Prediction of the Indirect Advanced Oxidation of Acid Orange 7 using a 3D RVC Cathode for H\textsubscript{2}O\textsubscript{2} Production in a Divided Electrochemical Reactor

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Abstract: A three dimensional reticulate vitreous carbon piece is used to design an electrode for the cathodic O\textsubscript{2} reduction reaction in a divided (by a Nafion\textsuperscript{117} membrane) parallel plate reactor. The anode is a commercial stainless steel mesh. This approach allows producing H\textsubscript{2}O\textsubscript{2} at low energy (6.85 kWKg\textsuperscript{-1}H\textsubscript{2}O\textsubscript{2}) in a low ionic acidic medium (0.05M Na\textsubscript{2}SO\textsubscript{4}, pH 2). Under these conditions the H\textsubscript{2}O\textsubscript{2} can be activated, in the presence of 1 mM Fe\textsuperscript{2+}, as soon as it is produced to develop the Fenton Reagent. It is found that Acid Orange 7 indirect oxidation (in the concentration range of 0.07 to 0.19 mM) by Fenton process follows a first order kinetic equation. From each experimental AO7 oxidation the main parameters (a, mM and k, min\textsuperscript{-1}) of the first order kinetic equation are obtained. These parameters can be correlated with AO7 concentration in the concentration range studied. A semi-empirical chemical model to predict AO7 degradation, in the electrochemical reactor, can be developed taking into account the main equations derived from experimental data. The prediction of the main parameters (H\textsubscript{2}O\textsubscript{2} electro-produced, oxidation rate, energy required, electrolysis time) shows good agreement with the experimental data. Therefore, it was found that 1.83 kWhm\textsuperscript{-3} are needed to oxidize 0.191 mM AO7 in 3h. The chemical model can be used to predict both time and the energy required to treat a textile effluent with a variable pollutant organic load.

Keywords: Reticulated vitreous carbon, O\textsubscript{2} Reduction, Acid Orange 7, Fenton process, Parallel plate reactor.

1. INTRODUCTION

The main work in the textile industry is the conversion of fibers into yarns, which are converted into fabrics that are finally pigmented. Each year roughly 9x10\textsuperscript{8} kg of 10,000 different dyes are produced and consumed globally in wet processing operations [1-4]. Dye concentrations are in the range from 10 to 10,000 mg/L depending on the process. Approximately, 15% of the dye production is lost during the synthesis and dyeing operations [5-7]. No wonder textile industry is one of the most important sources of colored effluent discharges. As a result, the generation of contaminated wastewater can cause environmental problems unless properly treated before its disposal. In general, Industrial wastewater treatments are mainly focused to primary and secondary processes. However, such conventional treatment systems are not very effective in removal of color and other organic pollutant [8].

Moreover, dye chemical structures are very stable to sun-light, biological activity and hence not readily removed by conventional treatments (such as physical, chemical and biological processes). Therefore, the advanced oxidation processes (AOP) are among the most promising techniques for the environmental destruction of organic dyes in textile effluents due to the generation of very reactive radicals. In this work the acid orange 7 (AO7) is chosen as model pollutant. AO7 is widely used in wool textile dyeing, paperboard Industries and belongs to the azo dye group (characteristic by the chromophore –N=N–) used in textile industries. Recently, several AOP based technologies have been applied to oxidize textile effluents containing different AO7 concentrations. Among them it can be mentioned the synergistic effect of an electrochemical process coupled with peroxydisulfate, activated with ferrous ions as source of radicals (SO\textsubscript{4}*), to oxidize 0.1 mM AO7 in 60 minutes [9]. In other study, the kinetics of AO7 discoloration by means of SO\textsubscript{4}* radicals were as well investigated [10]. In the same way, a powerful reduction agent, zero-valent aluminum (2g L\textsuperscript{-1}), was coupled with ultrasonic irradiation (20 kHz, 300W), as source of OH* radicals, to oxidize 0.057 mM AO7 in 30 minutes [11]. The energy recuperation from 0.6 mM AO7 aqueous solutions, by means of a microbial fuel cell coupled with an aerobic system while the textile effluent was been treated, was as well documented [12].
The objective of this work is to develop a simple semi-empirical chemical model to predict AO7 oxidation in the range of 0.07 to 0.19 mM by means of Fenton reaction. A three dimensional reticulate vitreous carbon (RVC) piece is used to design an electrode for the cathodic O2 reduction reaction in a divided parallel plate reactor. This approach allows the production of H2O2 at low energy in a low ionic acidic medium. Under these conditions the H2O2 can be activated, in the presence of 1 mM Fe2+, as soon as it is produced to generate the Fenton reagent. Such conditions, and for a given electrolysis time, the amount of H2O2 produced/activated can be predicted by the Faraday’s law (from a straight line). Under the hypothesis that each activated mole of H2O2 will take two moles of electrons from AO7, the fraction of H2O2 activated provides a measure of the efficiency of the AO7 oxidation process. Taking into account that AO7 oxidation rate follows a straight line. Under the hypothesis that each activated mole of H2O2 will take two moles of electrons from AO7, the fraction of H2O2 activated provides a measure of the efficiency of the AO7 oxidation process.

