



EFFECT ON DISCOLORATION BY NONTHERMAL PLASMA IN DISSOLVED TEXTILE DYES: ACID BLACK 194

EFFECTO DE DECOLORACIÓN POR PLASMA NO TÉRMICO EN COLORANTES TEXTILES DISUELTOS: NEGRO ÁCIDO 194

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Abstract

In this work, we show that cold plasma (electrical discharge) acting on the liquid-atmosphere interface can change some macroscopic and microscopic parameters of wastewater with dissolved dyes, a process characterized by the study of physical and chemical variables, such as the voltage and current of the electrical discharge, temperature, volume, absorbance, electrical conductivity, pH, chemical oxygen demand (COD), and total organic carbon (TOC). The dye used is Acid Black 194 (AB194) in a water solution (250 mL) with a concentration of 0.1 mM and the addition of FeSO₄ at 1.0 mM. The initial values of pH and electrical conductivity were 2.54 and 1.55 μS/cm, respectively, at a temperature of 21.5 °C. Nonthermal plasma was generated with a DC power supply at a potential of 700 V and 133 mA, which was maintained throughout the process, until an exposure time of 45 min. This physicochemical method is environmentally friendly because it does not generate polluting waste.

Keywords: degradation, cold plasmas, textile dyes.

Resumen

Este trabajo muestra que el plasma frío (descarga eléctrica) que actúa sobre la interfaz líquido-atmósfera puede cambiar algunos parámetros macroscópicos y microscópicos del agua residual con tintes disueltos; el proceso se caracteriza por el estudio de variables físicas y químicas, como voltaje y corriente de la descarga eléctrica, temperatura, volumen, absorbancia, conductividad eléctrica, pH, Demanda Química de Oxígeno (DQO) y carbono orgánico total (COT). El colorante usado es el Negro Acido 194 (NA 194) en una solución acuosa de 250 mL con una concentración de 0.1 mM y la adición de FeSO₄ a 1.0 mM; los valores iniciales de pH y conductividad eléctrica fueron de 2.54 y 1.55 μS/cm respectivamente a una temperatura de 21.5 °C. El plasma no térmico se generó con una fuente de voltaje DC a un potencial de 700 V y 133 mA que se mantuvo durante todo el proceso, hasta un tiempo de exposición de 45 minutos. Este método físico-químico es amigable con el medio ambiente porque no genera desechos contaminantes.

Palabras clave: degradación, plasma frío, colorantes textiles.

1 Introduction

Recently, the demand in the consumption of personal inputs has increased. One of the main reasons of that is the increase of the population. For example, one of these personal inputs is the use of clothing and footwear, basic nowadays, which in turn has caused the industry to increase the demand for water for this use. Wastewater contains dyes and

garbage that affect the ecosystem (Téllez et al., 2017), which, together with inadequate handling of drinking water, are factors that have impacted drinking water's scarcity. This has led to the development of different processes for complete biodegradation of textile effluents contaminated with azo dyes, because some products of anaerobic reduction are considered potentially carcinogenic or mutagenic for humans and toxic for aquatic organisms (Ayadi et al., 2016).

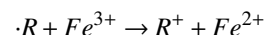
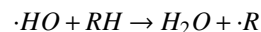
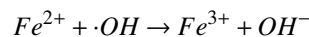
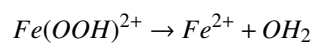
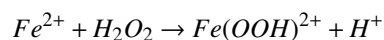
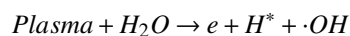
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The effects of water pollution from the waste produced by different industrial processes where dyes are involved worldwide are known and considered catastrophic for life. The presence of a large amount of wastewater is responsible for unwanted phenomena in nature, such as the drastic decrease in photosynthesis and photolysis, which results in a decrease in dissolved oxygen and contributes to the eutrophication of water constituents (Kadam et al., 2013). In industries that use colorants, the textiles consume between 25 and 250 m³ of water for every ton of product, which makes it one of the highest water-demanding sectors and the largest consumer of colorants in its final products, such as dyeing, printing, and finishing (Chacón et al., 2006; Gonçalves et al., 2005). Conventional methods for the degradation of azo dyes that use aerobic processes have not been so efficient, since many of them are only adsorbed on sludge or flocs and others pass without being altered (Lin et al., 1996). In other works, anaerobic/aerobic combined biological processes have been used with not so favorable results. The advanced methods of oxidation have been shown to be efficient in the treatment of residual water with textile dyes, such as Fenton and photo-Fenton (Salazar et al., 2011). Currently, plasmas at atmospheric pressure are used as a technology that can help in the discoloration and degradation of these types of water, showing a greater efficiency than that of conventional methods. The application of a high voltage and current for the generation of plasmas at atmospheric pressure has been shown to be efficient and capable of degrading textile dyes dissolved in water. The production of this kind of plasma can be categorized into direct current, pulsed alternating current, dielectric barrier, and radio frequency, each one with some physical characteristic that is used for the treatment of these types of water according to the physicochemical characteristics of the solutions. For this work, a corona-type plasma was generated with a power of 130 W, using air at atmospheric pressure. Electric discharge was carried out with direct current. The contribution of electrons necessary to generate the plasma comes from a source of voltage, producing reactive radicals such as hydroxyl (OH) radicals and free electrons that are responsible for the breaking of the double bonds of the dye. Corona plasmas are classified based on their degree of ionization as nonthermal cold plasmas, and they have a property where the resulting particles, such as atoms, ions, and electrons, have different temperatures, a characteristic that makes them very useful in many applications. Besides that, they can be relatively easy to produce in a laboratory. Different

