Electrochemical Oxidation of the Azo Dye Ponceau 4R by Electro-Fenton Process

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Abstract— The focus on food color additives is continuously increasing due to their presence in waters and to their health effects. The mineralization of Ponceau 4R in a synthetic solution by electro-Fenton process using an undivided glass electrochemical cell, with a graphite-felt cathode and a platinum anode has been studied. The electrolysis were performed using different supporting electrolytes such as Na2SO4, NaCl, NaNO3 and using different catalysts such as CuSO4, Ag2SO4, FeSO4 in order to define the optimum degradation parameters. The reaction kinetic had an absolute constant rate of 8.24 x 10²M⁻¹sc⁻¹. The repeatability of the experiments was investigated. The total organic carbon indicates that 23.5% of mineralization yields were achieved after 4h of treatment and decay in the mineralization current efficiency was observed to be 23.29%. The ions chromatography analysis has shown that all nitrogen is converted to NO₃⁻, except sulfate ions, were not detectable in the medium.

Keywords— Mineralization, azo dyes, Ponceau 4R, Advanced Oxidation Process, electro-Fenton.

I. INTRODUCTION

Color is the first sensory parameter by which food quality and flavor are judged (1). Hence, synthetic food colorant are highly suggested by producers in the industry for a variety of features such as their stability to light, oxygen, pH, their low microbiological contamination as well as their relatively low production cost (2; 3). The most popular synthetic colorants widely used in food industry are the azo dyes (4-6). Various studies have shown that more than 100,000 dyes are commercially available with an estimated annual production of over 7 × 10⁷ tons of dye-stuff, when 60-70% of them are azo dyes (7-9). Azo dyes contain one or more azo groups (-N=N-) as chromophore, being linked to benzene, naphthalene or to both rings with lateral -OH and -SO₂H groups, which allows for increasing their water solubility (3; 4). Azo dyes degradation products are considered to be carcinogen and teratogen, i.e toxic hazards prohibited in many countries (5; 6; 1). This led to its ban in the European Union for being food additives (5). It has been reported by the European Food Safety that food azo dyes can be dangerous due to their connection to children hyperactivity (3; 6). They come in the second place after polymers in terms of the number of new compounds submitted for registration in the U.S under the Toxic Substance Control Act (TSCA) (6).

Industries such as textile, cosmetic, paper, leather, light-harvesting arrays, agricultural research, photo-electrochemical cells, pharmaceutical and food produce large volumes of wastewater polluted with high concentration of dyes and other components (7; 6). From an environmental standpoint, these dyes are toxic for both aquatic organisms and human being (8; 3; 7; 9). In fact, their presence in water, even with small proportions has an unfavorable impact on aesthetic merit, gas solubility and water transparency (7; 4). Indeed, azo dyes are very stable in the environment. They are recalcitrant to conventional biological and physicochemical treatment (8; 3; 4). Consequently, the discharge of wastewater into rivers and lakes is problematic, due to the serious damage caused to aquatic biota. This results in a significant impact on photosynthesis and oxygenation, along with their resistance to natural degradation (10; 9).

Considerable efforts have been made by researches in order to overcome, the impurities of wastewaters from industries that use dyes. Over the last decade, emerging alternative technologies for the efficient degradation of a large variety of dyes has been introduced by several Advanced Oxidation Processes (AOPs) (11). These processes involve chemical, photochemical or electrochemical techniques (12; 13). They are considered as the most effective methods used to treat water and wastewater that contain toxic and non-biodegradable pollutants nowadays. This is due to their environmental compatibility, versatility and safety, since they operate under mild conditions (14; 15; 16). The AOPs have been optimized for the removal of toxic and refractory organic pollutants from water under the action of very reactive and non-selective transient oxidizing species such as the hydroxyl radicals •OH (3; 17; 18; 14). These techniques are mainly based on the continuous generation of the dominant oxidizing species •OH. These species are able to react to most organics due to its high standard redox potential (E° = 2.80 V/SHE) (19; 14; 12). They are found to react unselectively and effectively against organic pollutants, by converting them into non-toxic products like CO₂, H₂O and inorganic salts. This may be achieved by means of hydrogen atom abstraction reaction, electron transfer, or electrophilic addition to II system (13).

