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# **Electrochemical oxidation treatment of Direct Red 23 aqueous solutions: Influence of the operating conditions**

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## 1 **Abstract**

2 A comparative study of the degradation of Direct Red 23 (DR23) dye aqueous solutions by  
3 **electrooxidation** was investigated using different anodes: **carbon graphite (CG)**, dimensionally  
4 stable anode (DSA), Magnéli phase  $Ti_4O_7$ , and boron doped diamond (BDD). Stainless steel  
5 (SS) and **CG** plates were tested as cathodes. The effect of operating parameters on the  
6 degradation kinetic of the dye was studied. In this study, NaCl and  $Na_2SO_4$  were selected as  
7 supporting electrolytes; the former was found to be more suitable for the degradation of  
8 DR23. The degradation of the dye follows a pseudo-first-order kinetic in both media. Higher  
9 total organic carbon (TOC) efficiency was achieved by BDD/**CG** cells. Thus, the treatment  
10 efficiency obtained using a current density of  $5 \text{ mA cm}^{-2}$ , and DR23 concentration of  $60 \text{ mg}$   
11  $L^{-1}$  was about 86 % using both NaCl and  $Na_2SO_4$  electrolyte, at 6 h electrolysis time. The  
12 energy consumptions per **g** TOC removed were found to be 2.05 and 2.6 kWh **g** $^{-1}$  TOC in  
13 NaCl and  $Na_2SO_4$  electrolytes, respectively.

14 **Keywords:** **Electrooxidation**, Direct Red 23 dye, organic degradation, mineralization,  
15 wastewater treatment.

## 16 **1. Introduction**

17 Nowadays, organic dye pollutants become a serious threat to the environment. Even in a small  
18 quantity, they present a source of turbidity, eutrophication, non-aesthetic pollution; and their  
19 discharge is particularly troublesome. Dyes present a higher biochemical stability due to their  
20 high molecular weight and aromatic rings which are difficult to eliminate [1]. Azo dyes  
21 constitute a real problem to the aqueous system and human health due to their side effects  
22 such as carcinogenicity, skin irritation, allergy, acute toxicity, and mutagenicity [2,3]. Several  
23 means were investigated to treat wastewaters containing recalcitrant pollutants; conventional  
24 ones are usually ineffective. Although usual treatments such as precipitation,

25 biodegradation coupled to membrane separation, coagulation, flocculation, adsorption [4–7],  
26 and electrocoagulation [8–12] were experienced for discoloration, they have common  
27 drawbacks of generating sludge [8,13]. To overcome these problems, electrochemical  
28 advanced oxidation processes (EAOPs) present a promising way to treat persistent pollutants  
29 [2,14,15] due to the unique characteristics such as high efficiency, high mineralization, and  
30 nonhazardous waste produced [3]. The interest related to EAOPs application for water  
31 treatment is linked to their easy manipulation being ecofriendly methods. In terms of  
32 sustainability, their installations can be supplied by renewable energies [16–18]. These  
33 technologies are easily automatable, viable, decentralizable and finally adaptable according to  
34 the nature of the effluents to be treated. The duration of the treatment can be optimized  
35 according to the biorefractoriness of the effluent to finally end up with a biodegradable  
36 solution after treatment [19]. The driving force is the in-situ generation of highly oxidant  
37 agents mainly  $\cdot\text{OH}$  radicals with a higher oxidation potential (versus standard hydrogen  
38 electrode (SHE))  $E^\circ (\cdot\text{OH}/\text{H}_2\text{O}) = 2.80 \text{ V/ SHE}$  [20–22]. These reactive entities are able to  
39 destroy unselectively organic and organometallic contaminants until their complete  
40 mineralization into  $\text{CO}_2$ , water, and inorganic ions [23,24]. They are considered the main  
41 oxidizing species for the removal of organic pollutants in EAOPs, where hydroxyl radicals  
42 can be generated in the bulk solution (homogeneous  $\cdot\text{OH}$ , denoted  $\cdot\text{OH}$ ) and/or at the anode  
43 surface (heterogeneous  $\cdot\text{OH}$ , marked  $\text{M}(\cdot\text{OH})$ , where M refers to anode material) [25,26].  
44 Depending on the used anode and its potential window for water discharge,  $\text{M}(\cdot\text{OH})$  may be  
45 physisorbed in case of non-active anodes and chemisorbed in case of active anodes [24–26].

46 Electrochemical oxidation (electrooxidation) is an environmentally friendly method for the  
47 treatment of water and wastewater, constitutes a direct way to produce  $\text{M}(\cdot\text{OH})$  radicals  
48 without using chemicals, where electrons are the only reagents [27].  $\cdot\text{OH}$  production generally  
49 requires higher  $\text{O}_2$  overpotential anodes (M) (Eq. (1)) [2]. Several electrodes have been used

50 for the **electrooxidation** such as PbO<sub>2</sub>, doped SnO<sub>2</sub>, IrO<sub>2</sub>, DSA (dimensionally stable anodes)  
51 that are mainly mixed metal oxide anodes, or Pt and BDD (boron doped diamond) [20]. SnO<sub>2</sub>  
52 and PbO<sub>2</sub> electrodes have a short life-time service and release toxic ions to the solution [1]. Pt  
53 electrode is expensive which prevents it from being used for the scale-up. On the other hand,  
54 BDD, a non-active anode, presents a wide potential window for water discharge; that provides  
55 a promising condition for industrial-scale wastewater treatment. **This** anode is able to generate  
56 weakly physisorbed hydroxyl radical [1]. Moreover, it can generate relatively weak oxidants  
57 such as reactive oxygen species O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>, chlorine species, peroxodisulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>),  
58 peroxodiphosphate (P<sub>2</sub>O<sub>8</sub><sup>4-</sup>), or peroxodicarbonate (C<sub>2</sub>O<sub>6</sub><sup>2-</sup>) species [28–31]. This non-active  
59 anode exhibits a good chemical and electrochemical stability and a long life time service [1].  
60 DSA, an active anode, formed by a mixture of metal oxides, has the property of generating  
61 hydroxyl radicals and a higher electrocatalytic activity for chlorine evolution reaction [32].  
62 This property is due to the redox reaction of the transition metal elements which act as active  
63 sites for chlorine atom adsorption [1]. Comparing BDD and DSA activity, unlike BDD, DSA  
64 has low ability to electro-generate **M(•OH)**. **It** has a high stability, large production of Cl<sub>2</sub>, and  
65 chlorine-oxygen species, which are endowed with lower oxidant power than •OH, but with  
66 interesting activity [33]. Therefore, direct oxidation of organics presents a sluggish kinetic  
67 reaction on DSA surface and the secondary reaction is favored [1]. Recently, ceramic  
68 electrodes based on sub-stoichiometric TiO<sub>2</sub>, especially, Ti<sub>4</sub>O<sub>7</sub> were reported to be an  
69 alternative to BDD anodes. They are characterized by a high electrical conductivity and a  
70 low-cost due to their preparation using TiO<sub>2</sub>, the most abundant feedstock on the planet [34].  
71 Moreover, concerning their electrochemical efficiency, they behave as non-active anodes,  
72 yielding to a higher electrochemical mineralization efficiency compared to DSA [35,34].  
73 Table 1 shows a brief summary of the recent application of **electrooxidation** in the treatment  
74 of targeted organic pollutants.



75

**(Table 1)**

76 Considering the negative effect of dyes to the environment, this paper aimed to study the  
77 degradation and mineralization of Direct Red 23 (DR23) as an azo naphthalene dye from its  
78 aqueous solution. It is well known that azo dyes, containing a double bond N=N, are toxic and  
79 their by-products are carcinogenic and mutagenic to the life being. According to this, previous  
80 papers reported its elimination using photocatalytic degradation [41–45], UV-assisted AOPs  
81 [46], persulfate oxidation [47], UV/H<sub>2</sub>O<sub>2</sub> process using carbon nanotube particles [48,49],  
82 adsorption process [50], enzymatic process [51], photo-electro Fenton [52,53], **electro Fenton**  
83 **[54]**, ozonation and ultrasonolysis processes [55]. Nevertheless, the degradation and  
84 mineralization of DR23 using **electrooxidation** remain unstudied. **Electrooxidation**, the most  
85 popular and low cost technique, is considered as an effective technique to treat dyeing  
86 solutions since it can degrade it by in-situ **M(·OH)** generation and/or by mediating active  
87 oxidants [56]. It does not need any chemical reagent addition such as Fe<sup>2+</sup> unlike the electro-  
88 Fenton process. **Electrooxidation** efficiency depends on the operating conditions such as  
89 temperature, pH, electrolyte medium, and electrode materials **[33,56–58]**. Therefore, this  
90 work aims to study the discoloration and mineralization of DR23 aqueous solution using  
91 **electrooxidation** as the most widely used and powerful electrochemical process. To the best of  
92 our knowledge, degradation/incineration of this dye is not yet performed. **This study**  
93 **compared the efficiency of its removal using different powerful known anodes. BDD anode is**  
94 **known by its higher potential for the removal of organic pollutants. However, its main**  
95 **drawback is its higher cost. Therefore, this comparative study can be useful to highlight the**  
96 **possible use of other powerful anodes in order to achieve similar efficiencies of those of BDD**  
97 **anode.** The effect of different operating conditions was studied under galvanostatic mode  
98 using different anode/cathode cells in chloride and sulfate media. **As the concentration of salts**

99 (electrolytes) differs from an industry to another, the chosen concentrations fall in the range  
100 of the used amounts in textile industry, presenting the minimum of supporting electrolyte that  
101 promotes the easy follow of discoloration kinetic and prevents side reactions and ohmic drop  
102 [59,60]. The amount of salts 25 mM NaCl (conductivity = 2.5 mS cm<sup>-1</sup>) and 12.5 mM Na<sub>2</sub>SO<sub>4</sub>  
103 (conductivity = 2.3 mS cm<sup>-1</sup>) were chosen to perform all the experiments in a constant 25 g-  
104 equivalent of supporting electrolyte medium. Discoloration experiments of the dye solutions  
105 were achieved in various operating conditions using different anode materials to compare  
106 their efficiency for the removal of DR23. The range of tested parameters was chosen based on  
107 some pretests and on different relevant literatures [23,61]. Mineralization efficiency, based on  
108 total organic carbon (TOC) measurement, mineralization current efficiency (MCE%), and  
109 energy consumption during the electrolysis were investigated.

110

## 111 2. Materials and methods

112 Direct Red 23 (DR23), the chosen pollutant to formulate the synthetic wastewater, is  
113 generally used in viscose cellulose fiber dyeing for silk, wool, paper, and pulp dyeing. It is an  
114 azo naphthalene dye (C<sub>35</sub>H<sub>25</sub>N<sub>7</sub>Na<sub>2</sub>O<sub>10</sub>S<sub>2</sub>, molar mass of 813.73 g mol<sup>-1</sup>, color index C.I.  
115 29160), of analytical grade, purchased from Sigma Aldrich and used without any further  
116 purification. Required amount of DR23 was dissolved in ultrapure water to prepare the  
117 desired concentrations. Sodium hydroxide, sulfuric acid, sodium chloride, and sodium sulfate,  
118 were analytical grades from Prolabo and Fluka. All solutions were prepared with ultrapure  
119 water obtained from a Millipore Milli-Q system with resistivity > 18 MΩ cm at 25 °C.