experimental systems have been built according to each specific purpose for each of the plasmas, all showing advantages among them, but most of the reactors are of pulsed corona discharge type, so they were taken as a reference for the determination of the efficiency in the relative energy (Malik et al., 2010). Various authors made efforts to make the technology of the treatment of wastewater have satisfactory results, and the production of plasmas applied to this type of processes has been studied in detail (Ghodbane et al., 2014; Gómez et al., 2017). A catalyst is a substance that changes the activation energy of a reaction, causing an increase in the reaction rate without it being consumed itself. This is because the catalyst causes an alternate mechanism faster than what the reaction would have without it. Generally, the catalyzed mechanism causes a decrease in the activation energy. A large percentage of catalysts are metallic substances, metal oxides, or acids (e.g., Fe, Co, Ni, Pd, Pt, Cr, Mn, W, and Ag). For this reason, it commonly used, due to transition metal, which is a good catalyst for reactions that include hydrogen and hydrocarbons, as is the case in dyes. This is because those molecules interact easily with those metals.

The mechanism of the process was reported in previous work (Vergara et al., 2017):



where R is used to describe the reacting organic compound.

In the present work, we focus on the physicochemical study of the interaction of nonthermal corona plasmas produced by a DC source at atmospheric pressure in an aqueous solution with a commercial dye AB194. The chemical parameters studied show the degradation of the dye, such as pH, electrical conductivity, chemical oxygen demand

(COD), total organic carbon (TOC), and adsorption spectra. The quantified physical variables in this work, such as the discharge current and voltage, sample temperature, volume, and optical emission spectra, contribute to the understanding of the formation of interacting species to achieve degradation.

2 Materials and methods

The generation of the plasma used for the physical process of interaction with water was carried out in the Advanced Physics Laboratory, Autonomous University of the State of Mexico, where the plasma was characterized by optical emission spectroscopy, in addition to the determination of the electrical variables, temperature, and volume. The experimental system used for degradation is shown in Fig. 1 (Vergara et al., 2017). Emission spectra are obtained by means of an Ocean Optics spectrometer HR4000CG-UV-NIR connected to an optical fiber. A temperature meter is connected in situ, which is an LM35 sensor, in an operating range of -55 to 150 °C, with a input voltage of 4 – 30 V and a resolution of ± 0.25 °C, connected to an Arduino Leonardo microcontroller in an analog input. Discharge into the atmosphere–liquid interface is achieved by providing a flow of electrons through a high-voltage source, Keysight N8937A, which is monitored throughout the time of discharge with a Tektronix TDS3014B, also simultaneously measuring the current with a multimeter BK Precision 5491B.

A 50 mM stock solution of $\text{FeSO}_4 + 0.1$ M of H_2SO_4 was prepared. For this, 3.475 g of FeSO_4 was weighed and diluted in a small volume of water, and

then 1.34 mL of H_2SO_4 [18.75 M] was added and the solution was homogenized in a 250 mL graduated flask. Sulfuric acid was added to obtain an acidic pH of less than 3 , since at a pH above this value, iron salt precipitates, which does not guarantee the homogeneity of the solution. From this solution, 5 mL (1.0 mM) is taken and added to the water solution with a dye, obtaining a volumetric solution (250 mL) for the plasma treatment.

