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 Na_2SO_4, $NaCl$, $NaNO_3$, and using different catalysts such as $CuSO_4$, $AgSO_4$, $FeSO_4$ in order to define the optimum degradation parameters. The reaction kinetic had an absolute constant rate of $8.24 \times 10^9\,M^{-1}s^{-1}$. 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 NO_3^-, 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 7×10^5 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 $-SO_3H$ 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 CO_2, H_2O and inorganic salts. This may be achieved by means of hydrogen atom abstraction reaction, electron transfer, or electrophilic addition to Π 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 H_2O_2 generation nowadays (3).This technology is based on Fenton reaction [1], in which one of the Fenton reagent, H_2O_2 is produced electrochemically. Moreover, Fe^{2+} is added to the medium in catalytic quantities and regenerated in situ, in a cyclic way, through the reduction of Fe^{3+} at the cathode [2].

$$Fe^{2+}_{(aq)} + H_2O_{2(aq)} \rightarrow Fe^{3+}_{(aq)} + OH^-_{(aq)} + \cdot OH_{(aq)} \qquad (1)$$

$$Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)} \qquad (2)$$

H_2O_2, which is essential to the Fenton reaction, is generated through the reduction of molecular oxygen using a suitable cathode, according to reaction [3]. O_2 or air gas is injected into the reaction medium up to saturation, at optimum pH 3.

$$O_{2(g)} + 2H^+_{(aq)} + 2e^- \longrightarrow H_2O_{2(aq)} \qquad (3)$$
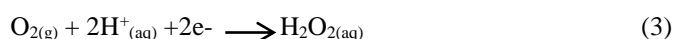
The main advantages of using EFP over more conventional Fenton's reagents is due to the cathodic regeneration of Fe^{2+}, which was previously introduced in reaction [2]. This results in the speedup of the Fenton's reaction as well as the enhancement of the mineralization process, allowing for directly using Fe^{3+} ions (3; 12). Moreover this process is environment-friendly since it does not require harmful chemical reagents since Fe^{2+} ions, H_2O_2, 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), CO_2 and H_2O 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), C.I. 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 $\lambda_{max} = 510$ nm.
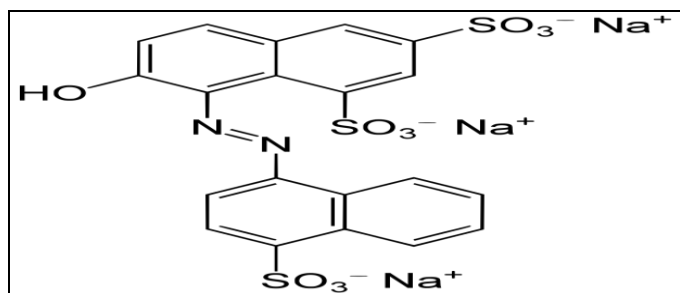

Fig. 1. Molecular structure of Ponceau 4R.

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 (H_2O_2/Fe^0) (11; 28), photo-Fenton process (28), photodegradation in a quartz labyrinth flow reactor with immobilized TiO_2 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) with or without H_2O_2 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 H_2O_2(EO–H_2O_2), electro-Fenton (EFP) 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, $NaNo_3$, Na_2SO_4) and catalysts (Fe^{2+}, Ag^{2+}, Cu^{2+}) 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 ($C_{20}H_{11}N_2Na_3O_{10}S_3$) was obtained as powder from a Tunisian food industry and was used without further purification. Heptahydrated ferrous sulfate ($FeSO_4·7H_2O$), a ferrous ion source, was supplied by VWR BDH Prolabo. Anhydrous sodium sulfate (Na_2SO_4), an inert supporting electrolyte, was purchased from Acros organics. All other chemicals were analytically graded VWR BDH Prolabo and Sigma-Aldrich. and were used without further purification.

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 Mersen) of 27 cm^2 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 H_2SO_4, its value is measured with a Mettler Toledo EL20 pH-meter. Prior to the electrolysis, continuous O_2 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 O_2 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 $\lambda_{max} = 510$ nm. This is computed in the following expression:

$$Color\ removal\ (\%) = \frac{ABS_o - ABS_t}{ABS_o} \times 100 \qquad (4)$$

Where ABS_o and 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-V$_{CPH-CPN}$ Total Organic Analyzer SCHIMADZU. Organic carbon compounds were combusted and converted to CO_2, 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 chemiluinescenece 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:

$$TOC\ removal\ (\%) = \left(1 - \left(\frac{TOC_t}{TOC_0}\right)\right) \times 100 \qquad (5)$$

Where TOC_0 and TOC_t are the measures of the total organic carbon at reaction time (0 and t).

