

Electrochemical treatment of paper mill wastewater by electro-Fenton process

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Abstract

The electrochemical oxidation of organics in paper mill wastewater belonging to Halfa industries (Tunisia) was performed by galvanostatic electrolyses using electro-Fenton (EF) process. The effect of several operating parameters, such as applied current density, electrodes material, air pressure and the presence of sodium chloride (NaCl) was evaluated. In particular, carbon felt (CF), modified carbon felt (MCF) and gas diffusion electrode (GDE) were used as cathode while Ti/IrO₂-Ta₂O₅ and Boron Doped Diamond (BDD) as anode. Total Organic Carbon (TOC) measure was chosen as reference parameter to assess the extent of the treatment. The experimental results show that, by adopting the optimal set of operative conditions, EF can allow a high removal of TOC. It was shown that better performances can be achieved increasing the complexity of the treatment, by using sufficiently long electrolysis time or BDD as anode, MCF or GDE as cathode or the addition of NaCl.

23 Keywords: Electro-Fenton, paper mill wastewater, modified carbon felt, pressurized electro-Fenton;
24 electrochemical oxidation, AOP

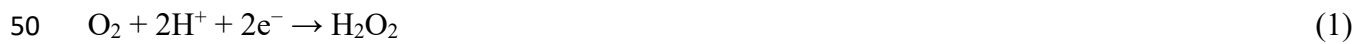
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26 **1. Introduction**

27 The pulp and paper mill industry is characterized by an intensive use of water and by the generation
28 of a large volume of wastewater (up to 60 m³/ton of paper produced [1]), harmful for the biotic
29 compartment [2] and characterized by an high level of chemical oxygen demand [3]. These effluents
30 present suspended solids, heavy metals and sulphur compounds along with lignin and its derivatives
31 [4]. Due to the presence of recalcitrant substances, paper mill wastewater have a very low
32 biodegradability, resulting in a reduced effectiveness of biological processes [5]. Hence, advanced
33 oxidation processes are necessary for the treatment of the embedded organic compounds. According
34 to literature, electrochemical treatments are some of the most interesting and effective processes for
35 treating wastewater contaminated by resistant organic pollutants [6, 7]. In particular, intensive
36 research efforts were devoted to the study of electrochemical advanced oxidation processes (EAOPs),
37 including anodic oxidation (AO), both direct and mediated [8], using conventional and modified
38 anodes [9], and electro-Fenton (EF) with homogeneous and heterogeneous catalyst [10, 11].
39 However, in spite of the fact that the effectiveness of electrochemical methods has been largely
40 proved for synthetic wastewater, less studies were devoted to the treatment of real wastewater. In
41 particular, the utilization of EAOPs for the treatment of pulp and paper mill wastewater has been
42 attempted by various authors [12–18]. Studies were focused mainly on the synergy with physical
43 processes [12], direct electrochemical oxidation [13, 14] and electrocoagulation [16, 17] or on
44 coupled electrochemical processes [11, 19, 20] while slightly less attention has been devoted to the
45 optimization of the sole EF process, even if it is one of the most mature EAOPs [21].

46 In EF process, H₂O₂ is produced by oxygen reduction (eq. 1) at cathode usually consisting of
47 carbonaceous materials and hydrogen peroxide reacts with catalytic amounts of Fe²⁺ to generate the
48 •OH radicals in the solution (eq. 2) [22].

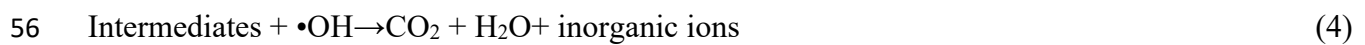
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53 These formed •OH reacts rapidly with organics, leading to their oxidation (eq. 3 and 4):

54



57

58 The advantages of this process with respect to conventional Fenton process is the continuous electro-
59 generation of H₂O₂ and the cathodic regeneration of Fe²⁺ from cathodic reduction of Fe³⁺. However,
60 the performances of EF are usually limited by the low solubility of oxygen that leads to slow mass
61 transfer of oxygen to the cathode, thus giving rise to slow generation of hydrogen peroxide. In
62 previous works it was shown that it is possible to minimize such problem by using various approaches
63 [23] such as the use of innovative cathodes, including gas diffusion electrodes (GDEs) [11, 22] and
64 modified carbon felts (MCF) [22, 24, 25]; jet-cells [26]; microfluidic cells [23, 27, 28]; and,
65 pressurized reactors [24, 29, 30].

