



# An effective electroanalytical approach for the monitoring of electroactive dyes and intermediate products formed in electro-Fenton treatment

Bakhta Bouzayani<sup>a,c</sup>, Elvira Bocos<sup>a</sup>, Sourour Chaâbane Elaoud<sup>c</sup>, Marta Pazos<sup>a</sup>,  
 Maria Ángeles Sanromán<sup>a</sup>, Elisa González-Romero<sup>b,\*</sup>

<sup>a</sup> Department of Chemical Engineering, University of Vigo, Campus As Lagoas-Marcosende, 36310 Vigo, Spain

<sup>b</sup> Department of Analytical and Food Chemistry, University of Vigo, 36310 Vigo, Spain

<sup>c</sup> Laboratory of Physical Chemistry of the Solid State, Department of Chemical, University of Sfax, 3000 Sfax, Tunisia

## ARTICLE INFO

### Keywords:

Reactive Black 5  
 H-Acid  
 Electro-Fenton  
 Linear Sweep Voltammetry  
 Screen-printed carbon electrodes  
 Dye degradation monitoring

## ABSTRACT

Reactive Black 5 (RB5) is an electroactive diazo dye compound derivate of H-acid (coupling reaction), which cannot be effectively degraded by conventional or biological processes. In this work, the feasibility of electro-Fenton (EF) process to treat a simulated effluent polluted by RB5 dye and the effectiveness of electroanalysis by Linear Sweep Voltammetry (LSV) to monitor RB5, intermediates and by-products during the EF treatment have been demonstrated. Several variables on the electrochemical behaviour of RB5 have been determined under EF experimental conditions. The key factors are scan rate and dye concentration (in the presence and the absence of iron) and their effect on shape, position and height of RB5 peaks have been determined to obtain the best sensitivity and selectivity in the voltammetric analysis. Moreover, the iron appears as a strong electrocatalyst that promotes the electron transfer for the oxidation reaction of RB5 on screen-printed carbon electrode, in part, due to a very stable coordinate complex formed with RB5. Besides that, the degradation profiles have revealed the main stages along the EF process and the voltammetric kinetic data has given selective information about the RB5 degradation and the evolution of the electroactive products generated. The formation of aromatic/cyclic organic intermediates, and evolution of carboxylic acids, as well as the inorganic ions released during the treatment were validated by other techniques and a plausible pathway is proposed based on the obtained results.

## 1. Introduction

Around 80,000 tons of synthetic dyes are annually used by a large variety of industries such as textile, leather tanning, hair colouring, food products, etc. [1]. However, 1–10% of employed dyes are lost during their consumption and production, generating 87 million litres of wastewater per day [2]. The important volumes of consumed water and wastewater generated provide aquatic environments with colour and odour, causing an irreparable damage on these ecosystems. Such enormous scale production and the later discharge of these substances into the water streams cause not only non-aesthetic conditions but also eutrophication, entailing a potential risk for living beings health [3]. Within this context, concerns among population and scientific community have force the environmental authorities to create more severe laws in matter of pollution and concentration limits of some chemical. As an example, attempts in this direction in Europe have included the redaction of the Directive 2002/61/EC, created to establish restrictions on the dyeing market and concentration limits of 70 ppm in the use of

certain azocolourants [4].

Dyes use to be classified according to their chromophore group, being the azo class ( $-N=N-$ ) the most used ones at industrial scale. Reactive Black 5 (RB5) is an electroactive diazo dye derivate from H-acid, which is considered having irritating and toxic properties for living beings. Moreover, apart from azo groups RB5 present sulfonic acid groups to increase water solubility that also increase the recalcitrant character of this compound [5]. Severe damages on the ecosystems and aquatic organisms due to their extremely high persistence and low biodegradability [6].

Lamentably, conventional wastewater treatment plants (WWTP) cannot achieve the complete elimination of these azo dyes. Consequently, numerous efforts have been addressed on research of alternative water technologies able to degrade these pollutants [7–10]. As an example, Electrochemical Advanced Oxidation Processes (EAOPs) are currently considered promising candidates able to achieve a complete and quick mineralization of nonbiodegradable organic matter [11]. These processes comprise the generation of hydroxyl radicals ( $\cdot$

\* Corresponding author.

