



## Elimination of AB210 dye in residual textile water by glow-discharge plasma application

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Received 7 August 2018; Accepted 2 January 2019

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### ABSTRACT

Owing to the global population growth and economic development in several developing countries, the availability of clean drinking water is a problem that has been growing in parallel with the continual increase in water consumption. Atmospheric nonthermal plasma discharge is inexpensive and safe in comparison of other toxic chemical methods of wastewater treatment. Here, the results of treating wastewater containing the Acid Black 210 (AB210) dye, at a concentration of 0.5 mM, are presented. In this process, Fe<sup>2+</sup> filings are used as a catalyst. The treatment was carried out by means of plasma generated at atmospheric pressure on the surface of water. The effectiveness of the degradation of AB210 was quantified at different treatment times, 0–180 min, obtaining a 99.9% removal rate of the dye. The experiments were performed at an initial volume of 250 mL, and the electrical conductivity, pH, chemical oxygen demand (COD), and total organic carbon (TOC) were determined. The changes in the spectral range (200–1,100 nm) of the plasma during wastewater treatment were studied.

*Keywords:* Plasma; Wastewater; Azo textile dye; TOC

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### 1. Introduction

Dyes thrown into rivers and lakes hinder the process of photosynthesis, consume oxygen, and are toxic and carcinogenic. Moreover, they can be absorbed by microorganisms and react with biologically important molecules [1]. Industrial wastewater discharges into natural effluents lead to serious consequences in aquatic ecosystems, for example, reduction of sunlight needed in photosynthesis and degradation of dissolved oxygen [2]. Of the total water used by the industrial sector worldwide, 25% is used by the textile

industry [3]. Wastewater from the textile and tanning industries represents a serious environmental and technological problem owing to the large quantities of nonbio-degradable organic chemicals present in it, including dyes that are mainly used in the textile industry. Thousands of tons of these dyes contaminate large volumes of waste that is discharged into water bodies without a proper treatment. These contaminants hinder photosynthesis within aquatic systems because they consume oxygen and cause the eutrophication of water bodies, as well as the generation of anaerobiosis processes in which greenhouse gases are produced [4]. Dyes are stable

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and toxic compounds, which complicates their degradation in wastewater treatment plants that operate on the basis of physical operations and conventional chemical and biological processes.

The concentrations of dyes in wastewater are usually lower than that of any other chemical compound, but because of their high molar extinction coefficients (indicating how strong a substance absorbs light at a wavelength, per unit molar concentration), even extremely low concentrations (0.01 mM) produce waste streams with strong coloration.

The dye AB210 or Acid Black 210 (C<sub>34</sub>H<sub>25</sub>N<sub>11</sub>O<sub>11</sub>S<sub>3</sub>), which has a molecular weight of 938.02 g/mol (IUPAC: 4-amino-6-((4-((4-((2,4-diaminophenyl)azo)phenyl)amino) sulphonyl)phenyl)azo)-5-hydroxy-3-[(4-nitrophenyl)azo] naphthalene-2,7-disulphonic acid) is used in many industries that produce paints, ceramics, plastics, leather, and inks, among others. It is also widely used in the textile industry, in fiber dyeing (its chemical structure is shown in Fig. 1.) [5,6]. AB210 presents high resistance to washing; therefore, it cannot be removed by conventional methods, hence making the use of advanced oxidation processes (AOPs) necessary.

This dye was obtained from the textile and tanning industries, where it is used in dyeing leather and wool. It has an azo-type chemical bond (–N=N–) in its molecule; this chromophore group is responsible for the absorption of light, giving the molecule a color. The molecular structure of this dye is shown in Fig. 1. In this study, the degradation of this dye AB210 was performed using plasma generated at atmospheric pressure.

The aim of this study was to evaluate the effect of the interaction of plasma water with AB210 and the catalyst in an aqueous solution at an initial concentration of 0.5 and 1.0 mM, respectively, by atmospheric plasma produced at the liquid–air interface. In this investigation, Fe<sup>2+</sup> filings were used as a catalyst for the reaction. The reaction kinetics was determined using ultraviolet–visible (UV–Vis) spectrophotometry, total organic carbon (TOC), and chemical oxygen demand (COD). The optical emission spectrum, in the range 200–1,100 nm, of the plasma during the water treatment was studied. In addition, we determined the catalyst concentration with the greatest efficiency in the reactor for this dye, as well as the optimum applied voltage. The results, hence, provide information on the subsequent application of this process to wastewater treatment on an industrial scale.

