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Phenol Red Degradation Using a Synergetic Method (Electrochemical Oxidation with Ozone) in Batch and Continuous System

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The degradation of phenol red (as a model of phenolic contamination) in aqueous solution was studied coupling two advanced oxidation processes in batch and continuous mode. Using an ozonation process in batch mode only 5% of COD removal in 30 min, is obtained. Electrochemical oxidation process in batch mode with electrodes of diamond doped with boron (DDB) as anode and stainless steel as cathode, removes 31% of COD in 120 minutes However, when the processes are coupled in batch mode reach 13.7% of COD removal in 30 minutes. In other hand, electrochemical oxidation process (DiaClean® cell) in continuous mode removes 38.4% of COD in 120 minutes. Coupling ozone with electrochemical oxidation (DiaClean ® cell) in continuous mode, a 46% of COD removal is achieved in 30 minutes. Samples of this treatment were analyzed in an ionic chromatographic equipment, it was detected that the main products formed in the degradation of phenol red were acetate and fumarate.

Keywords: Phenol red, Degradation, Ozone, Electrochemical oxidation, DiaClean® cell

1. INTRODUCTION

In previous decades, water contamination has been treated by conventional methods, such as biological processes, filtration, flocculation, sedimentation, etc. However, due to the high toxicity of persistent contaminants, these technologies are no longer efficient for water treatment [1].

The presence of persistent compounds in effluents is becoming more common, so it is necessary to use more intensive technologies for the degradation of these polluting substances. One of the best alternatives for treating these water pollutants is the use of advanced oxidation processes (AOP's). These processes include the formation of hydroxyl radicals (HO•), species of great oxidizing power due to its high redox potential (2.80V) which attack organic molecules degrading them, reducing their toxicity and increasing their biodegradability [2-4].

One of the most efficient AOP's to eliminate pollutants of wastewater is electrochemical oxidation. The main advantage of this process is the formation of oxidizing species such as hydroxyl radicals or ozone that are produced directly by the electrolysis of water [5]. These processes only need the application of electric current, which avoids the addition of other chemical reactive.

An important part in electrochemical oxidation treatments is the electrode material, especially the anode, which is where hydroxyl radical formation occurs. The most efficient materials found are boron doped diamond (BDD) thanks to its physical and chemical properties, such as, high electrical conductivity, mechanical, chemical and electrochemical stability. In addition, BDD electrodes promote the formation of oxidizing species, such as peroxosulfates, peroxocarbonates, ozone and hydrogen peroxide [6,7].

Nowadays, there are commercial technologies that use BDD electrodes to treat and disinfect wastewater in continuous flow, such as DiaCell® with BDD/Si electrodes or DiaClean® these technologies are designed to be used on a large scale to electro-treat wastewater [8].

Research such as, Souza, et al., 2015, studied the degradation of the herbicide 2,4-D (100 mg dm^{-3} and 3 g L^{-1} NaCl as electrolyte) using a DiCell 401 reactor with BDD/Si electrodes, achieving its complete mineralization by fixing the number of electrodes in bipolar form [9].

Cano, et al., 2016 report the use of DiaCell 401 with up to four compartments and BDD/Si electrodes connected in bipolar form and DiaCell 1001 with 10 compartments and with BDD/Si electrodes as anode and stainless steel as cathode connected in monopolar form, to disinfect wastewater from a treatment plant in Ciudad Real Spain, they report the formation in high concentrations of hypochlorite for the DiaCell 101 reactor and the formation of high concentrations of chloramines in the DiaCell 401 reactor due to its bipolar arrangement [8].

Another AOP's is the ozone, a powerful oxidant that has been used to treat drinking water [10], the main objective in the treatment of wastewater using ozone is to optimize and improve the disinfection and removal of organic pollutants present in the water [11].

Several investigations have been reported in the literature indicating the degradation of organic compounds with ozone treatments. Ohrhon, et al., 2017 report the degradation of triclosan (3 mg L^{-1}) in synthetic water and wastewater (Ankara, Turkia) using ozone (5 mg L^{-1}) obtaining 99.7% degradation in synthetic water and 88.1% in wastewater. The difference in the percentage of degradation is due to the fact that wastewater contains high concentrations of natural organic matter that break down ozone and prevent the formation of hydroxyl radicals [12].