66 In this work the treatment of a real paper mill wastewater was performed by EF using various kinds
67 of cathodes (namely, carbon felt, MCF and GDE) and anodes (Ti/IrO₂-Ta₂O₅ and Boron Doped

68 Diamond), at various current densities in both conventional and pressurized cells, in order to evaluate
69 in depth the EF process for the removal of organics by such wastewater.

70

71 **2. Experimental**

72 2.1. Electrolysis system

73 Two different systems were used to carry out the electrolyses. System (I) was an undivided
74 conventional three-electrode glass cell equipped with *i.* a gas bubbler; *ii.* a SCE reference electrode;
75 *iii.* a carbon felt (CF); a modified carbon felt (MCF) or a gas diffusion electrode (GDE) cathode; *iv.*
76 and a Ti/IrO₂-Ta₂O₅ (DSA[®] from ElectroCell AB) or a BDD (Condias) anode. System (II) was made
77 up of a stainless steel (AISI 316) cell with a cylindrical geometry, previously showed in detail [29].
78 Briefly, the high pressure cell was equipped with a gas inlet/outlet, electrical connections for the
79 electrodes (CF or MCF as cathode and DSA[®] as anode), a pressure gauge and a dip tube connected
80 to an external valve that was used to withdrawal the liquid sample. System (II) was pressurized by air
81 (99.999% purity, supplied by Air Liquide) and the operating pressure was controlled by a pressure
82 reducer. All the experiments were carried out under galvanostatic mode using an Amel 2549
83 potentiostat/galvanostat at room temperature. The electrolytic solution, i.e. the treated sample, of 50
84 mL was continuously stirred by using a magnetic stirrer (600 rpm). The surface area of both cathode
85 and anode electrode was 2.8 cm²; the current densities were computed as the ratio between the current
86 intensity and the geometric wet surface area. Experiments were repeated at least twice in order to
87 check the reproducibility of the data.

88

89 2.2 Chemicals

90 The paper mill effluents samples used were taken from Halfa industries (Tunisia) where the
91 wastewater is discharged. The typical characteristics of the raw wastewater are given in Table 1.

92 As synthetic catalyst 0.5 mM of ferrous sulphate heptahydrate, ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, in analytical grade from
93 Fluka) was used. Sulfuric acid from Sigma–Aldrich was added in solution to adjust pH to the target
94 value. The paper mill wastewater was filtered using a vacuum filtration apparatus equipped with a
95 dry paper membrane (0.45 μm average diameter pores).

96

97 Table 1. Characteristics of paper mill wastewater as received.

Parameter	Value
Color	brown
pH	6.6
conductivity (mS/cm)	3.14
TOC (mg/L)	115

98

99 2.3. Instruments and analytical procedures

100 During the experiments, bulk samples were taken from the reactor at regular intervals and analysed
101 with a Shimadzu TOC-L analyser. With respect to the initial value (TOC_0), the percentage of TOC
102 removed at time t was calculated as follows:

$$103 \quad \%(\text{TOC}) = \frac{\text{TOC}_0 - \text{TOC}(t)}{\text{TOC}_0} * 100$$

104 The instantaneous value of the current efficiency (CE) was determined similarly to [31]. Briefly,
105 CE(t) is the ratio of the current of electrons theoretically needed for the observed oxidation (TOC_0 -
106 $\text{TOC}(t)$) and the actual amount of energy provided to the cell:

$$107 \quad \text{CE}(t) = \frac{FnV(\text{TOC}_0 - \text{TOC}(t))}{Mit}$$

108 where I is the potentiostatic applied current for the time span t , F the Faraday constant (96485.33 C
109 mol^{-1}), V the treated volume. Organic content is always considered as an equivalent amount of glucose

110 (in terms of carbon atoms), so that n and M are the 24 moles of electrons exchanged during the
111 oxidation of a mole of glucose and its molecular weight, respectively.