## 2. Experimental setup

A batch reactor (Fig. 2), which was designed and built in collaboration between the Advanced Physics Laboratory (FC-UAEMex) and the Environmental Analysis and Sustainability Laboratory (EESuX-UAEM), was used to produce plasma on the surface of the liquid sample; this system has been described in previous studies [3,7].

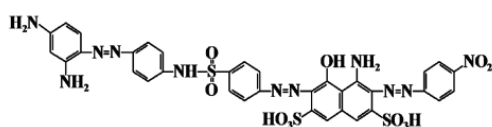


Fig. 1. Molecular structure of AB210 [6].

The plasma was generated with a DC voltage source (HP Mod. 6525 A, 4.0 kV, 50 mA), at a constant power of 80 W. Samples with the AB210 dye, at a concentration of 0.5 mM, were treated by plasma. At the beginning of each treatment, we performed measurements using calibrated electrodes of pH, electrical conductivity, and temperature, using an HQ40d potentiometer. UV–Vis spectra were recorded in the 300–800 nm range using an HACH DR6000 spectrophotometer. The COD was determined using vials of 0–150 mg/L range in order to obtain the amount of oxygen required to oxidize organic matter. The TOC was determined with a midrange vial (15–150 mg/L). The COD and TOC were determined by the HACH methods.

The experiment was conducted at the Environmental Analysis and Sustainability Laboratory of the Universidad Autónoma del Estado de Morelos. The analyses were carried out at different treatment times (0, 15, 30, 45, 60, 75, 90, 105, 120, 135, 150, 165, and 180 min). The initial values of the distilled water used in the experiments were pH = 6.4, conductivity = 31.7 μS/cm, and temperature = 25.0°C. Subsequently, when the Fe<sup>2+</sup> filings (1.0 mM) were added, the values of these parameters became pH = 8.27, electrical conductivity = 90.7 μS/cm, and temperature = 25.0°C. In addition, the measured absorbance at a wavelength of 607 nm was 4.74. The optical emission spectrum in the range 200–1,100 nm was obtained using a StellarNet EPP2000 spectrometer.

### 2.1. Preparation of Acid Black 210

The AB210 solution was prepared at a concentration of 0.5 mM (0.1174 g) to create a volume of 250 mL. This solution was placed in a volumetric flask, and 1.0 mM Fe<sup>2+</sup> was added as a catalyst. The initial absorbance of the solution was measured using an HACH DR6000 spectrophotometer. In order to do this, 1.0 mL of the solution was taken and diluted with 2.0 mL of distilled water. A quartz cell was placed with the dye solution in a spectrophotometer. For this dye, the characteristic peak absorbance was at 320, 455, and 604 nm. In order to identify whether the use of a greater or a lesser amount of catalyst affects the degradation

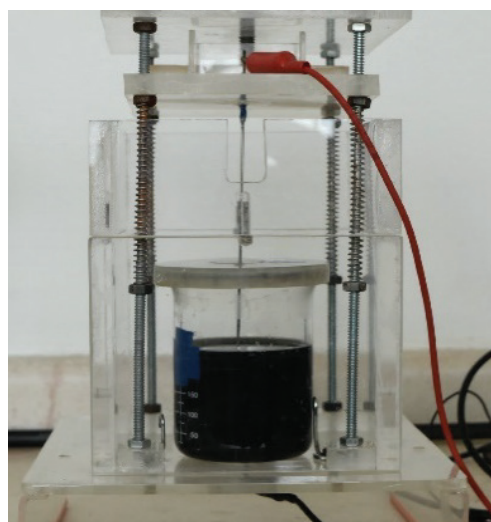


Fig. 2. Plasma treatment reactor at atmospheric pressure.

process, different percentages of iron filings were used (50%, 80%, 100%, 120%, and 150%), considering 100% as 1.0 mM. The mixture was a heterogeneous solution of the dye with water and the catalyst.

2.2. Calculation of the energy yield ( $G_{50}$ )

The plasma generated in the reactor is a corona discharge, so the relative energy efficiency ( $G_{50}$ ) was determined. The yield value was calculated in terms of  $G_{50}$ ; this yield value expresses the amount of pollutants converted in the function of the energy supplied and required for 50% conversion of the pollutant:

$$G_{50} = 1.8 \times 10^6 \frac{C_0 V_0 M}{P t_{50}} \tag{1}$$

where  $C_0$  is the molar concentration of the pollutant at  $t = 0$ ,  $V_0$  is the volume of the treated solution in liters,  $M$  is the molecular weight of the pollutant,  $P$  is the electrical power of the reactor in watts, and  $t_{50}$  is the time in seconds required for 50% conversion.  $G_{50}$  is expressed in grams/kilowatt-hour (g/kWh) [8].