One of the disadvantages in use of ozone in wastewater degradation treatments is that ozone reacts slowly with some organic substances such as inactive aromatics or saturated carboxylic acids, which prevents it from reaching full mineralization, that is why it has to be coupled with another method that helps achieve mineralization [13].

Regarding the synergy between treatments of electrochemical oxidation with ozone, several investigations have been reported in the literature, among them the published by Rosales, et al., 2017, studied the degradation of endosulfan (Thiodan® 35) in an ozone-electrochemical oxidation coupled system with BDD electrodes (current density of 60 mA cm^{-2}). They report COD removal for electrochemical treatment achieved 97% in 100 minutes, for ozonation treatment 77% COD removal in 100 minutes and for coupled treatment it was 94% COD removal in 40 minutes [14,15].

A compound that has been studied extensively in terms of its degradation by advanced oxidation processes is phenol. Phenol and its derivate are a family of aromatic compounds are environmental concern, because they present a wide variety of uses, such as, pharmaceuticals, pesticides, fungicides, etc. are stable compounds, toxic and difficult to degrade by microorganisms [16-19]. The Environmental Protection Agency has classified phenol and its derivate as priority pollutants, that is, as a dangerous chemical [20].

One of the phenol derivate is phenol red, it is an organic compound used in several applications, one of the most important in chemical laboratories as a pH indicator, it is also used as a bromination catalyst and as estrogenic properties [21]. Therefore, in this study, phenol red was chosen as a model phenolic contamination.

Therefore, the main objective of the present study is to evaluate the coupled system ozone-electrochemical oxidation in batch and continuous system (DiaClean®) in the degradation of phenol red in aqueous solution, analyzing the effect of applied current density and the feed flow to the continuous electrochemical reactor.

2. MATERIALS AND METHODS

2.1 Reagents and Chemicals

All the chemicals, which have been used, were analytical reactants without further purification. Phenol red was purchased from Analytikal, Absolute Ethanol ACS from Fermont, sodium sulfate anhydrous from Reasol, concentrated phosphoric acid from Sigma Aldrich, potassium trisulfonate of indigo from Sigma Aldrich, monobasic potassium phosphate from J. T. Baker. Distilled water was used for all experiments.

2.2 Synthetic solution

Solution of 5 mg L^{-1} of phenol red in 0.05 M of Na_2SO_4 was used in all experiments. Solution was prepared diluting 100 mg of phenol red in 100 mL of ethanol in continuous stirring, completing 1L of solution with Na_2SO_4 0.05 M, obtaining a concentration of 100 mg L^{-1} of phenol red. Aliquots from this solution were taken to prepare solutions of 5 mg L^{-1} of 1 and 3 L.

2.3 Ozonation Treatment in batch mode

The ozone treatment in batch mode was carried out in a glass bubbling reactor with a capacity of 1.2 L, which has an entry of the gas into the reactor, entry of the phenol red solution and one exit where the residual ozone is transported to the ozone destroyer (Pacific Ozone Heated Catalytic Ozone destruct).

It also has a porous filter that allows a more even distribution of the gas within the liquid. Samples were taken at different times during 30 minutes in order to determine COD and UV-Vis.

The ozone used was produced in an electric shock generator (Pacific Ozone Technology, Mod.). The concentration of ozone was determined with the colorimetric technique of indigo blue [18], 9.4 mg O_3 L^{-1}.

2.4 Electrochemical oxidation Treatment in batch mode

The electrochemical oxidation treatment in batch mode was carried out in an electrochemical cell made of glass with a capacity of 1.2 L, internal diameter of 6.7 cm and a height of 39.5 cm, also has a faucet for taking samples located 10 cm from the base of the reactor. The electrodes used were; as an anode, a METAKEM® Diamond Doped with Boron (BDD) electrode, and as a cathode, a food grade commercial stainless steel 304 electrode (Chromium 18 to 20% and Nickel 8 to 10.5%). The area of each electrode is 50 cm^2, with 20 cm high and 2.5 cm wide.