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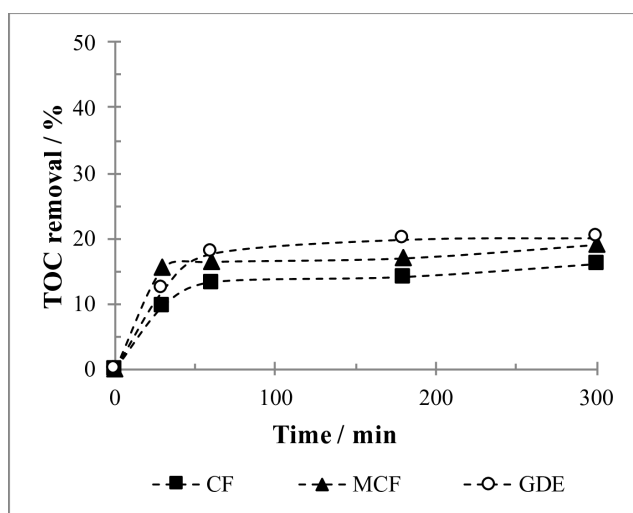
113 3. Results and discussion

114 3.1 First electrolyses in the absence of Fe(II)

115 First electrolyses were performed in the absence of iron under galvanostatic conditions with a carbon
116 felt cathode and a DSA[®] anode (Ti/IrO₂-Ta₂O₅) with a stirring rate of 600 rpm, a current density of
117 20 mA cm⁻², pH =3, with 50 mL of a real paper-mill wastewater. In the absence of Fe(II), oxidation
118 of organics takes place mainly directly at DSA[®]-anode surface and indirectly by means of cathodic
119 produced H₂O₂ [32]. As shown in Fig. 1, a quite low abatement of TOC occurred in this case, thus
120 showing the poor efficacy of both DSA[®] anode and H₂O₂ for the oxidation of organics present in this
121 real wastewater. In particular, after 60 min a very slow abatement was recorded. As an example, at
122 carbon felt cathode after 1 and 5 h the removal of TOC was about 13 and 16 %, respectively. Since
123 the generation of hydrogen peroxide is expected to strongly depend on the nature of the cathode [26,
124 29], the electrolyses were repeated using two cathodes more effective for the cathodic conversion of
125 oxygen to H₂O₂:

- 126 • A modified carbon felt obtained by addition of a carbon black/polytetrafluoroethylene
127 (CB/PTFE) mixture on the carbon felt (MCF), which allows, according to the literature, to
128 increase the generation of H₂O₂ and the removal of organics by EF [33].
- 129 • A gas diffusion electrode GDE characterized by a thin and porous structure which favours the
130 percolation of the injected gas across its pores to contact the solution at the carbon surface.
131 These electrodes possess a large number of active surface sites leading to a very fast O₂
132 reduction and large accumulation of H₂O₂ [22, 34–36].

133 As shown in Fig. 1, the abatement of TOC slightly increased replacing CF with MCF and GDE,
134 as a result of the higher generation of H₂O₂. However, in all cases, a very small removal of TOC
135 occurred.



136

137 Figure 1. Electrochemical treatment of pulp and paper mill wastewater with DSA[®] anode and
138 different carbonaceous cathodes in the absence of Fe(II) under amperostatic conditions with $i = 20$
139 mA cm⁻². Cathode: carbon felt (CF), modified carbon felt (MFC) and gas diffusion electrode (GDE);
140 Anode: DSA[®]; V = 50 mL; pH = 3; stirring rate = 600 rpm.