3. Results

The corona plasma at atmospheric pressure is an AOP in which different oxidizing species, such as radicals (H, O, and OH) and some molecules ( $H_2O_2$ ,  $O_3$ , etc.), are produced and combined with different physical and chemical effects, such as pyrolysis, UV photolysis, and electro hydraulic cavitation. Therefore, the correct monitoring of the physical and chemical parameters involved in the process of mineralization of organic pollutants by plasma is of great interest, owing to its multiple industrial applications.

The absorption spectrum of AB210 in the visible range (300–800 nm) is shown in Fig. 3. Three characteristic peaks were identified at 320, 455, and 604 nm, which are due to the triple azo bond ( $-N=N-$ ) of the contaminant. It is possible

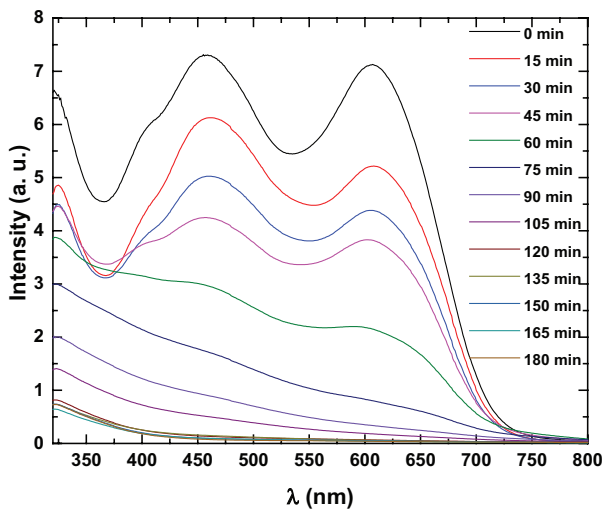


Fig. 3. Absorption spectrum of the AB210 dye.

to observe that the intensity of the characteristic peaks of absorption of the dye diminishes as a function of the time of treatment with plasma. Fig. 4 shows the calibration curve of AB210, where the red line indicates the mathematical adjustment to a straight line, whose adjustment equation is as follows:

$$y = 0.07143 + 8.23729x \tag{2}$$

This equation relates the value of absorbance with the concentration of the dye in the solution as follows:

$$\text{Dye concentration} = \frac{\text{Absorbance} - 0.07143}{8.23729} \tag{3}$$

Knowing the concentration of the dye at a certain time, it is possible to obtain the percentage of removal of the contaminant in the following way:

$$\% \text{ Degradation} = \left[ \frac{\text{Initial dye concentration} - \text{Dye concentration}}{\text{Initial dye concentration}} \right] \times 100\% \tag{4}$$

The distilled water used to prepare the solution has an initial pH of 6.4. By adding the dye, the pH increases to 8.27 owing to the effect of the dye. Here, no adjustment of the pH was performed, in order to prove the effectiveness of the dye, without adding any agent other than the plasma and the iron filings. It was observed that the plasma treatment reduced the pH level of the water in a time-dependent manner. Fig. 5 shows the behavior of pH and electrical conductivity as a function of treatment time. Plasma promotes an increase in the  $H^+$  concentration, owing to the process of dissociation of water molecules, resulting in a decrease in pH from 8.27 to 3.2 and an increase in the electrical conductivity from 90.7 to 221.9  $\mu\text{S}/\text{cm}$ . In other words, the pH decreases by 61.3% and the electrical conductivity increases by 59.1%.