Each electrode was previously cleaned, the BDD electrode had an anodic polarization pretreatment with 0.05 M Na_2SO_4 solution at a current density of 30 mA cm^{-2} for 30 minutes. The stainless steel electrode was sanded to remove roughness, washed with soap and running water and rinsing with distilled water. Reported results are the average of three tests.

The effect of current density was studied applied three different values 10, 20 and 30 mA cm^{-2}. Samples were taken at different times during 120 minutes in order to evaluate COD and UV-Vis.

2.5 Coupled treatment in batch mode

The coupled treatment in batch mode ozone-electrochemical oxidation was carried out in a jacketed glass reactor with a capacity of 1.2 L, the reactor has one inlet for the gas and another to introduce the solution of phenol red and the electrodes. Reactor also has two outputs, one for carry the residual ozone to the ozone destroyer, and other for taking samples. The electrodes used for this treatment, as well as the ozone concentration used, are the same as those described in the individual ozone and electrochemical oxidation treatments. Samples were taken at different times during 30 minutes in order to determine COD and UV-Vis.

2.6 Electrochemical oxidation treatment DiaClean® cell in continuous mode

The electrochemical oxidation treatment in continuous mode DiaClean® cell Model 101 with electrodes of BDD as anode and stainless steel as cathode was installed with peristaltic pump Masterflex BT Cole-Parmer Modelo 77111-6, source power GW Instek Modelo GPR-1820HD and feeding tank.

The feeding tank was a cylinder shape of acrylic with a capacity of 10 L internal diameter of 19 cm and a height of 60 cm. The recirculation of the solution through the whole system was through a pipe for drinking water of Polypropylene Random Copolymer. The effect of the feed flow (Q) to the reactor was studied applying three different values 7, 14 y 22 L min^{-1}. Samples were taken at different times during 120 minutes in order to determine COD and UV-Vis.

2.7 Coupled treatment DiaClean® cell-ozone in continuous mode

The coupled treatment in continuous mode, uses the previously DiaClean® cell electrochemical described system but now the reservoir has a diffuser gas of pumice stone (diameter of 17 cm and height of 3 cm) installed in the bottom of the tank in which ozone is added. Samples were taken at different times during 30 minutes in order to determine COD and UV-Vis.

2.8 Physicochemical Analysis

The phenol red was spectrophometrically monitored in a UV-Vis spectrophotometer Perkin Elmer precisely Lambda 25 UV-Vis spectrometer, between 200 and 600 nm. The spectrums were taken of phenol red before and during each treatment at different times. Chemical Oxygen Demand was analyzed using the American Public Health Association Standard Procedures [18], using a Hach DR 5000.

Ionic chromatographic equipment Thermo Scientific Model DIONEX Aquion®, self-sampling AS-DV with conductivity detector was used to determine byproducts in degradation of phenol red for each treatment. The method was performed with phase mobile of NaOH 30 mM (injection volume 125 μL and flow of 1.5 mL min^{-1}) and column AS11-HC with 250 mm in length and 4 mm of diameter.

3. RESULTS AND DISCUSSION

To examine the degradation of phenol red in each treatment, the absorption spectra of the samples taken at different time intervals were obtained, and the percentage of degradation was calculated in the maximum intensity band at λ_{max} of 432 nm (visible region) of phenol red as follows in (Eq. 1) [20].

$$\%\,Degradation = \left(\frac{A_0 - A_t}{A_0}\right) * 100 \qquad (1)$$

Where A_0 and A_t are initial absorbance and absorbance after treatment at different time intervals, respectively. Reported results are the average of three tests.

3.1 Ozonation treatment in batch mode

During the ozonation treatment of phenol red, the absorption spectra were obtained at elapsed treatment time. Figure 1a shows that 98% of degradation is obtained at 30 minutes. The absorption spectra can be observed in the figure 1b, the absorption spectra change over the treatment time, the intensity of the main band ($\lambda_{max\,=}$ 432 nm) start to decrease after the first 10 minutes, at 30 minutes this intensity drop off.