To identify whether the presence of ferrous sulfate (FeSO_4) increases the efficiency in the degradation process plasma and in advanced oxidation processes (AOPs) (Lin et al., 1996), different mixtures with distilled water and 0.1 mM dye to AB194 were performed, varying the concentration of FeSO_4 ; the reagent FeSO_4 was added in varying percentages (50 , 80 , 100 , and 120%), where 100% corresponds to 1.0 mM. The sample was prepared with a total volume of 250 mL in a volumetric flask, and distilled water (pH = 6.0) was used, which was added to the dye AB194 (0.1 mM) and diluted. A solution of 1.0 mM FeSO_4 was added to this mixture and stirred to obtain a homogeneous solution. The process was conducted at room temperature, and the baseline and after-treatment parameters such as pH, electrical conductivity, and volume were monitored. Samples were not exposed to natural light after treatment. Previous work has shown that the simple heating of the solution is not capable of causing degradation (Vergara et al., 2017), due to only have FeSO_4 and the solution with dye, without H_2O_2 , which starts the degradation process; while hydrogen peroxide is produced when the solution interacts with the plasma. In addition, if the sample does not interact with the plasma, no change in the value of the absorbance will exist, even if it has the catalyst.

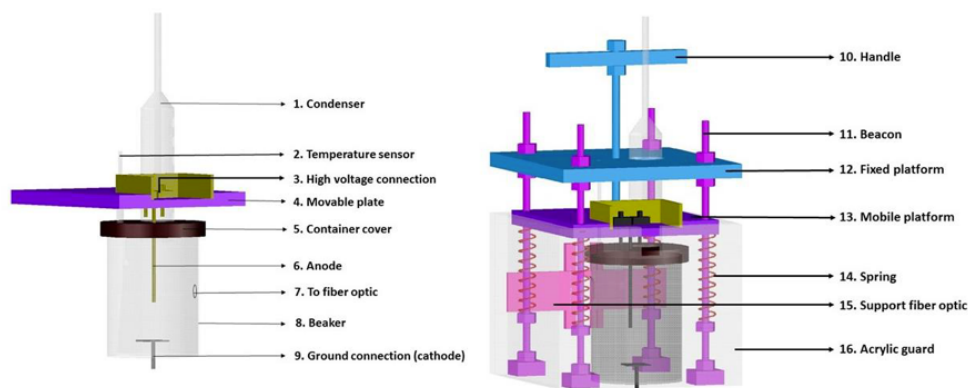


Fig. 1. Experimental system.

The plasma was generated at a constant voltage and current of 1.0 kV and 130 mA, respectively. For monitoring the decomposition of the dye at different times, a spectrophotometer (DR6000 HACH) and some reagents for COD and TOC were used. This analysis was performed at the Laboratory of Analysis and Environmental Sustainability.

3 Results and discussion

3.1 Calibration curve

To determine the concentration of the sample solution, at different times of degradation, a calibration curve is made (Fig. 2). The calibration curve is drawn by preparing several solutions at a known concentration (0.5 mM) of the dye. In each of these solutions, the absorbance is determined at 574 nm for this case, with a HACH DR6000 spectrophotometer, and the data is plotted as concentration (mM) versus Absorbance (ABS) where the relation of these is obtained by means of the equation of the straight line, $y = mx + b$, by means of least squares, where y is the ABS, x is the known concentration of the dye, m is the slope of the line, and b is the ordinate to the origin.

Through this equation, it is possible to determine the concentration of the sample during the experimentation of degradation by means of the AOP by cold plasma. The ABS is obtained directly, and later the concentration of the dye AB194 is calculated by the equation of the straight line, with $= \frac{(y-b)}{m}$.

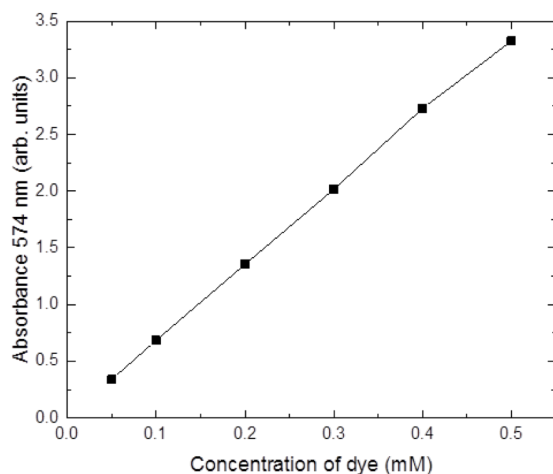


Fig. 2. Calibration curve of AB194.

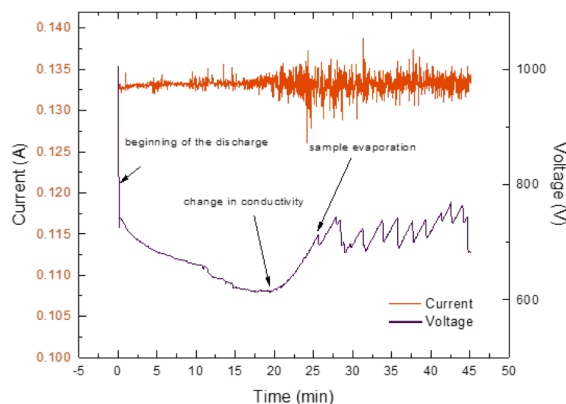


Fig. 3. Behavior of current and voltage in all time treatments.

