



Routes for the electrochemical degradation of the artificial food azo-colour Ponceau 4R by advanced oxidation processes



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ABSTRACT

The performance of three electrochemical advanced oxidation processes, namely electro-oxidation with electrogenerated H_2O_2 (EO- H_2O_2), electro-Fenton (EF) and photoelectro-Fenton (PEF) for the treatment of aqueous solutions of the food azo dye Ponceau 4R in an undivided cell with a BDD anode and an air-diffusion cathode was compared in terms of colour, dye concentration and total organic carbon (TOC) removals. PEF treatments in ultrapure water with Na_2SO_4 were performed to assess the effect of current density, as well as supporting electrolyte and dye concentrations. At 100 mA cm^{-2} , solutions of 130 mL of 254 mg L^{-1} of the dye in $0.05 \text{ M Na}_2\text{SO}_4$ became colourless and totally mineralized after 50 and 240 min, respectively, which can be explained by the synergistic action of BDD($\cdot\text{OH}$) at the anode surface and homogeneous $\cdot\text{OH}$ formed in the bulk from Fenton's reaction promoted in the presence of Fe^{2+} catalyst. Furthermore, UVA photons induced the continuous Fe^{2+} regeneration and photolytic decomposition of refractory intermediate complexes. In that aqueous matrix, the cleavage of the dye molecules proceeded through several reaction routes to yield *N*-containing and non-*N*-containing derivatives with one or two aromatic rings, short-chain aliphatic carboxylic acids and inorganic ions. Oxalic and oxamic acids and sulfate ions were accumulated at different rates in EO- H_2O_2 , EF and PEF. The three methods allowed the progressive decontamination of Ponceau 4R solutions in a real water matrix even without the addition of electrolyte, although complete TOC abatement after 360 min at 33.3 mA cm^{-2} was only ensured by the iron-catalyzed PEF process.

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1. Introduction

Currently, food additives such as preservatives and colouring agents are among top food safety concerns in industrialized countries, despite being carefully regulated by national and international authorities. Indeed, their effects become uncontrolled when unintended targets, particularly children or some highly sensitive person (HSP) with allergies or food intolerances, are routinely exposed to them upon drinking water consumption. According to the International Food Information Council (IFIC) and the US Food and Drug Administration (FDA), colour additives include dyes, pigments and any other substance applied to a food, drug, cosmetic or the human body to impart colour [1]. Azo compounds are the most widespread synthetic colouring substances in the food industry, as occurs in many other sectors [2,3], but the negative impact of the so-called food azo-colours has been much less investigated than

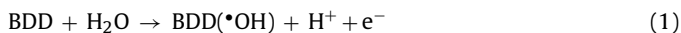
that of their textile counterparts so far. These dyes present one or more azo ($-\text{N}=\text{N}-$) bonds and usually exhibit complex structures that confer them large stability against physicochemical attack and bio/photodegradation, thus becoming persistent in water [3].

Ponceau 4R ($\text{C}_{20}\text{H}_{11}\text{N}_2\text{O}_{10}\text{S}_3\text{Na}_3$, trisodium 2-hydroxy-1-(4-sulphonato-1-naphthylazo)-naphthalene-6,8-disulphonate, also known as Acid Red 18, New Coccine or additive E124 in the industry, CI 16255, $\lambda_{\text{max}} = 508 \text{ nm}$) is a paradigmatic case of sulphonated azo dye employed to give red colouring to foodstuffs. Lately, serious concerns have arisen since the intake of Ponceau 4R is plausibly connected to asthma and insomnia and it may increase children's hyperactivity and intolerance [4]. As a result, in 2009, the European Food Safety Authority reduced the acceptable daily intake from 4.0 to $0.7 \text{ mg (kg body weight)}^{-1}$ [5]. Despite being negative in *in vitro* genotoxicity as well as in long-term carcinogenicity studies, the topic is still controversial [6]. For instance, Ponceau 4R is currently not approved in the United States, Canada, Norway and Finland, and it is listed as a banned substance by some authorities [7]. Since information about the safety of water containing Ponceau 4R and other related azo dyes

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remains inconclusive [8], the best way to reduce risks is to develop much more effective water treatment technologies that ensure their complete removal before reaching end users. The great ability of advanced oxidation processes (AOPs) such as heterogeneous photocatalysis [9,10], ozone-electrolysis with Pt anode [11], chemical Fenton's reagent [12,13] and photo-Fenton [13] to degrade Ponceau 4R has been demonstrated. For the two latter Fenton-based AOPs, however, scarce information was provided, only describing a similar decolourization and mineralization rate in ultrapure water in both cases. Note that those studies did not evaluate the possible influence of a more complex water matrix and the formation of by-products, which is crucial for establishing the actual viability of both techniques. Conversely, to the best of the authors' knowledge, the performance of the electrochemical AOPs (EAOPs) to destroy this dye has not been reported yet.

