water surface. The main chemical reactions observed are [18] (R1, R2, R7 and R8):

$$
*H + O2 → *HO2 k = 10-10 \frac{cm3}{s}
$$
 (7)

$$
{}^{*}HO_{2} + {}^{*}HO_{2} \rightarrow H_{2}O_{2} + O_{2} \quad k = 2 \times 10^{-6} \frac{\text{cm}^{3}}{s}
$$
 (8)

These reactions describe the identification in the emission spectrum of the plasma of the •OH band, which is the main radical that aids the decomposition of organic matter in the solution. Another possible process arising from the presence of nitrogen in generating the plasma in the air is described in reaction (9), where •OH radical can also be generated through the dissociative excitation process of  $H<sub>2</sub>O$  (gas) by excited nitrogen atoms [24]:

$$
N_2^* + H_2O_{(gas)} \to N_2 + OH_{(gas)}^* + H
$$
\n(9)

To characterize the corona discharge used in the treatment, the temperature and electron density were obtained. To determine the temperature of the applied plasma, in the process of degradation of the dye in water, the values of *H*<sup>α</sup> and  $H_{\beta}$  were considered and inserted into Eq. (4), obtaining a value of 2.4 eV. Considering the value obtained from the electron temperature and hydrogen ionization energy, using Eq. (5), the value obtained from the electron density of the plasma was  $5.69 \times 10^{12}$  particles/cm<sup>3</sup>.

Another important parameter that must be taken into account is the economic cost of the treatment. In this work, only the cost attributed to electricity consumption is considered relevant because of the other costs, such as those related to electrode wear, are minimal and, therefore, can be neglected. The electrical cost can be calculated according to Eq. (10) [25]:

Table 3

Principal species identified in the treatment's optical emission spectrum of the corona discharge

Species	$\lambda$ (nm)	Transition	Energy (eV)
OН	284.0	$A^{2}\Sigma^{+} - X^{2}\Pi$	3,064 Å system
	309.5		
N,	337.0	$C^3\Pi_u - B^2\Pi_u$	Second positive system
	357.5		
	375.5		
	380.5		
$H_{\rm B}$	487.0	$2 - 4$	2.5497
Na	590.0	$2p^{6}3s - 2p^{6}3p$	2.1023
$H_{\alpha}$	656.5	$2 - 3$	1.8887
O*	777	$3p^5P \rightarrow 3s^5S$	1.8427

$$
Electric \cos t = \frac{a \cdot I \cdot t_{\text{treatment}}}{V} \tag{10}
$$

where *U* is the voltage with which the plasma is generated (V), *I* is the intensity of the electric current (A),  $t_{\text{treat}}$ .  $m_{\text{cent}}$  is the treatment time (h), *V* is the volume of the sample (m3 ) and the electricity cost is expressed in USD/kWh (0.04 USD/kWh in Mexico). In this study, the values of the variables are:  $U = 1.0$  kV,  $I = 80$  mA, *t*-treatment = 60 min and  $V = 250$  mL. Therefore, the cost of treating 1 m<sup>3</sup> of solution with RhB dye for 60 min amounted to 3.20 USD (80 kWh/m<sup>3</sup> ) like reported in Torres et al. [22] whose value was  $1.28$  USD  $(32 \text{ kWh/m}^3)$  in 60 min. This cost is lower than that incurred in other treatments such as Fenton and photo-Fenton, in which expensive chemical reagents are used.

#### *3.1. Limitations and recommendation for future work*

One of the greatest limitations of this type of treatment system (batch) is the proportional increase in electrical energy and treatment time depending on the volume of solution treated. However, this type of study serves to provide basic knowledge that allows mitigating this type of limitation. It is recommended to modify the treatment system instead of being static that allows the treatment of contaminated water at constant flow, since it has been experimentally proven by this research group that this allows the treatment of larger volumes of solution in similar times. The use of heterogeneous catalysts allows them to be removed after treatment, for this reason the use of catalysts of this type is recommended.