### 120 2.1. Description of the electrochemical process

121 The elimination of DR23 by electrooxidation, in a batch study, was carried out with 230 mL  
122 of the dye solution in a 250 mL Pyrex beaker. The electrolysis was performed in an undivided

123 electrolytic cell where different electrode combinations were used. All used electrodes except  
124 for  $\text{Ti}_4\text{O}_7$  anode were purchased from different suppliers. Four anodes were tested:  
125 dimensionally stable anode (DSA), ( $\text{Ti}/\text{RuO}_2\text{-IrO}_2$  (4 cm  $\times$  6 cm  $\times$  0.2 cm) from Baoji Xinyu  
126 Guang Ji Dian Limited Liability Company, China), which can be prepared as reported by Yu  
127 et al. [62], boron doped diamond (BDD) thin-film deposited on a niobium substrate (4 cm  $\times$  6  
128 cm  $\times$  0.2 cm) from CONDIAS, Germany, fabricated as described by Fryda et al. [63], carbon  
129 graphite (CG)(expanded graphite sheet PSB-860, (4 cm  $\times$  6 cm  $\times$  0.4 cm), purchased from  
130 SHIELD SEALING & Packing CO., LTD, China, prepared as indicated by Liu et al. [64],  
131 and  $\text{Ti}_4\text{O}_7$  (4 cm  $\times$  6 cm  $\times$  0.2 cm ) thin film deposited on Ti substrate from Saint Gobain  
132 Research Provence (France) prepared as described elsewhere [65,66].  $\text{Ti}_4\text{O}_7$  was synthesized  
133 by plasma coating of prepared  $\text{TiO}_x$  ( $x < 2$ ) particles (20–60  $\mu\text{m}$ ) on a Ti substrate (4 cm  $\times$  6  
134 cm) as described by Ganiyu et al. [65]. Ti substrate surface was pretreated by sandblasting in  
135 order to obtain a rough surface. By applying coating conditions reported by Ganiyu et al. [65],  
136 a continuous thick film of 100  $\mu\text{m}$  and 95% density was achieved. The prepared electrode  
137 mainly contains  $\text{Ti}_4\text{O}_7$  phase with the presence of  $\text{TiO}_2$  rutile and  $\text{Ti}_3\text{O}_5$  as indicated by X-ray  
138 diffraction. The plasma-sprayed coating has a typical electronic conductivity of  $10^3 \text{ S cm}^{-1}$ .  
139 The tested cathodes were CG (4 cm  $\times$  6 cm  $\times$  0.4 cm), and AINSI 304 Stainless steel (SS)  
140 plate (4 cm  $\times$  6 cm  $\times$  0.4 cm). Electrolysis was conducted under galvanostatic conditions, by  
141 applying a constant current using a digital DC supply unit, ELC model ALR3002M. For all  
142 electrodes, 30  $\text{cm}^2$  is kept constant as the submerged geometric surface area. The distance  
143 between these electrodes was 1.5 cm, and they were connected to the DC power supply. The  
144 pH variation was monitored using HANNA pH meter. Prior to each experiment, compressed  
145 air (Flow air, 1.5  $\text{L min}^{-1}$ ) was bubbled for 10 min through the cell to saturate the solution  
146 with dissolved oxygen. All electrolyses were performed in triplicate and averaged at room



147 temperature ( $20 \pm 2$  °C), and the solutions were homogenized with magnetic stirring (600 rpm)  
148 during the treatment to allow efficient mass transfer.

## 149 2.2. Analytical procedure

150 The discoloration was monitored using Shimadzu spectrophotometer UV-VIS 1800 at the  
151 maximum adsorption wavelength ( $\lambda_{\max} = 502$  nm), to assess the decrease in chromophore  
152 absorption bands by taking different aliquots of 2 mL at different times. Calibration curve of  
153 DR23 absorbance was prepared using known aqueous solutions with different concentrations  
154 (20, 30, 40, 60, 80, 100, and 200 mg L<sup>-1</sup>). The color removal was computed using (Eq. (2)):

$$\text{Color removal (\%)} = \left( \frac{A_0 - A_t}{A_0} \right) \times 100 \quad (2)$$

155 where  $A_0$  and  $A_t$  are the initial and final dye absorbance.

156 Total Organic Carbon (TOC) measurements were determined by injecting samples of 50  $\mu$ L  
157 through thermal catalytic oxidation at 680 °C using TOC-L SHIMADZU analyzer equipped  
158 with a manual injector. The TOC removal was then calculated using (Eq. (3)):

$$\text{TOC removal (\%)} = \frac{\text{TOC}_0 - \text{TOC}}{\text{TOC}_0} \times 100 \quad (3)$$

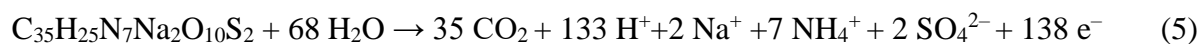
159 where  $\text{TOC}_0$  and TOC stand for the initial and TOC (mg L<sup>-1</sup>) at a given reaction time,  
160 respectively.

161 The mineralization current efficiency, MCE%, was estimated by (Eq. (4)) [67]:

$$\text{MCE\%} = \frac{nFV_s\Delta(\text{TOC})_{\text{exp}}}{4.32 \times 10^7 \times m \times I \times t} \times 100 \quad (4)$$

162 where  $F$  is the Faraday constant (96487 C mol<sup>-1</sup>),  $V_s$  is the solution volume (L),  $\Delta(\text{TOC})_{\text{exp}}$  is  
163 the experimental TOC change (mg L<sup>-1</sup>) at a given time,  $4.32 \times 10^7$  is an homogenization factor

164  $(3600 \text{ s h}^{-1} \times 12,000 \text{ mg of C mol}^{-1})$ ,  $m$  is the number of carbon atoms of DR23 (35 atoms),  $I$  is  
165 the applied current (A) and  $t$  is the electrolysis time (h).  $n$  is the electron transfer number per  
166 mole of DR23 taken as 138 considering the total mineralization according to the following  
167 reaction Eq. (5):



168 The energy consumption, EC, ( $\text{kWh g}^{-1} \text{ TOC}$ ) was determined using (Eq. (6)) [68]:

$$\text{EC (kWh g}^{-1} \text{ TOC)} = \frac{E_{\text{cell}} I t}{(\text{TOC}_0 - \text{TOC}_t) V_s} \quad (6)$$

169 where  $E_{\text{cell}}$  is the average voltage applied (V),  $I$  is the applied current intensity (A),  $t$  is the  
170 treatment time (h),  $\text{TOC}_0$  and  $\text{TOC}_t$  are the TOC values ( $\text{mg L}^{-1}$ ) at the initial time and at a  
171 given electrolysis time  $t$ , respectively, and  $V_s$  is the solution volume (L). In all trials,  
172 degradation was monitored using UV-Vis technique while mineralization was followed by  
173 TOC-meter.

### 174 **3. Results and discussion**

#### 175 *3.1. Parameters influencing the degradation of DR23*

##### 176 *3.1.1. Effect of electrode materials and supporting electrolyte*

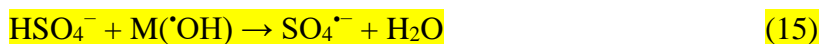
177 Although **electrooxidation** is a process essentially based on the power of the anode in the  
178 electrolytic cell, the cathode can help improve the efficiency of the process, which depends on  
179 the nature of the electrode used. The electrode materials influence the degradation rate of  
180 organic pollutants since their efficiency depends on their ability to generate oxidizing species  
181 such as  **$\text{M}(\bullet\text{OH})$**  and/or chlorine **and sulfate active** species on the anode and  $\text{H}_2\text{O}_2$  on the  
182 cathode. The former species are the main oxidizing agents for the destruction of pollutants.  
183 Therefore, this study focused on the role of the nature of the anode and cathode materials in  
184 addition to the supporting electrolyte to set the effective combination to get rid of DR23.

185 Therefore, four anodes including dimensionally stable anode (DSA), boron-doped diamond  
186 (BDD),  $\text{Ti}_4\text{O}_7$ , and CG, were tested and compared using CG, and stainless steel (SS) as  
187 cathodes. The degradation was carried out using  $40 \text{ mg L}^{-1}$  DR23,  $8.3 \text{ mA cm}^{-2}$  current  
188 density, and  $25 \text{ mM NaCl}$  or  $12.5 \text{ mM Na}_2\text{SO}_4$ , at natural pH ( $\text{pH} = 6.0$ ), to set the effect of  
189 electrode combination, Figure 1. In all cases, color removal increased progressively with  
190 electrolysis time and this increase depends on the added salt. In these trials, the pH remained  
191 almost constant with variations close to  $\pm 0.3$  pH units in  $\text{Na}_2\text{SO}_4$  medium, whereas it changes  
192 in  $\text{NaCl}$  where the final pH evolves to be near to neutral at the end of electrolysis, in the case  
193 of BDD and DSA, and acidic for  $\text{Ti}_4\text{O}_7$ . The drop of the pH to acidic values using Magnéli  
194  $\text{Ti}_4\text{O}_7$  may have a beneficial effect on the stability of hydroxyl radicals that requires acidic  
195 conditions [69]. Similar observation was already reported by Salazar et al. [33] indicating that  
196 the active chlorine evolution changes the final pH of the solution as a function of electrodes  
197 and electrolysis time.

198 Comparing the activity of anode materials, DSA,  $\text{Ti}_4\text{O}_7$ , and BDD anodes show a higher  
199 degradation activity compared to CG, whatever the medium. Although the CG anode may  
200 contribute to the degradation of DR23 by the  $\text{M}(\cdot\text{OH})$  radicals formed, during electrolysis, its  
201 surface burns over time, damaging it and limiting its reuse. Carbon-based materials such as  
202 CG undergo incineration, and their corrosion depends on various parameters such as pH,  
203 current and the presence of  $\text{NaCl}$ . This corrosion occurs even at low currents [70,71].

204 Regarding the electrolytic media, the higher discoloration activity was found in  $\text{NaCl}$   
205 supporting electrolyte. In the presence of sulfate ions, compared to DSA anode, BDD and  
206  $\text{Ti}_4\text{O}_7$  are known being able to generate reactive sulfate species,  $\text{S}_2\text{O}_8^{2-}$  and  $\text{SO}_4^{\cdot-}$ , depending  
207 on the pH and applied current density, through direct oxidation on the anode surface or the  
208 reaction with  $\text{M}(\cdot\text{OH})$  (Eqs. (7)-(15)(12)) [72–76]. The electro-generated sulfate active  
209 species may contribute to the solution degradation in addition to the strong oxidant  $\text{M}(\cdot\text{OH})$

210 radicals [72,77–79]. However, for DSA, the lower degradation efficiency could be attributed  
211 to the strong adsorption of  $M(\cdot\text{OH})$  that can limit the discoloration rate [33].

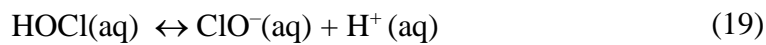
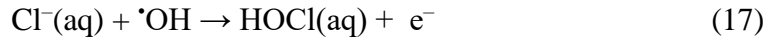


212 These sulfate active species are known by their higher standard potential being 2.01 V/SHE  
213 for  $\text{S}_2\text{O}_8^{2-}$  and 2.6 V/SHE for  $\text{SO}_4^{\cdot-}$  [72,80,81]. However, the higher bleaching properties of  
214 chloride active species compared to sulfate active species are reported in many cases. For  
215 example, the effects of different electrolytes ( $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{HClO}_4$ ) on Alizarin  
216 Red S (ARS) degradation using BDD anode, were studied and compared. A fast complete  
217 discoloration of ARS was achieved within 6 min using  $\text{NaCl}$  electrolyte [82].

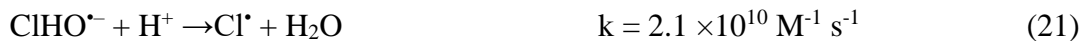
218 Regarding the obtained results, the  $\text{NaCl}$  supporting electrolyte was used for further  
219 investigations on the degradation of DR23.