Figure 3 shows the measurements of current and voltage, which were taken using BK Precision 5491B multimeters. At the beginning of the discharge, a drop in the supplied voltage can be observed, from 1000 V to 700 V. This fall is related to the energy needed to carry out the electrical breakdown. At this point, the current suddenly increases until an average of 133 mA. In the first 20 min, the applied voltage decreases until a minimum value of 615 V; this is correlated with the behavior of electrical conductivity, which in the same time range exhibits an increase in its value. However, the current stays constant. With a treatment time of 20 min, the voltage increases to 700 V. At this time, the conductivity begins to decrease. From this point (25 min approximately), the current and voltage exhibit fluctuations, around 130 mA and 700 V, respectively, since the sample reaches a temperature of 90 °C (Fig. 4) and the losses by evaporation become more evident, resulting in a change in the level of the sample, with a consequent change in the separation distance between the liquid–air interface and the anode. To avoid this variation and to keep the current constant, the height of the anode was changed manually, resulting in the fluctuations described above.

Figure 4 shows the behavior of the temperature of the samples during the time of interaction with the plasma. All samples showed similar growth at different treatment times. Starting at an average temperature inside the laboratory of 21.5 °C and reaching a maximum value of 90 °C, this value remains constant as a function of time. The samples were prepared using distilled water, adding FeSO₄ as a catalyst.

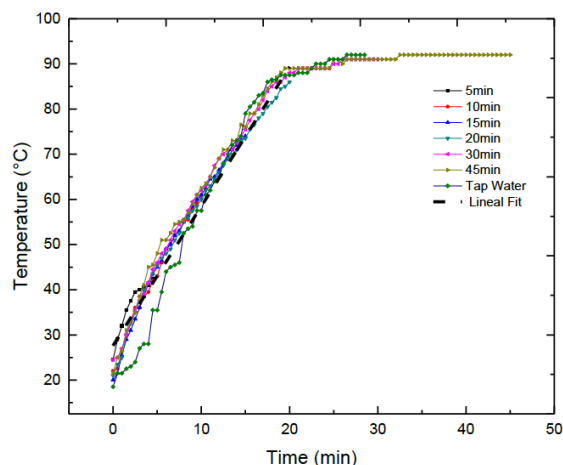


Fig. 4. Temperature of the sample at different interaction times.

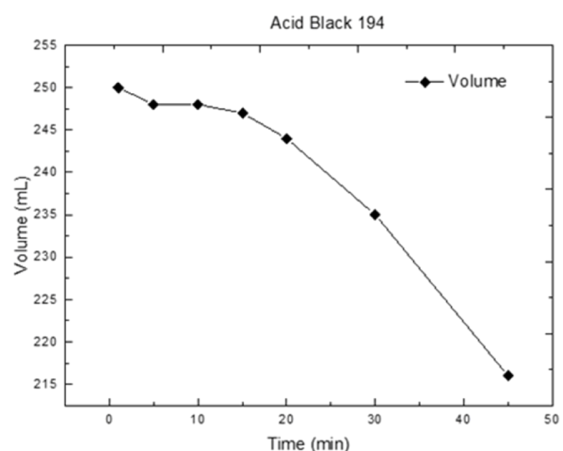


Fig. 5. Lost volume of sample with a dye.

As the temperature of tap water and that of the samples were observed, a comparison of water with a dye and tap water was made at the same time of exposure and same parameters of current and voltage, showing that water with a dye exhibits a 9 °C higher temperature than tap water in the time interval of 5 min of treatment. After 20 min, both samples reached 87 °C. The temperature increased to 90 °C after 30 min until the end of the process, with this being the maximum value reached during the plasma-sample interaction process. By performing a linear adjustment, it is observed that the increase is similar in all cases, so that, in the range of 0–5 min, the temperature increases by 17.5 °C, from 5 to 10 min by 16.2 °C, from 10 to 15 min by 14.9 °C, and from 15 to 20 min by 10.9 °C. This allows saying that degradation was not caused by heating since it exhibits the same behavior, but by the formation of hydroxyl produced by the corona discharge. A temperature sensor (LM35)

was used, placed in the same position within the treated samples. This data was acquired by means of an Arduino Leonardo card with the same code at 30 s of capture. The increase in temperature is attributed to the flow of electric current by Joule's effect since the system tries to dissipate the electric power supplied and does that in the form of heat.