# **4. Conclusions**

A 99% mineralization percentage of the Rhodamine B textile dye was achieved, in a time of 60 min, using plasma and iron filing  $(Fe^{2+})$  as a catalyst. The final TOC and COD values were  $0.06$  mg C/L and  $0.02$  mg O<sub>2</sub>/L, respectively. Temperature and the emission of  $CO_2$  as a function of the time of treatment by corona discharge plasma of the solution with RhB dye were measured, the maximum value of  $CO_2$  was obtained in 20 min (109 arb. units) and the maximum temperature was 87.4°C, which indicates that the increase in temperature is not the reason why  $CO<sub>2</sub>$  production increases, but rather by plasma treatment. Nitrates and nitrites were determined, in 60 min the values were 208 and 10 mg/L, respectively. The energy yield value  $(G_{50})$  was 1.99 g/kWh. These results indicate that the use of iron filings as a catalyst accelerates the degradation process and facilitates the mineralization of the colorant. From the optical spectrum of plasma emission, different species were identified (e.g., OH, N<sub>2</sub>, Na, H<sub>α</sub>, and H<sub>β</sub>). The OES revealed that the presence of the catalyst increased the •OH production, which favored the dye degradation and reduces the necessary treatment time. The cost of treating  $1 \text{ m}^3$  of an aqueous solution of RhB dye, with an energy consumption of 80 kWh/ $m<sup>3</sup>$ , was estimated at few dollars.

# **Acknowledgments**

The authors would like to thank H. Huertos (EESX) for the experimental support. This research was supported by DGAPA IN105519, PRODEP DSA/103.5/15/6986, PROMEP 103.5/13/6626, PRODEP CA-5511-6/18-8304, PII-43/ PIDE/2013, CONACyT 268644, and UAEM 4307/2017/CI.

# **References**

- [1] G. Panomsuwan, T. Morishita, J. Kang, R. Rujiravanit, T. Ueno, N. Saito, Degradation of synthetic dye in water by solution plasma process, J. Korean Soc. Mar. Eng., 40 (2016) 888–893.
- [2] S. Meiyazhagan, S. Yugeswaran, P.V. Ananthapadmanabhan, P.R. Sreedevi, K. Suresh, Relative potential of different plasma forming gases in degradation of Rhodamine B dye by microplasma treatment and evaluation of reuse prospectus for treated water as liquid fertilizer, Plasma Chem. Plasma Process., 40 (2020) 1267–1290.
- [3] Y. Chen, Y. Li, X. Zhang, A. Zhu, Y. Huang, Z. Liu, K. Yan, Degradation of aqueous Rhodamine B with gaseous streamer corona plasma, IEEE Trans. Plasma Sci., 43 (2015) 828–835.
- [4] M. Magureanu, D. Piroi, N. Bogdan Mandache, V. Parvulescu, Decomposition of methylene blue in water using a dielectric barrier discharge: optimization of the operating parameters, J. Appl. Phys., 104 (2008) 103306, 1–7, doi: 10.1063/1.3021452.
- [5] M.I. Stefan, Advanced Oxidation Processes for Water Treatment: Fundamentals and Applications, IWA Publishing, United Kingdom, 2018, pp. 635–637.
- [6] C. Torres-Segundo, J. Vergara-Sánchez, P.G. Reyes-Romero, A. Gómez-Diaz, M.J. Rodríguez-Albarrán, H. Martinez-Valencia, Effect on discoloration by non-thermal plasma in dissolved textile dyes: Acid black 194, Rev. Mex. Ing. Quim., 18 (2019) 939–947.
- [7] R. Sabarish, G. Unnikrishnan, Novel biopolymer templated hierarchical silicalite-1 as an adsorbent for the removal of Rhodamine B, J. Mol. Liq., 272 (2018) 919–929.
- J. Gu, C. Luo, W. Zhou, Z. Tong, H. Zhang, P. Zhang, X. Ren, Degradation of Rhodamine B in aqueous solution by laser cavitation, Ultrason. Sonochem., 68 (2020) 105181, 1–12, doi: 10.1016/j.ultsonch.2020.105181.
- J. Fan, H. Wu, R. Liu, L. Meng, Z. Fang, F. Liu, Y. Xu, Nonthermal plasma combined with zeolites to remove ammonia nitrogen from wastewater, J. Hazard. Mater., 401 (2021) 123627, 1–8, doi: 10.1016/j.jhazmat.2020.123627.
- [10] P. Manoj Kumar Reddy, B. Ramaraju, Ch. Subrahmanyam, Degradation of malachite green by dielectric barrier discharge plasma, Water Sci. Technol., 67 (2013) 1097–1104.
- [11] M.A. Malik, Water purification by plasmas: which reactors are most energy efficient?, Plasma Chem. Plasma Process., 30 (2010) 21–31.
- [12] G.G. Raju, Collision cross sections in gaseous electronics part I: what do they mean?, IEEE Electr. Insul. Mag., 22 (2006) 5–23.
- [13] NIST. Available at: https://www.nist.gov/
- [14] V.K. Unnikrishnan, K. Alti, V.B. Kartha, C. Santhosh, G.P. Gupta, B.M. Suri, Measurements of plasma temperature and electron density in laser-induced copper plasma by time-resolved spectroscopy of neutral atom and ion emissions, Pramana-J.  $\vec{P}$ hys., 74 (2010) 983–993.
- [15] H.R. Griem, Principles of Plasma Spectroscopy, Cambridge University Press, United Kingdom, 1997.
- [16] J. Feng, Z. Wang, Z. Li, W. Ni, Study to reduce laser-induced breakdown spectroscopy measurement uncertainty using plasma characteristic parameters, Spectrochim. Acta, Part B, 65 (2010) 549–556.
- [17] B. Jiang, J. Zheng, S. Qiu, M. Wu, Q. Zhang, Z. Yan, Q. Xue, Review on electrical discharge plasma technology for wastewater remediation, Chem. Eng. J., 236 (2014) 348–368.
- [18] H. Ghodbane, O. Hamdaoui, J. Vandamme, J.V. Durme, P. Vanraes, C. Leys, A.Y. Nikiforov, Degradation of AB25 dye in liquid medium by atmospheric pressure non-thermal plasma