220 In the case of BDD and DSA anodes, the presence of  $\text{NaCl}$  leads to generate electro-active  
221 chlorine oxidizing species such as  $\text{Cl}_2$ ,  $\text{HClO}$ , and  $\text{ClO}^-$ , once chloride ions undergo oxidation

222 as reported by Degaki et al. [83] and Jalife-Jacobo et al. [56] following the reactions (Eqs.  
 223 (16)-(19)). Furthermore, the low evolution of chlorine on DSA surface favors the generation  
 224 of active chlorine species during the oxidation of chlorides [68].



225 It should be noted that the stability of these oxidizing agents in the solution depends on its pH.  
 226 The  $\text{pK}_a$  of HOCl/ClO<sup>-</sup> couple is given equal to 7.55 [68]. Globally, chlorine, Cl<sub>2</sub> is the  
 227 predominant species when pH < 3.00, hypochlorous acid, HOCl for 3.00 < pH < 7.50, and  
 228 hypochlorite ion, ClO<sup>-</sup> for pH > 7.55 [67,84]. However, other species of chlorine, ClO<sub>2</sub><sup>-</sup>,  
 229 ClO<sub>3</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup>, with low oxidizing power were mentioned in the literature [85].  
 230 However, in the case of Ti<sub>4</sub>O<sub>7</sub>, the oxidation of Cl<sup>-</sup> according to Eq. (16) do not occurs on  
 231 Ti<sub>4</sub>O<sub>7</sub> surface as reported by Wang et al. [86]. They reported that the degradation of organics  
 232 is mainly attributed to M(<sup>•</sup>OH) radicals formed at the anode surface beside the synergic effect  
 233 of chlorine active species formed as follow: (Eqs. (20)-(24)).



234 Moreover, in terms of reactivity, they reported that hydroxyl radicals are more reactive than  
 235 the produced chlorine species. Their lower reactivity leads to their accumulation in the cell

236 with less oxidation potential to form  $\text{ClO}^-$ ,  $\text{ClO}_2^-$ ,  $\text{ClO}_3^-$ , and  $\text{ClO}_4^-$  as presented in Eqs. ((25)-  
237 (28)) [87].



238 Regarding the negative impact of  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$  on health (disturbance of the normal  
239 functions of the thyroid gland and carcinogenic effect) [86], the low production of these  
240 species in the case of  $\text{Ti}_4\text{O}_7$  present an advantage for this electrode for their large scale  
241 application in **electrooxidation** of organic pollutants [86].

242 As it can be seen in **Figure 1**, the highest degradation of DR23 is obtained using DSA/**CG**  
243 system in the presence of chloride ions. In this case, the discoloration of the solution results  
244 mainly from the dye's chromophore destruction by active chlorine species which are formed  
245 at the testing pH solution. Similar results are carried out by others studying the degradation of  
246 Reactive Blue 19 dye using a BDD or DSA anode in a flow reactor [83].

247 The oxidation power of DSA/**CG** and DSA/SS are almost similar, the difference is due to the  
248 contribution of **CG** cathode which may generate  $\text{H}_2\text{O}_2$  (Eq. (29)) unlike the SS cathode which  
249 promotes mainly oxygen reduction via 4 transferred electrons. It is well known that cathodes  
250 made of carbon materials promote the formation of  $\text{H}_2\text{O}_2$  via two-electron oxygen reduction  
251 reaction (ORR) at low current density according to the reaction (Eq. (29)) **[88,89]**. The  
252 generation of oxidant species,  $\text{H}_2\text{O}_2$  on the cathode is more favorable in acidic medium. In  
253 addition, carbonaceous materials have significant catalytic performance for accelerating the  
254 activation of in-situ generated  $\text{H}_2\text{O}_2$  into hydroxyl radicals that enhances the degradation and  
255 mineralization efficiency [90,91].



256 Sopaj et al. [92] stated that the stainless steel cathode generates very low H<sub>2</sub>O<sub>2</sub> amounts, for  
 257 the operating conditions, current densities of 2.4 to 5 mA cm<sup>-2</sup>, Pt anode, 50 mM Na<sub>2</sub>SO<sub>4</sub>, pH  
 258 = 3.00, under continuous air bubbling conditions. In the previous work, the hydrogen  
 259 peroxide amount was determined by titration of the complex (1:1) formed between Ti(IV) and  
 260 H<sub>2</sub>O<sub>2</sub> by measuring its color intensity in acidic media, at a wavelength of 423 nm.

261 Likewise, the difference of discoloration efficiency obtained for both Ti<sub>4</sub>O<sub>7</sub> and BDD using  
 262 CG and SS cathodes could be interpreted by the generation of H<sub>2</sub>O<sub>2</sub> on CG surface. As  
 263 presented in the Figure 1, the discoloration in the case of Ti<sub>4</sub>O<sub>7</sub> is almost coincident with that  
 264 of DSA. Similar result was observed by He et al. [93] using Ti<sub>4</sub>O<sub>7</sub> and DSA anode for the  
 265 discoloration of methyl orange solution. In NaCl medium, the discoloration follows the order:  
 266 DSA/CG ≈ Ti<sub>4</sub>O<sub>7</sub>/CG > DSA/SS ≈ Ti<sub>4</sub>O<sub>7</sub>/SS > BDD/CG > BDD/SS. The lower degradation  
 267 in the case of Ti<sub>4</sub>O<sub>7</sub> and BDD compared to DSA anode can be attributed to the consumption  
 268 of M(•OH) due to chlorine (Eqs. ((25)-(28)) [34]. In contrast, active anodes, endowed with  
 269 high oxygen evolution overpotential, the oxidation of target molecules mainly occurs directly  
 270 on the anode surface by the adsorbed hydroxyl radicals electro-generated according to  
 271 reaction (Eq. (1)). However, the oxidation rate strongly depends on the applied current density  
 272 and mass transfer in the cell as the pollutants must reach the anode surface [1]. It was reported  
 273 that the oxidation of pollutants by M(•OH) generated by inactive anodes leads to high removal  
 274 efficiency; these reacting species are adsorbed physically onto the anode surface and react  
 275 with the pollutant in the interface of solid/solution [94,95]. Hence, the treatment cost may  
 276 increase according to the electrolysis time. The use of effective intermediate oxidizing agents  
 277 obtained by electro-generating active chlorine species leads to indirect oxidation by mass  
 278 transfer to the bulk of the solution, which hinders the above limitation. Based on these  
 279 assertions, color removal is principally dependent on the active chlorine species

280 concentrations produced by the used electrodes as suggested by Salazar et al. [33]. These  
281 authors recognized that the production of chlorine species on DSA anodes is higher than what  
282 was generated on BDD anodes whatever the pH and current density. Similar results were  
283 carried out by Malpass et al. [96] using BDD and DSA anodes for the degradation of both the  
284 pesticide atrazine and cyanuric acid by **electrooxidation** in NaCl and Na<sub>2</sub>SO<sub>4</sub> supporting  
285 electrolytes. Therefore, DSA, Ti<sub>4</sub>O<sub>7</sub>, or BDD anode, and **CG** as the cathode were chosen to  
286 study the operating conditions effect on the degradation of DR23 for the sake of comparison  
287 in NaCl medium.

288

289 **(Figure 1)**

290

### 291 *3.1.2. Effect of NaCl concentration*

292 The study of NaCl electrolyte deserves special attention since Cl<sup>-</sup> has an ubiquitous character  
293 [15]. The electrical conductivity of the solution plays an important role in the degradation  
294 reaction. Good conductivity leads to a faster electron transfer, a better degradation ratio, and  
295 energy saving [8,69]. In chloride media, the reduction of organic compounds occurs mainly  
296 by indirect oxidation other than direct oxidation, due to strong in-situ electro-generated  
297 reactants, which may transform target pollutants into less harmful compounds. As was already  
298 reported before, the main oxidizing agents are active chlorine, hypochlorous acid, or  
299 hypochlorite ions, those reactants are produced anodically from chloride as indicated in  
300 reactions (Eqs. ((16)-(19)) [1,8]. It is well known that increasing the concentration of the  
301 supporting electrolyte affects color removal, which positively impacts the conductivity of the  
302 solution and reduces the cell voltage leading to decrease the energy consumption.

303 To study the effect of supporting electrolyte on the removal of 60 mg L<sup>-1</sup> of DR23, different  
304 concentrations of NaCl, 12.5, 25, 50, and 75 mM were investigated. Experiments were carried



305 out under  $5 \text{ mA cm}^{-2}$  current density and at natural pH of the solution ( $\text{pH} = 6.0 \pm 0.4$ ), for  
306 DSA/CG,  $\text{Ti}_4\text{O}_7/\text{CG}$ , and BDD/CG cells, as shown in Figure 2a, 2b, and 2c, respectively. The  
307 same behavior was observed for DSA,  $\text{Ti}_4\text{O}_7$ , and BDD, the color removal increases when the  
308 concentration of NaCl increases, illustrating the positive impact on the degradation of DR23.  
309 The enhancement of the efficiency is related to the increase of production-mediated oxidants  
310 and the decrease of the selectivity for oxygen evolution due to the increase of  $\text{Cl}^-$   
311 concentration as reported by Jager et al. [39].

312 The total discoloration requires 40 min for a concentration of 12.5 mM of NaCl where it  
313 requires only 20 min using 50 mM or 75 mM of NaCl in all electrolytic cells tested. On the  
314 other hand, the discoloration rate is slower for BDD/CG system compared to DSA/CG and  
315  $\text{Ti}_4\text{O}_7/\text{CG}$ , in the same operating conditions. The kinetic of discoloration fits with the pseudo-  
316 first order kinetic model with  $R^2$  almost equal to unity. As shown in Figure 2d, the kinetic  
317 rates enhance from  $0.080$  to  $0.173 \text{ min}^{-1}$ , from  $0.079$  to  $0.197 \text{ min}^{-1}$ , and from  $0.069$  to  $0.1514$   
318  $\text{min}^{-1}$  when the concentration of NaCl increases from 12.5 to 75 mM, for  $\text{Ti}_4\text{O}_7$ , DSA and  
319 BDD, respectively. The higher kinetic rate in the case of DSA anode and especially for 75  
320 mM of NaCl is related to the higher accumulation of active chlorine species formed in the  
321 medium. This behavior is in complete agreement with the reported literature of the  
322 degradation of organic compounds being enhanced with NaCl concentration [97–100]. As  
323 mentioned by Ganiyu et al. [73] the generation of reactive chlorine species is particularly high  
324 using DSA anodes. However, in the case of BDD, less active chlorine species can be  
325 simultaneously generated by the action of  $\text{M}(\cdot\text{OH})$  according to the reactions (Eqs. ((25)-  
326 (28)), where  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$  are considered as unwanted by-products [85,101]. These species  
327 were endowed with low oxidizing power, they limit the electrochemical degradation of  
328 organics and constitute a scavenger for hydroxyl radicals as reported by Dominguez et al.  
329 [85]. Furthermore, the higher kinetic rates in the case of  $\text{Ti}_4\text{O}_7$  may be attributed to the less

330 formation of  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$  and the stability of hydroxyl radicals under acidic conditions as  
331 mentioned before.

