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1 **Electrochemical treatment of a synthetic wastewater containing a sulphonated azo**  
2 **dye. Determination of naphthalenesulphonic compounds produced as main by-**  
3 **products.**

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9 **Abstract**

10 The electrochemical treatment of wastewaters from textile industry is a promising  
11 technique for substances which are resistant to biodegradation. This paper deals with the  
12 electrochemical decolourisation / degradation of synthetic solutions containing a  
13 reactive dye, C.I. Reactive Orange 4. Oxidation, reduction and oxido-reduction  
14 processes were evaluated using Ti/SnO<sub>2</sub>-Sb-Pt and stainless steel electrodes as anode  
15 and cathode, respectively. Electrolyses were performed at galvanostatic conditions in a  
16 filter press reactor. Decolourisation and degradation were followed by means of total  
17 organic carbon (TOC), chemical oxygen demand (COD) measurements and high  
18 performance liquid chromatography (HPLC). It was found a higher mineralisation rate  
19 for oxidation while oxido-reduction process gave more oxidised species. The kinetics of  
20 decolourisation was of pseudo-first order in all cases. The reduction process was the  
21 slowest process to decolourise. Gas chromatography-mass spectrometry (GC-MS) was  
22 employed to investigate the main intermediate compounds, confirming the presence of  
23 2-amino-1, 5-naphthalenedisulphonic acid (2A15NDS) in solution. When this  
24 compound was generated, it was gradually degraded during the oxidation and oxido-  
25 reduction processes indicating the feasibility and durability of Ti/SnO<sub>2</sub>-Sb-Pt

26 electrodes. However, during the electrochemical reduction process, this compound was  
27 continuously generated but it was not degraded.

28  
29 *Keywords: electrochemical wastewater treatment, reactive dye, naphthalensulphonic*  
30 *compound, derivatisation, GC-MS.*

31  
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## 38 **1. Introduction**

39

40 Over the last few decades, society has become increasingly sensitive towards the  
41 protection of the environment. **Taking into account that dyes are, by definition,**  
42 **highly visible materials, even minor releases into the environment may cause the**  
43 **appearance of colour.** In addition to this, many dyes are toxic and/or mutagenic to  
44 aquatic life [1]. **Due to** the large degree of aromatic rings present in the dye molecules  
45 and the stability of modern dyes, biological treatment is ineffective for their degradation  
46 [2, 3]. Moreover, as the number of sulphonic groups increases, the solubility of the dye  
47 in water increases too which implies a serious problem for their removal. The particular  
48 case of reactive dyes is of special interest because they undergo, to a certain extent, a  
49 hydrolysis reaction. The hydrolysed dye is no longer capable of reacting with the fibre  
50 and so must be washed out of the fibre after dyeing is complete. Then, the hydrolysed

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51 dye and any unreacted dye inevitably end up in the dyehouse effluent. Recently, these  
52 problems have been partially reduced with the development of more selective fibre-  
53 reactive systems, such as bifunctional reactive dyes, showing significantly improved  
54 processing conditions [4]. However, a practical reactive dye system which is completely  
55 free of the problem of hydrolysis has not been found yet. For this reason, an alternative  
56 approach to addressing the problem of colour and toxicity in textile dyeing effluent has  
57 involved the development of effluent treatment methods such as ozonation [5, 6],  
58 advanced oxidation processes [7-10], enzymatic [6] or adsorption processes [11] for the  
59 removal of different dyes. In this sense, over the past 10 years, the electrochemical  
60 techniques have been found of special interest for textile wastewater remediation due to  
61 advantages such as high efficiency, ease of operation and environmental compatibility  
62 since there is no need of adding chemicals [12]. Electrocoagulation methods have been  
63 investigated in order to remove textile dyes and several consumable materials as iron  
64 [13, 14] or aluminium [15] have been employed. Besides, electrochemical oxidation  
65 with non-soluble anodes has been investigated [13, 16-28]. The degradation products in  
66 the oxidation of azo dyes are typically carbon dioxide, nitrogen and sodium sulphate,  
67 with the possible formation of aromatic esters, phenols, aromatic amines, etc. First of  
68 all, the azo group is oxidized and, later, the decomposition products [29]. Moreover,  
69 electrochemical reduction of dyes is an attractive alternative for the decolourisation of  
70 highly coloured concentrated dyestuff solutions [18-21, 30-37].  
71 Since, in the 1960s, Henri Bernard Beer started studying the electrocatalytic behaviour  
72 of mixed metal oxides for the evolution of chlorine and oxygen [38-40], several oxide  
73 coatings have been investigated as a key factor in the development of **Dimensionally**  
74 **Stable Anodes (DSA) as electrodic materials**. From all DSA electrodes studied, a  
75 good candidate because of its considerable potential is SnO<sub>2</sub> and, especially, Sb-doped

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76 SnO<sub>2</sub> (Ti/SnO<sub>2</sub>-Sb). This kind of electrodes combine three important aspects: they  
77 present high **chemical** and electrochemical stability as a consequence of the rather large  
78 band gap (roughly 3.5 eV), high electrical **conductivity and high oxygen evolution**  
79 overpotential ( $\eta_{O_2}$ ). This last property contributes to the anodic oxidation of many  
80 organic pollutants in aqueous solution since oxygen evolution represents an unwanted  
81 leakage current, reducing the overall current efficiency and the available oxidation  
82 potential [41-43]. **To** increase the service life of Ti/SnO<sub>2</sub>-Sb electrodes it **was**  
83 **demonstrated that little amounts of platinum in the coating increase the service life**  
84 **several orders of magnitude** [41]. In general, the service life of these electrodes, as  
85 DSA-type electrodes, is affected by several factors that should be considered. **The**  
86 **electrolyte employed is one of them. Numerous electrolytes have been employed in**  
87 **several studies. Some of them are:** H<sub>2</sub>SO<sub>4</sub> [18, **44**], KNO<sub>3</sub> [**45**], HClO<sub>4</sub> [**46**], NaF [**18**],  
88 Na<sub>2</sub>SO<sub>4</sub> [**20, 21, 47**] and NaCl (or KCl) [**16, 18, 22, 48, 49**]. **In the case of chloride,**  
89 **although it enhances the efficiency of the process, it affects directly the coating**  
90 **stability reducing the service life.** In addition, **its use** can be limited by the production  
91 of undesirable toxic chlorinated by-products. **The generation of these chlorinated**  
92 **compounds has been confirmed in some cases by GC-MS analysis [50, 51].** In  
93 contrast, sulphate is an inert supporting electrolyte and any reactive species **are**  
94 **produced** during the electrolysis, except under special conditions where **persulphate**  
95 **may be generated** [17, 52].

96  
97 The first objective of this work **was** to study the electrochemical treatment of a  
98 synthetic solution containing **the reactive azo dye C.I. Reactive Orange 4** (Colour  
99 Index Number 18260), **using** Na<sub>2</sub>SO<sub>4</sub> as electrolyte and Ti/SnO<sub>2</sub>-Sb-Pt as anode. **Azo**  
100 **dyes are considered** the major outlet for naphthalenesulphonic compounds. **These**

101 compounds may be more harmful to the aqueous environment than the dye  
102 molecule. For this reason, the second purpose of this paper was to determinate the  
103 presence or not of these compounds during and after the electrochemical  
104 treatment.