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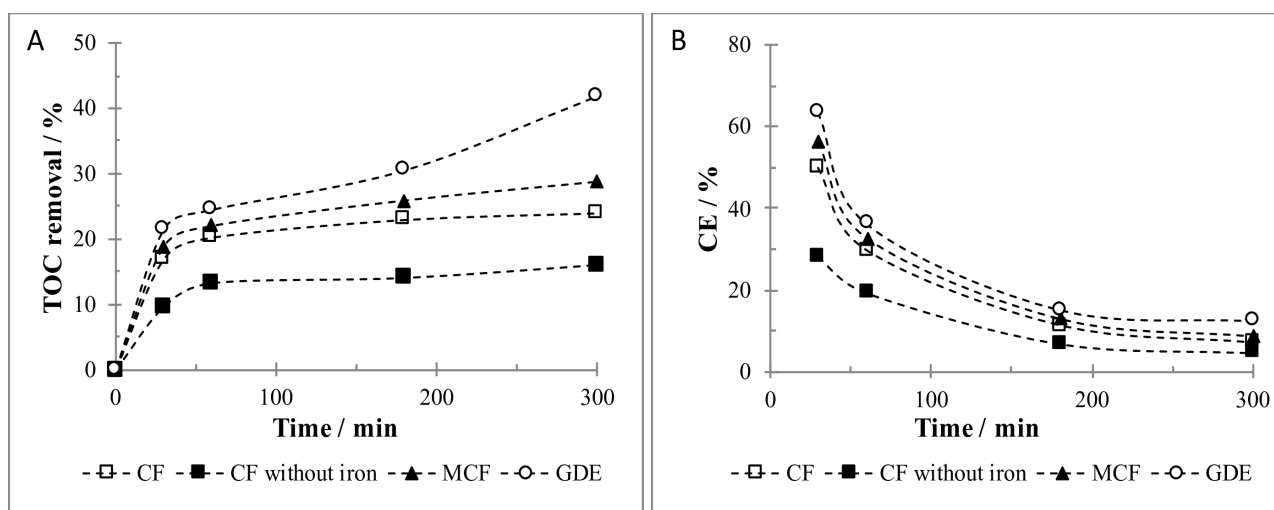
142 3.2 EF process

143 3.2.1 Effect of the nature of the cathode

144 In order to evaluate the performance of EF process, some electrolyses were repeated using carbon felt
145 as cathode and DSA[®] as anode at 20 mA cm⁻² in the presence of Fe(II) 0.5 mM. As shown in Fig. 2,
146 when Fe(II) was added to the solution, the removal of TOC after 5 h increased from 16 % to about
147 24 % thus demonstrating that EF process is useful for the oxidation of organics present in paper mill
148 wastewater. An initial fast abatement occurred (17 % after 30 min) with a very high current efficiency
149 (close to 50 % after 0.5 h), followed by a very slow abatement (24 % after 5 h) coupled with a drastic
150 decrease of the CE (about 7 % after 5 h) (Fig. 2). It seems reasonable to assume that in the first part

151 of the electrolysis, the oxidation involves the organics that are more easily oxidizable, while the
152 second part of the process involves the oxidation of more resistant organics.