332 **(Figure 2)**

333

334 *3.1.3. Effect of current density*

335 The current density is a direct controlled parameter; it affects the degradation rate and the  
336 energy consumption. Figure 3a, 3b, and 3c present the current density variation effect on the  
337 elimination rate of 60 mg L<sup>-1</sup> of DR23 using 25 mM of NaCl at pH = 6.0 for DSA, BDD, and  
338 Ti<sub>4</sub>O<sub>7</sub> anodes, respectively. The increase in the current density enhances the color removal  
339 and regulates the ability of hydroxyl radical and active chlorine generation on anode surfaces  
340 [56,102,103]. The total discoloration occurred around 40 min for a density of 2.5 mA cm<sup>-2</sup>  
341 and decreased to be only 10 min using 15 mA cm<sup>-2</sup> on the tested anodes. However, the  
342 discoloration is almost faster in the case of DSA/CG system; this is due to the greater electro-  
343 generation of active chlorine species [1]. The apparent kinetic rates increased about three  
344 times from 0.055 to 0.291 min<sup>-1</sup>, from 0.045 to 0.237 min<sup>-1</sup>, and from 0.0831 to 0.182 min<sup>-1</sup>  
345 when the current density increased from 2.5 to 15 mA cm<sup>-2</sup>, for DSA/CG, BDD/CG, and  
346 Ti<sub>4</sub>O<sub>7</sub>/CG cells, respectively, Figure 3d. Similarly, the electrochemical oxidation kinetic rate  
347 of Acid Brown 98 using Ti/Ru<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> composite anode increases from 0.036 to 0.062 min<sup>-1</sup>  
348 when the current density increases from 5 to 20 mA cm<sup>-2</sup> [99]. Likewise, Paniza et al. [1]  
349 investigated a comparison between indirect oxidation on DSA anode and direct oxidation on  
350 BDD surface of Acid Brown 98, they reported that the degradation enhanced with increasing  
351 the current density for both electrodes while the discoloration of the solution is almost faster  
352 on DSA anode. Regarding K<sub>app</sub> values, Ti<sub>4</sub>O<sub>7</sub> anode leads to a faster degradation compared to  
353 DSA and BDD anode in similar operating conditions under lower current densities (2.5 and 5  
354 mA cm<sup>-2</sup>). However, applying a current density above 5 mA cm<sup>-2</sup> could not further increase

355 the discoloration of DR23 solutions in the case of  $\text{Ti}_4\text{O}_7$ , where the apparent kinetic rates  
356 exhibit little changes. For higher current densities (10 and 15  $\text{mA cm}^{-2}$ )  $K_{\text{app}}$  follows the order:  
357  $K_{\text{app}}(\text{DSA}) > K_{\text{app}}(\text{BDD}) > K_{\text{app}}(\text{Ti}_4\text{O}_7)$ . This result was consistent with the degradation of  
358 tetracycline using  $\text{Ti}/\text{Ti}_4\text{O}_7$  anode [104]. This behavior can be attributed to the limited mass  
359 transfer rate of DR23 toward the  $\text{Ti}_4\text{O}_7$  at a higher current density and/or, to some extent,  
360 enhances some side reactions such as  $\text{O}_2$  evolution and increases the energy consumption  
361 [104,105].

### 362 (Figure 3)

363

#### 364 3.1.4. Effect of the concentration of DR23

365 Figure 4a, 4b, and 4c present the effect of the concentration of DR23 on the color removal,  
366 using 25 mM NaCl and 5  $\text{mA cm}^{-2}$  as the current density. As the concentration of dyes in  
367 textile wastewater is ranged from 5 to 230  $\text{mg L}^{-1}$  as reported by Yaseen et al. [60], the tested  
368 concentrations of DR23 were 60, 80, 100, and 200  $\text{mg L}^{-1}$ . The increase of the initial  
369 concentration decreases either the efficiency of the discoloration, Figure 4a, 4b, and 4c, and  
370 the kinetic rate Figure 4d. The apparent kinetic rate constants decreased from 0.101 to 0.070  
371  $\text{min}^{-1}$ , from 0.093 to 0.065  $\text{min}^{-1}$ , and from 0.134 to 0.046  $\text{min}^{-1}$  when the concentrations of  
372 DR23 increased from 60 to 200  $\text{mg L}^{-1}$  in DSA/CG, BDD/CG, and  $\text{Ti}_4\text{O}_7/\text{CG}$  cells,  
373 respectively. Generally, longer times of treatment are required to attain the same color  
374 removal efficiency with the increase of the initial concentration of DR23, due to the  
375 considerable slower discoloration rate at higher pollutant load [2]. This behavior can be  
376 related to the greater amount of organics in solution to react with the similar amount of  
377 oxidizing species, associated with the propensity of dye molecules to form clusters at high  
378 concentration, thus decreasing dye diffusion rate to the anode surface [106]. With the increase  
379 of DR23 concentration, the accumulation of intermediates and by-products is expectable,

380 which are thereafter competing with the colored compounds to react with the same amount of  
381 active chlorine in the case of DSA and either with  $M(\cdot OH)$  in the case of BDD and  $Ti_4O_7$   
382 anodes. Consequently, a smaller proportion of organics compared to the initial pollutant  
383 concentration is oxidized. Abdel-Aziz et al. [106] reported that increasing the initial  
384 concentration of dyes from 50 to 100 mg L<sup>-1</sup> decreased the color removal from 60 to 41% and  
385 from 70 to 46% for methylene blue and methyl blue, respectively, during the first 10 min of  
386 treatment using 2.5 g L<sup>-1</sup> of NaCl at pH = 3 and under 42.55 mA cm<sup>-2</sup>. Similar behavior was  
387 also reported elsewhere with increasing concentration of organic pollutants [98].

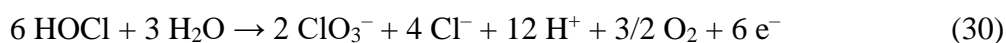
388 **(Figure 4)**

389

#### 390 3.1.5. Effect of initial pH

391 Figure 5a, 5b, and 5c present the effect of initial pH on the color removal of 60 mg L<sup>-1</sup> of  
392 DR23 using 25 mM NaCl under a current density of 5 mA cm<sup>-2</sup>. The higher color removal  
393 efficiency is achieved at pH = 3.00 using DSA/CG system. When the initial pH increased, the  
394 effectiveness of the degradation decreases dramatically by increasing the pH from 5.00 to  
395 11.00. For BDD/CG cell, the effectiveness of the degradation remains sensibly constant in the  
396 pH range of 3.00 to 9.00, while it decreased slightly at pH = 11.00. Therefore, the direct  
397 oxidation of DR23 on the BDD anode is efficient over a wide pH range. Serrano [107]  
398 reported the effect of acidic pH on the performance of the discoloration of the solution and  
399 explained the faster oxidation in the presence of active chlorine. This behavior is related to  
400 oxidizing power given by the standard potential of each produced chloride species, i.e. HOCl  
401 and Cl<sub>2</sub> have the highest standard potential ( $E^\circ (HOCl/Cl^-) = 1.49$  V/SHE) compared to Cl<sub>2</sub>  
402 ( $E^\circ (Cl_2/Cl^-) = 1.36$  V/SHE) and ClO<sup>-</sup> ( $E^\circ (ClO^-/Cl^-) = 0.89$  V/SHE). In addition, Rajkumar  
403 et al. [98] attributed the decrease of the efficiency of the elimination of Reactive Blue 19 in  
404 chloride medium using DSA anode to the decreased production of chlorine/hypochlorite at

405 higher pH conditions, due to the formation of chlorate or perchlorate with a low oxidizing  
406 potential according to the following reactions (Eqs. (30), (31)).



407 The pH variation during electrolysis can be attributed to the formation of these species (insert  
408 panels (Figure 5a and 5b)). In the case of the Magnéli phase  $\text{Ti}_4\text{O}_7$  (Figure 5c), the  
409 degradation of DR23 was highly influenced by the initial pH value. The best efficiency was  
410 obtained for  $\text{pH} = 3$  and it decreased with increasing the pH value. After 30 min of  
411 electrolysis time the discoloration achieved was 97%, 97%, 95%, 94%, and 84% using pH 3,  
412 5, 7, 9, and 11, respectively.

413 The pH drops during the first 30 min in the case of  $\text{Ti}_4\text{O}_7$  contrarily to the case of using DSA  
414 and BDD anodes (insert panel (Figure 5c)). This behavior can be attributed to the slow  
415 formation of  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$  on the surface of  $\text{Ti}_4\text{O}_7$  due to the absence of **direct oxidation of**  
416  $\text{Cl}^-$ , where it is mainly oxidized according to Eq. (20) and (21) [86]. This fact was also  
417 observed by Wang et al. in the case of perfluoroalkyl acids treatment using  $\text{Ti}_4\text{O}_7$ , where they  
418 reported that no appreciable chlorate and perchlorate was formed during the first 8 h of the  
419 treatment [87]. Similar results was observed by Gui et al. [108] in the case of methyl orange  
420 degradation.

421 Wang et al. [86] observed the higher accumulation of free chlorine using  $\text{Ti}_4\text{O}_7$  compared to  
422 BDD anode suggesting their less readily oxidation potential on the  $\text{Ti}_4\text{O}_7$ , which highlights its  
423 advantage in application for electrochemical oxidation treatment of organic pollutants in  
424 chloride medium.

425 However, to ensure the maximum mineralization efficiency in the subsequent part, the  
426 solution pH will be adjusted to acidic (pH = 3.00) during the electrolysis. In general, it is well  
427 known that hydroxyl radical formation is better in acidic media [26,69]. Therefore, the higher  
428 efficiency at various solution pH promotes the practical implementation of **electrooxidation**  
429 process to treat wastewaters.

### 430 (Figure 5)

431

## 432 3.2. Mineralization

### 433 3.2.1. Effect of electrode system on the mineralization efficiency of DR23

434 To determine the best treatment to eliminate DR23 by **electrooxidation**, the mineralization  
435 efficiency was investigated. **Figure 6** presents a comparison of the mineralization efficiency of  
436 DR23 in terms of TOC removal, using different electrode systems. Operating conditions were  
437 fixed at 60 mg L<sup>-1</sup> of DR23, pH = 3.00, 5 mA cm<sup>-2</sup> with 25 mM of NaCl (**Figure 6a**) or 12.5  
438 mM of Na<sub>2</sub>SO<sub>4</sub> (**Figure 6b**). The pH value was maintained at 3.0 ± 0.3 by adding acidic  
439 solution during the electrolysis time, in the case of NaCl medium. As shown in **Figure 6a** and  
440 **6b**, TOC removal increased steadily for about 1.5 h before slowing down with prolonged  
441 electrolysis time. The highest rate of TOC removal was achieved using BDD/**CG** system,  
442 around 86% using either NaCl or Na<sub>2</sub>SO<sub>4</sub> electrolytes, after 6 h of electrolysis. Meanwhile,  
443 BDD/SS system, whose activity comes just below the former, presents the mineralization  
444 efficiency of 73 and 82 % in NaCl and Na<sub>2</sub>SO<sub>4</sub> electrolytes, respectively, under similar  
445 experimental conditions. It is evidenced that the use of **CG** cathode enhanced the breakdown  
446 of DR23 in NaCl medium, with a relative increase of 18%, unlike Na<sub>2</sub>SO<sub>4</sub>, which may be  
447 attributed to the activity of **CG** cathode to generate H<sub>2</sub>O<sub>2</sub>, contributing to the mineralization of  
448 the dye. Furthermore, for all other systems, the use of **CG** cathodes allows higher TOC