105

## 106 2. Experimental

107

### 108 2.1. Chemicals and reagents

109 Ultrapure water from an Elix 3 Millipore Milli-Q RG system with a resistivity near to  
110 18.2 MΩ cm was used for the preparation of all solutions. Dye solutions of 0.8 g L<sup>-1</sup>  
111 were simulated from the commercial product according to real concentrations  
112 found in textile effluents [53]. This concentration was also selected according to the  
113 detection limits of the different systems to ensure an optimal monitorisation of the  
114 different parameters.

115 All synthetic dye solutions were previously hydrolysed by NaOH solution addition  
116 obtaining an alkaline pH (about 10-13) as a result of the substitution of the two  
117 chlorine atoms by OH<sup>-</sup> groups, giving the hydrolysed form.

118

119 Moreover, when electrochemical reduction and electrochemical oxidation were studied,  
120 a blank solution consisting of 0.5 M NaOH + 0.1 M Na<sub>2</sub>SO<sub>4</sub> was used in a separated  
121 compartment. It is important to highlight that NaOH was not used as electrolyte, it  
122 was only used to obtain the same alkaline pH that the hydrolysed dye solution. NaOH  
123 and Na<sub>2</sub>SO<sub>4</sub> were supplied by Merck (p.a.).

124 Methanol 99+ % and sulphuric acid 95-97 % used for the solid phase extraction (SPE)  
125 were supplied by Merck. N, N-dimethylformamide (DMF) employed in the

126 **derivatisation process** was supplied by Scharlau, hexane 99+ % was purchased from  
127 Fluka Analytical, sodium thiosulphate and potassium iodide 99+ % from Aldrich and  
128 trifluoroacetic anhydride (TFAA) 99+ % from Fluka. Moreover, all  
129 naphthalenesulphonic compounds 98+ % were obtained either as free acids or as  
130 sodium salts from Sigma, Fluka and Merck. 2-aminonaphthalene 99 % was purchased  
131 from Panreac.

132

## 133 2.2. *Electrochemical experiments*

134 The electrolyses of the **dye solutions were** carried out **using a divided filter press**  
135 **reactor for the electrochemical oxidation and the electrochemical reduction. In this**  
136 **case, anodic and cathodic compartments were separated by means of a Nafion 117**  
137 **(DuPont) cationic membrane. For the electrochemical oxido-reduction it was**  
138 **employed the undivided mode of the filter press reactor.** A stainless steel electrode  
139 was employed as cathode and Ti/SnO<sub>2</sub>-Sb-Pt electrode with mesh geometry was used as  
140 anode. The working volume was 0.45 L in all cases. All the experiments were carried  
141 out under galvanostatic conditions with a power supply (Grelco GVD310 0-30Vcc / 0-  
142 10 A). The applied current density was 125 mA cm<sup>-2</sup> and the total applied specific  
143 charge (Q<sub>final</sub>) was 240 Ah L<sup>-1</sup>. This value of total applied specific charge permitted to  
144 compare the final samples **when parameters such as TOC and COD are practically**  
145 **invariable.** Samples were collected at two different points of the electrolysis. The first  
146 sample was taken at the moment of complete decolourisation. This is when the  
147 unbroken azo group in solution was only 1 % (determined by means of kinetics  
148 calculations). The second sample was the final sample and it was always taken at Q<sub>final</sub>  
149 = 240 Ah L<sup>-1</sup> [54].

150

151 *2.3. Preparation of the doped SnO<sub>2</sub> electrodes*

152 The electrodes of doped tin dioxide were prepared following a standard thermal  
153 decomposition method of the salt precursor on a titanium substrate [41, 55-57].  
154 Titanium electrodes with mesh geometry (8 cm x 6 cm) were first pre-treated to  
155 eliminate the superficial layer of TiO<sub>2</sub> (an electric semiconductor). Moreover, a higher  
156 roughness was obtained which favours the electrocatalytic oxide adherence to the Ti  
157 support. This pre-treatment consisted of degreasing with acetone using ultrasounds for  
158 10 min. Following, the titanium supports were etched for 1 h in a boiling solution of  
159 oxalic acid (10 %). After that, the supports were rinsed with ultrapure water and the  
160 precursor solution was brushed on the Ti mesh. This precursor solution contained 10 %  
161 SnCl<sub>4</sub>·5H<sub>2</sub>O (provided by Aldrich) + 1 % SbCl<sub>3</sub> (purchased from Fluka) + 0.252 %  
162 H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (supplied by Merck) dissolved in a mixture of ethanol (provided by  
163 Panreac) + HCl (supplied by Merck). Afterwards, the electrodes were introduced in an  
164 oven at 400 °C for 10 min. In this phase of the procedure, the decomposition of the salt  
165 and the formation of the metal oxide occurred. This process was successively repeated  
166 until a weight increment of about 2 mg cm<sup>-2</sup> was obtained. Finally, a final thermal  
167 treatment at 600 °C was applied for 1 h.

169 *2.4. Solid phase extraction (SPE) of the samples*

170 The SPE of polar and hydrophilic aromatic sulphonic acids was done using a LiChrolut  
171 EN polymeric sorbent (from Merck) based on a polystyrene-divinylbenzene. This  
172 provides high extraction efficiency for polar and hydrophilic aromatic sulphonic acids  
173 [58]. Before extraction, each SPE cartridge was conditioned by passing 4 mL of  
174 methanol and 5 mL of water (acidified to pH = 3 using sulphuric acid). Then, the  
175 aqueous samples were loaded. The next stage consisted of drying the sorbent using a



176 Diafragm-Vacuum Pump MD4C, Vacuum Brand GMBH+CO, set at 15 psi (negative  
177 pressure) during 15-20 min. **Once dried the extract, it was dissolved in 4 mL** of  
178 methanol. **After evaporating the methanol, the extract was lately dissolved in DMF**  
179 **for its derivatisation.**

180 **Samples from** the electrochemical reduction and electrochemical oxido-reduction of  
181 C.I. Reactive Orange 4 solution, the pH was also adjusted to pH = 3 with sulphuric acid.  
182 **Samples from** electrochemical oxidation presented already acid pH since hydroxyl  
183 groups were oxidised.