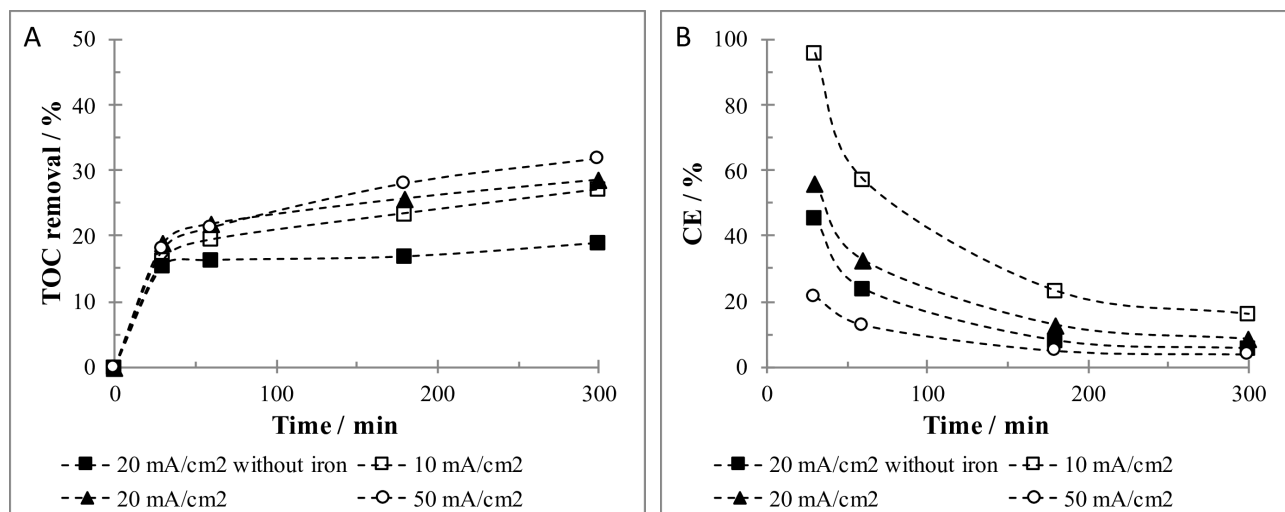
153 It has been shown in the literature that the performances of the EF process depend strongly on the
154 nature of the cathode. For this reason, the electrolyses were repeated using MCF and GDE. Indeed,
155 the use of a MCF cathode allowed an increase of the TOC removal (29 % after 5 h). A further higher
156 abatement of TOC was achieved using a GDE (about 40 % after 5 h), according to the fact that this
157 cathode gives rise to a higher generation of H₂O₂. As a consequence, the nature of the cathode affected
158 also the CE that, after 5 h, increased from about 7 to 13 % replacing the carbon felt with the GDE,
159 while intermediate results were achieved using MCF.



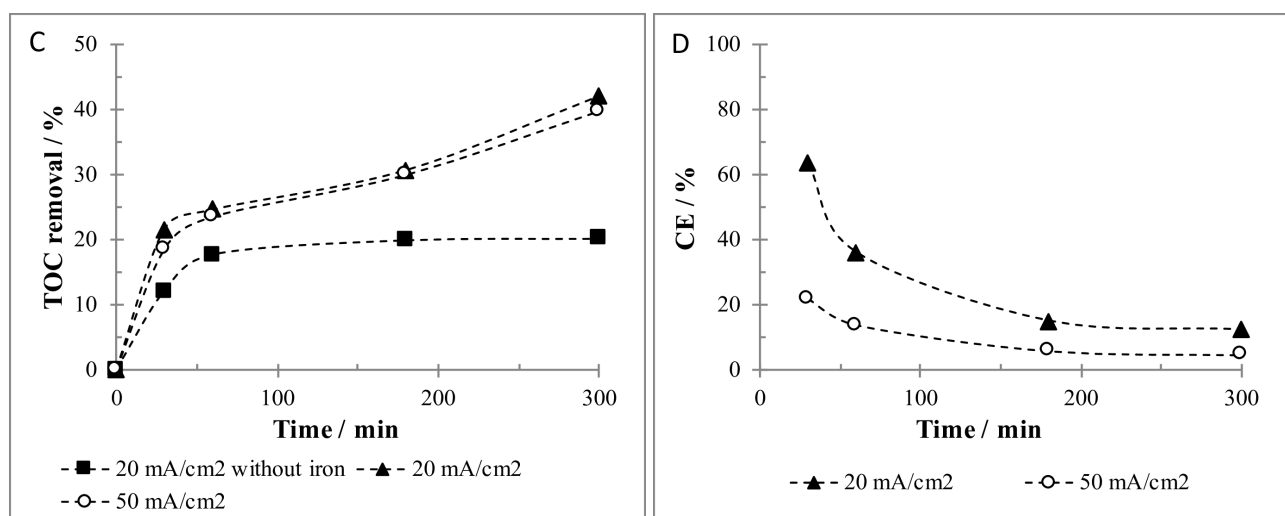
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161 Figure 2. Electrochemical treatment of paper mill wastewater with DSA[®] anode and different
162 carbonaceous cathodes in the absence and presence of Fe(II) under amperostatic conditions with $i =$
163 20 mA cm^{-2} . Fig. 2A and 2B report the TOC removal and the current efficiency (CE) (%),
164 respectively. Cathode: carbon felt (CF), modified carbon felt (MFC) and gas diffusion electrode
165 (GDE); Anode: DSA[®]; V = 50 mL; pH = 3; stirring rate = 600 rpm; [Fe²⁺] = 0.5 mM when present.