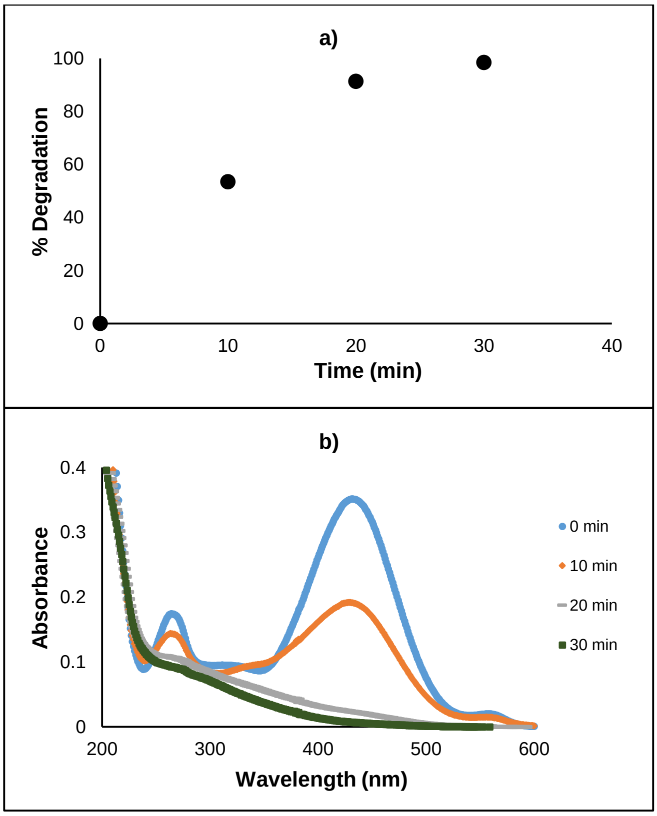

Figure 1. a) % of degradation at λ_{max} (432 nm) and b) UV-Vis spectra of phenol red (5 mg L^{-1}) in ozonation treatment (9.4 mgO_3 L^{-1}) in batch mode, regarding time.

The decrease in the absorbance of the bands (decrease of intensity) is due to the reaction of ozone with dye which is favored in acidic medium. This behavior has been reported in several publication of dyes degradation with ozone. El Hassani et al., 2019, studied the degradation of methyl orange dye by catalytic ozonation with Ni, reporting the decrease of the bands (465nm, maximum intensity) reaching a 72% of mineralization in 60 minutes of treatment. Tehrani-Bagha et al., 2010, investigated the degradation of a textile dye (reactive blue 19) by ozonation, report similar results, the high intensity band of the dye (595nm) decrease as increase treatment time, reaching complete decolorization after 45 minutes [22,24].

On the other hand, the figure 1b also shows the formation of peaks in wavelength of 264 nm that correspond to the aromatics compounds, this peaks decrease due to the degradation of aromatic species and formation of by-products.

3.2 Electrochemical oxidation treatment in batch mode

In the electrochemical oxidation treatment using BDD electrodes as anode and stainless steel as cathode, the influence of current density (*j*) was studied at 10, 20 y 30 mA cm^{-2} in order to evaluate this effect on the degradation of phenol red (5 mg L^{-1} and 0.05 M of Na_2SO_4 as electrolyte) in batch mode. Figure 2a, shows the degradation percentage of the three current density values (*j*) studied; this figure indicates that reduction increases as a function of electrolysis time and the applied current density. After 120 minutes of treatment a 56%, 59% and 69% is obtained for 10, 20 y 30 mA cm^{-2} respectively.