2. THEORETICAL APPROACH

2.1. H2O2 Production

On carbon surface the oxygen reduction reaction (ORR) takes place simultaneously by both 4-electron and 2-electron pathways [13]. In a slightly acidic solution ORR on a RVC cathode surface will produce a mixture of H2O2/H2O in the reactor catholyte compartment, according to equations (1) and (2).

\[ O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \]  \hfill (1)
\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \]  \hfill (2)

H2O2 electro-production is normally assisted by O2 evolution on a Pt anode surface. However, it is possible to decrease the energy for H2O2 production if a low energy anodic reaction is chosen. Thus, on a Fe-anode the spontaneous electro-production of Fe2+ is expected in an acidic anolyte. But, under anode potential, Fe2+ can be oxidized to Fe3+, according to

\[ Fe^{2+} + e^- \rightarrow Fe^{3+} \]  \hfill (3)

Reaction (3) is a less energy demanding reaction than O2 evolution. An additional advantage of this approach is that iron ions are produced in the anolyte reactor side and they can be used, in future work, to develop the Fenton reaction by adding H2O2.

For a given electrolysis time \( t \), the amount of H2O2 is evaluated by the Faraday’s law considering the current efficiency \( f \), as depicted by equation (4).

\[ m_{H_2O_2} = \frac{I_{Cell} t}{2 F} \cdot \phi \]  \hfill (4)

Where \( m_{H_2O_2} \) is the number of moles of H2O2 produced on a RVC surface, \( I_{Cell} \) is the cell current (A), and \( F \) is the constant of Faraday (C mol\(^{-1}\)).

2.2. Fenton Reaction

The interactions of soluble iron cations (Fe\(^{II}\)/Fe\(^{III}\)) with H2O2 give a near-stoichiometric generation of a strong oxidant that is responsible for organic oxidation. This route is developed through a very complex chemistry and it is called Fenton process [14]. In 1934 it was proposed [15] the hydroxyl radical (OH•) as the most feasible strong oxidant. Since then OH• has been widely accepted while its existence is still controversial [16-18] and it was not settled satisfactorily. However, it is clear that such strong oxidant is capable of oxidizing organic pollutants in mild conditions. Under this approach different wastewater treatments [19-21] can be developed. The generation of H2O2 in acidic media can be represented by the following reaction:

\[ H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \]  \hfill (5)

In this way, the fraction of the organic conversion (or the fraction of the H2O2 activated by iron ions during the Fenton process) provides a measure of the efficiency of the oxidation process. This fact allows the use of a theoretical assessment of the efficiency of the AO7 oxidation process, as depicted by reaction (6):

\[ C_{10}H_{11}O_2N_2SNa + 34H_2O_2 \rightarrow 16CO_2 + NaHSO_4 + 2NH_3 + 36H_2O \]  \hfill (6)

Hence, the stoichiometric conversion of 1 mole of AO7 (MW= 350 g mol\(^{-1}\)) to CO\(_2\) requires up to 34 moles of hydrogen peroxide by considering that sulfur and nitrogen atoms are converted to HSO\(_4^-\) and NH\(_3\), respectively.