166



167



168 Figure 3. Effect of current density on the removal of TOC of pulp and paper mill wastewater with
 169 DSA[®] anode at MCF (Fig. 3A) and GDE (Fig. 3C) and on the current efficiency (Fig. 3B for MCF
 170 and 3D for GDE). Anode: DSA[®]; V = 50 mL; pH = 3; stirring rate = 600 rpm; [Fe²⁺] = 0.5 mM when
 171 present.

172

173 3.2.2 Effect of the current density

174 It has been shown that the performances of EF process can strongly depend on the adopted current
 175 density i [32]. Indeed, the increase of the current density can enhance the generation of H₂O₂ in the
 176 absence of mass transfer limitations. First experiments were performed at MCF at 10, 20 and 40 mA
 177 cm⁻². The increase of the current density resulted in a slight enhancement of the TOC abatement (Fig.

178 2A), but in a strong decrease of the current efficiency (Fig. 2B). As an example, after 5 h at 10 mA
179 cm⁻² a decrease of TOC of about 27% was achieved with a CE of 16 %; when the electrolysis was
180 repeated at 50 mA cm⁻², the removal of TOC after 5 h increased to about 32 %, but a very low current
181 efficiency of about 4 % was obtained. Hence, at current densities higher than 10 mA cm⁻², the kinetic
182 of the cathodic reduction of oxygen is limited by the mass transfer of oxygen to the cathode and an
183 increase of the current density resulted mainly in an enhancement of cathodic competitive processes,
184 such as the hydrogen evolution (eq. 5) and the cathodic reduction of H₂O₂ to H₂O (eq. 6), and,
185 possibly, in a faster anodic oxidation of H₂O₂ to oxygen (eq. 7).

186



190

191 Since the higher abatement of TOC were obtained using a GDE cathode (see previous paragraph),
192 the effect of *i* was evaluated also using a GDE cathode at 20 and 50 mAcm⁻². However, also in this
193 case, the increase of *i* resulted in a very small change of TOC removal (Fig. 3C) and in a drastic
194 decrease of CE (Fig. 3D) which, after 5 h, respectively were of about 12 and 5 % at 50 and 10 mA
195 cm⁻².