#### 185 2.5. Derivatisation procedure

186 **Sulphonated compounds have in general poor thermal stability and low volatility**  
187 **so it is necessary to transform sulphonic groups into volatile derivatives.** Taking  
188 into account the high volatility of thiols, the **derivatisation method used** in this work  
189 **consisted of sulphonic groups reduction.** For that purpose, iodide and trifluoroacetic  
190 anhydride in dimethylformamide were used **[59, 60]**. Solutions of 2-naphthaleneamine  
191 and naphthalene-2-sulphonic acid were directly prepared by dissolving 0.1 mmols of  
192 these reagents in 2 mL of DMF. On the other hand, solutions of 2-amino-1-  
193 naphthalenesulphonic acid (2A1NS) and 2-amino-1, 5-naphthalenedisulphonic acid  
194 (2A15NDS) in DMF were prepared by dissolving the residue recovered after the SPE  
195 process (see section 2.4) from aqueous solutions containing 0.1 mmol of reagent.  
196 Following to this, 1 mmol of potassium iodide and 1 mmol of TFAA was added to the  
197 DMF solution. After reacting at 60 °C during 1 h, the next stage of the process consisted  
198 of the addition of the exact volume of sodium thiosulphate (5 % aqueous) necessary **to**  
199 **decolourise the dark brown solution.** Finally, the derivatised products were extracted  
200 into 1 mL of hexane. Once the derivatisation process finished, the initial amino and

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201 sulphonic groups were **transformed** into amide and thiol groups, respectively. **This**  
202 **process was also carried out for samples from the electrochemical treatments.**

203

## 204 *2.6. Analyses and instruments*

205 TOC measurements were performed using a Shimadzu TOC-VCSN analyser based on  
206 the combustion-infrared method. Initial and final samples were diluted **to obtain the**  
207 **appropriate concentration according to the operating range of the system.** The  
208 instrument operated at 720 °C and 20 µL sample injection with an air (free of CO<sub>2</sub>) flow  
209 rate of 150 mL min<sup>-1</sup>. COD values were also determined with a Spectroquant<sup>®</sup> analyser.  
210 The method employed for COD measurements is analogous to EPA 410.4, US Standard  
211 Methods 5220 D and ISO 15705. The breakdown intermediates after the  
212 electrochemical treatments have been studied by means of high-performance liquid  
213 chromatography (HPLC). The system employed was a Hitachi Lachrom-Elite  
214 Chromatographic System equipped with diode array detector. This system also  
215 **permitted** to obtain the UV-Visible spectra of dye solutions. The chromatographic  
216 separations were performed on a Lichrospher 100 RP-18 C column with 5 µm packing  
217 using a similar method to that in EN 14362-2:2003/A. The mobile phase composition  
218 was methanol (eluent A)/aqueous buffer solution KH<sub>2</sub>PO<sub>4</sub>-Na<sub>2</sub>HPO<sub>4</sub> (eluent B) with pH  
219 6.9. Separation was accomplished at a flow rate of 1 mL min<sup>-1</sup>, at 25 °C and injection  
220 volume of 80 µL. The detection wavelength was set at 486 and 258 nm. At the  
221 beginning of the chromatographic separations, the gradient elution consisted of 15 %  
222 methanol – 85 % aqueous buffer and it was progressively modified to 30% methanol –  
223 70 % aqueous buffer within 10 min.

224 GC-MS analyses were also performed **using** a Shimadzu GC-MS-QP2010 gas  
225 chromatograph-mass spectrometer equipped with a secondary electron multiplier

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226 dinode (MSD) and a Teknokroma S Meta X5, P/N TR-820232 capillary column (30 m  
227  $\times 0.25$  mm I.D.  $\times 0.25$   $\mu$ m film) was employed under the following conditions: carrier  
228 gas (helium) flow rate 30 mL min<sup>-1</sup>; injection port temperature 250 °C. GC temperature  
229 program was as follows: 120 °C for 4 min, followed by a 10 °C min<sup>-1</sup> ramp to 250 °C for  
230 analytical samples. The GC temperature program for samples from electrochemical  
231 processes was as follows: 140 °C for 4 min, followed by a 10 °C min<sup>-1</sup> ramp to 275 °C;  
232 injection port temperature, 250 °C. Mass spectra were acquired in the electron impact  
233 mode with a m/z scan from 40 to 1000; scan speed of 2000; interval 0.5 s; ion source  
234 temperature, 200 °C.

235

### 236 3. Results and discussion

237

#### 238 3.1. TOC and COD analyses. Oxidation and mineralisation process

239 COD and TOC concentrations were determined in order to know the feasibility of  
240 oxido-reduction and oxidation processes to degrade dye solutions. Figure 1 shows TOC  
241 and COD removals obtained at  $Q_{\text{final}} = 240$  Ah L<sup>-1</sup>. It can be observed that almost 50 %  
242 of the initial organic carbon disappeared after the oxido-reduction process while the  
243 COD removal reached a higher value (72 %). These results indicate that, although there  
244 is a partial mineralisation of the initial solution, the intermediates generated during the  
245 oxido-reduction show certain stability in solution compared to oxidation process. In the  
246 case of the oxidation process, the mineralisation degree is higher than COD  
247 removal. Then, these results give a general idea of the degradation during the  
248 oxidation process. This higher mineralisation rate could be possible due to the  
249 previous oxidation of the intermediates which makes them more easily mineralised. This  
250 can be evaluated considering the ratio COD/TOC at two significant points of the

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251 **electrolyses**: the moment of complete decolourisation and the end of the electrolyses.  
252 As it will be explained in the next section, the moment of complete decolourisation  
253 corresponds to the presence of only 1 % of the dye remaining in solution. In the case of  
254 the oxidation process, it was observed an increase in COD/TOC ratio from 0.99 to 1.18.  
255 This reveals that, although there is lesser TOC concentration in the final sample, it is  
256 more difficult to oxidise these organic compounds since more **moles** of oxygen are  
257 needed. **Contrary to this**, during oxido-reduction process the COD/TOC ratio  
258 decreased from 0.70 to 0.62 confirming the presence of organic compounds stable in  
259 solution that **are gradually** oxidised.

260

### 261 *3.2.HPLC analyses and kinetics of decolourisation*

262 HPLC technique was employed to evaluate the variation of dye concentration with  
263 electrolysis time **and the generation of intermediates during the electrochemical**  
264 **processes**. For this purpose, representative chromatograms were obtained at two  
265 different wavelengths. Figure 2 shows the chromatographic evolution obtained at 486  
266 nm for different values of applied specific charge (Q) (Fig. 2-a, Fig. 2-b and Fig. 2-c).  
267 This wavelength corresponds to the maximum absorbance of the chromophore group (-  
268 N=N-) so the peak observed at **the** retention time (Rt) of around 2.4 minutes is **in** direct  
269 relation to the quantity of dye present in solution whose azo group is unbroken.  
270 Therefore, evaluating the area of this peak it is possible **to study the decolourisation**  
271 **kinetics**. It is important to point out that the shift of this chromatographic peak with  
272 time is due to structural changes of the dye molecule as a result of the electrochemical  
273 treatment. This involves polarity changes which affects slightly **the** retention time  
274 value. However, although retention time varies, the UV-Visible spectrum associated to  
275 the chromatographic peak always showed the band at 486 nm; indicating the presence