449 removals than those of SS cathodes, in the same operating conditions. DSA/CG cell, endowed  
450 with a good activity in degradation, presents the worst mineralization efficiencies in chlorine  
451 and sulfate medium; they reached only 25 and 28 % TOC removal respectively. Between the  
452 two extreme results, Ti<sub>4</sub>O<sub>7</sub>/CG, Ti<sub>4</sub>O<sub>7</sub>/SS, CG/SS and CG/CG systems present intermediate  
453 efficiencies. However, Ti<sub>4</sub>O<sub>7</sub>/CG and Ti<sub>4</sub>O<sub>7</sub>/SS yield to a close efficiency to that of BDD  
454 anode in NaCl medium. After 6h of electrolysis time, TOC removals achieved using  
455 Ti<sub>4</sub>O<sub>7</sub>/CG and Ti<sub>4</sub>O<sub>7</sub>/SS were 60 and 51% in NaCl and 44 and 42% in Na<sub>2</sub>SO<sub>4</sub>, respectively.  
456 CG/SS and CG/CG reached 36 and 39 % in NaCl electrolyte and reached 45 and 51 % in  
457 Na<sub>2</sub>SO<sub>4</sub> electrolyte, respectively. Several authors have suggested that the mineralization  
458 process is improved using a chloride ion as a supporting electrolyte [20,56]. Oturan [25]  
459 reported that BDD thin film anode has a higher oxidation and/or mineralization power for the  
460 treatment of organic pollutants in sulfate medium. This is due to the generation of physisorbed  
461 M(<sup>•</sup>OH) which are more available for destruction of organics than in the case of metallic  
462 oxide anodes and DSA. Active anodes such as DSA and graphite have a low value of oxygen  
463 evolution overpotential and permit only the partial oxidation of organics [109]. Salazar et al.  
464 [33] compared the mineralization of Disperse Yellow 3 dye on BDD, Ti/Ru<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub>, and  
465 Ti/Pt anodes in Na<sub>2</sub>SO<sub>4</sub> and NaCl supporting electrolytes and achieved 90% TOC removal  
466 with BDD in sulfate solution, while the percentage is up to 50% for other anodes, irrespective  
467 of the operating conditions. They reported that DSA anode is more active in NaCl medium,  
468 followed by BDD and Ti/Pt due to higher production of effective chlorine species which  
469 depend on pH and anode material. Likewise, Yang et al. [110] reported that the order of the  
470 mineralization of Imatinib drug decreases in the order: BDD > Ti<sub>4</sub>O<sub>7</sub> > Pt > DSA. They  
471 evaluated the TOC removal efficiency in Na<sub>2</sub>SO<sub>4</sub> media, achieving total mineralization at 8 h  
472 treatment using BDD anode. They also mentioned that the mineralization rate was 61%, 78%,  
473 and 82% by Pt, DSA, and Ti<sub>4</sub>O<sub>7</sub> anodes, respectively.

474 DR23 mineralization in BDD/CG system is mainly occurred by direct and mediated  
475 electrochemical oxidation on the BDD surface in sulfate and in chloride media, respectively.  
476 Physisorbed  $M(\bullet OH)$  radicals, the strong oxidant, are considered as the main oxidant in  
477 sulfate solution, while homogenous oxidation prevails in the chloride solution in the bulk of  
478 the solution or near the anode surface. The trend of the TOC removal curve obtained by  
479 BDD/CG in NaCl medium, Figure 6a, unlike in  $Na_2SO_4$ , Figure 6b, shows that the  
480 mineralization can still increase with the electrolysis time, confirming that the by-products are  
481 still breakdown. Jalife-Jacobo et al. [56] have found the same results studying the degradation  
482 of diazo dye congo red on BDD/SS cell and reported a favorable synergy between the free  
483  $M(\bullet OH)$  and the active chlorine species leading to a faster mineralization using NaCl. On the  
484 other hand, various by-products may be formed which are highly recalcitrant to oxidation by  
485 the action of  $M(\bullet OH)$  generated conjugated to that of oxidant species such as persulfates in  
486  $Na_2SO_4$  medium.

487 Based on (Eq. (6)), the energy consumption per g of TOC removed is presented in Figure 6c  
488 using different electrode cells at  $5 \text{ mA cm}^{-2}$  after 6h electrolysis time. The energy  
489 consumption, EC, at the end of electrolysis using BDD/CG is lower compared to other  
490 systems. It is about 2.05 and 2.60 kWh  $g^{-1}$  TOC for NaCl and  $Na_2SO_4$ , respectively. The same  
491 trends which corroborate our findings were already reported [33]. This result highlights  
492 clearly the low EC and the efficiency of BDD anode for DR23 treatment in solutions  
493 containing chloride salts.

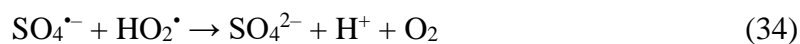
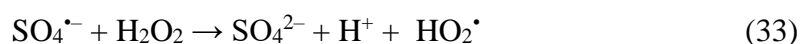
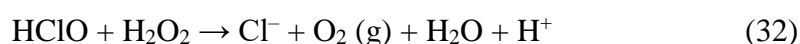
### 494 (Figure 6)

495

496 3.2.2. *Effect of current on the mineralization efficiency*

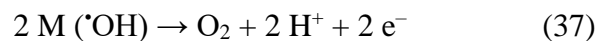
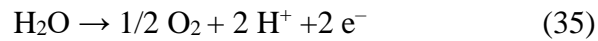


497 The effect of current density on TOC removal in the case of BDD/CG is presented in Figure  
 498 7a and 7b for NaCl and Na<sub>2</sub>SO<sub>4</sub>, respectively. In the case of NaCl (Figure 7a), increasing the  
 499 current density from 2.5 to 15 mA cm<sup>-2</sup> increases the TOC removal value and reduce the time  
 500 required for total mineralization. After 6h, the obtained TOC removal values were 80%, 86%,  
 501 94%, and 95% using 2.5, 5, 10, and 15 mA cm<sup>-2</sup>, respectively. On the other hand, in the case  
 502 of Na<sub>2</sub>SO<sub>4</sub>, the variation of TOC removal (%) vs. current density is shown in Figure 7b. As  
 503 can be seen from the results, the increase of current density over 5 mA cm<sup>-2</sup> does not  
 504 significantly improve the TOC removal % after 6h of electrolysis. The mineralization reached  
 505 was 74%, 86%, 91%, and 92% using 2.5, 5, 10, and 15 mA cm<sup>-2</sup>, respectively. The  
 506 uncompleted mineralization can be attributed to the formation of recalcitrant and toxic by-  
 507 products like chloroderivatives that are slowly degraded by active chlorine species and  
 508 M(•OH), in the case of NaCl. In addition, the TOC removal efficiency can be affected by the  
 509 consumption of M(•OH) by sulfate (Eqs. (13)-(15)) or chloride ions (Eq. (20)), and the  
 510 decomposition of H<sub>2</sub>O<sub>2</sub> by HOCl or SO<sub>4</sub><sup>•-</sup> (formed through the reaction between sulfate ions  
 511 and •OH (Eqs. (14), (15)) as presented in Eqs. (32)-(34) [111].



512 Besides the increase of the kinetic of TOC removal with the current density, the  
 513 mineralization current efficiency, MCE%, decreased by increasing applied current density  
 514 values, Figure 7c and 7d. MCE% values were significant for 2.5 mA cm<sup>-2</sup> at 2h of  
 515 electrolysis; they were about 7.5% and 5.2% for NaCl and Na<sub>2</sub>SO<sub>4</sub>, respectively. For both  
 516 electrolytes, increasing the electrolysis time reduces the MCE% due to the formation of short  
 517 chain carboxylic acids that resist to the mineralization [61]. The increase in the current density

518 enhances the side reaction of oxygen evolution on BDD surface (Eq. (35)) as well as the  
519 recombination of  $\cdot\text{OH}$  in the bulk (Eq. (36)) or oxidation of  $\text{M}(\cdot\text{OH})$  at the anode (Eq. (37))  
520 [21].



521 To evaluate the feasibility of the process and the reliability of the electrodes, the energy  
522 consumption, EC ( $\text{kWh g}^{-1}$  TOC) was computed using (Eq. 4) and its trend is presented in  
523 [Figure 7e](#) and [7f](#). The increase of current density increases the energy consumption with  
524 electrolysis time. It is clear from [Figure 7e](#) and [7f](#) that  $5 \text{ mA cm}^{-2}$  requires a low EC, about  
525  $2.05 \text{ kWh g}^{-1}$  TOC and  $2.6 \text{ kWh g}^{-1}$  TOC using NaCl and  $\text{Na}_2\text{SO}_4$ , respectively, to achieve 86  
526 % of TOC removal after 6h of electrolysis. From MCE% and the energy consumption,  $5 \text{ mA}$   
527  $\text{cm}^{-2}$  was suggested as the optimal value for efficient mineralization of DR23 under fixed  
528 experimental conditions.

529 **(Figure 7)**

530

#### 531 **4. Conclusion**

532 In summary, the treatment of DR23 was investigated by **electrooxidation** process in a batch  
533 reactor using different electrode configurations in operating conditions of current densities  
534 ( $2.5, 5, 10, \text{ and } 15 \text{ mA cm}^{-2}$ ) under values of pH about 3.00, 5.00, 6.00, 7.00, 9.00, and 11.00,  
535 and 25 mM NaCl or 12.5 mM  $\text{Na}_2\text{SO}_4$  as the supporting electrolyte, at  $20 \text{ }^\circ\text{C}$ . The  
536 effectiveness of different electrode combinations was compared during the degradation and  
537 mineralization of DR23 solution. The results demonstrate that using BDD,  $\text{Ti}_4\text{O}_7$ , or DSA

538 anodes coupled with CG or SS cathode is found to be helpful for a good discoloration in NaCl  
539 medium. In addition, the discoloration rate increases by increasing the electrolysis time,  
540 current density, concentration of supporting electrolyte, and decreases by increasing the pH  
541 and the concentration of the dye. The best mineralization efficiency obtained for DR23  
542 solutions was achieved with the BDD/CG, followed by BDD/SS with slight efficiency when  
543 using CG cathode in both saline solutions. The mineralization of 60 mg L<sup>-1</sup> of DR23 with  
544 BDD/CG system reaches about 86% of TOC removal in either chloride or sulfate solution,  
545 using 5 mA cm<sup>-2</sup> at 6 h of electrolysis time. From MCE% and the energy consumption, 5 mA  
546 cm<sup>-2</sup> was suggested as an optimal value for efficient mineralization of DR23 under fixed  
547 experimental conditions using BDD/CG system. The energy consumption and MCE% were  
548 2.05 kWh g<sup>-1</sup> TOC and 2.5%, and 2.6 kWh g<sup>-1</sup> TOC and 2.6%, using NaCl and Na<sub>2</sub>SO<sub>4</sub>,  
549 respectively, after 6h of treatment.

550 The future trend and perspective of this study should focus on the identification of aliphatic  
551 intermediates and inorganic ions to propose a mineralization pathway of DR23 and  
552 investigate the ecotoxicity assessment of the final effluent to verify that toxicity has been  
553 efficiently removed. Likewise, electrochemical behavior of the studied anodes and formed  
554 active species in chloride and sulfate salts seem to be of importance. In addition, a comparison  
555 between electrooxidation and other processes such as electro-Fenton process will be  
556 performed to enhance the efficiency and reduce the treatment time.

557

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565

#### 566 **Conflict of interest**

567 On behalf of all authors, the corresponding author states that there is no conflict of interest.

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970 **Table 1.** Recent studies on decontamination of dye solutions by anodic oxidation method.