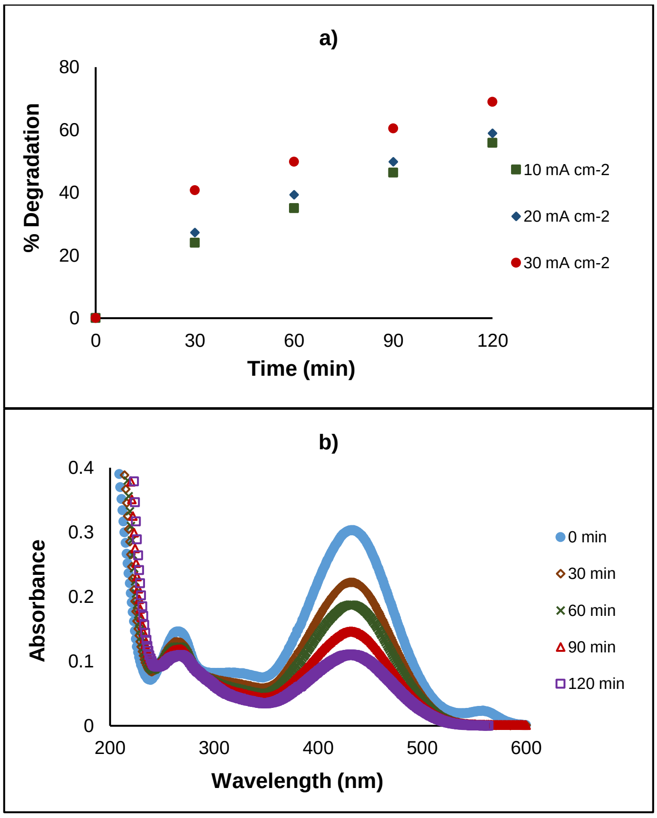

Figure 2. a) % degradation of three current density (*j*) studied at λ_{max} (432 nm), 10, 20 and 30 mA cm^{-2}, b) Absorbance Spectrum of the electrochemical oxidation treatment in the degradation of phenol red in batch mode. Conditions: 30 mA cm^{-2}, 5 mg L^{-1} of phenol red, 0.05 M Na_2SO_4.

The increase of degradation percentage using a higher current density has been reported previously, this effect is explained in terms of the increase of current density accelerate the formation of HO• and secondary oxidizing species increasing the direct and indirect oxidation reactions [25,26],

Figure 2b, shows the absorbance spectrum in the degradation of phenol red using the electrochemical oxidation treatment with a current density of 30 mA cm^{-2}, note that the absorbance abatement is less when compared with the ozone treatment.

3.3 Coupled treatment ozone-electrochemical oxidation in batch mode

In the coupled treatment ozone-electrochemical the conditions used were: ozone concentration of 9.4 mg O_3 L^{-1} and a current density of 30 mA cm^{-2}. Figure 3a, shows that the degradation was 99% in 30 minutes. Figure 3b, shows absorbance spectrum and the influence of the time in the degradation of phenol red.