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

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

$$MCE(\%) = \frac{(\Delta TOC)exp\ nFVs)}{4.32 \times 10^7\ mIt} \qquad (6)$$

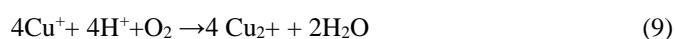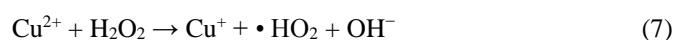Where F is the Faraday constant (96,487 C mol^{-1}), Vs is the solution volume (dm^3), $\Delta(TOC)_{exp}$ is the experimental TOC abatement (in mg dm^{-3}), 4.32×10^{-7} is a conversion

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 × 10^{-2} mM, [Na$_2$SO$_4$] = 50 mM, pH = 3, V=250 mL, I =250 mA). The curves illustrated in Fig. 2 clearly show that FeSO$_4$ leads to best degradation rate, compared to CuSO$_4$ and Ag$_2$SO$_4$. This result may be explained by the higher oxidative potential of Fe^{3+}/Fe^{2+} (E^0=0.77 V/SHE) compared to Cu^{2+}/Cu$^+$ (E^0=0.16 V/ SHE) (32). In fact, in acidic conditions, Cu$^+$ is oxidized by oxygen to Cu^{2+}. As explained in (7), (8) and 9, the reaction between Cu^{2+} and H$_2$O$_2$ is performed by molecular oxygen, which allows for reducing the effective Cu^{2+} available to react with H$_2$O$_2$ (33; 21).

$$Cu^{2+} + H_2O_2 \rightarrow Cu^+ + \bullet HO_2 + OH^- \qquad (7)$$

$$Cu+ + H_2O_2 \rightarrow Cu_2^+ + \bullet HO + HO^- \qquad (8)$$

$$4Cu^+ + 4H^+ + O_2 \rightarrow 4\ Cu_2+ + 2H_2O \qquad (9)$$

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 × 10^{-2} mM P4R in 50 mM of Na$_2$SO$_4$, NaCl and NaNO$_3$ 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 Na$_2$SO$_4$ and is slightly decreased in the NaCl medium followed by NaNO$_3$. This can be attributed to the highest conductibility of SO$_4^{2-}$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 SO$_4^{2-}$ ~ClO^{4-} < NO^{3-}<< Cl$^-$ compared to other medium. This difference can be attributed to the use of an air diffusion cathode instead of a carbon felt one (23).
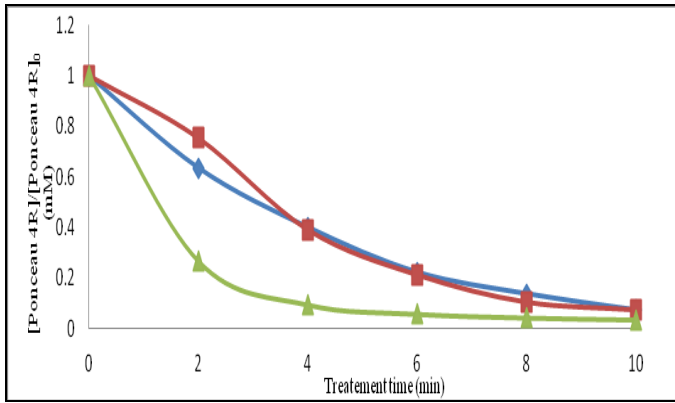
Fig. 2. Effect of the chemical nature of the catalyst on the degradation of P4R by EFP. Catalyst: CuSO4(◊),Ag2SO4(□), FeSO4(Δ). [P4R]0=6.6 × 10-2 mM, [catalyst]=0.5 mM, [Na2SO4] = 50 mM, pH = 3, V=250 mL, I =250 mA.
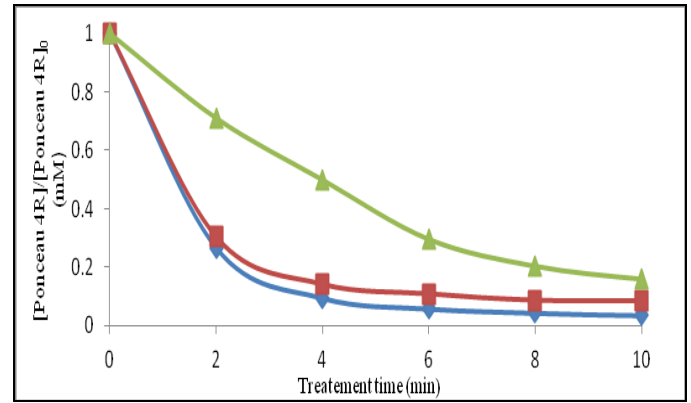