Pollutants	Conditions	Maximum degradation	References
Acid red18	-Ti/ Graphite felt/ Granular activated carbon (GAC) in fluidized bed.  -Optimal conditions: $C_0 = 100 \text{ mg L}^{-1}$ , 100 mM NaCl, pH = 3, $j = 20 \text{ mA cm}^{-2}$ , GAC = $250 \text{ mg L}^{-1}$	96.5% of color removal and 84.8% of COD removal at 45 min	[3]
Acid blue 29	-Sn-Cu-Sb/SS  -Optimal conditions: $C_0 = 60 \text{ mg L}^{-1}$ , $j = 10 \text{ mA cm}^{-2}$ , pH = 7, 50 mM $\text{Na}_2\text{SO}_4$	100% of COD removal at 600 min	[2]
Orange G	-BDD/SS  -Conditions: $100 \text{ cm}^3$ of 0.52-6.34 mM of Orange G azo dye, pH 3, 50 mM $\text{Na}_2\text{SO}_4$ , and current density between 33.3 and $150 \text{ mA cm}^{-2}$	-100 %TOC removal in less than 330 min operating at $j \geq 66.7 \text{ mA cm}^{-2}$  -100% Color removal at 396 min-at $150 \text{ mA cm}^{-2}$ .	[36]
indigo carmine	-BDD/SS  -Conditions: indigo carmine up to $0.9 \text{ g L}^{-1}$ , 50 mM $\text{Na}_2\text{SO}_4$ , pH 3.0-10.0, and 100, 300, and 450 mA at $35^\circ\text{C}$ .	TOC reduced with current. 100% mineralization drops from 600 min at 100 mA to 300 min at 450 mA.	[37]

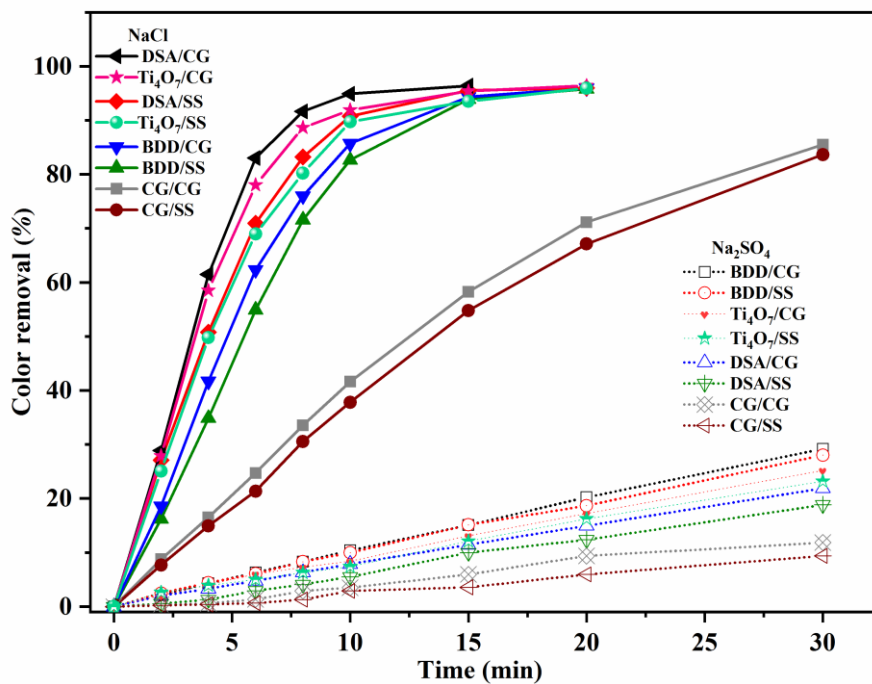
Methyl Violet	-BDD or Pt/SS	- BDD, >97% TOC decay	[38]
	-Conditions: 100 cm <sup>3</sup> of 100 mg L <sup>-1</sup> , 50 mM Na <sub>2</sub> SO <sub>4</sub> , pH 3.0-7.4, current density 33.3- 150 mA cm <sup>-2</sup>	with 18 Ah dm <sup>-3</sup> (360 min) at pH 3.0 and 15 Ah dm <sup>-3</sup> (300 min) at pH 7.4	
		- Pt TOC decay, close to 22% and 33% at pH 3.0 and 7.4.	
Reactive Black 5	-Ti/RuO <sub>2</sub> /IrO <sub>2</sub> /TiO <sub>2</sub> /SS	-100 % of color removal and 33% of COD decay at 15 min.	[39]
	Optimal conditions: C <sub>0</sub> =300 mg L <sup>-1</sup> , 100 mA cm <sup>-2</sup> , 8 mM NaCl		
Methyl orange	-Ti <sub>4</sub> O <sub>7</sub> / Ti	-Complete color removal and 91.7% COD reached after 5 h electrolysis	[40]
	-Conditions: C <sub>0</sub> = 100 mg L <sup>-1</sup> , 10 mA cm <sup>-2</sup> , 100 mM NaCl		

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971 **COD:** Chemical Oxygen Demand; **TOC :** Total Organic Carbon; **SS:** stainless steel

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**Figure 1:** Kinetics of color removal (%) on different electrode materials; 40 mg L<sup>-1</sup> DR23, 25 mM NaCl or 12.5 mM Na<sub>2</sub>SO<sub>4</sub>, 8.3 mA cm<sup>-2</sup>, pH = 6.0.

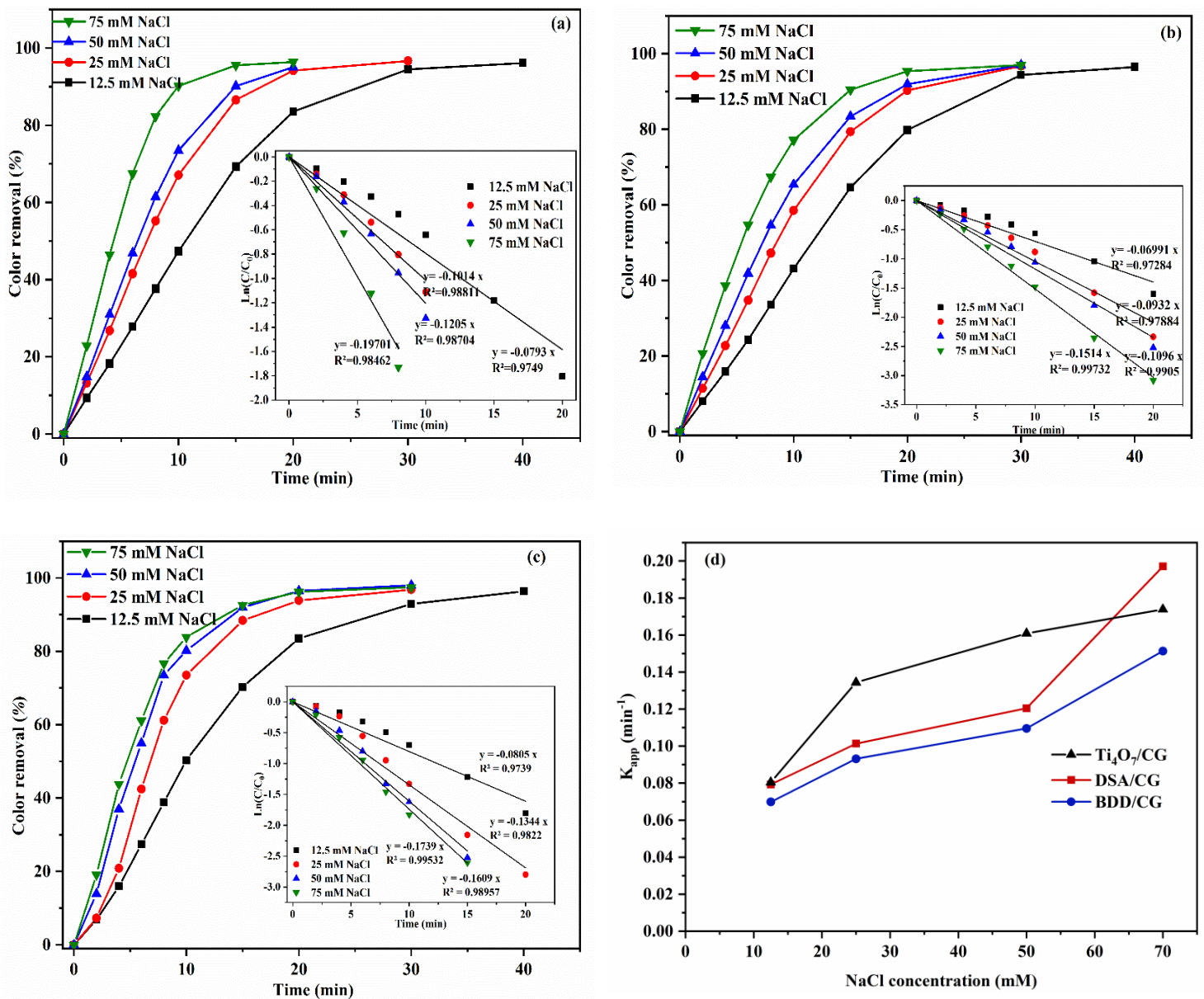


Figure 2: Effect of NaCl concentration,  $60 \text{ mg L}^{-1}$  DR23,  $\text{pH} = 6.0$ ,  $5 \text{ mA cm}^{-2}$ , (a) color removal (%), (a): DSA/CG, (b): BDD/CG, (c):  $Ti_4O_7/CG$ , and (d): the apparent kinetic rate constants vs. NaCl concentration. The insert panels are the kinetic analysis assuming a pseudo first order reaction.



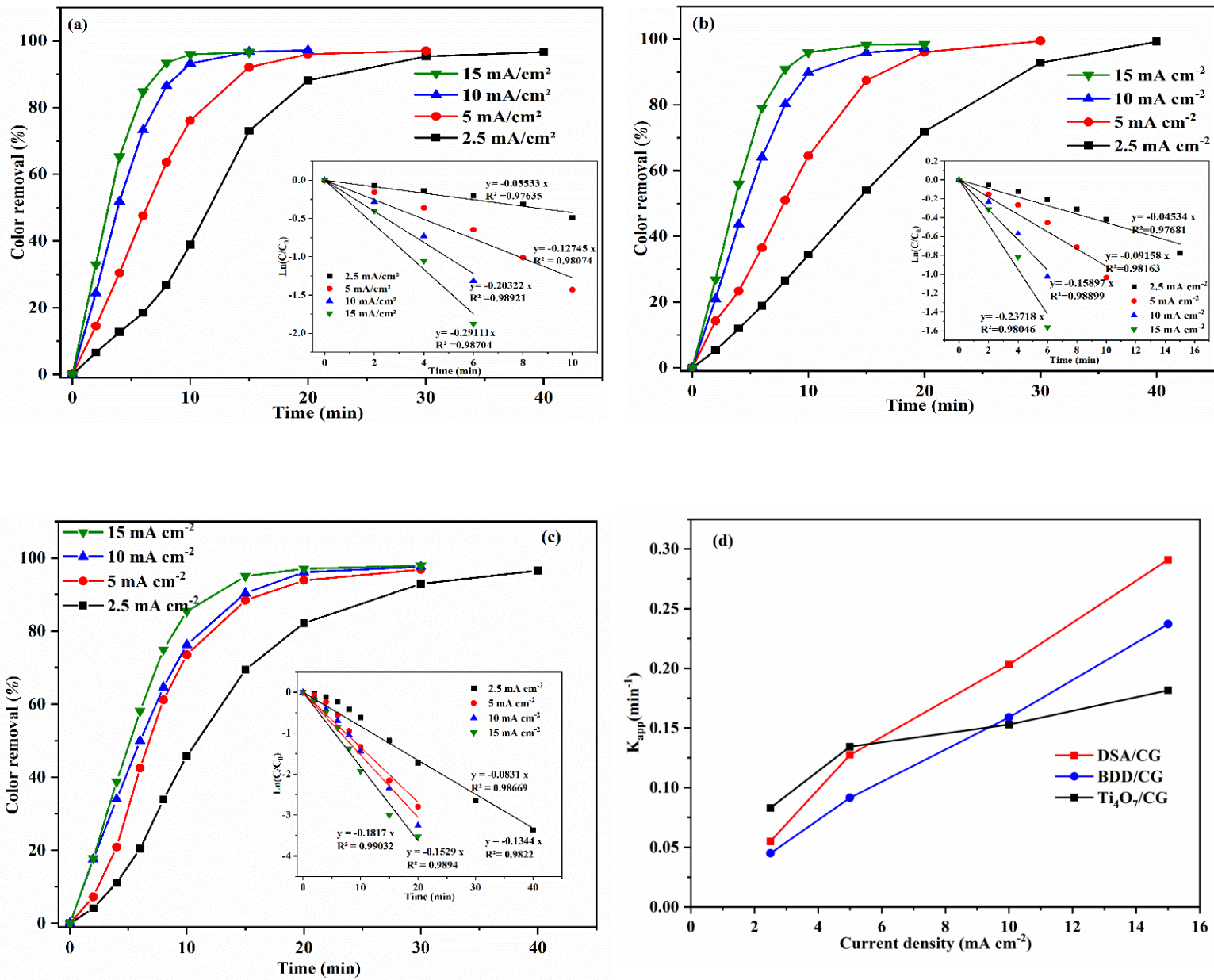


Figure 3: Effect of the current density, 60 mg L<sup>-1</sup> of DR23, 25 mM NaCl, pH = 5.89, (a): DSA/CG, (b): BDD/CG, (c): Ti<sub>4</sub>O<sub>7</sub>/CG, and (d): apparent kinetic rate. The insert panels are the kinetic analysis assuming a pseudo first-order reaction.