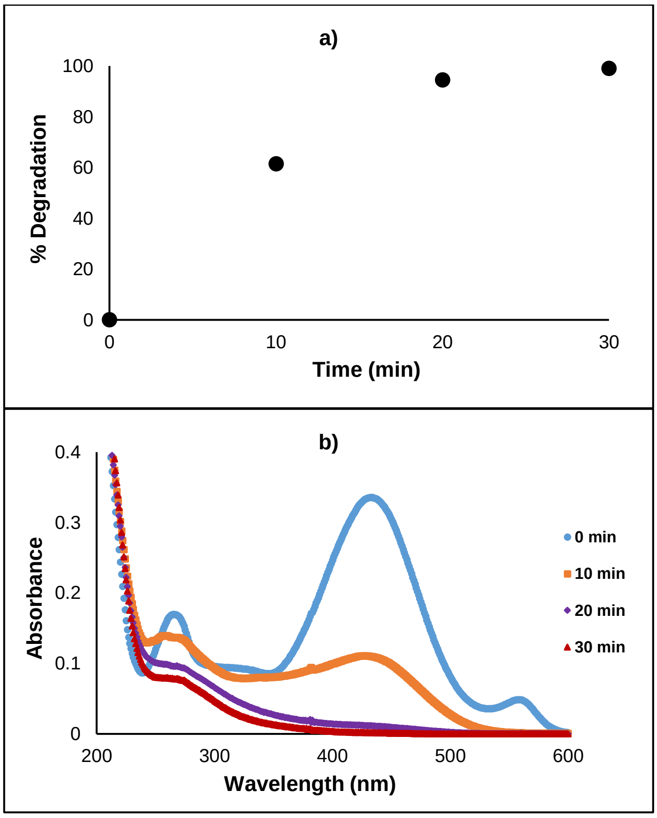

Figure 3. a) % of degradation of phenol red at λ_{max} (432 nm) and b) Absorbance Spectrum of the coupled treatment ozone-electrochemical oxidation in the degradation of phenol red, in batch mode. Conditions: 30 mA cm^{-2}, 5 mg L^{-1} of phenol red, 0.05 M Na_2SO_4, 9.4 mg O_3 L^{-1}.

As can observed in figure 3b, the decrease in the intensity of the bands carry out faster than the individual systems, which indicate that better results are obtained coupling advanced oxidation processes. Comparing the COD for each treatment, electrochemical oxidation treatment COD removal was 31% in 120 minutes, in ozanation treatment is obtained 5% in COD removal, and coupled treatment just 13.7% in COD removal in 30 minutes respectively. The low decrease is due the ethanol present in phenol red solution and the accumulation of by-products formed during each treatment such as carboxylic acids.

This results agree with Rosales et al., 2017, who studied the degradation of endosulfan (Thiodan® 35) using similar treatments, reporting an increase in COD removal in less treatment time when degradation was carry out in coupled system [15].

3.4 Electrochemical oxidation treatment (DiaClean® cell) in continuous mode

The absorbance spectrum in the degradation of phenol red in electrochemical oxidation treatment (DiaClean® cell) in continuous mode with a current density of 30 mA cm^{-2} and a feed flow of 22 L min^{-1}, shows that the bands decrease with the same characteristics of bands in batch mode. The difference of percentage degradation of phenol red in batch and continuous mode is due at treated volume in each one, since in batch mode was 1 L of phenol red solution and continuous mode was 3 L.

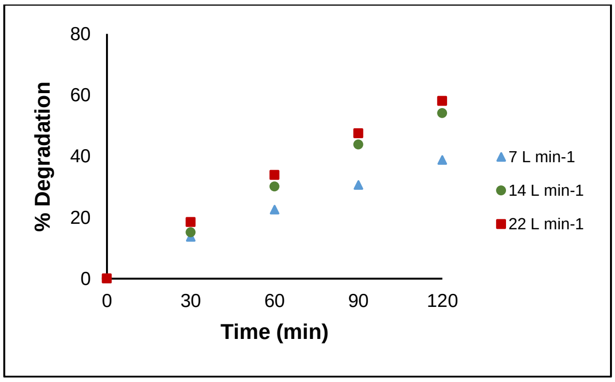

Figure 4. % of degradation of three feed flow (*Q*) studied in electrochemical treatment (DiaClean® cell), 7, 14 and 22 L min^{-1} in continuous mode. Conditions: 30 mA cm^{-2}, 5 mg L^{-1} of phenol red, 0.05 M Na_2SO_4, 3 L.

Figure 4, shows the percentage degradation of phenol red with different feed flow obtained 38.7%, 54% and 58% of degradation after 120 minutes in 7, 14 y 22 L min^{-1} respectively. As can observed in figure 4, the highest percentage of degradation is obtained with the feed flow of 22 L min^{-1}, which presents less time electrode contact than the other two flows. However, Rodriguez-Peña et al., 2019, report that the feed flow of 7 L min^{-1} (longer contact time with electrode) present major degradation of nonylphenol (initial concentration = 50 mg mL^{-1}) than the 14 and 22 L min^{-1}, applying a current density of 30 mA cm^{-2}. Armijos-Alcocer et al., 2017, studied the degradation of nonylphenol ethoxilate-7 (initial concentration = 500 mg mL^{-1}), using a feed flow of 12.6 L min^{-1} and 40 mA cm^{-2} of current density. This mean that degradation of contaminants depends of the structure of compound, the initial concentration and the current density applied, which change the feed flow for each case. [27, 28].

