



Prediction of H_2O_2 Electrogeneration on a RVC Cathode in a Parallel-Plate Cell for Treatment of Industrial Effluents

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Abstract

A parallel-plate cell was built to electrochemically generate H_2O_2 using two sizes of reticulated vitreous carbon (RVC) as cathode and stainless steel mesh as anode. It was possible to predict H_2O_2 electroproduction on a RVC cathode in a parallel-plate cell according to Faraday's law. Two RVC cathode lengths were evaluated. For the small RVC cathode (1.25 x 5 x 1 cm) different current values were evaluated. From this experimental setup, the optimal current obtained was 80 mA achieving H_2O_2 production efficiency of 81%. Experimental results were compared with theoretical results and it was found that the model fitted the experimental results fairly well (variation 0.5%). For the large RVC cathode (2.5 x 5 x 1 cm), another set of different current values was evaluated. From this experiment, the optimal current was determined to be 170 mA with an H_2O_2 production efficiency of 54%. These experimental results were also compared with theoretical results generating also a fairly good fit between them (variation 1.5%). Finally, using the large RVC cathode the removal of the dye BB9 (0.08 mM) was evaluated, 94% discoloration was achieved after 15 min of electrolysis and 90% of COD was achieved after 60 min.

Key words: Prediction, H_2O_2 production, parallel-plate cell, RVC design, BB9.

1 Introduction

The wastewater from the textile industry is characterized by the high amount and persistence of its contaminants. Textile industries generate effluents which are characterized by strong color, high COD and wide pH variation. When color is due to the presence of reactive dyes, it is an environmental problem because reactive dyes are usually difficult to biodegrade and they can remain in the environment for an extended period of time [1-3]. Electrochemical treatments are among of the most important oxidation processes because of their versatility, environmental compatibility and effectiveness in degrading different organic pollutants [4]. One of the methods used for treating industrial effluents containing organic pollutants, especially dyes used in the textile sector, is by using H_2O_2 as oxidizing agent [5-8].

Hydrogen peroxide is considered to be an environmentally friendly chemical; since it leaves no hazardous residues as other oxidants do [9-14]. It is a powerful and versatile chemical, since it reacts both as reducer and as oxidant. It is effective throughout the pH range, has high oxidation potential and, being a liquid, is easier to use [3,15-17]. For all these properties, H_2O_2 is used in a large number of applications, such as in pulp, paper and textile bleaching, chemical synthesis, metallurgy, electronic industry, water disinfection and detoxification of industrial effluents [18-22]. It has been reported that H_2O_2 can be electrochemically generated by reducing dissolved oxygen in acidic solutions [9,14]. The generated H_2O_2 can be coupled with Fe^{2+} to produce Fenton's reagent for either degradation or synthesis of organic compounds [23-25].

Electroproduction of Fenton reagent involves two electrode processes, resulting in hydrogen peroxide production at the cathode and evolution of oxygen at the anode [21]. Reticulated vitreous carbon (RVC), carbon, graphite felt or gas diffusion electrodes are used in H_2O_2 electrogeneration process [26]. These electrodes have been used in a variety of applications ranging from fuel cells to

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water and wastewater treatment and several studies focused on the carbon layer structure and the addition of catalyst to favor a particular reaction have been conducted [12]. RVC is a useful electrode material, particularly where high current densities, low electrical/fluid flow resistance, minimal cell volume loss to electrodes and large capacity to hold infused materials within controlled pore sizes are required. RVC has low density, low thermal expansion, high corrosion resistance and high thermal and electrical conductivities. It is an open-pore foamy material of honeycomb structure composed solely of vitreous carbon with exceptionally high void volume, high surface area, rigid structure and very high resistance to temperatures in non-oxidizing environments [13]. The skeletal structure of the material is brittle and needs support and its low volumetric carbon content means that care has to be taken to ensure uniform potential and current distribution through the material. For all these characteristics, RVC has been considered a good cathode material in H_2O_2 electrochemical generation [14]. This electrochemical technique leads to the chemical degradation of organic pollutants. The huge production rate of synthetic dyes and their intensive usage in the textile and other industries generates large quantities of colored wastewaters [27-28].

In this study, simulated and experimental H_2O_2 generation was conducted using a RVC cathode in a parallel-plate cell to estimate the H_2O_2 concentration achieved. Influential parameters such as cathodic potential, oxygen purity and mass flow rates, cathode surface area, pH of the solution and inert supporting electrolyte concentration were systematically examined during the experimental procedures and contrasted against the simulation results. Moreover, the performance of a parallel plate electrochemical cell that can activate H_2O_2 to oxidize organic molecules in toxic industrial effluents was also determined in this study. A series of tests were conducted in order to evaluate the oxidation of organic dye BB9.