Among the AOPs, electro-Fenton process was developed and has been widely used in the oxidation of various organic...
pollutants (20; 3; 7; 16). It is found to be the most efficient AOP with H₂O₂ generation nowadays (3). This technology is based on Fenton reaction [1], in which one of the Fenton reagents, H₂O₂ is produced electrochemically. Moreover, Fe²⁺ is added to the medium in catalytic quantities and regenerated in situ, in a cyclic way, through the reduction of Fe³⁺ at the cathode [2].

Fe³⁺(aq) + H₂O₂(aq) → Fe²⁺(aq) + OH⁻(aq) + •OH(aq)  
Fe²⁺(aq) + e⁻ → Fe²⁺(aq)  
H₂O₂, which is essential to the Fenton reaction, is generated through the reduction of molecular oxygen using a suitable cathode, according to reaction [3]. O₂ or air gas is injected into the reaction medium up to saturation, at optimum pH 3.

O₂(g) + 2H⁺(aq) + 2e⁻ → H₂O₂(aq)  
The main advantages of using EFP over more conventional Fenton’s reagents is due to the cathodic regeneration of Fe²⁺, which was previously introduced in reaction [2]. This results in the speedup of the Fenton’s reaction as well as the enhancement of the mineralization process, allowing for directly using Fe²⁺ ions (3; 12). Moreover this process is environment-friendly since it does not require harmful chemical reagents since Fe²⁺ ions, H₂O₂, and the produced hydroxyl radicals •OH are produced on-site (21; 16). Likewise the possibility of controlling the degradation kinetics of the dyes into low-molecular-weight compounds (e.g., small aldehydes, carboxylic acids or small inorganic compounds), CO₂ and H₂O allows for mechanistic studies. Moreover, electricity is a clean energy source that is used in the process, so that the overall process does not create secondary pollutants (18; 22; 19). Consequently, it is of great importance to find all affecting parameters and the optimum operating conditions that enhance the removal efficiently.

Ponceau 4R (P4R), CI. 16255, also called Acid Red18 is principally trisodium 2-hydroxy-1-(4-sulfonato-1-naphthylazo)-6,8 naphthalenedisulfo-natea food colorant, part of the azo dyes family. Its molecular structure is illustrated in Fig. 1, has a molecular weight of 604.46 g mol⁻¹ and a maximum wavelength of λ_max = 510 nm.

Some countries consider it as carcinogenic and therefore is banned including the US, Canada, Norway and Finland. Its usage remains, however, controversial in some European countries (5; 23; 9). In some other countries, it is still in use with limited quantities with a maximum of 100 mg/kg or mg/L in jellies, and a maximum of 50 mg/kg or 50 mg/L in candies and beverages (5). It is important to highlight the use of P4R in many other countries such as Tunisia, Brazil, Japan and China (4; 19) in the food industry to give red coloring to various foodstuffs such as alcoholic beverages, soft drinks, candies, syrups, bakery products, tomato sauce, cherry marmalade and yogurts (23). In fact, using days may have unfavorable impact on health, such as reproductive toxicity, neurobehavioral effects, mutagenic action, hyperactivity and potential carcinogenicity (5; 6; 23).

The destruction of P4R have been studied through a biological treatment (24), decolorization using bacteria (25), Ozonation (4), adsorption (26), oxidative degradation (27), Fenton (H₂O₂/Fe⁶⁺) (11; 28), photo-Fenton process (28), photodegradation in a quartz labyrinth flow reactor with immobilized TiO₂ bed (29) and in a mixture with two other dyes by EFP and UV photoelectron-Fenton (9). A. Thiam et al. compared the decolorization and mineralization of Ponceau 4R by electro-oxidation (EO) or without H₂O₂ production, EFP and photoelectro-Fenton (PEF) both using small undivided and divided batch cells with either Pt or BDD as the anode, whereas the cathode was a carbon-PTFE air-diffusion electrode (23). They studied the performance of three electrochemical advanced oxidation processes, as follows: electro-oxidation with electro-generated H₂O₂ (EO–H₂O₂), electro-Fenton (EF) and photoelectro-Fenton (PEF) in an undivided cell with a BDD anode and an air-diffusion cathode (30).