E-mail addresses: [ebocos@uvigo.es](mailto:ebocos@uvigo.es) (E. Bocos), [sourour.chaabane@fss.rnu.tn](mailto:sourour.chaabane@fss.rnu.tn) (S.C. Elaoud), [mcurras@uvigo.es](mailto:mcurras@uvigo.es) (M. Pazos), [sanroman@uvigo.es](mailto:sanroman@uvigo.es) (M.Á. Sanromán), [romero@uvigo.es](mailto:romero@uvigo.es) (E. González-Romero).

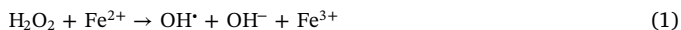
<http://dx.doi.org/10.1016/j.jelechem.2017.06.035>

Received 31 March 2017; Received in revised form 20 May 2017; Accepted 19 June 2017

Available online 20 June 2017

1572-6657/ © 2017 Elsevier B.V. All rights reserved.

OH), highly reactive species up to quickly attack the saturated aromatic rings of organic compounds until their complete elimination. Among them, EF treatment is the most known and popular EAOP [12]. Based in Fenton's reaction (1), on this process,  $\text{H}_2\text{O}_2$  is *in situ* electrogenerated at a carbonaceous cathode continuously fed with oxygen Eq. (2), while  $\text{Fe}^{2+}$  is electro-regenerated from  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  at the cathode surface Eq. (3) [12].



Hydroxyl radicals attack the organic compounds and the by-products generated may be carcinogenic substances in nature, being crucial the development and evaluation of alternative analytical approaches able to bring an accurate identification of these intermediates [13]. Usually, the evolution of pollutants and oxidation intermediates formed in EAOPs is evaluated by analytical techniques such as HPLC, HPLC-MS, GC-MS, UV-Vis Spectrophotometer, etc. However, some of them (HPLC-MS or GC-MS) have complex interpretation, being necessary long time of analysis (HPLC, HPLC-MS, GC-MS) and high volumes (GC-MS) of sample. Nonetheless, electroanalytical methodologies may be an interesting tool for monitoring both kind of inorganic and organic pollutants in water, which applicability on this field has been practically disregarded [14,15]. Recently, we have afforded in previous works the challenge of developing alternative electroanalytical approaches with high versatility and efficiency for monitoring electroactive pollutants and the intermediates generated in EF treatments [16–18]. These studies describe the use of traditional electroanalytical techniques such as Linear Sweep Voltammetry (LSV) or Differential Pulse Voltammetry (DPV) in combination with “screen-printed carbon electrodes” (SPCE), which indeed can be considered as very accurate and sensitive devices, being suited to detect contaminants even at trace levels (ppt) [19], a fundamental task to understand degradation mechanisms.

As a matter of fact, a study published by Bounab et al. [17] has demonstrated the potentialities of this methodology identifying electroactive compounds formed during the EF treatment of phenolic derivatives. More recently, Bocos et al. [18] reported in an interesting work the novelty of this system as a powerful tool able to partially elucidate the degradation mechanism of the ionic liquid 1-Butyl-3-methylimidazolium triflate during EF treatment. Remarkably, this new device allowed the authors to describe the strange behaviour found by Ionic Chromatographic (IC) analysis. As the molecule 1-Butyl-3-methylimidazolium triflate has 3 atoms of fluoride, it was expected to found a determined amount in the media as mineralization of organics occurs, however no sign of fluoride in solution was found. Eventually, by using the described electroanalytical system, authors could identify a strong interaction occurring between the anion triflate released in the treatment and iron used as catalyst. Thus, by coupling LSV with SPCE, the authors were able to quickly evaluate the evolution of the treatment causing low disruption of the system, since very little volumes of sample (50  $\mu\text{L}$ ) are necessary.

The core of this work deals with the application of LSV technique on the monitoring of the RB5 dye degradation and the electroactive intermediates formed during EF process. Likewise, the formation of aromatic/cyclic organic intermediates and evolution of carboxylic acids, as well as the inorganic ions released during the treatment were validated by other conventional techniques.