2 Materials and Methods

2.1 Electrochemical modeling

The electrochemical model used is mainly based on the hypothesis that the electrochemical cell always works in steady state and that the main electrochemical oxidation and reduction reactions are those depicted in Eq. (1) and (2). Electrochemical reactions (shown in Figure 1) were used to develop the model considering the following conditions: 1) the potential difference applied corresponds to the limiting current observed; and 2) the electrochemical reactions selected are the only ones that occur, therefore, the most important electrochemical transformation can be evaluated by Faraday's law [7-9].



2.2 Electrochemical experimental setup

Electrolysis were carried out using a potentiostat (AMEL 2051) coupled to a programmable function generator connected to the electrochemical cell. The electrochemical cell, also known as electrochemical cell,

reproduces a parallel-plate cell model. This type of reactor is the most common in the industry because of its numerous advantages such as: easy construction and assembly, variety of fabrication materials, uniform potential distribution, ease of operation, scaling up potential, different electrode configurations, simple electrical connections, and mass transport control [19]. The hydraulic circuit and the flow-cell of the reactor used are very similar to that showed elsewhere [21], see Figure 2.

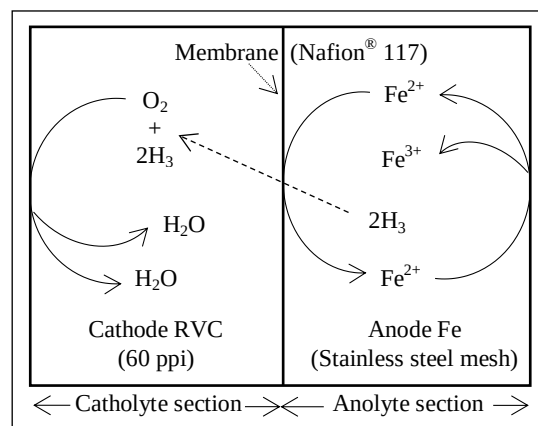


Figure 1: Main electrochemical reactions carried out in the electrochemical cell. Anolyte: 1L 0.8 M H_2SO_4 and Catholyte: 1L 0.05 M Na_2SO_4 at pH $\approx$ 2 with O_2 feed.

The electrochemical cell is coupled to a hydraulic circuit which includes a pair of glass containers [13,14]; one for the anolyte and one for the catholyte, both having a volume of 1000 mL. The connections of the components of the circuit are made with hose and valves. During the electrolysis, oxygen was dosed in the catholyte to keep it saturated of oxygen. Hydrogen peroxide released in the reaction was measured by titration with permanganometric method (KMnO_4). Flow rate through the reactor was 10 Lmin^{-1} for both catholyte and anolyte. Finally, a potential difference was applied to the cell in order to start the electrolysis (by a potentiostat BK Precision®).

The electrochemical cell prototype is constituted by four blocks of acrylic. Between them, a rubber gasket (hydraulic seal) was placed to prevent leakages. The blocks of acrylic (12 x 26 x 1 cm) were assembled with screws. Likewise, the electrochemical cell is divided into two compartments (cathodic and anodic compartments) in which the cathode and anode are placed, respectively. Both compartments are separated by a membrane (Nafion® 117) in order to avoid the mixture of the anolyte and catholyte fluids in the cell. However, due to its permeable capacity, the membrane allowed cations flux. What was intended is that protons of the anolyte, due to their high concentration, migrate to the catholyte compartment through the membrane surface. Anolyte and catholyte were kept in circulation by pumps (Iwaki Magnet Pump). Each compartment has inlets and outlets to allow fluids to flow from and to it. Moreover, each electrode has a feeder for power supply connection. The flow-cell setup used is very similar to that proposed by Alvarez-Gallegos and Pletcher [14], see Figure 3.