of the azo group in the structure. **The three processes presented pseudo-first order kinetics. From the regression equations shown in Table 1 of the kinetic plots (that is,  $\ln(A/A_0)$  versus  $Q$  where  $A$  is the area of the chromatographic peak detected at 486 nm. Kinetic plots not shown), it was possible to obtain the theoretical value of  $Q$  for a complete decolourisation. This is when the area of the chromatographic peak of the dye presented a diminution of 99 %.** These values of  $Q$  are indicated in red colour in Fig. 2. As it can be seen, the three electrochemical processes are able to decolourise the dye solution since the peak at 2.4 minutes is completely eliminated. Both oxido-reduction and oxidation processes required the same value of  $Q$  to decolourise the dye solution while the electrochemical reduction was the slowest process. This involves that the reduction process presented the lowest decolourisation rate constant ( $k$ ), as shown in Table 1. The oxido-reduction process kinetics presented two stages: in the first one the decolourisation rate constant ( $k_1$ ) was very similar **to that of** the oxidation process. In the second stage, the decolourisation rate constant ( $k_2$ ) becomes more than double of  $k_1$ . The value of  $Q$  at which the decolourisation rate changes from  $k_1$  to  $k_2$  (about 25 Ah L<sup>-1</sup>) practically coincides with the value of  $Q$  **of** complete decolourisation for oxido-reduction. This is not surprising considering that at the moment of complete decolourisation there is only 1 % of dye molecules with chromophore group in their structure. **Oxidation did not show any change** in the decolourisation rate indicating a different mechanism for the azo group cleavage. This can be observed in Fig. 2-d, Fig. 2-e and Fig. 2-f where the evolutions of the different chromatograms obtained at 258 nm (a wavelength of the UV region, typical of aromatic intermediates absorbance) for different values of  $Q$  are **shown**. These chromatographic evolutions include chromatograms at the moment of complete decolourisation (values of  $Q$  in red colour) and chromatograms of final samples ( $Q_{\text{final}} = 240 \text{ Ah L}^{-1}$ ). It can be

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301 observed a set of new components appeared during the electrolyses. It was **also**  
302 observed a greater number of peaks in chromatograms of oxidation process (Fig. 2-e)  
303 which **could be** associated with a more complex mechanism of degradation. This could  
304 be the reason why the oxidation process did not show any increase of decolourisation  
305 rate. Furthermore, it can be observed higher scales in oxido-reduction chromatograms  
306 which are in accordance with TOC removal results commented before. On the contrary,  
307 the smaller scale observed in chromatograms of oxidation process verifies the higher  
308 **mineralisation** rate.

309 **In the case of the** reduction process (Fig. 2-f), the final chromatogram showed a single  
310 peak which indicates the generation of a single intermediate compound. This  
311 chromatogram was compared with other chromatograms of standard commercial  
312 compounds (figures not shown) whose chemical structure is similar to several dye  
313 moieties postulated as possible by-products. Based on the so close values of  $R_t$  (about 2  
314 min) and the similarity degree of 99 % obtained by comparing the UV-Visible spectra  
315 [28, 37], it was found that 2-amine-1, 5-naphthalenedisulphonic acid (2A15NDS) would  
316 be the most similar compound to the main intermediate formed after the reduction  
317 process. It is also interesting to highlight that **this intermediate was also** formed during  
318 oxido-reduction and oxidation processes. Later, it was gradually degraded since the area  
319 of its chromatographic peak diminished as  $Q$  increased. **However, in the case of the**  
320 **reduction** process this compound was formed at low values of  $Q$  **and the area** of its  
321 corresponding chromatographic peak did not decrease during the overall process. **This**  
322 implies that this compound was not degraded during the reduction process (see Figure  
323 3). Several authors have also obtained sulphonated amines from reactive dyes treatment.  
324 Thus, Carliell and coworkers investigated the microbial decolourisation of textile  
325 wastewaters under anaerobic conditions obtaining not only 2-amine-1, 5-

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326 naphthalenedisulphonic acid but also 1, 7-diamine-8-naphtho-3, 6-disulphonic acid,  
327 among others intermediates [61].

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### 329 3.3. GC-MS analyses

330 Taking into account the previous results obtained by HPLC, GC-MS analyses were  
331 performed for unambiguous identification of the intermediate products formed in the  
332 liquid phase during the electrolyses.

333 As commented in the experimental section, sulphonated compounds present poor  
334 thermal stability as well as low volatility which make their GC-MS study more  
335 complicated. Then, it is necessary a derivatisation process where sulphonic and amino  
336 groups are converted into the corresponding thiol and amide groups, respectively [59,  
337 60]. In order to validate the derivatisation method, standard solutions in DMF of 2-  
338 naphthaleneamine and 2-naphthalenesulphonic acid were analysed. This part of the  
339 study consists in verifying the expected behaviour and structural changes of amino and  
340 sulphonic groups after derivatisation process. The chemical structures of these standard  
341 compounds before and after being derivatisated are given in Table 2-a. The GC-MS  
342 results (data also shown in table 2-a) confirmed the structural modifications after the  
343 derivatisation.

344 The aim of GC-MS analyses was to obtain the greatest information as possible in order  
345 to identify the main species present in samples from C.I. Reactive Orange 4  
346 electrochemical treatment. Then, considering the aqueous nature of these samples, it  
347 was also important to study aqueous solutions of standard compounds previously  
348 postulated as possible by-products after the electrochemical treatments (see section  
349 3.2.). For this purpose, standard aqueous solutions of 2A1NS and 2A15NDS were  
350 prepared, subjected to SPE process and derivatised. All ionic fragments found in the

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351 standard aqueous solutions were of particular interest because they were considered as  
352 reference for the identification of 2A15NDS as the main intermediate expected to be  
353 formed after the electrochemical treatments of the dye. Based on the results obtained for  
354 these standard compounds, it was possible to propose an overall degradation pathway  
355 for derivatised 2A15NDS which is shown schematically in Scheme 2. The proposed  
356 2A15NDS degradation mechanism can be discussed more thoroughly taking into  
357 account the results presented in Table 2-b. **This table** contains the chemical structures  
358 of 2A1NS and 2A15NDS before and after the derivatisation together with the  
359 chromatographic retention times and the information obtained from the full-scan  
360 electron impact ionisation (EI) mass spectra. The derivatised 2A1NS showed **a single**  
361 chromatographic peak at  $R_t = 11.9$  min. The corresponding EI mass spectrum presented  
362 different fragments. Peaks at  $m/z$  253 ( $F_5$ ),  $m/z$  234 ( $F_{11}$ ) and  $m/z$  216 ( $F_{12}$ ) suggest the  
363 successive cleavage of C-F bonds of  $M^+$  ( $m/z$  272, see  $F_1$  in scheme 2). Peak at  $m/z$  239  
364 corresponds to N-(2-naphthalene)trifluoroethanamide ion ( $F_2$ ) and peaks at  $m/z$  160 and  
365 158 belong to naphthalenethiol molecular ion ( $F_3$ ). With regard to derivatised  
366 2A15NDS it can be observed a greater number of chromatographic peaks. This could be  
367 due to the instability of the derivatised structure at high temperatures in the injection  
368 port or to secondary reactions during the derivatisation process. Nevertheless, the  
369 reproducibility of these results has been confirmed. The EI mass spectra of these  
370 chromatographic peaks showed different fragments whose postulated structures are  $F_2$ ,  
371  $F_3$ ,  $F_5$ ,  $F_6$ ,  $F_7$ ,  $F_8$ ,  $F_9$ ,  $F_{10}$  and  $F_{11}$ .