This paper introduces an extension to our previous work, referred to as the decolorization and mineralization of Ponceau 4R at pH 3 by EFP using a Platinum anode and a carbon felt cathode (19). This study focuses on the impact of different electrolytes (NaCl, NaNO₃, Na₂SO₄) and catalysts (Fe²⁺, Ag²⁺, Cu²⁺) on the discoloration efficiency, the reaction kinetics, on the COT abatement as well as the released ions after mineralization. The electrolyses were carried out under the optimized conditions selected in accordance with the conditions studied in our previous paper (19).

II. MATERIALS AND METHODS

A. Chemicals

Ponceau 4R (C₂₀H₁₄N₂Na₂O₁₀S₄) was obtained as powder from a Tunisian food industry and was used without further purification. Heptahydrated ferrous sulfate (FeSO₄·7H₂O), a ferrous ion source, was supplied by VWR BDH Prolabo. Anhydrous sodium sulfate (Na₂SO₄), an inert supporting electrolyte, was purchased from Acros organics. All other chemicals were electrolytically and in a mixture with two other dyes by EFP and UV photoelectron-Fenton (9). A. Thiam et al. compared the decolorization and mineralization of Ponceau 4R by electro-oxidation (EO) with or without H₂O₂ production, EFP and photoelectro-Fenton (PEF) both using small undivided and divided batch cells with either Pt or BDD as the anode, whereas the cathode was a carbon-PTFE air-diffusion electrode (23). They studied the performance of three electrochemical advanced oxidation processes, as follows: electro-oxidation with electro-generated H₂O₂ (EO–H₂O₂), electro-Fenton (EF) and photoelectro-Fenton (PEF) in an undivided cell with a BDD anode and an air-diffusion cathode (30).

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B. Electrochemical Apparatus and Procedure

Dye solution was prepared containing a concentration of 6.6 × 10⁻² mM of P4R. The ionic strength was maintained constant adding 50 mM of electrolytes. Catalytic ions were introduced to the synthetic samples prepared just before the beginning of the electrolysis. Electrolytic experiments were conducted in an open, cylindrical and non-divided cell of 250 ml capacity. The latter is equipped with two electrodes: a 3D
carbon felt (Carbone Lorraine RVG 4000 Menser) of 27 cm² area as a cathode and a spiral rod of platinum as an anode of 5.5 cm height. In all treatments, the anode was placed in the center of the electrochemical cell and was surrounded by the cathode, which covered its inner wall. All electrolyses were performed with a METRIX AX322 potentiostat by applying a constant current of 250 mA, found to be the optimum value as introduced in the previous paper (31). The temperature of the reaction medium is kept constant, by using a thermostated bath. The pH is maintained at 3 (19), by adding 0.1 M of H₂SO₄, its value is measured with a Mettler Toledo EL20 pH-meter. Prior to the electrolysis, continuous O₂ saturation at atmospheric pressure is performed by bubbling compressed air in the solution. This is performed 10 minutes before the electrolysis takes place to reach a steady O₂ concentration.

C. Analytical Methods

Color removal was monitored by measuring the decrease in absorbance using a single cell module, Life Science UV/Vis spectrophotometer BECKMAN DU-530, California by determining the absorbance at \( \lambda_{\text{max}} = 510 \text{ nm} \). This is computed in the following expression:

\[
\text{Color removal} \ (\%) = \left( \frac{\text{ABS}_0 - \text{ABS}_t}{\text{ABS}_0} \right) \times 100
\]

Where \( \text{ABS}_0 \) and \( \text{ABS}_t \) are the initial and final absorbance during the electrolysis at a time \( t \), respectively.