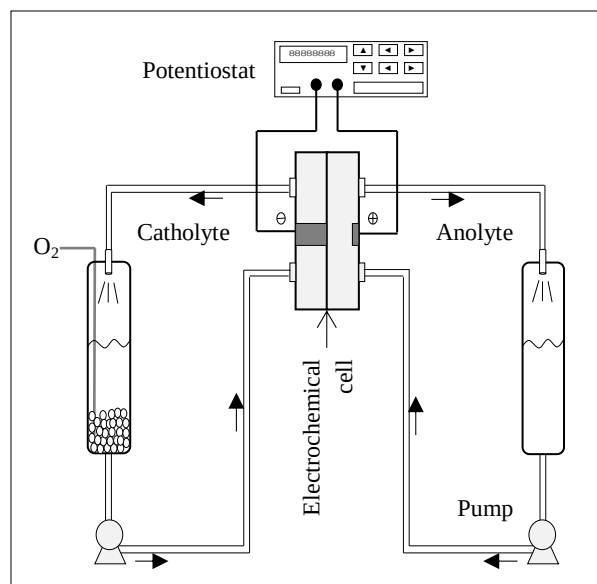


Figure 2: Hydraulic structure of the electrochemical cell

2.3 Electrode design

Reticulated vitreous carbon (RVC), 60 pores per linear inch (ppi) (Electrolytica Inc., NY), having a specific surface area of $40 \text{ cm}^2 \text{ cm}^{-3}$ was selected as the cathode material. The design was based on a cube-like shape having various dimensions (thickness, width and length). The width of the electrode is not a particularly troublesome parameter. However, the width of the electrode is linked to the cross sectional area A_x of the reactor canal and this parameter is related to the linear velocity of the electrolyte. According to Figueroa et al [21], a cross sectional area of 0.0005 m^2 was considered. From the width $\times$ thickness = cross sectional area relationship, an electrode width of 0.05 m and an electrode thickness of 0.01 m were considered. Once the dimensions (thickness and width) of the tridimensional electrode were selected, the production of hydrogen peroxide was conducted by the passage of the (oxygen saturated) electrolyte through the tridimensional electrode. The dissolved oxygen takes the electrons available on the electrode surface to convert into hydrogen peroxide [14]. Thus, the production of hydrogen peroxide is a function of the length of the electrode. For this reason, various RVC cathode lengths were evaluated.

A small RVC cathode ($1.25 \times 5 \times 1 \text{ cm}$) and a large RVC cathode ($2.5 \times 5 \times 1 \text{ cm}$) were evaluated. Superficial cathode area in the direction of current flow was 6.25 and 12.5 cm^2 , respectively. For the small RVC cathode, the following current values were evaluated: 60, 80, 100, 120 and 140 mA, with variable voltage. In the case of the large RVC cathode, another set of different current values were tested (170, 180, 190, 200 and 250 mA) with variable voltage. The potential applied to initiate the electrolysis was 2.0 V, and since the current remained constant, the applied potential was increased to 3.0V after 180 min for both RVC. Different currents were evaluated for different concentrations of H_2O_2 and the optimal current values were determined based on the efficiency gains. The RVC electrode was attached to stainless steel, the rest of the

collector's surface was isolated by insulating paint in order to ensure that all the current went to the RVC electrode. The cathode was placed in one of the acrylic blocks, as shown in Figure.4.

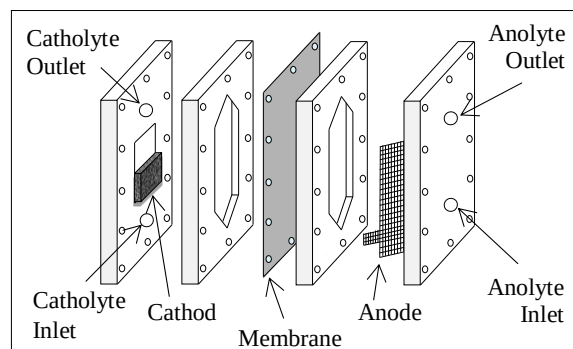


Figure 3: Electrochemical cell comprising a membrane, a cathode RVC and a stainless steel anode

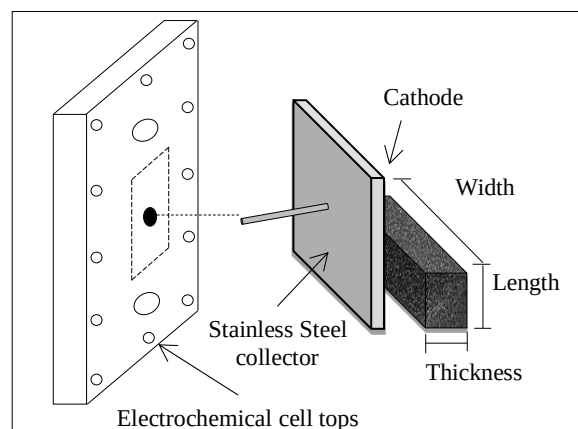


Figure 4: RVC cathode attached to a stainless steel collector using carbon glue, the rest of the collector was painted in order to isolate it and placed in an electrochemical cell top

Stainless steel mesh (304 SS, $10.5 \times 6.5 \text{ cm}$) with a slash to connect it to the power supply was selected as the anode material with the position near the membrane, between two gaskets, so the anode is placed a few millimeters away from the RVC cathode. Said material is characterized by its high resistance to corrosion and its low cost.