2.3. Prediction of Textile Effluent Discoloration

According to reactions (5) and (6), the theoretical oxidation of AO7 is a 68 electron oxidation reaction.
However, decolorizing a given AO7 amount requires only a small fraction of H₂O₂, as indicated by equation (5), because the color of the dyestuff is a function of the conjugated double bonds length in the aromatic molecule. The ring opening process should lead to an early discoloration in the oxidation process. However, the theoretical required amount of H₂O₂ for a discoloration of a given AO7 concentration is not easy to be found. But it can be experimentally determined in the electrochemical reactor by recording the evolution of the spectra (AO7 absorbance vs electrolysis time) at various stages during the oxidation process for a given AO7 concentration. From these experimental data and a calibration curve (AO7 concentration vs AO7 absorbance), it is possible to evaluate the required H₂O₂ concentration for a desired AO7 color abatement (or AO7 concentration). In fact, it is experimentally found that, for a given AO7 concentration the oxidation process lasts the required time to electro-produce the stoichiometric H₂O₂ amount in the electrochemical reactor, according to equation (6). The AO7 abatement follows an apparent first order kinetic equation and can be adjusted to the following linear equation (7):

\[
\ln[AO7]_t = -kt + \ln[AO7]_0
\]  

(7)

Where \(\ln[AO7]_t\) is the natural logarithm of the AO7 concentration (mM) at any time \(t\) during the electrolysis time, except for the first 10 minutes of AO7 oxidation, \(\ln[AO7]_0\) is the logarithm of a constant but it does not represent the initial AO7 concentration and \(k\) (\(\text{min}^{-1}\)) is the velocity constant of the reaction.

From a set of absorbance values vs electrolysis time, measured during the oxidation of different AO7 concentrations in the electrochemical reactor, it is possible to fit each experimental data to an apparent first order kinetic equation. Evidently, the absorbance values were first converted to concentration values by means of the Lambert-Beer law. From each experimental AO7 oxidation a pair of \(\ln[AO7]_0\) and \(k\) (\(\text{min}^{-1}\)) are obtained. These parameters can be correlated with AO7 concentration in the concentration range studied. In this way, for a given unknown AO7 concentration a pair of such parameters is obtained from the previous correlation. If such parameters are substituted in equation (7) and the time starts to increase, a theoretical AO7 oxidation is obtained as a function of the time. Except for the first minutes of the oxidation process, the AO7 concentration (or its absorbance) remaining in the solution can be predicted. Other useful information can be obtained as well, such as H₂O₂ electro-produced and the energy required at any time.

3. EXPERIMENTAL

3.1. Solutions and Chemicals

All aqueous solutions are prepared using laboratory tap water. The chemicals used in this work are reagent grade quality and used as received (Aldrich-Sigma or JT Baker). AO7, supplied by Ciba Specialty Chemicals, is used without further purification. The anolyte was 1 L of 0.8 M H₂SO₄, while the catholyte consisted of 1 L of 0.05 M Na₂SO₄ (pH 2, adjusted with H₂SO₄) plus a selected amount of AO7. The O₂ concentration in the catholyte was maintained constant by O₂ bubbling.

3.2. Electrodes and Cell

The electrochemical cell is a divided (by a Nafion® 117 membrane) parallel plate reactor, which is fully described elsewhere [22, 23]. However, its main features are described here. The cell is built with four acrylic pieces (to avoid leaks sheets of gaskets are collocated between them) and the channel dimensions are 10 cm x 5 cm. The cathode is a RVC (60 pores per inch, supplied by Electrolytica Inc. NY) machined to meet the required size (5 cm x 3.75 cm x 1 cm). The RVC electrode is glued to a stainless steel current collector surface by conductive silver epoxy (supplied by Pelco International) and the rest of the surface is insulated using insulator paint. The anode is a metallic gauze (10 cm x 5 cm) of commercial 304 stainless steel (304 SS). Its position is near the cation membrane, so the anode is placed a few millimeters away from the RVC cathode. Both electrolytes are pumped at a constant rate (7 liters per min). Electrochemical experiments are controlled by a direct current power supply (BK Precision) and the electrical charge, integrated from tabular data (current vs. time), is taken manually from a digital voltage display. Schemes of the reactor and hydraulic circuit are shown in Figures 1 and 2, respectively.