372 The final stage of this study was to analyse several dye-containing samples collected at  
373  $45 \text{ Ah L}^{-1}$  and at the end ( $240 \text{ Ah L}^{-1}$ ) of the electrolyses. The majority of the  
374 intermediate products were identified by comparing their mass spectra and retention  
375 times with those obtained for pure standards 2A1NS and 2A15NDS. In the case of the



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376 oxido-reduction, the EI mass spectra of the chromatographic peaks at  $R_t = 12.3$  min,  $R_t$   
377  $= 14.3$  min and  $R_t = 14.5$  min showed the fragments  $F_2$ ,  $F_6$ ,  $F_7$ ,  $F_8$ ,  $F_9$  and  $F_{10}$ . The  
378 majority of these moieties were also observed for the standard 2A15NDS degradation  
379 so it can be confirmed that this compound is formed as an intermediate during the  
380 oxido-reduction. On the other hand, it is interesting to highlight the decrease in intensity  
381 of the chromatographic peaks from sample at  $45 \text{ Ah L}^{-1}$  to final sample. This indicates  
382 the gradual degradation of 2A15NDS which is formed at the first stage of the  
383 electrolysis. In fact, this result was also observed in chromatograms of samples  
384 collected during and after the electrochemical oxidation. EI mass spectra of samples  
385 from oxidation also showed two new fragments at  $m/z$  270 ( $F_1$ ) and  $m/z$  255 ( $F_5$ )  
386 coming from the cleavage of C-SH and C-F bonds of the theoretical structure for the  
387 derivatised 2A15NDS.

388 The generation and subsequent degradation of different aromatic amines formed during  
389 the electrochemical treatment of azo dyes have been also studied by other authors.  
390 Muthukumar and co-workers studied the electrochemical removal of the dye Acid  
391 Orange 10 [13]. The cleavage of the azo linkage resulted in the formation of aniline and  
392 1-amino-2-naphthol-6, 8-disulfonic acid as intermediates. These intermediates were  
393 later degraded. Vaněrková and co-workers also studied the electrochemical degradation  
394 of C.I. Acid Yellow 9 and C.I. Reactive Black 5. In this case, high-performance liquid  
395 chromatography/tandem mass spectrometry demonstrated the generation of different  
396 aromatic amines [62]. It is important to highlight that in both cases NaCl was used as  
397 electrolyte so the process of azo dye and intermediates degradation is faster and more  
398 effective. In this work, the electrolyte was  $\text{Na}_2\text{SO}_4$  avoiding the formation of  
399 organochlorinated compounds.

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400 On the contrary, GC-MS analyses of samples obtained during and after the  
401 electrochemical reduction process showed the opposite behaviour. The intensity of the  
402 main chromatographic peaks increased from the sample at 45 Ah L<sup>-1</sup> to final sample.  
403 This increase of intensity of the chromatographic peaks indicates the continuous  
404 formation of 2A15NDS by breakage of the azo group leading to the amino group during  
405 the electrochemical reduction. The EI mass spectra analysis revealed the generation of  
406 the following fragments: F<sub>1</sub>, F<sub>2</sub>, F<sub>5</sub>, F<sub>6</sub>, F<sub>7</sub>, F<sub>8</sub>, F<sub>9</sub> and F<sub>10</sub>. Then, the presence of the  
407 different fragments coming from the degradation of 2A15NDS in samples from the  
408 electrochemical treatment of C.I. Reactive Orange 4 verify the generation of this  
409 compound during the oxido-reduction, oxidation and reduction processes.

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#### 412 **4. Conclusions**

413 The main conclusions of this work can be summarised in the following points:

- 414 • TOC and COD **measurements** revealed a higher mineralisation rate for  
415 oxidation process while oxido-reduction process **generated** highly oxidised  
416 intermediates.
- 417 • HPLC technique demonstrated that the three electrochemical processes are able  
418 to decolourise the dye solution. The decolourisation followed a pseudo-first  
419 order kinetics for the three processes. The applied specific charge (Q) to  
420 decolourise by means of oxido-reduction and oxidation processes was similar.  
421 The reduction process was the slowest process to decolourise.
- 422 • Chromatograms from samples after the oxidation process presented a higher  
423 number of peaks which means higher number of intermediates. On the contrary,

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424 the electrochemical reduction showed a single chromatographic peak indicating  
425 the generation of a main compound as intermediate.

- 426 • By means of HPLC technique and UV-Visible spectroscopy, it was found that  
427 the nature of this **major** intermediate is similar to 2-amino-1, 5-  
428 naphthalenedisulphonic acid. This intermediate was formed; during the three  
429 electrochemical processes studied in this work.
- 430 • HPLC and GC-MS technique also demonstrated that oxido-reduction and  
431 oxidation degraded this intermediate after being formed while electrochemical  
432 reduction generated this compound continuously but did not degrade it.
- 433 • Naphthalenesulphonic compounds with amino groups were successfully  
434 derivatised by the system sodium iodide-dimethylformamide-trifluoroacetic  
435 anhydride. Although the presence of two sulphonic groups in the aromatic  
436 structure makes more complicated the resolution of chromathograms and mass  
437 spectra; it was possible the identification of the 2-amino-1, 5-  
438 naphthalenedisulphonic acid in the different analysed samples.

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632  
633 **Figure captions**

634  
635 Figure 1. TOC and COD removal percentages measured after oxido-reduction and  
636 oxidation processes at 240 Ah L<sup>-1</sup>. Synthetic dye solution of 0.8 g L<sup>-1</sup> C.I. Reactive  
637 Orange 4 in 0.1 M Na<sub>2</sub>SO<sub>4</sub>. Processes performed at 125 mA cm<sup>-2</sup>. Electrode area = 48  
638 cm<sup>2</sup>; V<sub>sol</sub> = 0.45 L.

639  
640 Figure 2. Evolution of HPLC chromatograms obtained during the electrochemical  
641 processes of a synthetic dye solution of 0.8 g L<sup>-1</sup> C.I. Reactive Orange 4 and 0.1 M  
642 Na<sub>2</sub>SO<sub>4</sub>. Processes performed at 125 mA cm<sup>-2</sup>. Electrode area = 48 cm<sup>2</sup>; V<sub>sol</sub> = 0.45 L.

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643 (a) electrochemical oxido-reduction process. Detection wavelength set at 486 nm; (b)  
644 electrochemical oxidation process. Detection wavelength set at 486 nm; (c)  
645 electrochemical reduction process. Detection wavelength set at 486 nm; (d)  
646 electrochemical oxido-reduction process. Detection wavelength set at 258 nm; (e)  
647 electrochemical oxidation process. Detection wavelength set at 258 nm; (f)  
648 electrochemical reduction process. Detection wavelength set at 258 nm

649

650 Figure 3. Area evolution of chromatographic peak at  $R_t = 2$  min observed by HPLC and  
651 detection wavelength set at 258 nm of a synthetic dye solution of  $0.8 \text{ g L}^{-1}$  C.I. Reactive  
652 Orange 4 in  $0.1 \text{ M Na}_2\text{SO}_4$  treated by oxido-reduction, oxidation and reduction.