2.4 Oxidation of industrial effluents

Electrolytes were prepared for electrolysis purposes in order to evaluate the electrogeneration of H_2O_2 . The catholyte was constituted by: 1L of 0.05 M Na_2SO_4 at $\text{pH} \approx 2$, adjusted with H_2SO_4 . The anolyte contained 1L of 0.8 M H_2SO_4 . Since high electrolyte concentrations are not usually feasible for effluent treatment by H_2O_2 electrogeneration, the inert supporting electrolyte (i.e., Na_2SO_4) was used only at the low concentration described earlier [3]. For dye degradation, 0.001 M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added to the catholyte to activate H_2O_2 . Synthetic wastewater was prepared using organic azo dyes (distributed by Ciba Specialty Chemicals). A concentration

of 0.08 mM BB9 was evaluated for discoloration using the electro-assisted Fenton reaction. The discoloration was observed by absorbance in a spectrophotometer (Thermo Scientific Genesys 10UV). Finally energy consumption (E_w , in WhL^{-1}) was calculated from Eq. (3), taking into account the electrolysis time ($t_{\text{electrolysis}}$, in h), assuming an average cell current (I_{Cell} , in Amperes), cell voltage (E_{Cell} , in Volts) and the volume of catholyte ($V_{\text{Catholyte}}$, in L).

$$E_w = \frac{(E_{\text{Cell}})(I_{\text{Cell}})(t_{\text{electrolysis}})}{V_{\text{Catholyte}}} \quad (3)$$

This approach could be attractive for effluent treatment because of its low energy consumption for color removal in industrial effluents [21].

3 Results and Discussion

3.1 Electrochemical predictive model

The hypothesis was that the electrochemical cell works in a steady state, where the parameters do not vary with time and thus the volumetric flow (m^3s^{-1}) is constant. The initial concentration of the electroactive species decreases as a function of the electrode length and the current observed anywhere in the electrode corresponds to the limit current. Under mass transport limitations, the overall performance of a cell can be written in terms of the average mass transport coefficient, k_{m,O_2} , as described in Eq. (4):

$$I(H_2O_2)_L = 2F A_e V_e k_{m,O_2} c_{O_2} \phi \quad (4)$$

Where $I(H_2O_2)_L$ is the limiting current (amperes) for H_2O_2 production; F is the Faraday constant ($96,485 \text{ C mol}^{-1}$), A_e is the specific area ($4000 \text{ m}^2\text{m}^{-3}$) and V_e the specific volume (thickness x width x length) of the RVC cathode, c_{O_2} is the O_2 concentration, k_{m,O_2} is the mass transport coefficient for O_2 , and ϕ is the current efficiency for H_2O_2 production [14,19]. Modeling the production of H_2O_2 aims to predict the amount of H_2O_2 accumulated during a given time. The amount of H_2O_2 obtained is represented by Faraday's law [19], Eq. (5) as:

$$m_{H_2O_2} = \frac{q\phi}{2F} \quad (5)$$

Where $m_{H_2O_2}$ is the amount (moles) of H_2O_2 when the electrolyte saturated with O_2 passes through the length of the three-dimensional electrode; q is the theoretical charge (in coulombs) passed through the cell and ϕ is the current efficiency for hydrogen peroxide production. Combining Eq. (4) and Eq. (5), H_2O_2 production is obtained as a function of the residence time in Eq. (6). The residence time along the electrode is equal to the electrode length divided by the linear velocity of the electrolyte. We thus obtain Eq. (7):

$$m_{H_2O_2} = t A_e V_e k_{m,O_2} c_{O_2} \phi \quad (6)$$

$$m_{H_2O_2} = \frac{L}{v} A_e V_e k_{m,O_2} c_{O_2} \phi \quad (7)$$

Where: t is the electrolysis time. The rest of the parameters have already been defined. The electrogeneration of H_2O_2 is simulated through O_2 concentration. During the passage of an O_2 saturated aqueous solution through a 60 ppi RVC cathode, O_2 is reduced as a function of the length of the electrode, while H_2O_2 and H_2O are concurrently generated [19]. For instance, a RVC piece may be hypothetically divided into five 0.5 cm long segments. The parameters of each segment being the same, and the volume of each segment being $0.5 \times 5 \times 1 \text{ cm}$, O_2 concentration progressively diminishes from the first to the last segment (see Figure 5).