3.3. Procedures

Absorbance spectra of the withdrawn solutions with time are recorded by using a spectrophotometer (HACH® DR/4000 UV-Vis). The analysis of the electro-produced H₂O₂ is carried out by the permanganate method [24]. Catholyte samples are periodically taken and immediately analyzed for H₂O₂. The results are tabulated as: time (min), observed current (A), and concentration (mM) of H₂O₂ produced. The electrical charge is evaluated from a numerical integration of the area under the curve of the recorded current as a function of time. The cumulative current efficiency for H₂O₂ production is evaluated by Faraday’s laws. The
energy consumption ($E_W$, in kWh m$^{-3}$) for H$_2$O$_2$ electro-production, or AO7 oxidation, can be calculated from equation (8) by taking into account the electrolysis time ($t$, in h), assuming an average cell current ($I_{Cell}$, in A), cell voltage ($\Delta E_{Cell}$, in V) and the volume of catholyte ($V_{Catholyte}$, in m$^3$).

$$E_W = \frac{(\Delta E_{Cell}) (I_{Cell}) t}{V_{Catholyte}}$$  \hspace{1cm} (8)

4. RESULTS AND DISCUSSIONS

4.1. H$_2$O$_2$ Electro-Production

As soon as the ORR takes place on the RVC surface the H$_2$O$_2$ is formed and it can be eliminated from the electrode surface by three pathways [13]: a) desorption of H$_2$O$_2$ and transportation into the bulk solution (accumulation); b) electrochemical reduction of H$_2$O$_2$ and c) disproportionation of the H$_2$O$_2$ forming H$_2$O and O$_2$ which can again be involved into the reaction. The first mechanism is the most important for the aim of this work. In general, the first mechanism is expected to occur at low cathode energy, at medium cathode energy a mixture of H$_2$O$_2$/H$_2$O is probable, and finally at high energy a mixture of H$_2$O$_2$/H$_2$ is expected. In this way, H$_2$O$_2$ was investigated during 180 minutes in the two-electrode configuration electrochemical flow-cell, as a function of current applied (or cell potential, $\Delta E_{Cell}$).

Figure 3 shows data from three different electrolyzes to reduce O$_2$ at different cell currents. In the
energy range studied, the \(H_2O_2\) accumulation is always a linear function of the electrolysis time. When the cell current is set to 200 mA (●), \(\Delta E_{\text{cell}} = 2.05\) V, the current efficiency for \(H_2O_2\) production (●) is 35%. Under these conditions the energy needed (\(E_W\)) to produce 4 mM \(H_2O_2\) after 180 minutes of electrolysis is evaluated (from equation 8) in 1.23 kWhm\(^{-3}\) (9.04 kWkg\(^{-1}\) \(H_2O_2\)). When the experiment is repeated under the same experimental condition but the cell current is increased to 220 mA (○), \(\Delta E_{\text{cell}} = 2.07\) V, the \(\phi\) increased to 44%. The energy needed (\(E_W\)) to produce 5.75 mM \(H_2O_2\) after 180 minutes of electrolysis was 1.34 kWhm\(^{-3}\) (6.85 kWkg\(^{-1}\) \(H_2O_2\)). By increasing again the cell current to 250 mA (●), \(\Delta E_{\text{cell}} = 2.11\) V, the \(H_2O_2\) electro-production increased but the \(\phi\) (44%) did not increase further. Under these conditions the energy needed to produce 6.5 mM \(H_2O_2\) after 180 minutes of electrolysis is 1.58 kWhm\(^{-3}\) (7.15 kWkg\(^{-1}\) \(H_2O_2\)).