Considering that the magnitude of absorbance indicates the amount of light absorbed by the solution and the amount of the dye in the solution, treatment by plasma diminishes the

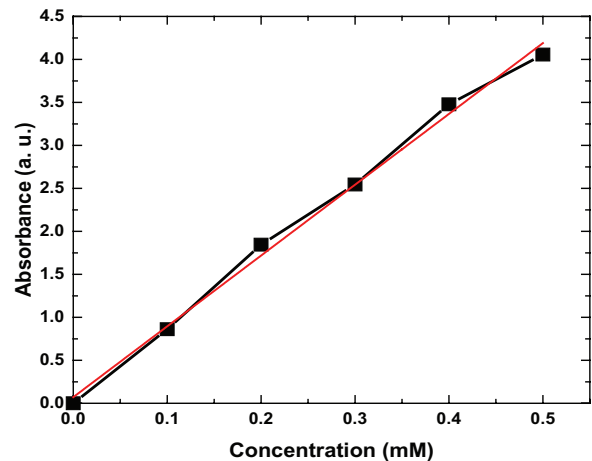


Fig. 4. Calibration curve of AB210.

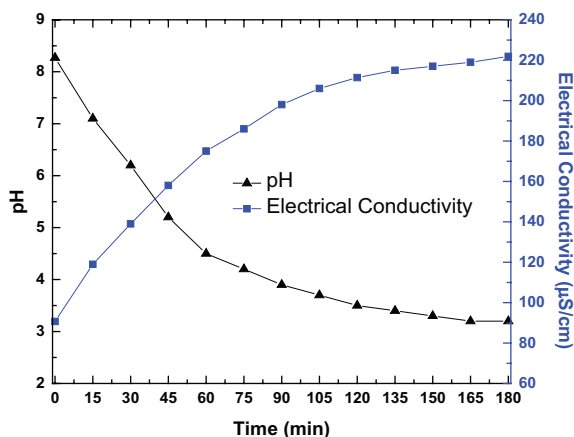


Fig. 5. Behavior of pH and electrical conductivity as a function of treatment time.

coloration of the solution and consequently the absorbance decreases, increasing the percentage of degradation. From Eqs. (3) to (4), the percentage of degradation of the dye as a function of the time of exposure with the plasma is observed in Fig. 6. At 180 min, it reached a value of 99.85%, indicating that the treatment is efficient in eliminating AB210. In addition, it was observed that, at 75 min of treatment, the percentage of removal was greater than 90%, which suggests its use at this particular time and its possible union with other AOPs to decompose the remaining 10%.

Monitoring of the TOC and COD in the solution is important because they provide information on the amount of organic matter in the solution, whose decrease indicates the successful removal of the dye. Fig. 7 shows the behavior of the COD and TOC with respect to the treatment time, with initial values of 678.85 and 786.85 mg/L, respectively. Furthermore, the error associated with the HACH method used to obtain the values of COD and TOC was 4% and 3%, respectively.

Both parameters were obtained during the 180 min treatment, at every 15 min of plasma treatment. After exposure to plasma, the dye was oxidized, decreasing its COD to 8.29 mg/L, and the TOC decreased to a value of 6.61 mg/L, that is, 98.7% and 99.15%. This allowed us to infer that the presence of plasma in the treatment contributes to the mineralization of the organic matter, converting it into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

Complete mineralization via the process of oxidation of the contaminants in water is generally expensive because of the intermediate products formed during the treatment. Because these tend to be increasingly resistant to complete chemical degradation and, in addition, they all consume energy (in this case, electrical power to produce the plasma) and chemical reagents (oxidizing catalysts), so the removal of contaminants is slower depending on the treatment time.

Using Eq. (1), for the AB210 dye in our reactor treated by plasma, the initial concentration was  $C_0 = 0.0005 \text{ M}$ , with an initial volume of  $V_0 = 0.25 \text{ L}$ ,  $M = 938.02 \text{ g/mol}$ , electrical power  $P = 80 \text{ W}$ , and  $t_{50} = 1,366 \text{ s}$ . Substituting those values into Eq. (1), the calculated value of  $G_{50}$  for this process becomes  $1.93 \text{ g/kWh}$ . This value is similar to those reported in the literature, indicating that the process is efficient and inexpensive compared with other AOPs (Table 1).

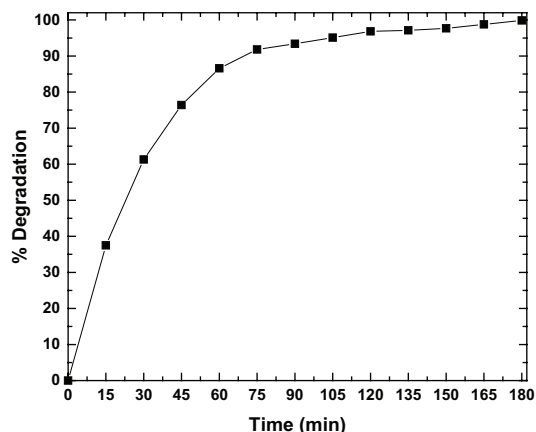


Fig. 6. Graph of the percentage of degradation vs. treatment time.