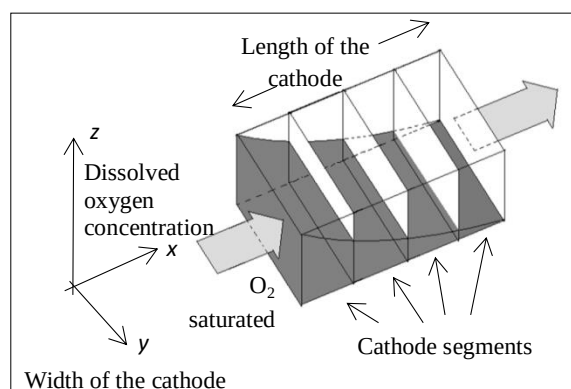


Figure 5: Simulation of H_2O_2 electrogeneration through O_2 reduction

3.2 Experimental electrochemical tests

After obtaining the theoretical results, experimental tests were performed. H_2O_2 electroproduction was carried out in a parallel-plate electrochemical cell divided by a cationic membrane (Nafion® 117) by means of O_2 reduction in the RVC (60 ppi) cathode. The catholyte was kept saturated with industrial oxygen. The anolyte and catholyte fluids remained constant (10 Lmin^{-1}) and were kept at room temperature and under atmospheric pressure. Samples (10 mL) were taken every 30 minutes, and H_2O_2 concentration was immediately determined by the permanganate method ($KMnO_4$) during an electrolysis total time of 180 min. Experiments were performed with different currents and two different-sized RVC cathodes, as stated in section 2.3. The water reaches the bottom of the cover and passes through the cathode and continues its journey to the top of the plate. The efficiency in the production of hydrogen peroxide was evaluated by means of the relation between the theoretical and experimental slopes as shown in Eq. (8).

$$\text{Efficiency} = \frac{\text{Experimental.slope}}{\text{Theoretical.slope}} \times 100 \quad (8)$$

The experimental slope was obtained by plotting the electrogenerated H_2O_2 concentration as a function of the charge (q). In every electrolysis experiment, the slope was

assessed by the least-squares method [19]. The theoretical slope is related to current efficiency by the production of hydrogen peroxide according to Faraday's law (Eq. 9):

$$m = cV = \frac{It}{nF} \quad (9)$$

Where m is the number of moles of H_2O_2 ; n the number of electrons transferred (2 electrons in this case); I is the current (amperes); t is the time (sec); c is the molar concentration of H_2O_2 ; V is the volume (liters) and q is the electrical charge (C). Faraday's law can be represented as a straight line with a positive slope $\left(\frac{1}{VnF}\right)$, intercepting the origin in the m versus q plane (Eq. 10). This equation is a straight line: $y = a + mx$, where the intercept (a) is zero and the slope (m) is $\left(\frac{1}{VnF}\right)$.

$$c = \left(\frac{1}{VnF}\right)q \quad (10)$$

Figure 6 shows the main results of the production of H_2O_2 as a function of the current applied in the electrochemical cell using the small RVC cathode ($1.25 \times 5 \times 1$ cm). The total amount of electrogenerated hydrogen peroxide was at the catholyte after 180 min of electrolysis. The influence of current on time-dependent changes of H_2O_2 concentration can be observed. By increasing current density, H_2O_2 generation rate increased mainly due to a greater charge passed into the cell. Indeed, H_2O_2 concentration accumulated in the solution is roughly proportional to applied current, and current at the beginning of the process is the same for all the processes.

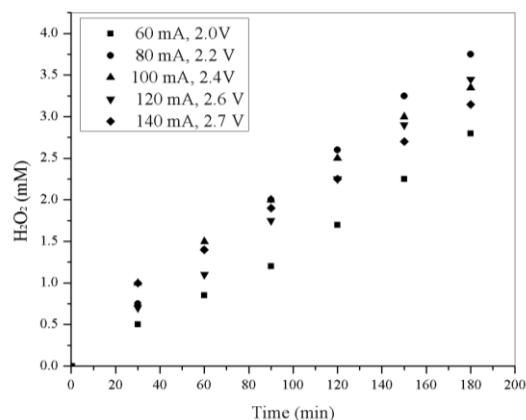


Figure 6: Electroproduction of hydrogen peroxide in an electrochemical cell, using the small 60 ppi RVC cathode ($1.25 \times 5 \times 1$ cm) and stainless steel anode, Catholyte: 1 L 0.05 M Na_2SO_4 , pH $\approx$ 2 and Anolyte: 1 L 0.8 M H_2SO_4 .

Figure 7 shows the different amounts of H_2O_2 generated with different applied currents using the large RVC cathode ($2.5 \times 5 \times 1$ cm). It is significant that the greatest amount of H_2O_2 was observed by applying a current of 180 which is very similar to applying a current of

170 but with the latter the highest efficiency of the four evaluated currents was obtained. For both RVC volumes, when $\Delta E_{cell} < 2$ Volts was applied, little current was observed but H_2O_2 was not detected, being probably under the limit of detection of the permanganate method. Under the condition: $2\text{Volts} < \Delta E_{cell} < 3\text{Volts}$, some current was observed and H_2O_2 concentration was detected. Besides, electrode thickness is important because, as it increases, potential drop (ΔE , in volts) through the electrode also increases.