## 2. Materials and methods

### 2.1. Chemicals

Reactive Black 5 (RB5) was purchased to Sigma Aldrich and used as

received. During electrochemical assays, an initial concentration of 100  $\text{mg L}^{-1}$  (50% of purity) was used in all cases.  $\text{Na}_2\text{SO}_4$  (10 mM) purchased to Sigma Aldrich was used as electrolyte. Iron (II) sulfate heptahydrate ( $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$ , used as catalyst source, 99%) was provided by Sigma-Aldrich and used as iron source.  $\text{H}_2\text{SO}_4$ , or NaOH were used to adjust the pH and purchased to Prolabo and Sigma Aldrich, respectively. Chromatographic mobile phases were prepared with acetonitrile (analytical grade, Sigma Aldrich) for HPLC analysis and the following inorganic salts:  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  (both from Fluka) for IC analysis. All solutions were prepared in Millipore filtered water and volumetric lab equipment. The following commercial products were used in the intermediate studies by voltammetric techniques: 4-Aminophenol (4AP), acetaminophen, sulfanilic acid, H-acid (4-Amino-5-hydroxynaphthalene-2,7-disulfonate), 1-Hydroxynaphthalene-4-sulfonate (1N4S), 4-Hydroxybenzene sulfonate (4PS), 1,2-Napthoquinone-4-sulfonate (12NQ4S), 4,5-Dihydroxynaphthalene-2,7-disulfonate (45N27S) from ACROS Organic and quinone (Q), hydroquinone (HQ), catechol, pyrogallol, 2-phenilendiamine (PDA), 2-Hydroxynaphthalene-3,6-disulfonate (2N36S) from Sigma-Aldrich.

### 2.2. Voltammetric analysis

Cyclic (CV) for electrode surface activation measurements and Linear Sweep Voltammetry (LSV) for electroanalysis of RB5 degradation studies were obtained with a potentiostat/galvanostat AUTOLAB PGSTAT30 connected to the SPCE through a connector DropSens DSC, where the electrochemical cell with a conventional three-electrode system is placed. The system was controlled by the General Purpose Electrochemical Experiments Software 4.9.05 (GPES 4.9.05). The cell configuration consists in a working electrode: carbon (DRP-C110) with a 4 mm diameter from DropSens Company (Spain), a pseudo-reference electrode of silver, and a carbon counter electrode. The volume dispense on the cell was 50  $\mu\text{L}$ , enough amount to cover the three electrodes system. The voltammetric measurements were carried out under room temperature. The LSV was the selected technique for monitoring the evolution of parent compound, RB5, and the electro-active compounds obtained from the EF experiments. Except when stated, the LSV voltammetric curves were recorded in a window potential range from  $-0.6 \text{ V}$  to  $1.2 \text{ V}$  at a scan rate of  $100 \text{ mV s}^{-1}$  and a step potential of 5 mV.

A “cleaning/activation” step of the working SPCE was required between successive runs and previously to any measurement in order to remove any impurity from the surface and to increase the active area on this working electrode [17–19]. For that, 5 cycles by CV in the potential range from  $-1.2$  to  $+1.0 \text{ V}$  at  $100 \text{ mV s}^{-1}$  in 0.05 M  $\text{H}_2\text{SO}_4$  solution were applied.

### 2.3. EF experiments

All experiments were carried out in a 0.25 L cylindrical glass reactor with 0.20 L of RB5 solution at initial pH of 3. The solution was continuously agitated with a magnetic stirring to avoid concentration gradients. Iron (0.25 mM) was added into the bulk as catalyst and  $\text{H}_2\text{O}_2$  was *in situ* electrochemically generated through the continuous aeration ( $1 \text{ L min}^{-1}$ ) on the cathode surface. The electric parameters were recorded with a multimeter (Fluke 175). A constant current density of 0.3 A was applied by two electrodes connected to a direct power supply (HP model 3662). Carbon felt (Carbon Lorraine, France) and boron doped diamond (BDD) (4–5  $\mu\text{m}$  diamond film thickness and doping level around 2500 ppm) supplied by DIACHEM® (Germany) were selected as cathode and anode, respectively. Carbon felt was placed on the inner wall of the cell, covering the total internal perimeter ( $6 \times 12 \text{ cm}$ ) while BDD ( $3 \times 3 \text{ cm}$ ) was centred in the reactor. All the experiments were carried out at ambient temperature.  $\text{Na}_2\text{SO}_4$  at concentration 0.01 M was added as electrolyte in order to increase the conductivity of the solution.

Download English Version:

<https://daneshyari.com/en/article/6662310>

Download Persian Version:

<https://daneshyari.com/article/6662310>

[Daneshyari.com](https://daneshyari.com)