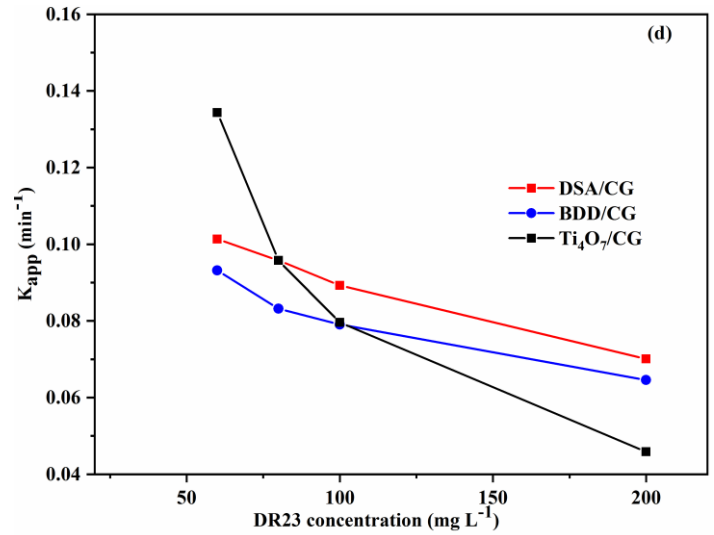
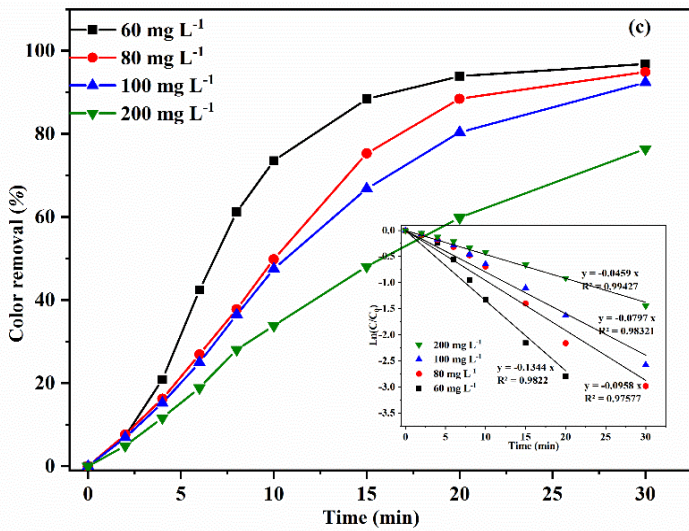
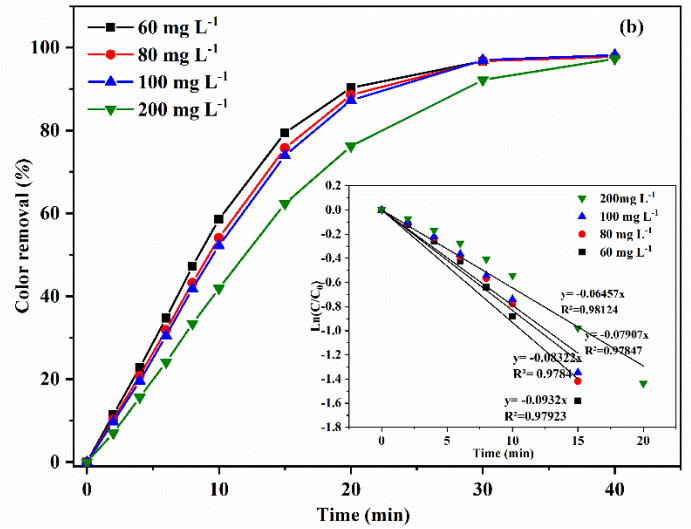
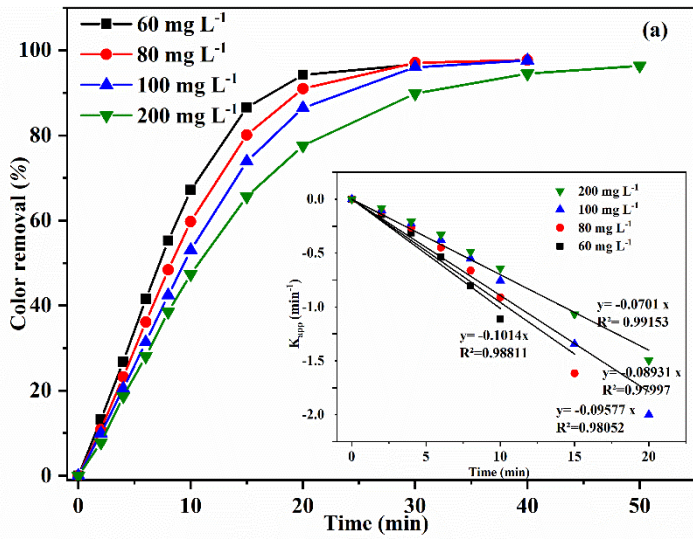


Figure 4: Effect of the initial dye concentration, 25 mM NaCl, pH = 5.89, 5 mA cm<sup>-2</sup> (a): DSA/CG, (b): BDD/CG, (c): Ti<sub>4</sub>O<sub>7</sub>/CG, and (d): variation of apparent kinetic rate. The insert panels are the kinetic analysis assuming a pseudo first order reaction.

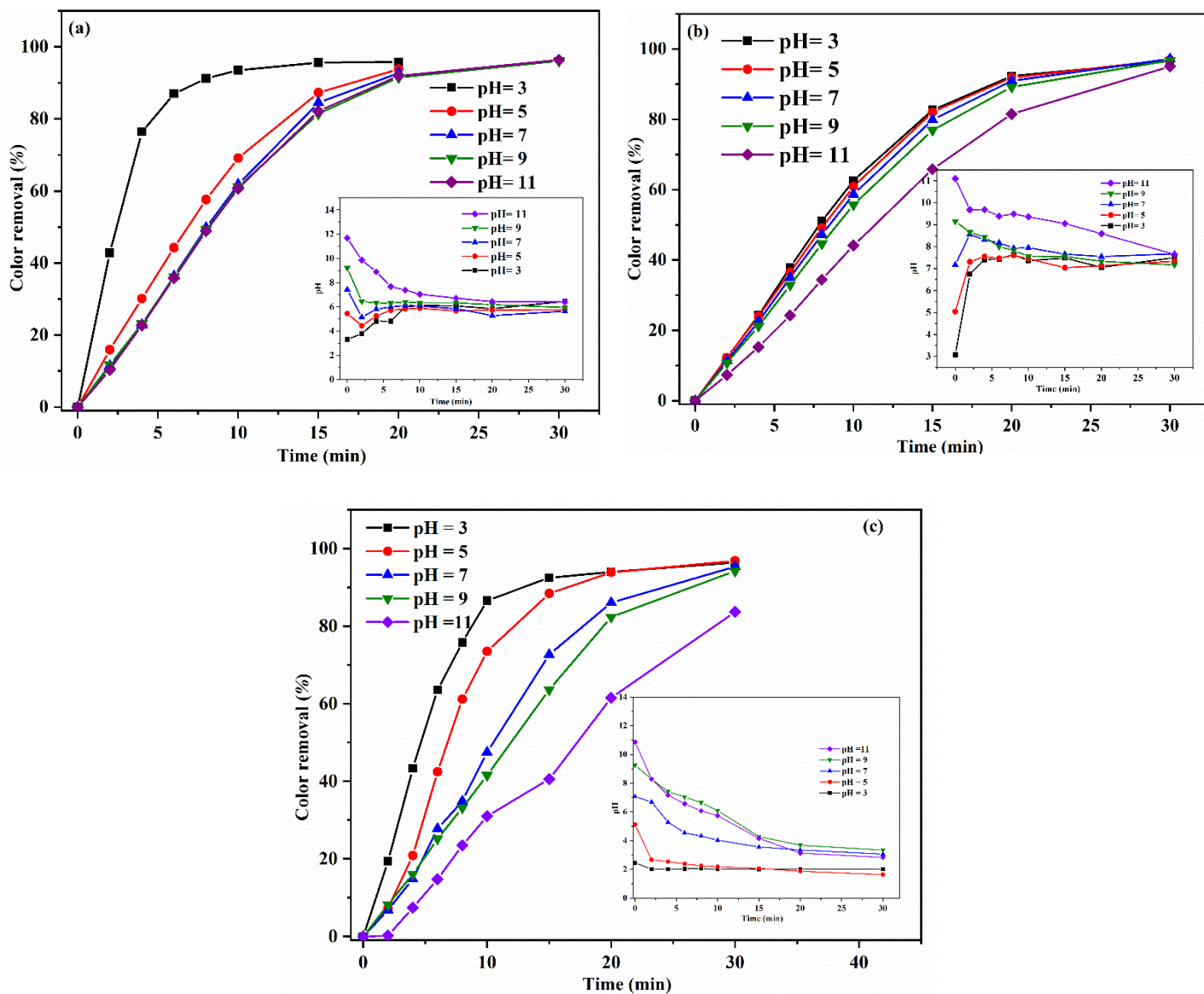


Figure 5: Effect of the initial pH on the color removal, 60 mg L<sup>-1</sup> of DR23, 25 mM NaCl, 5 mA cm<sup>-2</sup>. Insert panels: variation of pH vs. time, (a): DSA/CG, (b): BDD/CG, and (c): Ti<sub>4</sub>O<sub>7</sub>/CG