In Fig. 5, the lost volume behavior is observed during treatment with the plasma, from 0 to 45 min. It could be seen that, after 45 min, it has the largest volume loss of the order of 14%, mainly associated with the temperature increase by the interaction of the samples with the plasma. The generated steam is contained in the upper part of the experimental system in the condenser, which is at room temperature so that the condensation and the return of the drops do not affect the physical conditions of the sample. When observing the results of the temperature at 30 min of interaction, the percentage of volume loss was 6.4%; the absorption spectra indicate that 96.1% of the dye has degraded at this time, a value that can be considered as being capable of depositing in the tributaries.

This time in the treatment coincides when the temperature increases as a function of the treatment time, reaches its maximum at 20 min and then remain constant. Also, it is observed that, in the interaction interval between 5 and 10 min, 1.2% of the original volume is lost. The volume loss is 1.5%, 2.8%, 6.4% at 15, 20 and 30 min of treated time, respectively. Which implies that the plasma treatment does not affect the temperature or the volume loss to the addition of catalytic agents. This study was also carried out for samples without a catalyst, observing the same results. The degradation of AB194 was monitored and measured at the time of treatment of the sample. The absorbance observed at the wavelength of $\lambda = 574$ nm, corresponding to the maximum of the absorbance characteristic peak for this textile dye, accounts for the compartment in function of treatment time. Figure 6(a) shows the visible region of the spectrum, where it is possible to observe the spectral evolution of the AB194 solution for 0, 5, 10, 15, 20, 30, and 45 min of plasma treatment. The absorbance peaks corresponding to 30 and 45 min disappear completely following the discharge plasma treatment. The disappearance of the peaks in the 574 nm absorbance band, as shown in Fig. 6(b), suggests that the double bonds of the azo group (N=N), responsible for the characteristic black color of the dye, were broken in the first 5 min, which represents a 34.85% decrease in absorbance, compared to an untreated sample.

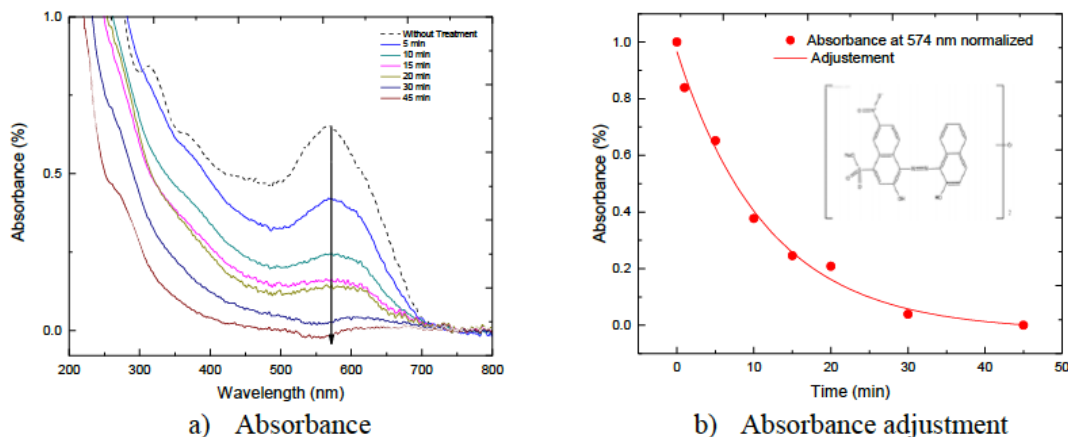


Fig. 6. (a) Absorbance as a function of the treatment time. (b) Absorbance adjustment.

The absorbance decreases in 0%, 34.85%, 62.35%, 75.47%, 79.22%, 96.1%, and 96.25% at 0, 5, 10, 15, 20, 30 and 45 min, respectively. In addition, the formation or recombination between the components of the dye is not observed. Electromagnetic radiation is absorbed only if its frequency coincides with the natural modes of vibration of the chemical bonds present in the molecule, which is why when absorption increases, peaks can be related to bonds. In the case of AB194, the absorption peak at 574 nm is associated with the double bond of N.

Soft absorption spectra, in the absence of peaks, are due to dispersion effects and not to absorption with a dependence on the suspended particles in the solution, demonstrating the double bonds of the chromophores.

Statistical normalization was made to the absorbance results in order to observe the general behavior in the degradation of the dye. Figure 6(b) shows this normalization. The values are adjusted to an exponential function of decay, where the coefficient of determination (R^2) is 0.9831, demonstrating the efficiency of the plasma when interacting with an organic sample.

The speed with which a certain concentration $c(t)$ of a dye is decomposed by the effect of plasma is directly proportional to the amount of dye at a certain time and is described as

$$\frac{dc(t)}{dt} = -kc(t)$$

The concentration of the dye $c(t)$ in a solution is a function of the time of exposure to plasma; that is, the organic compound degrades with the plasma interaction, forming new byproducts, which usually

tend to require more energy to be degraded, resulting in a form of an exponential decay function.