The solutions were filtered on Sartorius Minisart 0.4 μm GF prefilters. Total Organic Carbon (TOC) was measured by means of a TOC-VCPH-CPN Total Organic Analyzer SCHIMADZU. Organic carbon compounds were combusted and converted to CO₂, which was detected and measured by a non-dispersive infrared detector (NDIR). Dissolved Nitrogen compounds were combusted and converted into NO which was then mixed with Ozone chemiluminescence for detection by a photomultiplier. Reproducible TOC values were always obtained by using the standard NPOC (Non-Purgeable Organic Carbon) method. For each sample, each measurement was duplicated.

TOC removal percentage was estimated in the following equation:

\[
\text{TOC removal} \ (\%) = \left( 1 - \frac{\text{TOC}_0}{\text{TOC}_1} \right) \times 100
\]

Where TOC₀ and TOC₁ are the measures of the total organic carbon at reaction time (0 and 1).

The detection of released ions were monitored by ionic chromatography using an exchange anions resin as a stationary phase on a Metrosep Anion Dual 11 column, equipped with a condumetric detector. The mobile phase is a mixture of sodium carbonate 10⁻¹ M and sodium bicarbonate 10⁻³ M, under a flow rate of 1 ml/min.

The mineralization current efficiency (MCE) values at current I (in A) and time t (in h) was then estimated as follows:

\[
\text{MCE}(\%) = \left( \frac{\Delta \text{TOC}}{\text{V/F}} \times 10^{2} \right) \times \text{m} \times \text{m}^{-1} \times \text{h}^{-1}
\]

Where F is the Faraday constant (96,487 C mol⁻¹), V is the solution volume (dm³), \( \Delta \text{TOC} \) is the experimental TOC abatement (in mg dm⁻³), 4.32 \times 10² is a conversion factor to homogenize units (3600 s h⁻¹×12000 mg carbon mol⁻¹) and \( m \) is the number of carbon atoms of Ponceau 4R.

III. RESULTS AND DISCUSSION

A. Effect of catalyst matures on Ponceau 4R degradation:

In order to understand the effect of the catalyst nature on the EFP, its impact is investigated. All catalysts are added to the solution at the same concentration 0.5 mM, optimized in the previous study of Ponceau 4R mineralization (31) as well as other operating parameters such as ([P4R]₀=6.6 \times 10⁻² mM, [Na₂SO₄] = 50 mM, pH = 3, V=250 mL, I =250 mA). The curves illustrated in Fig. 2 clearly show that FeSO₄ leads to best degradation rate, compared to CuSO₄ and Ag₂SO₄. This result may be explained by the higher oxidative potential of Fe³⁺/Fe²⁺ (E⁰=0.77 V/SHE) compared to Cu²⁺/Cu⁺ (E⁰=0.16 V/ SHE) (32). In fact, in acidic conditions, Cu⁺ is oxidized by oxygen to Cu²⁺. As explained in (7), (8) and 9, the reaction between Cu²⁺ and H₂O₂ is performed by molecular oxygen, which allows for reducing the effective Cu²⁺ available to react with H₂O₂ (33; 21).

\[
\text{Cu}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^+ + \text{HO}_2 + \text{OH}^-
\]  

\[
\text{Cu}^+ + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^{2+} + \text{HO} + \text{HO}^-
\]  

\[
4\text{Cu}^{+} + 4\text{H}^+ + \text{O}_2 \rightarrow 4\text{Cu}^{2+} + 2\text{H}_2\text{O}
\]

Compared to the two previous catalysts silver, sulfate does not improve the efficiency of Ponceau 4R degradation. Moreover, it’s not in accordance with the ecological and economic side of the process, considering its price and toxicity. These results are consistent with previous studies that are introduced in the literature (34). Conclusively iron remains the most adequate catalyst considering its high reactivity, abundance, low commercial cost and last but not least, its environmental compatibility and low toxicity (33).