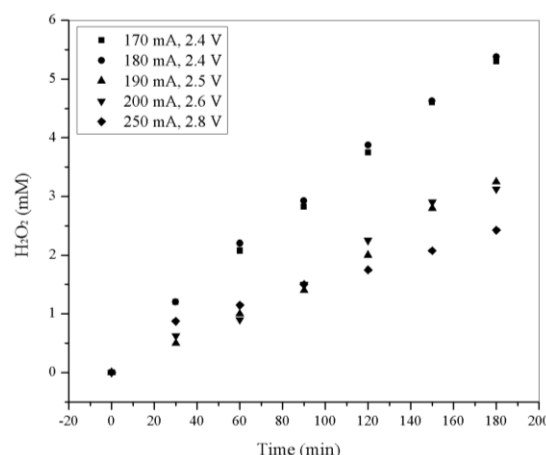


Figure 7: Electroproduction of hydrogen peroxide in an electrochemical cell using the large 60 ppi RVC cathode ($2.5 \times 5 \times 1$ cm) and stainless steel anode, Catholyte: 1 L 0.05 M Na_2SO_4 , pH $\approx$ 2 and Anolyte: 1 L 0.8 M H_2SO_4 .

The efficiency of every current applied for the two cathodes tested was obtained and the results are presented in Table 1. According to Table 1, when using the small RVC cathode ($1.25 \times 5 \times 1$ cm), the higher efficiency was obtained at 80 mA generating a concentration of 3.75 mM H_2O_2 , this current value being considered optimum. Using the large RVC cathode ($2.5 \times 5 \times 1$ cm), the highest efficiency was achieved at current value of 170 mA. The generated H_2O_2 concentration was 5.3 mM. In this case the optimal current was 170 mA (the same current was used for prediction).

Figure 8 shows the comparison among experimental and theoretical data for H_2O_2 production under the experimental conditions tested using the small RVC cathode ($1.25 \times 5 \times 1$ cm). H_2O_2 was accurately predicted by the model with an error rate of 0.5%.

Figure 9 shows the comparison among experimental and theoretical data for H_2O_2 production using the large RVC cathode ($2.5 \times 5 \times 1$ cm). Theoretical results generated with the model fitted reflect experimental trends fairly close (1.5% error rate). Both error values are considered small so it can be said that it is feasible to predict H_2O_2 electrogeneration by Faraday's law [15]. Moreover, it was found that electrode thickness was important because as it increases, the potential drops (ΔE , in volts) through the electrode. In order to oxidize the organic matter, activating H_2O_2 in presence of Fe^{2+} ions is required to produce Fenton's reagent. Thus, H_2O_2 will activate immediately after being electrogenerated.

The amount of active H_2O_2 was evaluated with the concentration obtained experimentally. It was found that about 90% of the generated H_2O_2 is activated to act as a powerful oxidant. According to previous reports [1], hydrogen peroxide production and current efficiency were higher in alkaline solution. However, as regards wastewater application, it is worth noticing that the efficiency is quite good even in acidic conditions because the electrolyte increases the pH level in the reaction zone, enhancing thus H_2O_2 formation [10,15].

3.3 Oxidation of a synthetic effluent

After predicting and evaluating H_2O_2 generation, the second stage of this work was to assess the oxidation of organic compounds through the electro-assisted Fenton process. The Fenton reaction was carried out in the cathodic compartment where electro-generated H_2O_2 reacted with the organic compounds in the presence of $\text{Fe}^{2+}/\text{Fe}^{3+}$ added as catalyst (Friedrich et al. 2004). The catholyte was constituted by 0.05 M Na_2SO_4 , 0.001M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (to activate H_2O_2), and 0.01 M H_2SO_4 (to ensure solution $\text{pH} \approx 2.0$) with O_2 feed. The anolyte was prepared using the above mentioned amount but with 0.8 M H_2SO_4 . In this study, it is recognized that the chemical interaction between H_2O_2 and $\text{Fe}^{2+}/\text{Fe}^{3+}$ produces a strong intermediate oxidant (FeO^{2+}) that is responsible for the organic oxidation.

Using the higher surface area cathode ($2.5 \times 5 \times 1$ cm), BB9 dye removal was evaluated (simulating an industrial effluent, this dye was used because it is the most common in jeans dyed fabrics). According to Eq. (1), one mole of H_2O_2 may accept up to two moles of electrons from the organic matter available to be oxidized. This means that the process may range from a highly selective oxidation in organic electro synthesis to the oxidation of the organic matter.