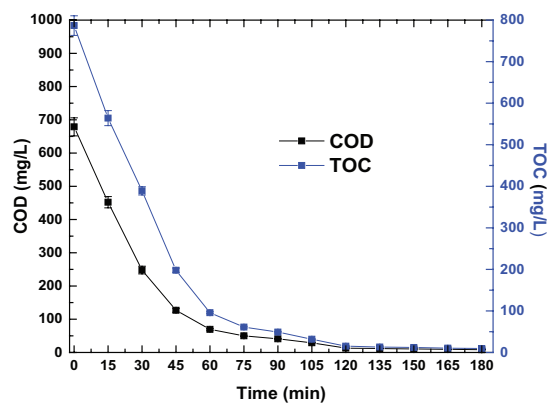


Fig. 7. Graph of COD and TOC vs. treatment time.

It can be seen in Table 1 that the  $G_{50}$  values are lower for other AOPs, the use of this process being feasible. Considering the amount of energy needed to eliminate 50% of the contaminant, which is obtained at 22.8 min, it is possible to use another method of lower cost to eliminate the residual dye.

In Fig. 8, it is possible to observe that the use of a greater or a lesser amount of catalyst affects the degradation process with plasma, in the same treatment time interval. The degradation of the dye was monitored at different concentrations of the catalyst (0.5, 0.8, 1.0, 1.2, and 1.5 mM) for 180 min, showing that, at 0.8 and 1.0 mM, the value of degradation is highly similar, with the ability to use only 0.8 mM of the catalyst for the next analyses. In addition, the use of a greater amount of iron is not favorable in this treatment either, because the final absorbance value decreases for 1.2 mM (99.32%) and for 1.5 mM (98.3%).

In order to be able to use this process on a large scale, it is necessary to reduce the applied energy, without diminishing the effective degradation of contaminants in the water. Therefore, we also studied the variation of the magnitude of the energy supplied to achieve the mineralization of the dye. Hence, we found that although the percentage decreases, it is possible to use only 1.0 kV to achieve a removal rate greater than 90%. In addition, the results show that applying more energy to the process is not more efficient; these results are shown in Fig. 9.



Table 1  
Comparison of the energy efficiency ( $G_{50}$ ) of this study with other similar studies and other advanced oxidation processes

Used dye	AOP's	Energy consumption g/kWh	Reference
Methylene Blue	Pulsed corona discharge	1.30	[9]
RhB	UV/H <sub>2</sub> O <sub>2</sub>	0.10	[10]
RhB	Ultrasound	0.20	[10]
RhB	Photocatalysis	0.20	[10]
RhB	Hydrodynamic cavitation	0.01	[10]
RhB	Electrical discharge plasma	0.078	[10]
AB210	Sonochemical	1.57	[11]
AB210	Glow-discharge plasma	1.93	Present work

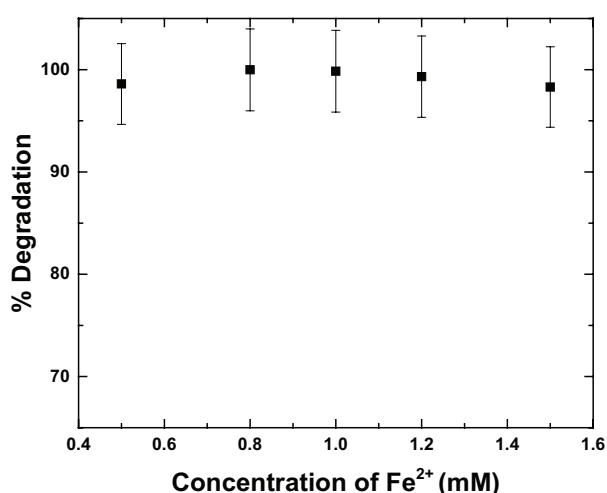


Fig. 8. Graph of % degradation vs. % concentration of Fe<sup>2+</sup>.