Fig. 3. Effect of the chemical natures of the electrolytes on the degradation of P4R by EFP. Electrolytes: Na2SO4(◊), NaCL(□), NaNO3(Δ). [P4R]0=6.6 × 10-2 mM, [FeSO4]=0.5 mM, [electrolytes] = 50 mM, pH = 3, V=250 mL, I =250 mA.

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 I. All experiments were carried out in an electro chemical cell of 250 mL, under optimal conditions, which are $[P4R]_0 = 6.6 \times 10^{-2}$ mM, $[Na_2SO_4]$=50 mM, pH=3, I=250 mA, $[Fe^{2+}]$=0.5 M, at 20 °C. 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. = $(S_r/x) \times 100$: relative standard deviation.

$S_r(x) = \sqrt{\dfrac{\sum_1^n (X_i - X)^2 -}{n-1}}$: standard deviation of repeatability.

$x = \sum_{i=1}^{ni} \dfrac{X_i}{n}$: arithmetic mean.

And n = 5: number of measurement carried out.

TABLE I. RESULTS OF REPEATABILITY TESTS

N° of trials	Color removal %	$S_r(X)$	X	S.R.D
1	93.8			
2	98.05			
3	99.02	1,83	96,87	1,88
4	96.23			
5	97.08			

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), ($[P4R]_0 = 6.6 \times 10^{-2}$ mM, $[Na_2SO_4]$=50 mM, pH=3, I=250 mA, $[Fe^{2+}]$=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.

$$k_{\text{Ponceau 4R}} = \frac{ln\frac{[AR18]_0}{[AR18]}}{ln\frac{[BA]_0}{[BA]}} \qquad (10)$$

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 ($[P4R]_0 = 6.6 \times 10^{-2}$ mM; I=250 mA ; $[Fe^{2+}]$=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 decolonization of the synthetic dyes reaches 100% (31). COT of Ponceau 4R decreased from 53.34 mg/L to 12.54 mg/L after 4h of treatment giving an abatement of 23.5% COT. 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).
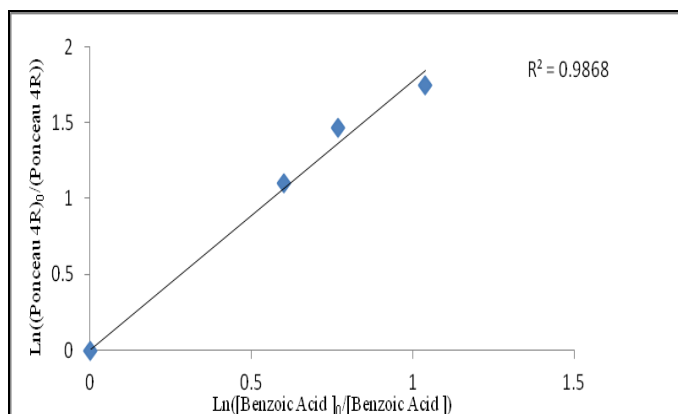
Fig. 4. Kinetic analysis for the pseudo-first order reaction of P4R and BA with hydroxyl radicals. $nPonceau\ 4R=nBA$. $[P4R]0 =6.6 \times 10^{-2}$ mM, $[Na_2SO_4]$ = 50 mM, pH = 3, V = 250 mL, I = 250 mA, $[Fe2+]$=0.5 mM.

Fig. 5. The concentration of NO3- ions released during the degradation of P4R solution. $[Ponceau\ 4R]0$ =0.16 mM, $[Na2SO4]$ = 50 mM, pH = 3, V = 250 mL, I = 250 mA, $[Fe2+]$=0.5 mM.