The experimental values for the dye concentration of AB194 were compared with an exponential function, related to Eq. (1) (Stará et al., 2009). The parameters of the exponential fit provide us with an initial concentration, $c_0 = 0.093$ mM, which agrees with the value obtained by means of Beer–Lambert law with a value of 0.095 mM and a percentage variation of 2.1% between both values. This initial concentration decreases with respect to time until 99.87% from the initial value for 45 min of plasma treatment.

$$c(t) = c_0 \exp[-k.t] + a, \quad (1)$$

where $c(t)$ is the time dependence concentration, c_0 is the initial concentration, k is the rate of dye removal, and a is the residual concentration.

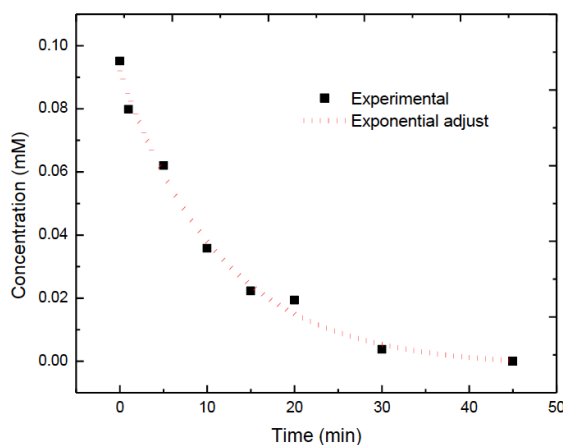


Fig. 7. Dye concentration (AB194) versus time.

This dye removal method has a rate of dye removal of $k = 0.085 \text{ min}^{-1}$ and a residual concentration of $a = 0.001 \text{ mM}$, close to zero, which shows that the experiment has a good response to the dye degradation. Considering that the chemical kinetics studies the speed with which the reactions are carried out under controlled conditions, the analysis carried out on the behavior of the concentration of the dye would be an analogy to the chemical kinetics, without the need to know the byproducts of the degradation process.

3.2 Calculation of Energy Yield (G_{50} AB194)

The plasma generated in the reactor is a corona discharge, so that 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 pollutant converted as a function of the energy supplied and required for 50% conversion of the pollutant:

$$G_{50} = 1.8 \times 10^6 \frac{C_0 V_0 M}{P t_{50}} \quad (2)$$

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). The initial concentration of the dye Acid Black 194 was $C_0 = 0.0001 \text{ M}$, the initial volume was $V_0 = 0.25 \text{ L}$, $M = 758.7 \text{ g/mol}$, the electrical power was $P = 130 \text{ W}$, and $t_{50} = 423 \text{ s}$. Substituting in the equation, the calculated value of G_{50} for this process is 0.621 g/kWh ; this value is similar to those reported in the literature (Malik et al., 2010), for reactors where processes are involved with corona plasmas like the one in this work. This calculation uses reactors that generate other plasmas, such as arc, luminescent, pulsed, microwave, dielectric, radiofrequency, or

hybrid systems, besides considering different factors such as pH, concentration, and chemical structure. The efficiency shows for the treatment using corona-type plasmas makes them to be considered as an efficient system of low energy consumption. For another type of photocatalysis processes such as Fenton and photo-Fenton, there is no calculation to estimate their energy efficiency. Fenton also uses electromagnetic radiation (UV light) to generate oxidizing agents, OH radicals, whereas plasma treatment generates radicals mainly by electronic impact. Likewise, both can use catalysts such as FeSO_4 to accelerate the degradation process.

Figure 8 shows the process of discoloration of the sample of the dye AB194 at different interaction times—5, 10, 15, 20, 30, and 45 min—with nonthermal plasma. It is observed that there is a loss of color at the time of treatment under the same physical and chemical conditions. The removal of COD and TOC concentration in the first 5 min of plasma treatment was 5%; however, it reached approximately 15% at 15 min, and at 45 min the removal was greater than 50%. The TOC had a similar behavior to that of the COD in the first 30 min, but at 45 min it reached 33% removal of the TOC. The effects on the chemical changes of the sample in pH and electrical conductivity are observed in Fig. 8. The behavior is determined since the pH is an important variable in the generation of the hydroxyl radicals responsible for degrading the organic components. For this, an analysis was carried out from pH 8 (basic) to pH 2 (acidic) for all the treatment times, with which the optimum value could be determined. Treated samples had an AB194 concentration of 0.1 mM and an initial volume of 250 mL with 1.0 mM FeSO_4 in acidic conditions. Studies have shown that, at acidic pH (2 to 4), degradation by nonthermal plasma is efficient. This degradation is associated with the oxidative capacity of the radical hydroxyl under acidic conditions (Ghodbane et al., 2014). This work shows that (similar to others) the process of oxidation by nonthermal plasma, the acidic pH degrades organic matter.