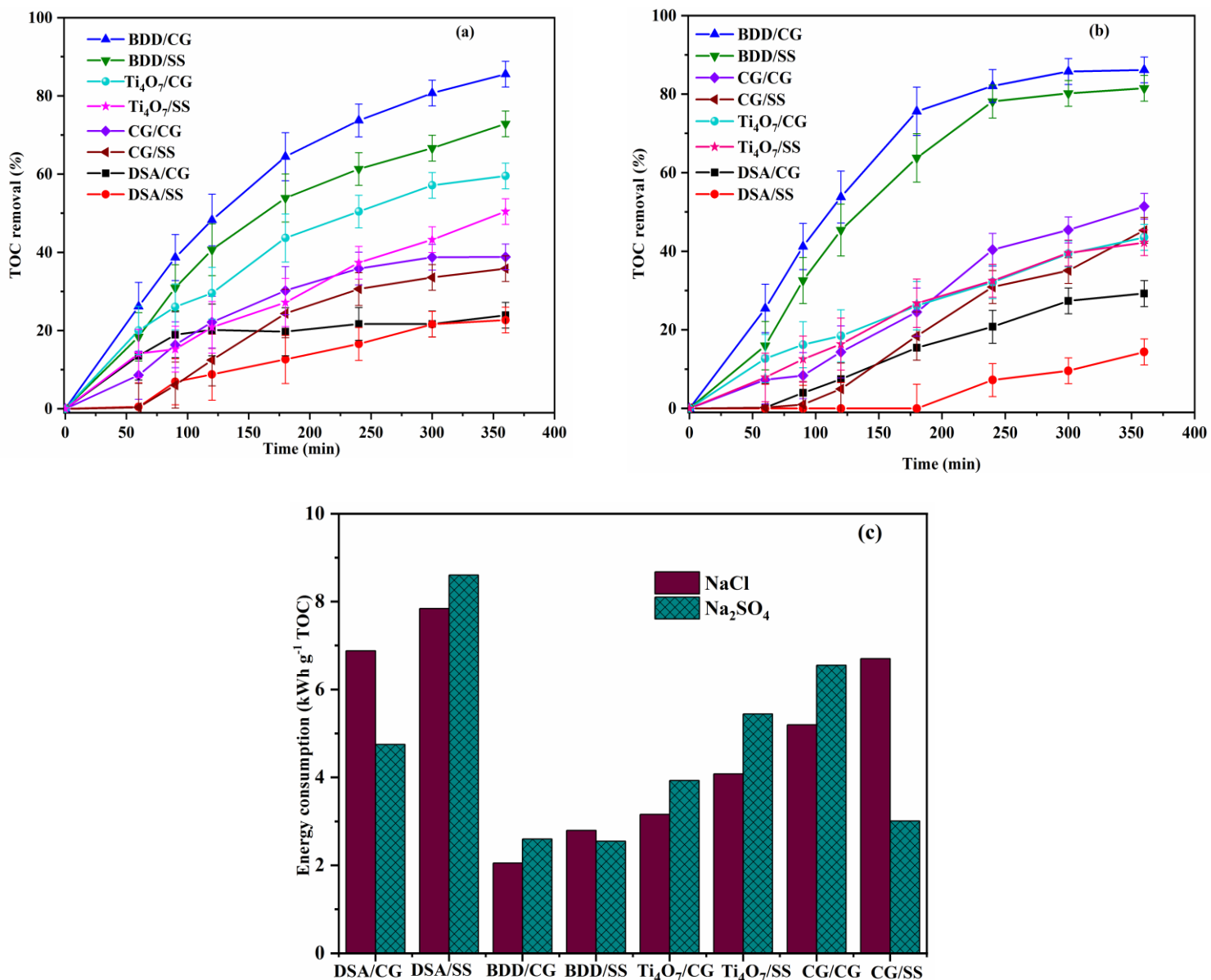


Figure 6: TOC removal vs. electrodes nature, 60 mg L<sup>-1</sup> of DR23, pH = 3.00, and 5 mA cm<sup>-2</sup>, after 6h of electrolysis time, (a): 25 mM NaCl, (b): 12.5 mM Na<sub>2</sub>SO<sub>4</sub>, (c): Energy consumption for tested systems, kWh g<sup>-1</sup> TOC

TOC

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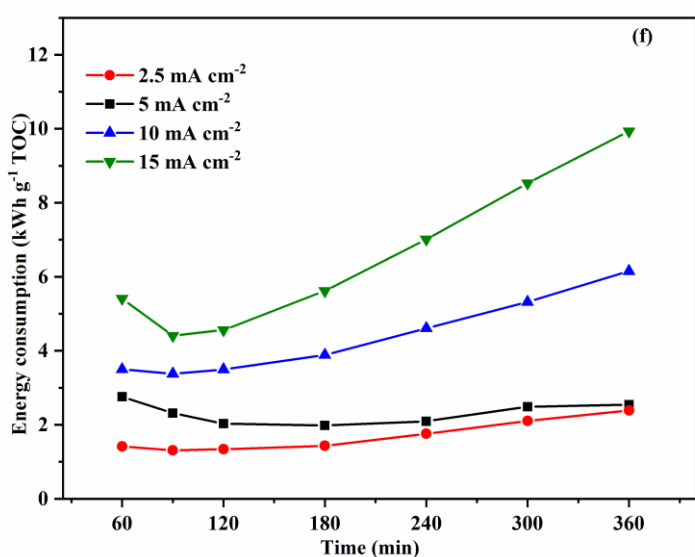
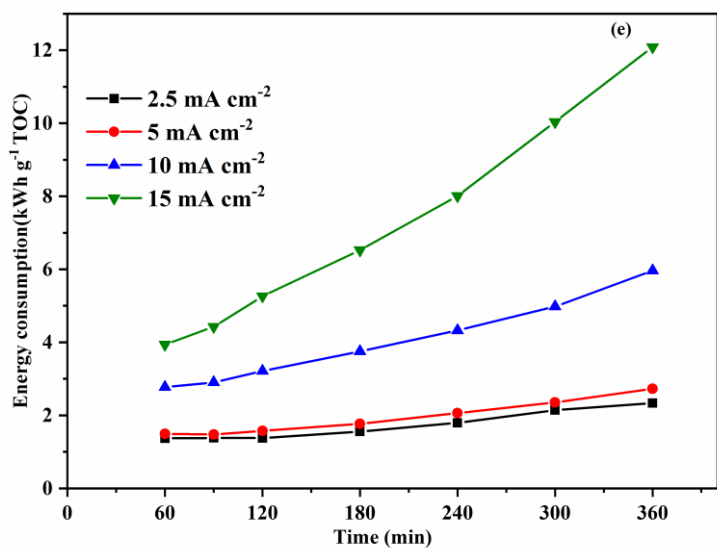
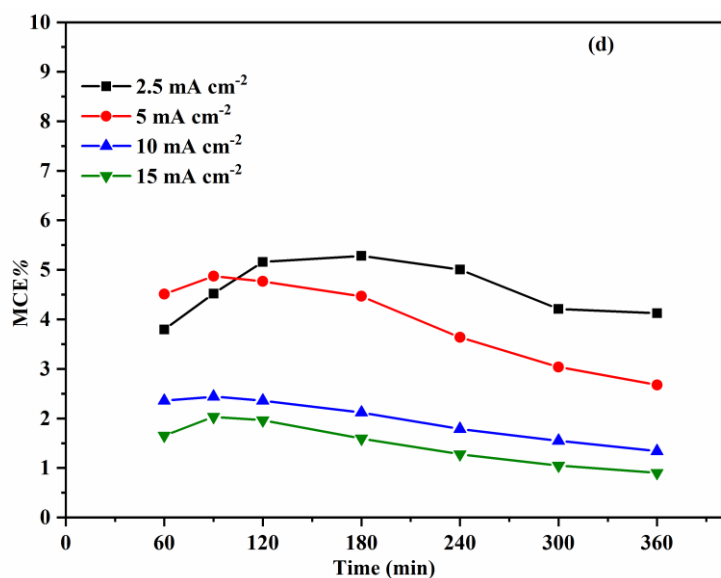
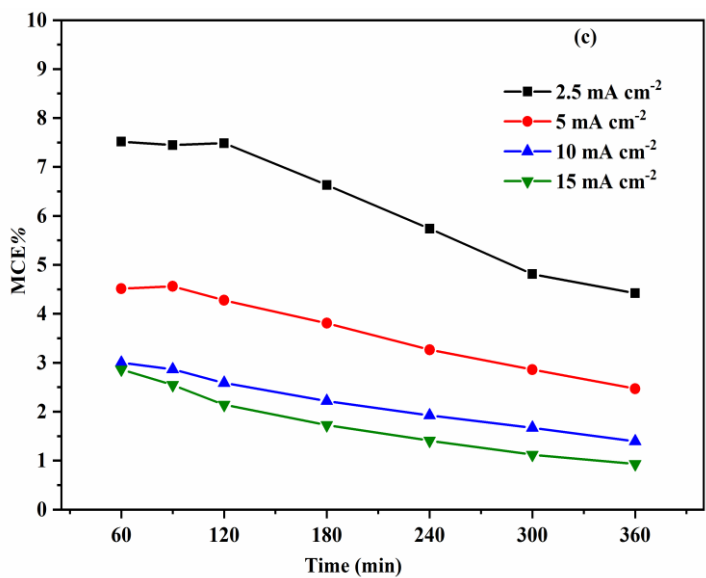
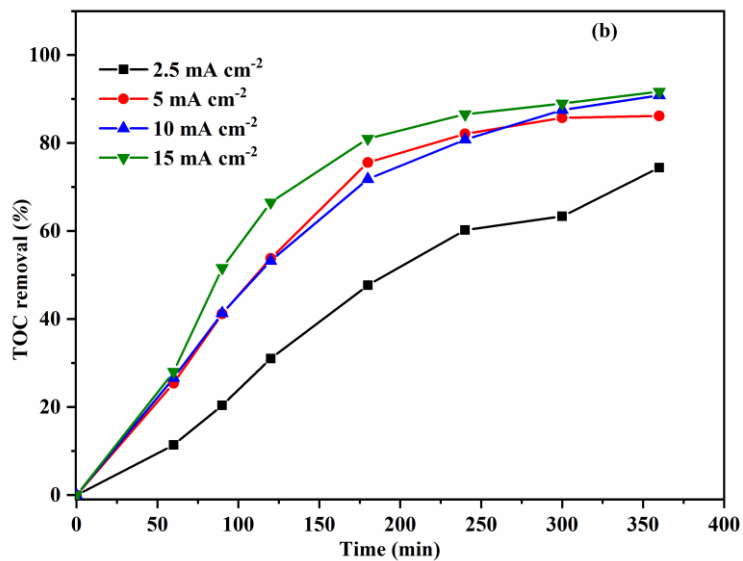
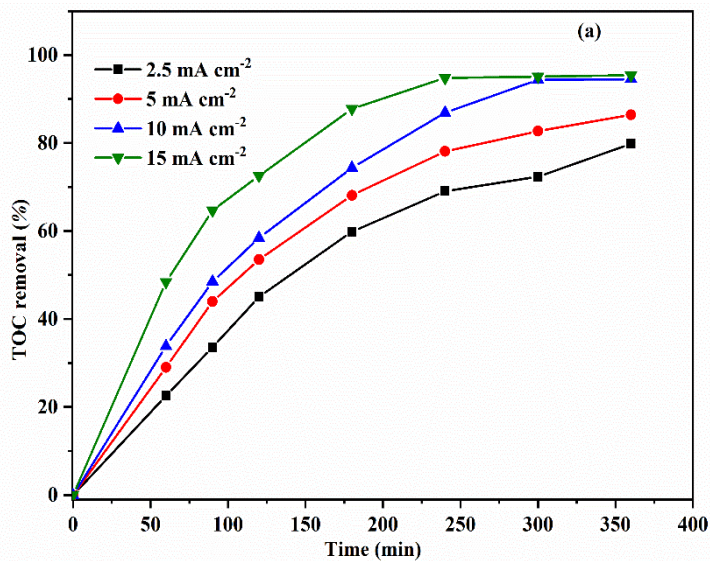


Figure 7: Effect of current on the mineralization of 60 mg L<sup>-1</sup> DR23 vs. time, (a, c, e) 25 mM NaCl, (b, d, f) 12.5 mM Na<sub>2</sub>SO<sub>4</sub>, pH = 3.00, BDD/CG, (a, b) TOC removal, (c, d) mineralization efficiencies (MCE%), (e, f) Energy consumption (kWh g<sup>-1</sup> TOC)

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