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 NO_3^- 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 insignificant 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):

$$C_{20}H_{11}N_2O_{10}S_3Na_3 + 48H_2O \longrightarrow 20CO_2 + 2NO_3^- + 3SO_4^{2-} +107H^+ +102e^- +3Na^+ \qquad (11)$$
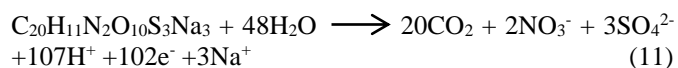
The current efficiency (MCE) values were calculated based on the TOC values. A decrease of 23.29 % in MCE value was observed after 4h of treatment. This decay in the current efficiency can be related to the accumulations of refractory molecules such as aliphatic carboxylic acids, which results in slowing the mass transport of reactants toward the anode (23; 12).
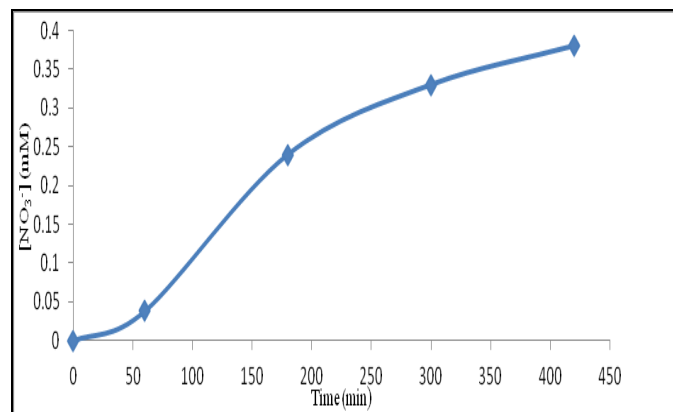
CONCLUSION

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 (Na_2SO_4, NaCl, $NaNO_3$) and catalyst nature ($CuSO_4$, $AgSO_4$.$FeSO_4$), are compared respectively. Both $FeSO_4$ and Na_2SO_4 allow for an optimum decolorization efficiency of 100% after 10 minutes of treatement. Moreover, this study shows that the absolute constant rate of the oxidation reaction is 8.24×10^9 $M^{-1}s^{-1}$, 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 NO_3^- ions. However, the sulfate released is insignificant when compared to the amount of sulfate already present in the medium.

REFERENCES

[1] Karthik Yamjala, Meyyanathan Subramania Nainar, Nageswara Rao Ramisetti. Methods for the analysis of azo dyes employed in food industry – A review. s.l. : Food Chemistry, 2015.

[2] F. A. Ozdemir Olgun, Demirata Ozturk, R. Apak. Determination of Synthetic Food Colorants in Powder Beverage Samples by On-line HPLC–Cupric Reducing Antioxidant Capacity (CUPRAC) Assay with Post-Column Detection. s.l. : Chromatographia, 2016.

[3] Brillas, Abdoulaye Thiam Ignasi Sires Jose A. Garrido Rosa M. Rodrıguez Enric. Decolorization and mineralization of Allura Red AC aqueous solutions by electrochemical advanced oxidation processes. s.l. : Journal of Hazardous Materials, 2015.

[4] Cristina Benincá, Patricio Peralta-Zamora, Célia Regina Granhen Tavares, Luciana Igarashi-Mafra. Degradation of an Azo Dye (Ponceau 4R) and Treatment of Wastewater from a Food Industry by Ozonation. Paraná : Ozone: Science & Engineering: The Journal of the International Ozone Association, 2013. Vol. 35.

[5] Aslihan Karatepe, Cagri Akalin, Mustafa Soylak. Solid-phase extraction of some food dyes on sea sponge column and determination by UV–vis spectrophotometer. s.l. : Desalination and Water Treatment, 2016.

[6] Mark A. Brown, Stephen C. De Vito. Predicting Azo Dye Toxicity. s.l. : Critical Reviews in Environmental Science and Technology, 1993. Vol. 23.

[7] Enric Brillas Carlos A, Martinez-Huitle. Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. s.l. : Applied Catalysis B: Environmental, 2014.

[8] Lazhar Labiadh, Mehmet A. Oturan, Marco Panizza, Nawfel Ben Hamadi, Salah Ammar. Complete Removal of AHPS Synthetic Dye from Water Using New Electro-Fenton Oxidation Catalyzed by Natural Pyrite as Heterogeneous Catalyst. s.l. : Journal of Hazardous Materials, 2015. HAZMAT 16780.

[9] Abdoulaye Thiam, Ignasi Sirés, Enric Brillas. Treatment of a mixture of food 1 color additives (E122, E124 and E129) in different water matrices by UVA and solar photoelectro-Fenton. s.l. : Water Research, 2015. 10.1016/j.watres.2015.05.057.