B. Effect of supporting electrolyte nature on Ponceau 4R degradation:

Electrolytes improve the solution conductivity, and accelerate the electron transfer, thus benefiting the EF reaction. Solutions of 250 ml containing 6.6 \times 10⁻² mM P4R in 50 mM of Na₂SO₄, NaCl and NaNO₃ as supporting electrolyte at pH 3.0 were comparatively treated at 250 mA. As it can be seen from the results shown in Fig. 3, the best performance is observed in the medium that contains Na₂SO₄ and is slightly decreased in the NaCl medium followed by NaNO₃. This can be attributed to the highest conductivity of SO₄²⁻electrolyte compared to Cl one as reported in the literature (35). In fact, our results are consistent with the results reported in the literature (35; 36). However, A. Thiam et al. showed that the decolorization efficiency for the EF treatment of Ponceau 4R with an air diffusion cathode is in the order of magnitude of SO₄²⁻ ≈ClO₄⁻ ≈NO₃⁻ ≈ CI⁻ compared to other medium. This difference can be attributed to the use of an air diffusion cathode instead of a carbon felt one (23).
C. Repeatability tests:

In order to estimate the relative standard deviation (SRD) of P4R, treated by EFP, a sequence of five tests has been conducted and summarized in Table 1. All experiments were carried out in an electro chemical cell of 250 mL, under optimal conditions, which are [P4R]=6.6 × 10^{-2} mM, [Na_2SO_4]=50 mM, pH=3, V=250 mL, I=250 mA.

The obtained results are summarized in Table 1. The SRD of P4R, treated by EFP, a sequence of five tests has been carried out in an electro chemical cell of 250 mL, under optimal conditions, which are [P4R]=6.6 × 10^{-2} mM, [Na_2SO_4]=50 mM, pH=3, V=250 mL, I=250 mA. The obtained results are summarized in Table 1. The SRD was found to be less than 2, as found in the study introduced by A. Thiam et al., where the degradation of P4R is reached by using three electrochemical advanced oxidation processes, as follows: electro-oxidation with electro-generated H_2O_2(EO-H_2O_2), electro-Fenton (EF) and photo-electro-Fenton (PEF) with a BDD anode (30). Consequently, we conclude that Ponceau 4R degradation with EFP using a carbon felt cathode and a Pt anode has a good repeatability (37).

With:

\[ R.S.D. = \frac{(S/X) \times 100}{S} \] : relative standard deviation.

\[ S = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1} \] : standard deviation of repeatability.

\[ x = \frac{\sum_{i=1}^{n} x_i}{n} \] : arithmetic mean.

And \( n = 5 \): number of measurement carried out.

<table>
<thead>
<tr>
<th>No of trials</th>
<th>Color removal %</th>
<th>S(X)</th>
<th>X</th>
<th>S.R.D</th>
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<td>5</td>
<td>97.08</td>
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</table>

D. Determination of the absolute rate constant of Ponceau 4R degradation:

Absolute constant rate of Ponceau 4R degradation by EFP at pH 3 was determined by competition kinetic methods. Benzoic acid (BA) was used as standard competitor as a well-known standard whose absolute constant is \( k_{BA} = 4.3 \times 10^{9} \) M^{-1}s^{-1} (34). Electrolysis of the aqueous solution containing P4R and BA was carried out under optimal conditions selected in accordance with the operating conditions found previously (31), ([P4R]=6.6 × 10^{-2} mM, [Na_2SO_4]=50 mM, pH=3, I=250 mA, [Fe^{3+}]=0.5 M, at 20°C). From the linear correlation observed in Fig. 4 and from (10), the absolute rate constant of Ponceau 4R was calculated.

\[ k_{Ponceau \text{4R}} = \frac{\ln \frac{[\text{BA}]_0}{[\text{BA}]}}{\ln \frac{[\text{P4R}]_0}{[\text{P4R}]}} \] (10)

The value found is 8.24 × 10^{9} M^{-1}s^{-1}, is in accordance with the range of 10^{9} - 10^{10} reported by many others studies about the reaction between aromatics compounds and hydroxyl radicals (38; 34).