4.2. AO7 Oxidation

The experimental 1 L 0.1911 mM AO7 (0.05 M \(Na_2SO_4\), pH 2) degradation was investigated by means of the electro-Fenton process carried out in the electrochemical reactor working at 220 mA (2.50 V). In theory, according to equation (6), 6.5 mM \(H_2O_2\) are needed to oxidize 0.1911 mM AO7 and the required time are 200 minutes (equation 9). Figure 4 shows a set of AO7 spectra (in the range 370 nm < \(\lambda\) < 700 nm) as a function of the electrolysis time. According to the observed absorbance at 130 minutes of the AO7 oxidation process, at least 96% of the initial AO7 concentration was abated (evaluated from a calibration curve absorbance vs AO7 concentration). The quantity of \(H_2O_2\) required for the AO7 discoloration process is evaluated by equation (9), and it is found to be 4.3 mM. The discoloration of 0.1911 mM AO7 requires 1.2 kWhm\(^{-3}\) of energy, according to equation (8). From Figure 4, a set of absorbance data are taken (\(\lambda_{\text{max}} = 485\) nm) during the discoloration process and converted to concentrations. Then, both parameters (\([AO7]_0, \tau\)) are fitted to equation (7). Figure 5 shows the \(\ln[AO7]_0\) vs \(\tau\); from such graph both constants (\(\ln[AO7]_0, k\)) are evaluated as -1.8478 and 0.0237, respectively.

The last two electrolyzes give better results than those obtained previously (7.8 kWkg\(^{-1}\) \(H_2O_2\)) in similar conditions for different authors [25]. Therefore, the best experimental conditions are represented by the electrolysis carried out at 220 mA with \(\Delta E_{\text{cell}} = 2.07\) V (○), which can be fitted to:

\[
[H_2O_2] = 0.0315(ET) + 0.218' R^2 = 0.9958
\]  

Where \([H_2O_2]\) is the hydrogen peroxide concentration (mM) and \(ET\) is the electrolysis time (min).

![Figure 3: Three different electrolyzes to reduce \(O_2\) at different cell currents. (●): 200 mA, \(\Delta E_{\text{cell}} = 2.05\) V, \(\phi = 35\%\). (○): 220 mA, \(\Delta E_{\text{cell}} = 2.07\) V, \(\phi = 44\%\). (●): 250 mA, \(\Delta E_{\text{cell}} = 2.11\) V, \(\phi = 44\%\). Catholyte 0.05M \(Na_2SO_4\) (pH 2), Anolyte 0.8 M \(H_2SO_4\). 60 ppi RVC Cathode (5 cm x 3.75 cm x 1 cm) and anode, 304 SS gauze (10 cm x 5 cm).](image-url)

![Figure 4: A set of AO7 spectra recorded during the discoloration process in the electrochemical reactor (220 mA, 2.50 V). Spectra from top to bottom: 20, 40, 60, 70, 80, 90, 105 and 130 minutes of electrolysis. 1 L 0.1911 mM AO7 (0.05 M \(Na_2SO_4\), pH 2). 60 ppi RVC Cathode (5 cm x 3.75 cm x 1 cm) and anode, 304 SS gauze (10 cm x 5 cm).](image-url)
shown in Table 1. As it is expected, the energy needed for AO7 discoloration is proportional to the AO7 concentration. Table 1 shows the required H₂O₂ concentration for the oxidation of a given AO7 amount (according to equation 6), its corresponding required energy (according to equation 8) and the oxidation cost. The electrolysis time can be evaluated from equation (9).

\[ k = -0.8105[mM \text{AO7}]^2 - 0.2371[mM \text{AO7}] + 0.0967; \quad R^2 = 0.9904 \]  

Equations (10) and (11) show the parameter \( k \) and \([\text{AO7}]_0\) as a function of AO7 concentration, respectively.

\[ [\text{AO7}]_0 = 0.0104e^{14.28[mM \text{AO7}]}; \quad R^2 = 9851 \]  

Using these equations at a given AO7 concentration (in the concentration range studied) a pair of \( \ln[\text{AO7}]_0 \) and \( k \) (min⁻¹) can be obtained. If such parameters are substituted in equation (7) and the time starts to increase, a theoretical AO7 oxidation rate, in the electrochemical reactor, for a wide range of AO7 concentrations can be simulated as a function of time. Figure 6 shows the AO7 abatement simulations (dotted line) for four different AO7 concentrations (0.07, 0.147, 0.176 mM). Simulations are compared against experimental data (●).