[10] Danielle F.M. Oliveira, Paulo S. Batista, Paulo S. Muller Jr, Valdemir Velani, Marcela D. França, Danilo R. de Souza, Antonio E.H. Machado. Evaluating the effectiveness of photocatalysts based on titanium dioxide in the degradation of the dye Ponceau 4R. s.l. : Dyes and Pigments, 2011.

[11] K. Barbusiński, J. Majewski. Discoloration of Azo Dye Acid Red 18 by Fenton Reagent in the Presence of Iron Powder. s.l. : Polish Journal of Environmental Studies, 2003. Vol. 12.

[12] Abdellatif El-Ghenymy, Francesc Centellas, Rosa María Rodríguez, Pere Lluís Cabot,José Antonio Garrido, Ignasi Sirés, Enric Brillas. Comparative use of anodic oxidation, electro-Fenton and photoelectro-Fenton with Pt or boron-doped diamond anode to decolorize and mineralize Malachite Green oxalate dye. Barcelona : Electrochimica Acta, 2015.

[13] Ali Ozcan, Yu cel Sahin, Mehmet A. Oturan. Complete removal of the insecticide azinphosmethyl from water by the electro-Fenton method - A kinetic and mechanistic study. s.l. : WATER RESEARCH, 2013.

[14] Ali Ozcan a, Yucel Sahin , A. Savas Koparal, Mehmet A. Oturan. Carbon sponge as a new cathode material for the electro-Fenton process: Comparison with carbon felt cathode and application to degradation of synthetic dye basic blue 3 in aqueous medium. s.l. : Journal of Electroanalytical Chemistry, 2008.

[15] Sourour Chaâbane Elaoud, Marco Panizza, Giacomo Cerisola, Tahar Mhiri. Coumaric acid degradation by electro-Fenton process. s.l. : Journal of Electroanalytical Chemistry, 2011.

[16] Minir Murati, Nihal Oturan, Jean-Jacques Aaron, Ahmad Dirany, Bruno Tassin, Zoran Zdravkovski, Mehmet A. Oturan. Degradation and mineralization of sulcotrione and mesotrione in aqueous medium by the electro-Fenton process: a kinetic study. s.l. : Environ Sci Pollut Res, 2011.

[17] Sergi Garcia-Segura, Alvaro Silva Lima Eliane, Bezerra Cavalcanti Enric Brillas. Anodic oxidation, electro-Fenton and photoelectro-Fenton degradations of pyridinium and imidazolium based ionic liquids in waters using a BDD/air-diffusion cell. s.l. : Electrochimica Acta, 2016. EA 26887.

[18] E. Rosales, M. A. Sanromán, M. Pazos. Application of central composite face-centered design and response surface methodology for the optimization of electro-Fenton decolorization of Azure B dye. s.l. : pringer-Verlag, 2011. 10.1007/s11356-011-0668-0.

[19] Nouha Ben Hafaiedh, Nizar Bellakhal. Mineralization of Synthetic and Industrial Food Effluent Containing Acid Red18 by Electro-Fenton Process using a Graphite-Felt Cathode. s.l. : International Journal of Science and Research (IJSR), 2015. Vol. 4. SUB154895.

[20] Jennifer A. Banuelos, Orlando Garcia-Rodriguez, Abdellatif El-Ghenymy,Francisco J. Rodrıguez-Valadez, Luis A. Godınez Enric Brillas. Advanced oxidation treatment of malachite green dye using a low cost carbon-felt air-diffusion cathode. s.l. : Journal of Environmental Chemical Engineering, 2016. Vol. JECE 1014.

[21] Puthiya Veetil Nidheesh, Rajan Gandhimathi. Comparative Removal of Rhodamine B from Aqueous Solution by Electro-Fenton and Electro-Fenton-Like Processes. s.l. : Clean Soil Air Water, 2013. 10.1002/clen.201300093.

[22] Enric Brillas, Ignasi Sires, and Mehmet A. Oturan. Electro-Fenton Process and Related Electrochemical Technologies Based on Fenton's Reaction Chemistry. s.l. : Chemical Reviews, 2009. Vol. 109.

[23] Abdoulaye Thiam, Enric Brillas, Francesc Centellas, Pere L. Cabot, Ignasi Sirés. Electrochemical reactivity of Ponceau 4R (food additive E124) in different electrolytes and batch cells. Barcelona : Electrochimica Acta, 2015.