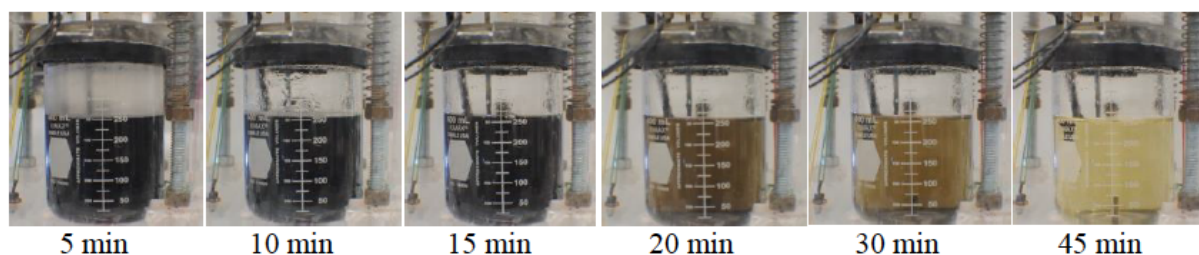


Fig. 8. Photographs of AB194 dye degradation as a result of the interaction with plasma.

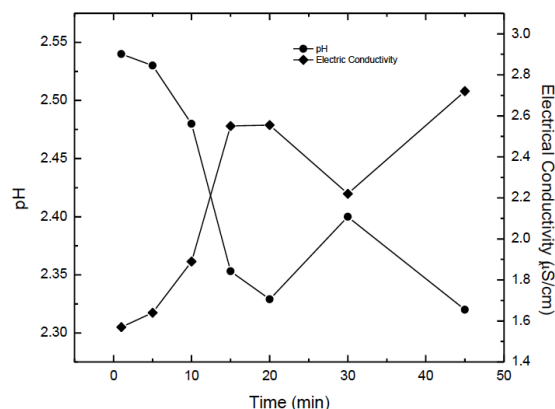


Fig. 9. pH and electrical conductivity as a function of the treatment time.

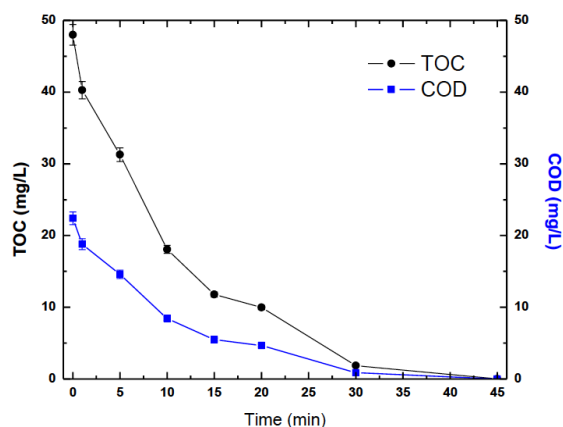


Fig. 10. TOC and COD as a function of the treatment time.

In this case, AB194 had a pH of 6 (no adjustment), and then we used H_2SO_4 to adjust the pH of the samples. We found that the optimum pH for the elimination of AB194 with plasma is 2.32. Figure 9 shows that the pH decreases and the electrical conductivity increases in the first 10 min. Subsequently, after 15 min, the pH was 2.35, and no significant changes occurred until the end of the treatment. On the other hand, the electrical conductivity showed a not so significant increase from 2.47 to 2.50 at the end of the treatment time. The pH behavior tends to acidify the solution (approximately 0.22 pH units). Electrical conductivity increases in the first 15 min; however, at 45 min, there is a slight decrease in this, reaching up to $2.75 \mu S/cm$.

In Fig. 10, the behavior in the degradation of the dye is observed as a function of the treatment time, and

the COD and TOC are determined. In both cases, there is a constant decrease with respect to plasma exposure. In the first 15 min of the degradation treatment of the AB194 textile dye, the removal percentage was 75% for the TOC, which indicates the chromophore. The percentage of removal of the TOC was 96% at 30 min. The behavior of COD was similar to that of TOC. These results show that a greater amount of hydroxyl radicals is generated in the first minutes of plasma treatment, which degrades the textile dye molecule.