![Figure 5: AO7 discoloration rate in the electrochemical reactor (220 mA, 2.50 V) as a function of the electrolysis time.](image)

<table>
<thead>
<tr>
<th>Experimental Parameters</th>
<th>mM AO7</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.07</td>
</tr>
<tr>
<td>[A]₀</td>
<td>0.028</td>
</tr>
<tr>
<td>k (min⁻¹)</td>
<td>0.076</td>
</tr>
<tr>
<td>DT / h</td>
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<tr>
<td>mM H₂O₂ RFO</td>
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<tr>
<td>kWhm⁻³ discoloration</td>
<td>0.36</td>
</tr>
<tr>
<td>mM H₂O₂ Oxidation</td>
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</tr>
<tr>
<td>Oxidation cost / €</td>
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</tr>
<tr>
<td>( \Delta E_{\text{cell}} )/ V</td>
<td>2.2</td>
</tr>
</tbody>
</table>

The oxidation cost for treating different AO7 concentrations is calculated based on the kWh price taken as 0.1€ [26]. These costs are advantageous when they are compared against similar AOP, such as Conductive-Diamond Electrochemical Oxidation (CDEO), Ozonation and Fenton process (FP). Several pollutants such as Butyric acid, 2-Propanol, 4-Chlorophenol, 2-Naphtol, Eriochrome Black T (EBT) and Olive oil (in the concentration range of 100 < mgL⁻¹ < 1000) were degraded by these AOP technologies. In particular the EBT treatment cost was 35, 99 and 46 € m⁻³ when the following AOP were applied, CDEO, Ozonation and FP, respectively [26].

From the data shown in Table 1 it is possible to correlate the parameters \([\text{AO7}]_0\) and \( k \) with AO7 concentration in the concentration range studied. Equations (10) and (11) show the parameter \( k \) and \([\text{AO7}]_0\) as a function of AO7 concentration, respectively.

\[ \ln[\text{AO7}]_0 = 1.8478, \quad k = 0.0237 \text{ min}^{-1}. \]
5. CONCLUSIONS

This work has shown that:

- $\text{H}_2\text{O}_2$ can be electro-produced with abundant and cheap feedstock (oxygen saturated tap water) in a divided parallel plate reactor. A commercial stainless steel (304 SS) mesh anode allows the $\text{H}_2\text{O}_2$ electro-production, in a low ionic acidic catholyte, which is energetically advantageous ($6.85 \text{ kWkg}^{-1} \text{ H}_2\text{O}_2$), and it follows a linear function of the electrical charge passed during the $\text{O}_2$ reduction.

- The $\text{H}_2\text{O}_2$ activation by $\text{Fe}^{2+}$ permits the development of Fenton reaction in the catholyte side and oxidizes AO7 at low energy requirements: $1.83 \text{ kWhm}^{-3}$ are needed to oxidize $0.191 \text{ mM AO7}$ in 3h.

- The oxidation of AO7 (in the concentration range of 0.07 to 0.191 mM) follows an apparent first order kinetic equation. The main parameters ([AO7]₀, $k$) of the first order kinetic equation can be expressed as functions of the AO7 concentrations.

- A semi-empirical chemical model to predict AO7 degradation, in the electrochemical reactor, can be developed taking into account the main equations derived from experimental data. The prediction of the main parameters ($\text{H}_2\text{O}_2$ electro-produced, oxidation rate, energy required, electrolysis time) shows good agreement with the experimental data.

- The chemical model is a useful tool to predict the oxidation rate of unknown concentration of AO7 inside the range studied.

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