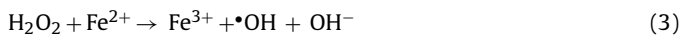
In the last decade, considerable effort has been devoted to the study of fundamentals and scale-up of electrochemical technologies for wastewater treatment, especially focusing on the destruction of organic matter by hydroxyl radicals [14–16]. Electro-oxidation (EO) is the most popular EAOP due to its simplicity, adaptability and outstanding performance of particular setups. This process relies on the electrocatalytic properties of the anode surface (M), since some materials like Pt only favour the partial conversion of contaminants by direct oxidation or under the action of chemisorbed oxides (MO), whereas others like boron-doped diamond (BDD) may promote the complete destruction of organic matter by physisorbed BDD(\bullet OH) formed as follows [17–23]:



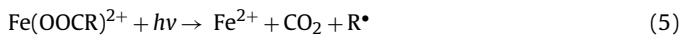
The use of undivided cells with a BDD anode and an active cathode can enhance the degree and/or rate of decontamination. Thus, in EO-H₂O₂, an air- or pure O₂-fed airtight or porous carbonaceous cathode is employed to electrogenerate H₂O₂ as follows [24–28]:



H₂O₂ is a weak oxidant, although it can be oxidized to HO₂ \bullet at the anode or be further activated in metal-catalyzed EAOPs like electro-Fenton (EF) and photoelectro-Fenton (PEF) [16]. In EF, the presence of low amounts of Fe²⁺ leads to the production of \bullet OH in the bulk through homogeneous catalysis via Fenton's Reaction (3) at optimum pH \sim 3 [29]. Organics are then destroyed upon the synergistic action of heterogeneous and homogeneous catalysis (BDD(\bullet OH) and \bullet OH, respectively).

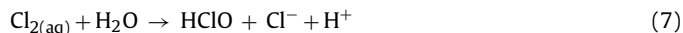


If an UVA lamp is used to irradiate the solution in the EF setup, then so-called PEF process, the mineralization is enhanced because UV photons induce the photoreduction of Fe(OH)²⁺ to Fe²⁺ via Reaction (4) and the photolysis of refractory Fe(III)-carboxylate products by Reaction (5) [16,29].



BDD anode has an extraordinary oxidation power that favours the production of oxidants such as H₂O₂, O₃, ferrate and peroxoaltes (S₂O₈²⁻, P₂O₈⁴⁻ and C₂O₆²⁻) depending on the aqueous matrix composition [16]. When the treated acidic solution contains Cl⁻ ions, \bullet OH and/or BDD(\bullet OH) (and UV in PEF) act in concomitance with active chlorine species (Cl₂ and HClO) produced in the bulk via Reactions (6) and (7) [3,14,16]. This medium, which is typical when treating real water matrices, is quite complex since oxychlorine anions [30–32], (oxy) chlorine radicals [33], chloramines [34],

trihalomethanes and haloacetic acids [35], as well as refractory chlorinated by-products, can appear.



Encouraging results have been obtained for the treatment of textile azo dyes by EAOPs with a BDD anode [36–40], and very recently we have even discussed the behaviour of two food azo dyes in such systems [41,42]. In the present work, aiming to gain more thorough knowledge about the fate of food azo-colours upon application of EAOPs, Ponceau 4R has been chosen as a model pollutant. It has been comparatively degraded in EO-H₂O₂, EF and PEF systems using an undivided BDD/air-diffusion cell. Most electrolyses have been carried out in ultrapure water with added Na₂SO₄ in order to investigate the effect of parameters like current density (*j*) and electrolyte and pollutant contents on the colour, dye concentration, and total organic carbon (TOC) removals. The reaction by-products identified by chromatographic techniques have allowed the proposal of various reaction pathways. The viability of the tested EAOPs to degrade Ponceau 4R in a real water matrix in the absence and presence of supporting electrolyte has been ascertained as well.

2. Experimental

2.1. Chemicals

Ponceau 4R (100% content) was purchased from Acros Organics. Anhydrous sodium sulfate, sodium chloride and lithium perchlorate used as supporting electrolytes, as well as iron(II) sulfate heptahydrate used as catalyst in EF and PEF, were of analytical grade supplied by Merck and Fluka. Oxalic, oxamic, fumaric, tartaric, formic and maleic acids used as standards were of analytical grade purchased from Merck, Avocado and Panreac. Sulfuric, hydrochloric and perchloric acids and sodium hydroxide used to regulate the pH were of analytic grade purchased from Merck, Acros Organics and Panreac. Organic solvents and other chemicals used were of high-performance liquid chromatography (HPLC) or analytical grade supplied by Sigma-Aldrich, Lancaster, Merck and Panreac. Solutions were prepared with ultrapure water obtained from a Millipore Milli-Q system with resistivity >18 M Ω cm at 25 °C. Some comparative trials were also carried out with a real water matrix collected from a secondary clarifier of a municipal wastewater treatment plant located in Manresa (Barcelona, Spain). Its main characteristics determined in the laboratory were: pH 7.3, specific conductivity = 1.9 mS cm⁻¹ (equivalent to ca. 0.010 M Na₂SO₄), TOC = 25 mg L⁻¹, 1.99 mM SO₄²⁻ and 10.3 mM Cl⁻. No iron ions were detected. This water was preserved at 4 °C and used the day after collection.

2.2. Electrochemical cells

The experiments were conducted in an open, undivided, cylindrical glass tank reactor of 150 mL capacity equipped with a double jacket for recirculation of thermostated water at 25 °C. The anode was a BDD thin-film electrode purchased from Adamant (at present, this material can be acquired from NeoCoat or Waterdiam), whereas the cathode was a carbon-polytetrafluoroethylene air-diffusion electrode purchased from E-TEK, mounted as described elsewhere [26] and fed with compressed air pumped at 1 L min⁻¹ for continuous H₂O₂ generation from Reaction (2). The geometric area of each electrode was 3 cm² and the interelectrode gap was 1 cm. All experiments were carried out using 130 mL of solutions at pH 3.0 under vigorous stirring with a magnetic bar at 800 rpm to ensure homogenization and the transport of reactants towards/from the electrodes. In EF and PEF, 0.50 mM Fe²⁺

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