Conclusions

We studied the effects that plasma's physical parameters, such as current and voltage, have on discoloration and degradation in samples with AB194 dye dissolved in 250 mL of water. The pH of the solution and the electrical conductivity were determined, besides the adsorption, COD, TOC, loss of volume, and temperature, demonstrating that the interaction of the plasma favors the process of degradation of the samples with a textile dye, allowing the evaluation of the physical and chemical effects of the system. Likewise, it was concluded that the resulting water does not require any other process because no waste is produced. The generated plasma is of corona type, with a value of G_{50} of 0.621 g/kWh in its efficiency energy to degrade 50% of the matter. This was produced at a power of 130 W. The magnitude shows the efficiency of the system, since we consider this value as adequate for this type of plasma at a dye removal rate of $k = 0.085 \text{ min}^{-1}$. The voltage and current of plasma generation are captured during the whole process in average values of 700 V and 133 mA, which ensures that the power of the plasma is the same. The initial temperature for all samples is $21.5^\circ C$, behaving in the same way for all cases up to a maximum temperature of $90^\circ C$ for the longest treatment time. With these temperature values, the volume loss by maximum heating is of the order of 14%, starting from 1.2% at 5 min. The discoloration of AB194 depends on the interaction time under the same conditions of initial concentration and volume. It is possible to confirm that complete elimination of the dye is reached at 45 min, whereas for 5, 10, 15, 20, 30, and 45 min, elimination was achieved at 34.85, 62.35, 75.47, 79.22, 96.1, and 96.25%, respectively, observed by the absorbance analysis. The degradation

rate of AB194 is not a function of pH and electrical conductivity of the sample, due to the results of 2.54 to 2.35, which correspond to an acidic medium and the electrical conductivity values of 1.55 to 2.75 $\mu\text{S}/\text{cm}$. The rate of degradation in the acidic medium (pH = 2 and 4) is explained by the fact that the OH radicals are eliminated by the hydroxide ions in basic solutions.

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References

- Ayadi, I., Souissi Y., Jlassi, I., Peixoto F. and Mnif, W. (2016). Chemical synonyms, molecular structure and toxicological risk assessment of synthetic textile dyes: A critical review. *Journal of Developing Drugs* 5, 100051, 1-4.
- Chacón, J. M., Leal, M.T., Sánchez, M., Bandala, E. R. (2006). Solar photocatalytic degradation of azo-dyes by photo-Fenton process. *Dyes and Pigments* 69, 144-150.
- Ghodbane, H., Nikiforov, A. Y., Hamdaoui, O., Surmont, P., Lynen, F., Willems, G., Leys, Ch. (2014). Non-thermal plasma degradation of anthraquinonic dye in water: Oxidation pathways and effect of natural matrices. *Journal of advanced oxidation technologies* 17, 372-384.
- Gómez, A., Torres, A. J., Vergara, J., Torres C., Reyes, P. G., Martínez, H., Saldarriaga, H. (2017). Physical-chemical characterization of the textile dye Azo AB52 degradation by corona plasma. *AIP Advances* 7, 1-11.
- Gonçalves, M.S.T., Pinto, E.M.S., Nkeonye, P., Oliveira, A.M.F. (2005). Degradation of C.I. Reactive Orange 4 and its simulated dyebath wastewater by heterogeneous photocatalysis. *Dyes and Pigments* 64, 135-139.
- Kadam, A. A., Lade, H. S., Patil, S. M., Govindar, S. P. (2013). Low cost CaCl_2 pretreatment of sugarcane bagasse for enhancement of textile dyes adsorption and subsequent biodegradation of adsorbed dyes under solid state fermentation. *Bioresource Technology* 132, 276-284.
- Lin, S. H. and Peng, C. F. (1996). Continuous treatment of textile wastewater by combined coagulation, electrochemical oxidation and activated sludge. *Water Research* 30, 587-592.
- Malik, M. A. (2010). Water Purification by plasmas: Which reactors are most energy efficient? *Plasma Chem Plasma Process* 30, 21-31.
- Salazar, R., Garcia, S., Ureta, M., Brillas, E. (2011). Degradation of disperse azo dyes from waters by solar Photoelectron-Fenton. *Electrochimica Acta* 56, 6371-6379.
- Stará, Z., Krčma, F., Nejezchleb, M. and Dušan Skalný, J. (2009). Organic dye decomposition by DC diaphragm discharge in water: Effect of solution properties on dye removal. *Desalination* 239, 283-294.
- Téllez-Pérez S. K., Castillo-Araiza, C. O., Huerta-Ochoa, S., Loera, O., Beristain-Cardoso, R. (2017). Biokinetic and zymographic study of the Acid Blue 74 dye biodegradation using activated sludge onto activated carbon. *Revista Mexicana de Ingeniería Química* 13, 971-982.
- Vergara, J., Torres, C., Montiel, E., Gómez, A., Reyes, P. G., and Martínez, H. (2017). Degradation of textile dye AB 52 in an aqueous solution by applying a plasma at atmospheric pressure. *IEEE Transactions on Plasma Sciences* 45, 479-484.