E. Electrochemical mineralization of Ponceau 4R:

The extent of oxidation of Ponceau 4R by EFP was monitored by estimating the Total Organic Carbone (TOC) at optimal conditions ([P4R]=6.6 × 10^{-2} mM; I=250 mA; [Fe^{3+}]=0.5 mM) during 240 minutes. As reported in our previous study, the degradation of Ponceau 4R under the same operating parameter achieves 73.2% COD removal, and the decolization of the synthetic dyes reaches 100% (31). CO2 of Ponceau 4R decreased from 53.34 mg/L to 12.54 mg/L after 4h of treatment giving an abatement of 23.5%.

This slow mineralization may be explained by the low oxidation power of Pt to remove the organic intermediates hardly oxidizable such as short-chain carboxylic acids (12; 7; 16). As reported in the literature introduced by A. Thiam and Al., in fact they investigate the mineralization of Ponceau 4R, by using photo-electron Fenton process, along with a BDD electrode. This allowed in obtaining a faster degradation, yet with a sigmoid curve, considered as a symptom of the formation of by-products that are slowly but progressively mineralized (30).
The mineralization of 6.6 × 10⁻² mM P4R into inorganic ions during electrolysis was investigated using ions chromatography analysis at 60 minutes, 180 minutes, 300 minutes and 420 minutes. The theoretical number of nitrogen released assuming that P4R is completely mineralized, was found to be 0.33 mM. Whereas, the N atoms forming the -N=N- bond were preferentially converted to NO₃⁻ ions. In fact, the analysis of nitrates invoked in the solution after 420 minutes of electrolysis, showed a concentration equal to 0.38 mM, as shown in Fig. 5. Conclusively, the overhead found during the analysis is, therefore, due to experimental errors. This result is consistent with the study that was previously introduced, which consisted of studying the mineralization of Ponceau 4R, by three AOP using BDD anode (30) and to similar treatment of other azo-dyes (3).

Regarding the sulfur content, the proportion of sulfate released in the medium is insignificantly compared to the amount already present in the medium, which is due to the sulfuric acid used to adjust the pH of the medium, the supporting electrolyte anhydrous sodium sulfate, and the catalyzer anhydrous sodium sulfate.

Based on our previous results, the theoretical number of exchanged electrons (n) per each substrate molecule is considered to be 102, assuming that P4R is completely mineralized, as shown in the following (11):

\[
\text{C}_2\text{H}_4\text{I}_2\text{N}_2\text{O}_3\text{S}_3\text{Na}_3 + 48\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 2\text{NO}_3^- + 3\text{SO}_4^{2-} + 107\text{H}^+ + 102\text{e}^- + 3\text{Na}^+ \tag{11}
\]

The current efficiency (MCE) values were calculated based on the TOC values. A decrease of 23.29 % in MCE value was observed after 4h of treatment. This decay in the current efficiency can be related to the accumulations of refractory molecules such as aliphatic carboxylic acids, which results in slowing the mass transport of reactants toward the anode (23; 12).

**CONCLUSION**

The mineralization of synthetic dye Ponceau 4R by electro-generated Fenton’s reagent has been optimized using an undivided electrochemical cell with a graphite-felt cathode and a platinum anode. The degradation of Ponceau 4R based on different electrolytes (Na₂SO₄, NaCl, NaNO₃) and catalyst nature (CuSO₄, AgSO₄, FeSO₄), are compared respectively. Both FeSO₄ and Na₂SO₄ allow for an optimum decolorization efficiency of 100% after 10 minutes of treatment. Moreover, this study shows that the absolute constant rate of the oxidation reaction is 8.24 × 10⁻⁹ M⁻¹s⁻¹ which was found based on the competition kinetics methods, using benzoic acid as standard competition substrate. The obtained results of TOC removal show a significant decrease of 23.5% after 4 hours, leading to MCE calculations, where the current efficiency decayed of 23.39%. Finally, the study of nitrogen by ions chromatography analysis shows that the N atoms forming the -N=N- bond are preferentially detected as NO₃⁻ ions. However, the sulfate released is insignificant when compared to the amount of sulfate already present in the medium.

**REFERENCES**