[24] S. Renganathan, W. Richard Thilagaraj, Lima Rose Miranda, P. Gautam, M. Velan. Accumulation of Acid Orange 7, Acid Red 18 and Reactive Black 5 by growing Schizophyllum commune. Chennai : Bioresource Technology, 2006.

[25] Taruna Joshi, Leela Iyengar, Karunakar Singh, Sanjeev Garg. Isolation, identification and application of novel bacterial consortium TJ-1 for the decolourization of structurally different azo dyes. Knapur : Bioresource Technology, 2008.

[26] Alexandro M.M. Vargas, André L. Cazetta, Alessandro C. Martins, Juliana C.G. Moraes, Edivaldo E. Garcia, Gisele F. Gauze, Willian F. Costa, Vitor C. Almeida. Kinetic and equilibrium studies:Adsorption of food dyes Acid Yellow 6, Acid Yellow 23, and Acid Red 18 on activated carbon from flamboyant pods. s.l. : Chemical Engineering Journal, 2011.

[27] Mohamed A. Salem, Shaker T. Abdel-Halim, Abd El-Hamid M. El-Sawy, Ahmed B. Zaki. Kinetics of degradation of allura red, ponceau 4R and carmosine dyes with potassium ferrioxalate complex in the presence of H2O2. Tanta : Chemosphere, 2009. Vol. 76.

[28] Cristina Beninca, Patrıcio Peralta-Zamora, Ronaldo Cardoso Camargo, Celia Regina Granhen Tavares, Everton Fernando Zanoelo, Luciana Igarashi-Mafra. Kinetics of oxidation of ponceau 4R in aqueous solutions by Fenton and photo-Fenton processes. s.l. : Reac Kinet Mech Cat, 2012.

[29] Sylwia Mozia, Maria Tomaszewska, Antoni W. Morawski. Photocatalytic degradation of azo-dye Acid Red 18. s.l. : Desalination, 2005.

[30] Abdoulaye Thiam, Enric Brillas, José A. Garrido, Rosa M. Rodríguez, Ignasi Sirés. Routes for the electrochemical degradation of the artificial food azo-colour Ponceau 4R by advanced oxidation processes. Barcelona : Applied Catalysis B: Environmental, 2016.

[31] Nouha Ben Hafaiedh, Nizar Bellakhal. Mineralization of Synthetic and Industrial Food Effluent Containing Acid Red18 by Electro-Fenton Process using a Graphite-Felt Cathode. Tunis : International Journal of Science and Research (IJSR), 2015. Vol. Volume 4. SUB154895.

[32] I. Naimi, N. Bellakhal. Removal of 17β-Estradiol by Electro-Fenton Process. Tunis : Scientific Research, 2012. Vol. 3.

[33] Choi, Alok D. Bokare Wonyong. Review of Iron-Free Fenton-Like Systems for Activating H2O2 in Advanced Oxidation Processes. Korea : Journal of Hazardous, 2014. HAZMAT 15895.

[34] Malak Maamar, Imen Naimi, Yassine Mkadem, Nebil Souissi, Nizar Bellakhal. Electrochemical Oxidation of Bromothymol Blue: Application to Textile Industrial Wastewater Treatment. Tunis : J. Adv. Oxid. Technol., 2015. Vol. 18. ISSN 1203-8407.

[35] Mohamed M. Ghoneim, Hanaa S. El-Desoky, Naglaa M. ZidanMohamed M. Ghoneim, Hanaa S. El-Desoky, Naglaa M. Zidan. Electro-Fenton oxidation of Sunset Yellow FCF azo-dye in aqueous solutions. Tanta : Desalination, 2011. Vol. 274.

[36] P.V. Nidheesh, R. Gandhimathi. Trends in electro-Fenton process for water and wastewater treatment: An overview. Tamilnadu : Desalination, 2012. Vol. 299.

[37] M. Zaied, N. Bellakhal. Electrocoagulation treatment of black liquor from paper industry. s.l. : Elsevier , 2008. Journal of Hazardous Materials 163 (2009) 995–1000.

[38] Ignasi Sirés, Elodie Guivarch, Nihal Oturan, Mehmet A. Oturan. Efficient removal of triphenylmethane dyes from aqueous medium by in situ electrogenerated Fenton's reagent at carbon-felt cathode. Marne-la-Vallée : Chemosphere, 2008. Vol. 72.