653

654 **Table 1. Regression equations obtained for a pseudo-first order kinetics model.**  
655 **Coefficients of determination ( $R^2$ ) and specific charges for a complete**  
656 **decolourisation ( $Q_{\text{decol}}$ ) are also shown.  $A_0$  and  $A$  are the areas of the**  
657 **chromatographic peak of the dye at the initial stage of the electrolysis and at**  
658 **different values of  $Q$ , respectively.**

659

660 Table 2. (a) Summary of GC-MS results of derivatised standard compounds studied in  
661 DMF media. (b) Summary of GC-MS results of derivatised standard compounds studied  
662 in aqueous media. Proposed fragments resulting from the different cleavages of the  
663 initial molecule also included. Program:  $120 \text{ }^\circ\text{C}$  (4 min) to  $250 \text{ }^\circ\text{C}$ ,  $10 \text{ }^\circ\text{C min}^{-1}$ .  
664 Injection:  $1 \text{ } \mu\text{L}$  (splitless),  $250 \text{ }^\circ\text{C}$ . Interface:  $250 \text{ }^\circ\text{C}$ .

665

666 Scheme 1. Molecular structure of the dye C.I. Reactive Orange 4.

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668 Scheme 2. Proposed fragments from the derivatised 2-amino-1, 5-  
669 naphthalenedisulphonic acid (2A15NDS) found in solution by means of GC-MS  
670 analyses.

Table 1

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Process	$\text{Ln} \frac{A}{A_0} = a \cdot Q + b$	$R^2$	$Q_{\text{deool.}} (\text{Ah L}^{-1})$ ( $A=0.01A_0$ )
Oxidation	$\text{Ln} \frac{A}{A_0} = -0.153 \cdot Q + 0.143^a$	0.991	32
	$\text{Ln} \frac{A}{A_0} = -0.130 \cdot Q + 0.142^b$	0.990	
Oxido-Reduction			29
	$\text{Ln} \frac{A}{A_0} = -0.343 \cdot Q + 5.420^c$	0.999	
Reduction	$\text{Ln} \frac{A}{A_0} = -0.076 \cdot Q + 0.277^a$	0.968	64

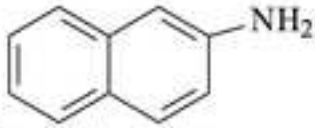
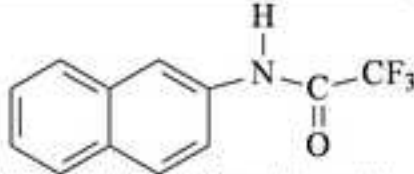
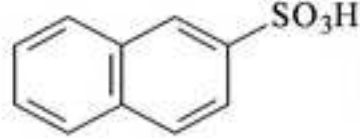
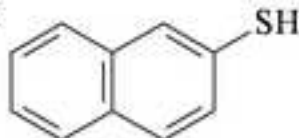
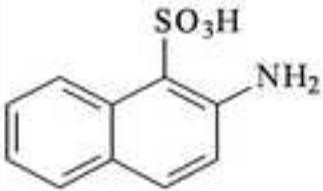
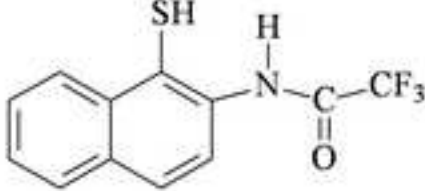
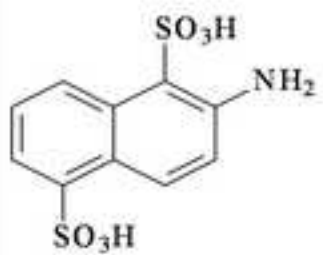
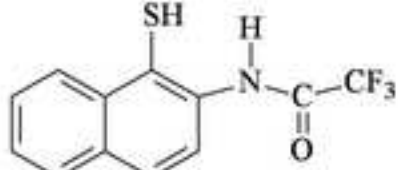
<sup>a</sup> Calculated from  $Q = 0$  to  $Q = 240 \text{ Ah L}^{-1}$

<sup>b</sup> Calculated from  $Q = 0$  to  $Q = 25 \text{ Ah L}^{-1}$

<sup>c</sup> Calculated from  $Q = 25$  to  $Q = 240 \text{ Ah L}^{-1}$

Table 2

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<b>(a) STANDARD SOLUTIONS IN DMF</b>				
Standard compound	Derivatised structure	Retention time (Rt)	m/z	
 2-naphthaleneamine	 N,(2-naphthalene)trifluoroethanamide	10.9	239	
 2-Naphthalenesulphonic acid	 2-Naphthalenethiol	10.3	160	
<b>(b) STANDARD AQUEOUS SOLUTIONS</b>				
Standard compound	Derivatised structure	Retention time (Rt)	m/z	Proposed fragment
 2-amino-1-naphthalenesulphonic acid (2A1NS)	 m/z = 272	11.9	253	F <sub>5</sub>
			239	F <sub>2</sub>
			234	F <sub>11</sub>
			215	F <sub>12</sub>
			158	F <sub>3</sub>
Standard compound	Derivatised structure	Retention time (Rt)	m/z	Proposed fragment
 2-amino-1,5-naphthalenedisulphonic acid (2A15NDS)	 m/z = 304	11.8	253	F <sub>5</sub>
			234	F <sub>11</sub>
			203	F <sub>7</sub>
			158	F <sub>3</sub>
		12.3	239	F <sub>2</sub>
			207	F <sub>7</sub>
		14.3	223	F <sub>6</sub>
			207	F <sub>7</sub>
		14.5	267	F <sub>10</sub>
			223	F <sub>6</sub>
	207	F <sub>7</sub>		

<b>Oxidation</b>	$k = 0.152^a$	
<b>Reduction</b>	$k = 0.076^a$	
<b>Oxido-reduction</b>	$k_1 = 0.130^b$	$k_2 = 0.343^c$