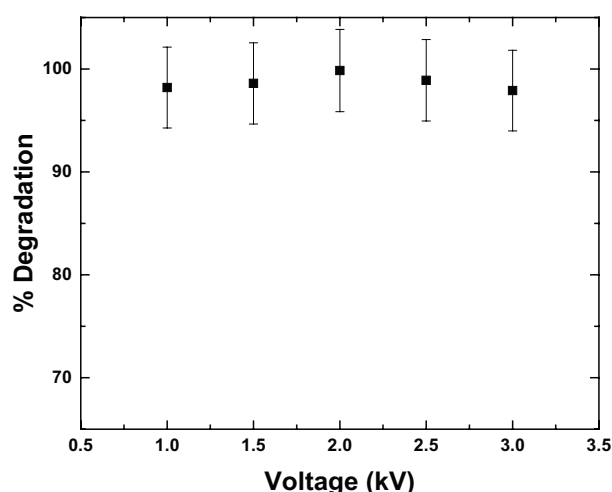


Fig. 9. Graph of % degradation vs. the applied voltage.

In typical optical emission spectrum of the plasma in the range 200–1,100 nm for this study, identifying the most intense species, which appear in all the spectra obtained during the treatment [3,7]. The optical emission spectrum

Table 2  
Principal species identified in the optical emission spectrum of the corona discharge used for the treatment [12]

Species	$\lambda$ (nm)	Transition	Energy (eV)
H <sub><math>\alpha</math></sub>	656.5	2–3	1.8887
H <sub><math>\beta</math></sub>	487.0	2–4	2.5497
OH	284.0	$A^2\Sigma^+ - X^2\Pi$ system	3064 A
	309.5		
N <sub>2</sub>	337.0	$C^3\Pi_u - B^3\Pi_g$	Second positive system
	357.5		
	375.5		
	380.5		
Na	590.0	$2p^63s - 2p^63p$	2.1023

was normalized with respect to nitrogen because the atmosphere used was air, where the most abundant gas is nitrogen. In addition, the bands of nitrogen are constant in intensity, and it is possible to observe that the intensity of the emission bands of OH<sup>\*</sup> is greater than that of N<sub>2</sub>. The difference is possible to infer owing to the great amount of oxygen in the solution in the presence of the dye, which favors the generation of OH<sup>\*</sup>. It is also possible to identify the characteristic doublet of sodium in the spectra with pollutants (D-lines). The species identified using optical emission spectroscopy is listed in Table 2.

Throughout the treatment, the most intense emission band was the one corresponding to the OH at 309.5 nm, which increases its intensity as a function of the time of exposure to plasma, because the plasma dissociates the water molecule, which favors the process of elimination of the dye. The plasma applied in water leads to the generation of the radicals OH<sup>•</sup> and H<sup>•</sup> via the dissociation and ionization of water molecules, mainly as described by the following reactions [13]:



#### 4. Conclusions

In this study, we produced plasma for the degradation of a textile dye, AB210, adding  $\text{Fe}^{2+}$  filings as a catalyst. The results indicate that treatment by corona plasma at atmospheric pressure eliminates the dye as a function of the treatment time (99.85% in 180 min). In addition, it is possible to infer that, for this dye, under the experimental conditions described, treatment would be sufficient for 120 min because a degradation rate of 96.82% is reached at this time. The decrease in the absorbance indicates that the chromophore groups are being divided and that the byproducts formed do not absorb in the studied region of the spectrum, so the sample at the end of the treatment does not show any coloration. The COD values show a decrease in the level of contamination because the intermediates require less oxygen. The behavior of TOC indicates the mineralization of the dye and its byproducts. The values for the removal of COD and TOC were 98.7% and 99.15% for 180 min of treatment. It is possible to use 0.8 mM of the catalyst and 1.0 kV of energy and achieve dye elimination rates greater than 90%, with the possibility of using another AOP that needs less energy to decompose the remaining 10%. The value of  $G_{50}$  for this process was 1.93 g/kWh, which is similar to compared with other dyes under these same conditions. The dye presents great resistance to be mineralized. The final pH and electrical conductivity values suggest a chemical pretreatment before water can be used, according to the official regulations for irrigation and other uses. The species identified in the plasma were  $\text{H}_\alpha$ ,  $\text{H}_\beta$ ,  $\text{OH}$ ,  $\text{N}_2$ , and Na by OES.

#### Acknowledgments

We are grateful to Neyfer Hernández (EESuX-UAEM) for her technical assistance. This research was supported by the projects DGAPA IN102916, PRODEP DSA/103.5/15/6986, PROMEP 103.5/13/6626 and PII-43/PIDE/2013, CONACyT 268644, and UAEM 4307/2017/CI.

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