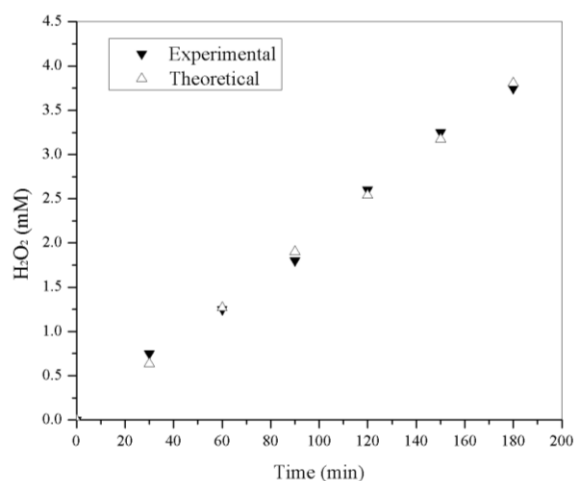


Figure 8: Concentration of hydrogen peroxide vs. electrolysis time for experimental and theoretical data using the small RVC cathode ($1.25 \times 5 \times 1$ cm) and stainless steel anode. Catholyte: 1 L 0.05 M Na_2SO_4 , $\text{pH} \approx 2$ and Anolyte: 1 L 0.8 M H_2SO_4 .

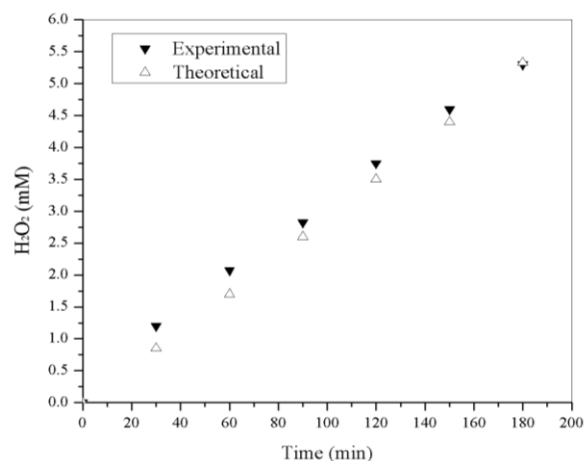
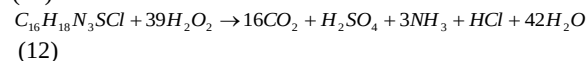
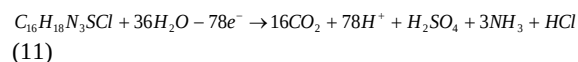


Figure 9: Concentration of hydrogen peroxide vs. electrolysis time for experimental and theoretical data using the large RVC cathode ($2.5 \times 5 \times 1$ cm) and stainless steel anode. Catholyte: 1 L 0.05 M Na_2SO_4 , $\text{pH} \approx 2$ and Anolyte: 1 L 0.8 M H_2SO_4 .

According to Eq. (11), it may be hypothesized that BB9 will lose 78 electrons during its oxidation. Furthermore, considering Eqs. (1) and (11), the theoretical amount of H_2O_2 required to mineralize BB9 can be calculated using Eq. (12).



If the amount of H_2O_2 required to discolor a certain quantity of BB9 is known, a stoichiometric equation could be established. Because the concentration of H_2O_2 generated and active within the reactor is known (4.8 mM), the amount of BB9 to be oxidized was determined. According to Figure 7 for large cathode, the greatest amount of H_2O_2 and the highest efficiency was observed by applying a current of 170 mA and the greater amount of H_2O_2 produced is 5.3. It was determined that about 90% of the H_2O_2 generated was activated H_2O_2 (it is estimated that 4.8 mM H_2O_2 were used to carrying out the discoloration process). The remaining 10% was not detected; possibly, the couple $\text{Fe}^{2+}/\text{Fe}^{3+}$ regeneration during the Fenton chemistry is not efficient due to chemical speciation. Other researchers report similar results [21].

The complete oxidation of BB9 in aqueous acidic solution involves 78 electrons and hence the stoichiometric conversion of 1 mol of BB9 requires 39 mol of H_2O_2 according Eqs. (9) and (10). The process generates and activates up to 4.8 mM of H_2O_2 , thus the maximum concentration of BB9 that can be eliminated is 0.12 mM. Therefore a lower concentration of 0.8 mM of BB9 was evaluated. From these experimental data, the following results were found: using a concentration of 0.08 mM BB9, 94% discoloration was achieved after 15 min of electrolysis using only 0.5 mM H_2O_2 , the theoretical charge was 145.8 C and 0.079 WhL^{-1} were consumed.