<sup>a</sup> Calculated from  $Q = 0$  to  $Q = 240 \text{ Ah L}^{-1}$

<sup>b</sup> Calculated from  $Q = 0$  to  $Q = 25 \text{ Ah L}^{-1}$

<sup>c</sup> Calculated from  $Q = 25$  to  $Q = 240 \text{ Ah L}^{-1}$



Figure 1  
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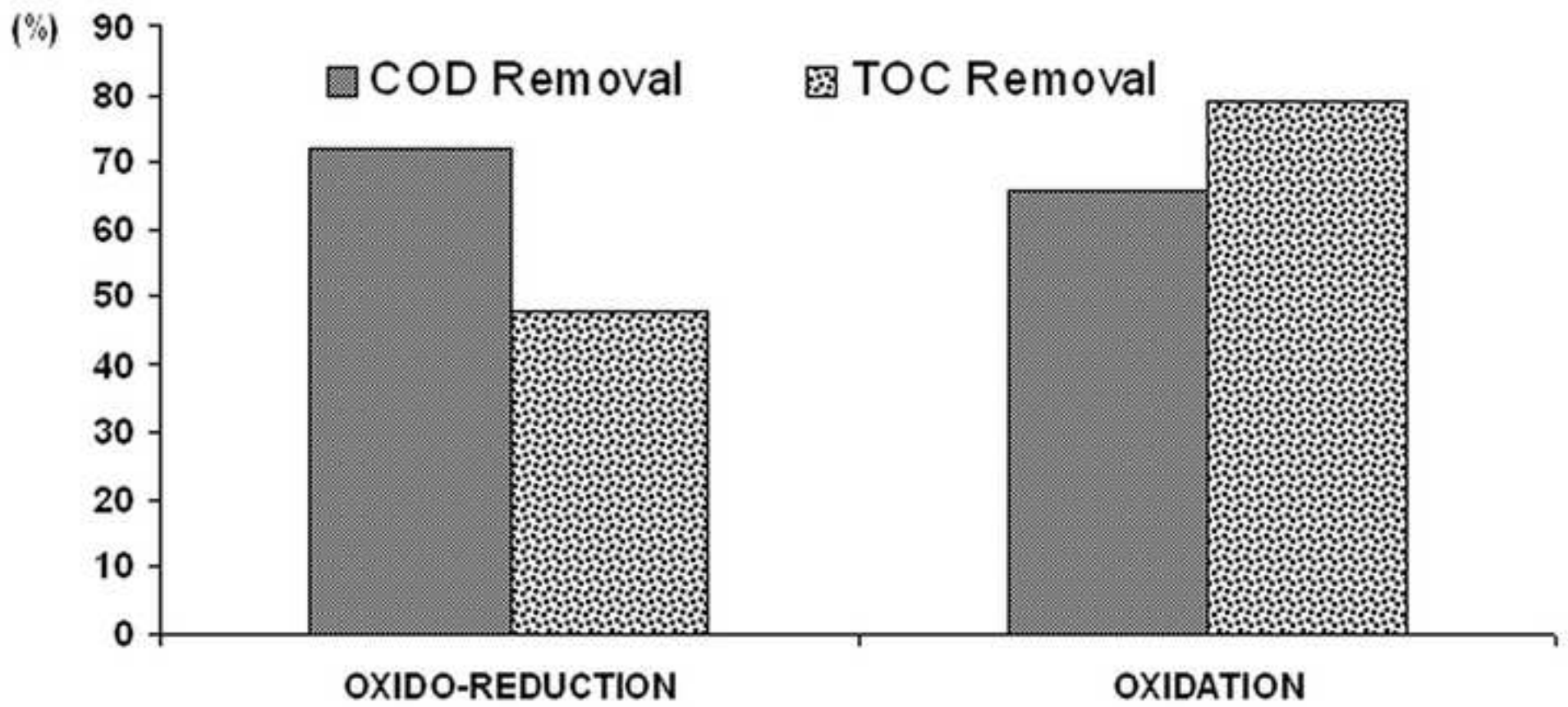