and plasma combination with photocatalyst  $\text{TiO}_2$ , Open Chem., 13 (2015) 325–331.

- [19] Ch. Sarangapani, N.N. Misra, V. Milosavljevic, P. Bourke, F. O´Regan, P.J. Cullen, Pesticide degradation in water using atmospheric air cold plasma, J. Water Process Eng., 9 (2016) 225–232.
- [20] P. Manoj Kumar Reddy, Ch. Subrahmanyam, Green approach for wastewater treatment—degradation and mineralization of aqueous organic pollutants by discharge plasma, Ind. Eng. Chem. Res., 51 (2012) 11097−11103.
- [21] A.T. Sugiarto, S. Ito, T. Ohshima, M. Sato, J.D. Skalny, Oxidative decoloration of dyes by pulsed discharge plasma in water, J. Electrostat., 58 (2003) 135–145.
- [22] C. Torres-Segundoa, J. Vergara Sánchez, E. Montiel Palacios, A. Gómez Díaz, P.G. Reyes Romero, H. Martínez Valencia, Discoloration and mineralization of Direct Orange 39

textile dye in water by atmospheric plasma and ferrous ion, Desal. Water Treat., 226 (2021) 362–371.

- [23] R. Zhou, R. Zhou, X. Zhang, J. Zhuang, S. Yang, K. Bazaka, K. (Ken) Ostrikov, Effects of atmospheric-pressure  $N_{2}$ , He, air, and  $O_2$  microplasmas on Mung bean seed germination and seedling growth, Sci. Rep., 6 (2016) 32603, 1–11, doi: 10.1038/ srep32603.
- [24] M.C. García, M. Mora, D. Esquivel, J.E. Foster, A. Rodero, C. Jiménez-Sanchidrián, F.J. Romero-Salguero, Microwave atmospheric pressure plasma jets for wastewater treatment: degradation of methylene blue as a model dye, Chemosphere, 180 (2017) 239−246.
- [25] D. Ghosh, C.R. Medhi, H. Solanki, M.K. Purkait, Decolorization of crystal violet solution by electrocoagulation, J. Environ. Prot. Sci., 2 (2008) 25–35.