3.5 Coupled treatment ozone-electrochemical oxidation (DiaClean® cell) in continuous mode

The coupled treatment ozone-electrochemical oxidation (Diaclean® cell) in degradation of phenol red was carry out using de optimal conditions studied in previous treatments, which are current density 30 mA cm^{-2}, 9.4 mg O_3 L^{-1} and feed flow 22 L min^{-1}. Figure 5 b), shows the absorbance spectrum of degradation of phenol red in a coupled treatment ozone-electrochemical oxidation (DiaClean® cell) in continuous mode, there is a significant decrease in absorption bands in the first two minutes of treatment reaching 88.9% of degradation as show in figure 5 a), continuing until 12 minutes where the band remains constants obtaining the maximum degradation of 95.5% till 30 minutes.

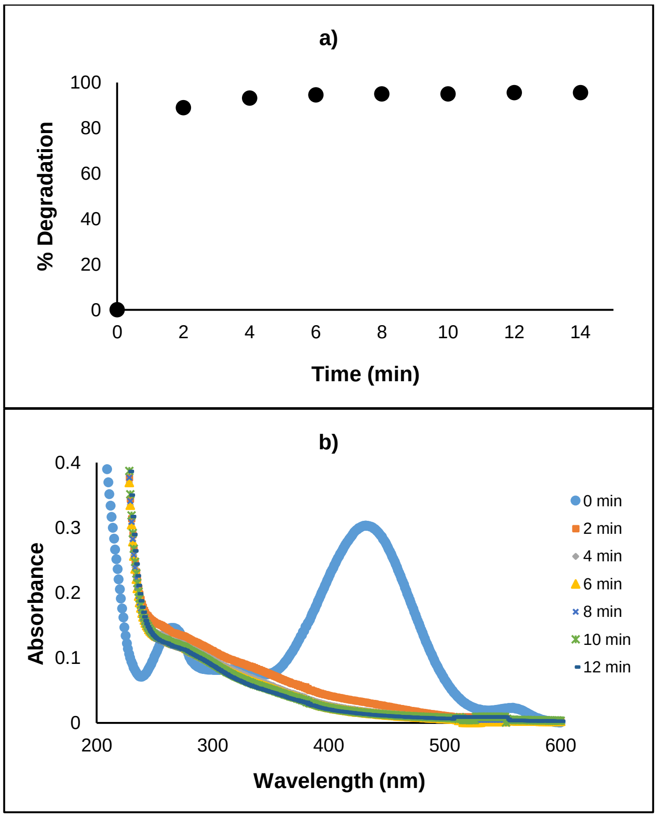

Figure 5. a) % of degradation of phenol red at λ_{max} (432 nm), and b) Absorbance Spectrum of the coupled treatment ozone-electrochemical oxidation (DiaClean® cell) in continuous mode. Conditions: 30 mA cm^{-2}, 5 mg L^{-1} of phenol red, 0.05 M Na_2SO_4, 9.4 mg O_3 L^{-1}, 22 L min^{-1}.

The difference in degradation of phenol red in coupled system in batch and continuous mode is significant, due the time to reach 95% of degradation in continuous system is needed 12 minutes (3 L of solution) and for batch system to reach 99% is needed 30 minutes (1 L solution), in addition, the COD removal increased, since in electrochemical and coupled ozone-electrochemical (DiaClean® cell) treatment in continuous mode reaches the 38.4% in 120 minutes and 46% in 30 minutes respectively.

3.6 Kinetics of degradation

The kinetic behavior of ozonation, electrochemical and coupled treatment in degradation of phenol red in batch mode was adjusted to a first order model (Eq. (2) and (3)).

$$r = -\frac{dA}{dt} = kA \qquad (2)$$

Where: A, absorbance (u. a.), t, time (min) y k (min^{-1}) rate constant.

Integrated equation: $$ln\left(\frac{A_0}{A_t}\right) = kt \qquad (3)$$

Kinetics degradation was analyzed from absorbance spectrum to λ_{max}= 432 nm. Figure 6 shows the kinetics degradation in ozonation and coupled ozone-electrochemical oxidation treatment with a rate constant of 0.0147 and 0.149 min^{-1} with a R^2 of 0,97 and 0,99 respectively.