Figure 2  
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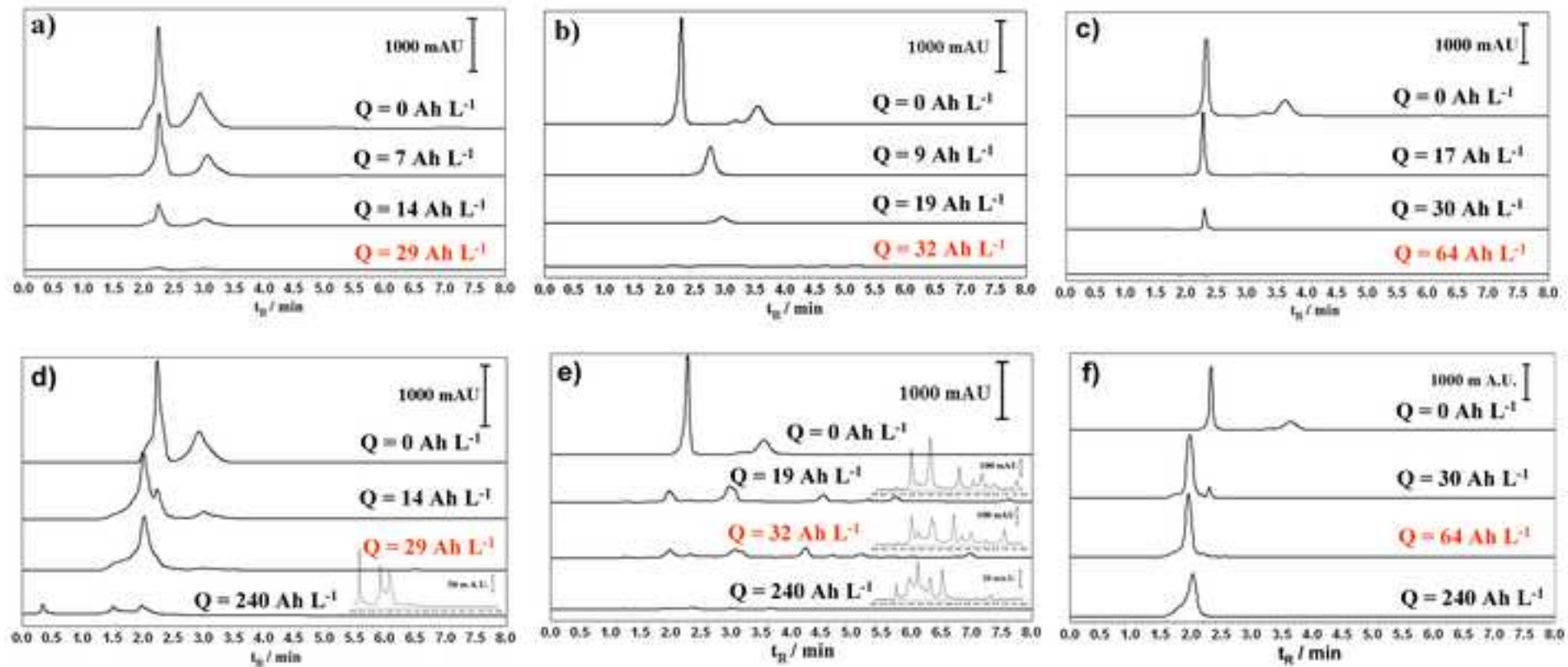
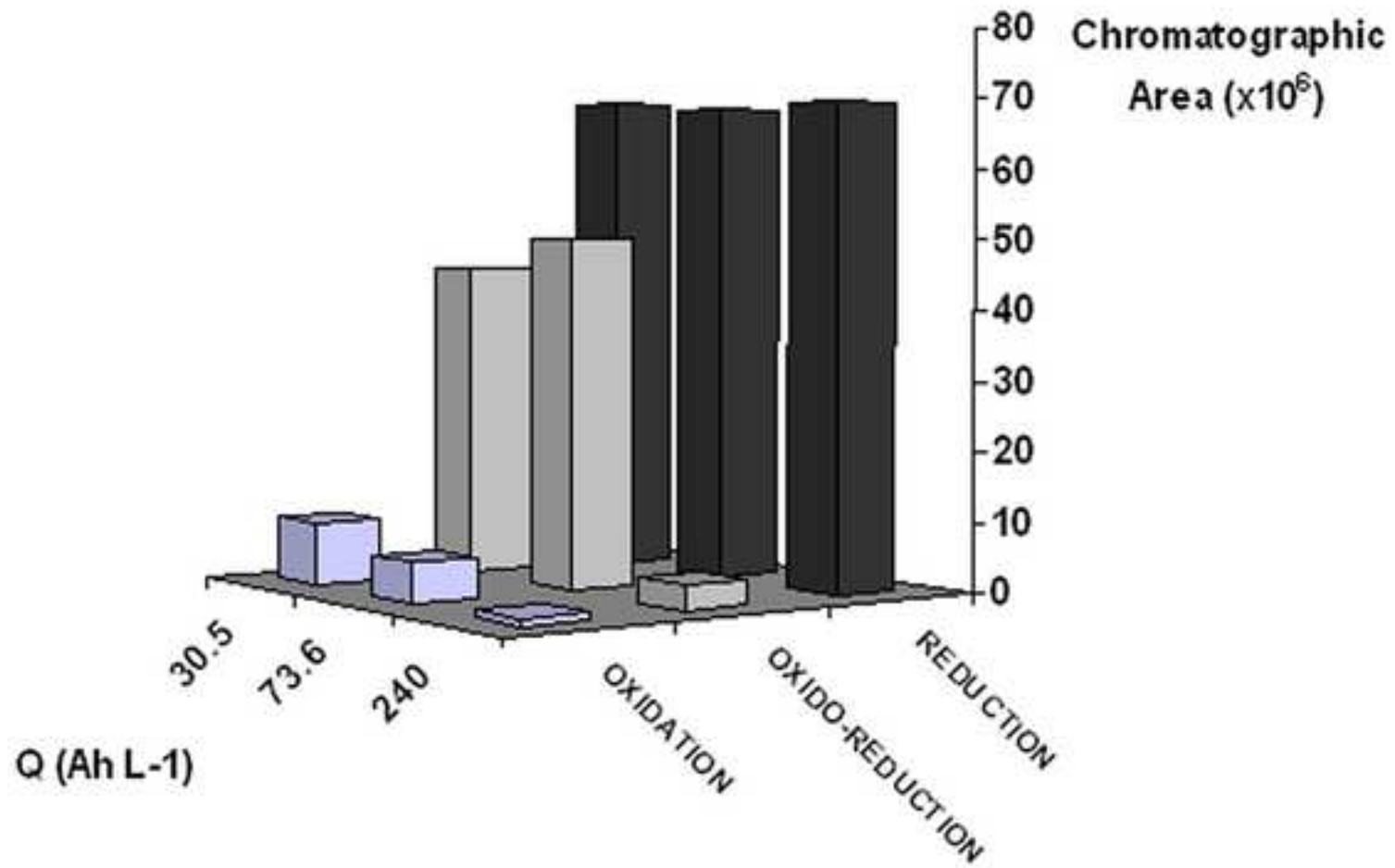
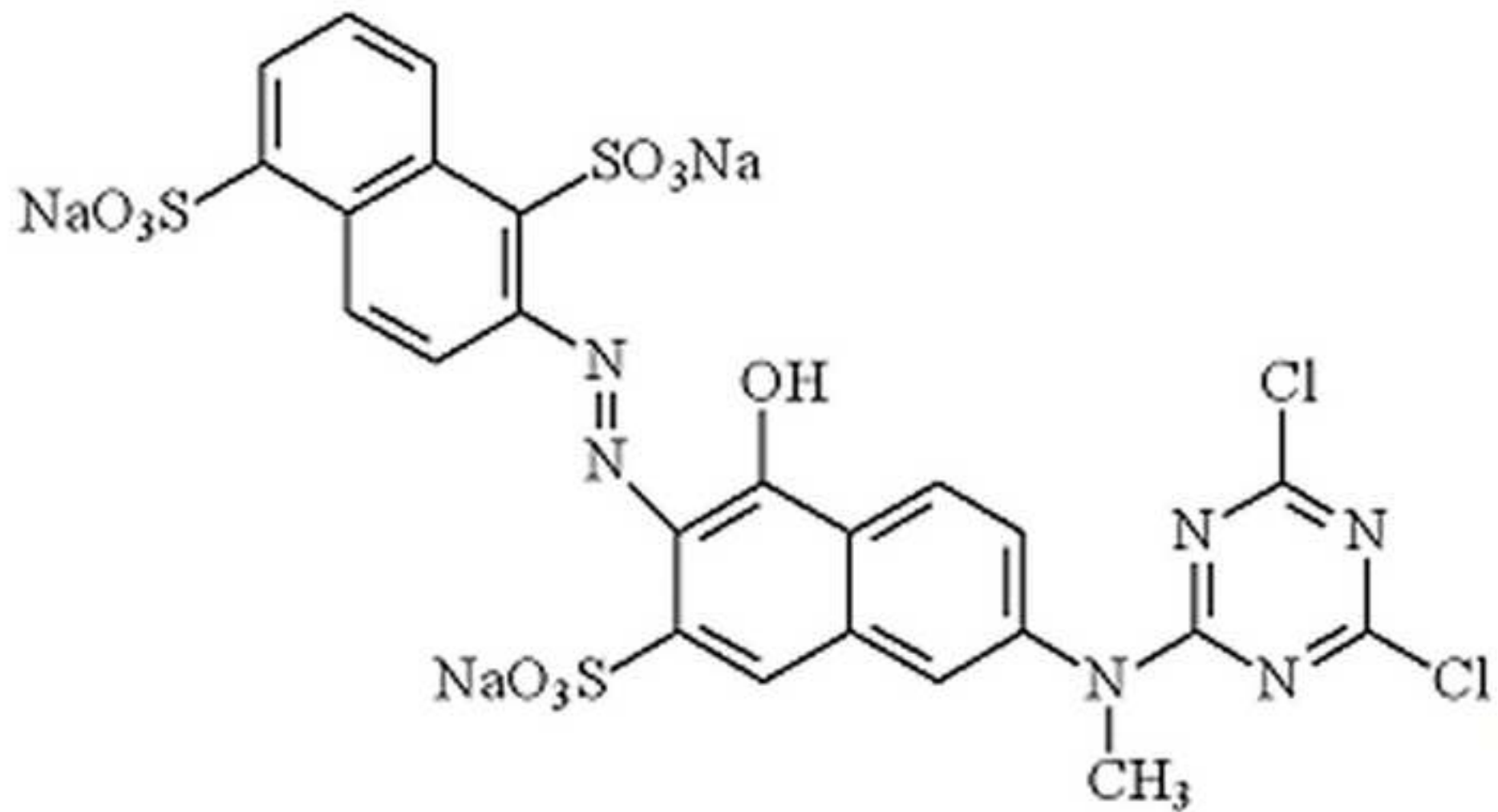


Figure 3  
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## Scheme 2

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