Table 1: Electrogenerated H_2O_2 efficiencies obtained for the different current values tested for the two RVC electrodes. Electrolysis was performed in a divided electrochemical cell (60 ppi 3D-RVC), stainless steel mesh anode and catholyte: 0.05 M Na_2SO_4 at $\text{pH} \approx 2.0$. Flow rate was 10 L min^{-1} , 180 min of electrolysis.

I_{cell} mA	ΔE_{Cell} Volts	q/C	H_2O_2 mM	Efficiency (%)	E_w Wh L^{-1}
RVC size: 1.25 x 5 x 1 cm					
60	2.0	648	2.8	79	0.360
80	2.1	864	3.75	81	0.504
100	2.3	1080	3.25	56	0.690
120	2.5	1296	3.45	50	0.900
140	2.7	1512	3.15	37	1.134
RVC size: 2.5 x 5 x 1 cm					
170	2.1	1836	5.3	54	1.071
180	2.2	1944	5.37	52	1.188
190	2.6	2052	3.25	30	1.516
200	2.7	2160	3.12	28	1.620
250	2.8	2700	2.42	15	2.100

Figure 10 shows spectra recorded for a solution. The discoloration was spectrophotometrically followed and the water was considered discolored when an absorbance $< 10\%$ of the original was achieved at the catholyte. During BB9 discoloration, the spectrum showed absorbance vs wavelength. Maximum absorbance was located at $\lambda_{\text{max}} = 665 \text{ nm}$. These results open a new perspective for further experiments with higher concentrations of BB9 and longer electrolysis time. To evaluate the oxidation organic, was determined by chemistry oxygen demand (COD), where it was found that at 40 min was obtained about 75% of reduction and 60 min was reduced to 90% using $2.0 \text{ mM H}_2\text{O}_2$.

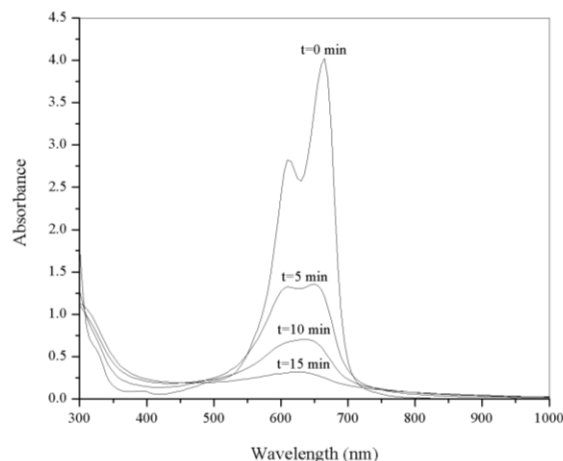


Figure 10: BB9 Degradation. Spectra recorded for solution (1L) containing 0.08 mM BB9 at $t=0 \text{ min}$ using the large 60 ppi RVC cathode ($2.5 \text{ cm} \times 5 \text{ cm} \times 1 \text{ cm}$). Both, stainless steel anode, Catholyte: $1 \text{ L } 0.05 \text{ M } \text{Na}_2\text{SO}_4$ $\text{pH} \approx 2$ and Anolyte: $1 \text{ L } 0.8 \text{ M } \text{H}_2\text{SO}_4$ with O_2 feed.

4 Conclusions

The electrochemical generation of H_2O_2 was verified experimentally and a predictive model based on the Faraday's law was developed. The experimental setup used included two different sizes of 60 ppi RCV cathodes and a stainless steel mesh anode using commercial oxygen to oxygenate the catholyte and several different voltage values were applied.

From experimental runs, the optimal current for the small RCV cathode was 80 mA , with a generation of $3.75 \text{ mM H}_2\text{O}_2$, i.e., an electrolysis efficiency of up to 81%. This trend was accurately predicted by the model with an error rate of 0.5%. With regard to the large RVC cathode, the optimal current was found to be 170 mA , twice as reported for the small RVC, with a H_2O_2 generation of 5.3 mM , i.e., a 54% efficiency. Theoretical results obtained with the model fitted this trend fairly well with a 1.5% error rate. Hydrogen peroxide concentrations were experimentally measured to determine the activated percentage. It was found that around 90% of the H_2O_2 generated may act as a strong oxidant.

It has been demonstrated that Fenton's reagent can be indirectly electroproduced in a flow-cell by cathodic reduction of dissolved oxygen on a RVC surface. Using a synthetic industrial effluent and the large RVC cathode, dye BB9 removal was evaluated and 94% discoloration was achieved after 15 min of electrolysis with 0.08 mM BB9 . Regarding COD, was reduced to 90% at 60 min.

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