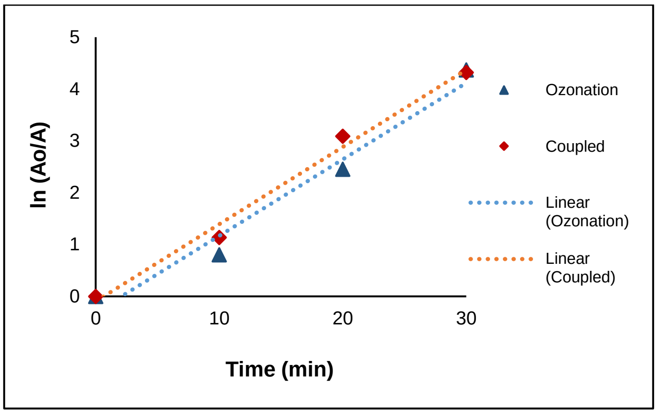

Figure 6. Kinetics of degradation in ozonation (9.4 mg O_3 L^{-1}) and coupled ozone-electrochemical oxidation treatment in batch mode (30 mA cm^{-2}, 5 mg L^{-1} of phenol red, 0.05 M Na_2SO_4, 9.4 mg O_3 L^{-1}) in 30 minutes of treatment respectively.

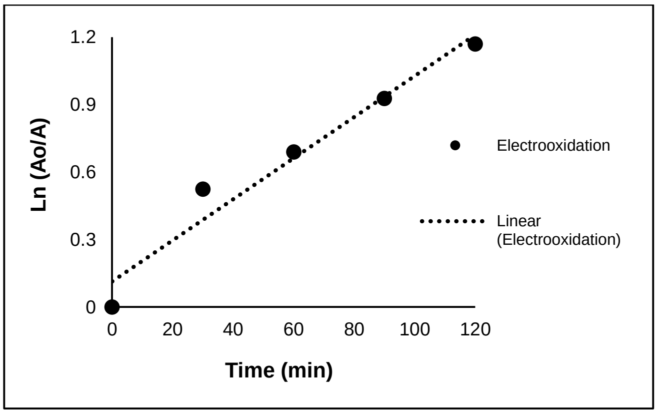

Figure 7. Kinetic of degradation in electrochemical oxidation treatment in batch mode (30 mA cm^{-2}, 5 mg L^{-1} of phenol red, 0.05 M Na_2SO_4) in 120 minutes of treatment.

Figure 7, shows the kinetic of degradation in electrochemical oxidation with a constant rate of 0.009 min^{-1} an a R^2 of 0.96.

3.7 By-products of degradation

Samples of each treatment were analyzed in an ionic chromatographic equipment. The main final products were fumarate ($[C_4H_2O_4]^-$) and acetate ($[C_2H_3O_2]^-$). The formation of fumarate was observed in coupled treatment ozone-electrochemical oxidation in batch mode, DiaClean® cell and coupled treatment ozone-DiaClean® cell in continuous mode in 30, 180 and 30 minutes respectively. Fumarate is the dissociate specie of fumaric acid, which indicates that carboxylic acids are being reached, therefore, biodegradable compounds are present in the treated solution.

In all the analyzed samples of each treatment, acetate formation was found in high concentrations, this behavior is attributed to the degradation of ethanol which is used as phenol red solvent and is present in aqueous solution.

4. CONCLUSIONS

The degradation of phenol red in aqueous solution in electrochemical oxidation, ozonation and coupled system was studied in batch and continuous mode. The optimal operating conditions was current density (j) 30 mA cm^{-2}, 9.4 mgO_3 L^{-1} and feed flow (Q) 22 L min^{-1}. The electrochemical oxidation (DiaClean® cell) treatment coupled with ozone was the more efficient treatment obtaining a 95.5% UV-Vis absorption in 12 minutes of treatment, reaching a 46% of COD removal in 30 minutes. The main products formed in the degradation of phenol red were acetate and fumarate.

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