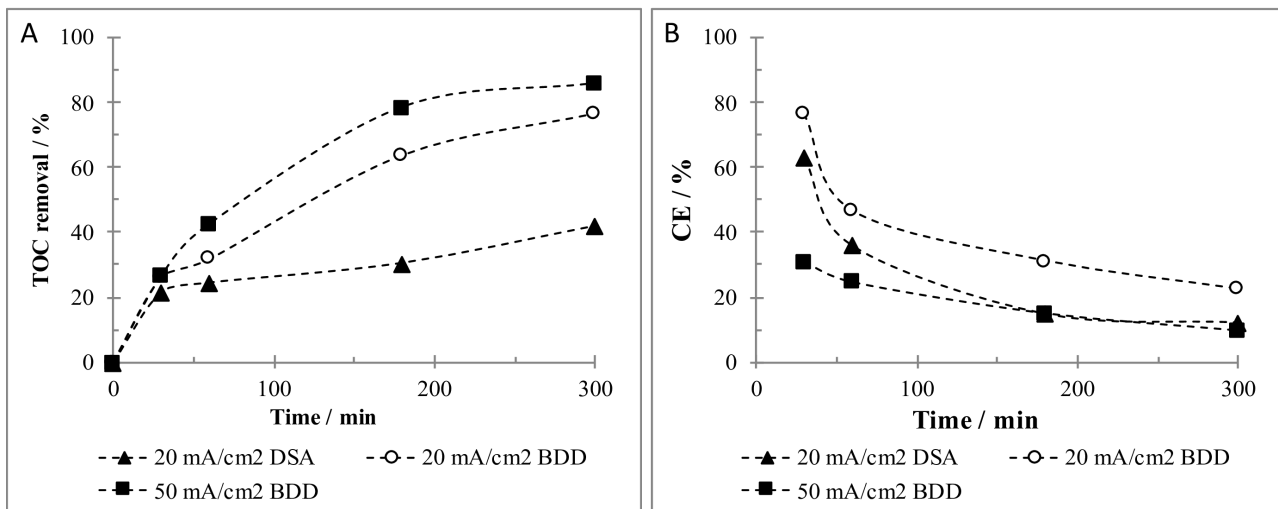
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197 3.2.3 Effect of the nature of the anode

198 The anodic mineralization of many organic pollutants can take place only at high anodic potentials
199 with simultaneous oxygen evolution, in order to avoid a decrease of the anode activity [11]. It has
200 been shown in literature that the anodic oxidation of organics strongly depends on the nature of the
201 anode [8, 11]. According to a simplified mechanism, proposed by Comminellis [37], selective

202 oxidation to stable compounds occurs with metal oxide anodes (MO_x) forming a so-called higher
203 oxide MO_{x+1} (chemisorbed hydroxyl radicals) such as IrO_2 , while combustion occurs with
204 physisorbed hydroxyl radicals, generated as an example at PbO_2 and Boron Doped diamond (BDD)
205 anodes. In particular, many authors have reported that BDD anodes are the more effective anodes for
206 the mineralization of many organic pollutants. Hence, the electrolyses of the adopted paper mill
207 wastewater were repeated at 20 mA cm^{-2} using BDD as anode.

208 As shown in Fig. 4, the replacement of DSA[®] with a BDD anode allowed to enhance the removal of
209 TOC from about 40 to 85 % after 5 h. Furthermore, the final CE increased from about 12 to 22 %.
210 The higher performances achieved with BDD are due to the fact that in this case both EF and anodic
211 mineralization cooperate effectively to the oxidation of organics and that the utilisation of BDD anode
212 allows to remove effectively also very resistant organics present in paper mill wastewater. Indeed,
213 Klidi and co-authors have recently shown that such kind of wastewater can be effectively treated by
214 direct anodic oxidation using BDD anode, with removal rates directly related to the applied electrical
215 power [14]. In order to evaluate the effect of current density also on this coupled process, the
216 electrolyses with BDD were repeated at 50 mA cm^{-2} . As shown in Fig. 4, the removal further
217 increased as a result of the higher charge passed. However, the CE decreased strongly in the last part
218 of the electrolysis, thus showing that both EF and anodic oxidation at this high current density are
219 partially under the kinetic control of the mass transfer of oxygen to the cathode for EF and of organics
220 to the anode for anodic oxidation.



221

222 Figure 4. Effect of anode on the removal of TOC of paper-mill wastewater with DSA[®] anode at MCF
 223 (Fig. 4A) and on the current efficiency (Fig. 4B). Anode: DSA[®] or BDD; V = 50 mL; pH = 3; stirring
 224 rate = 600 rpm; [Fe²⁺] = 0.5 mM.

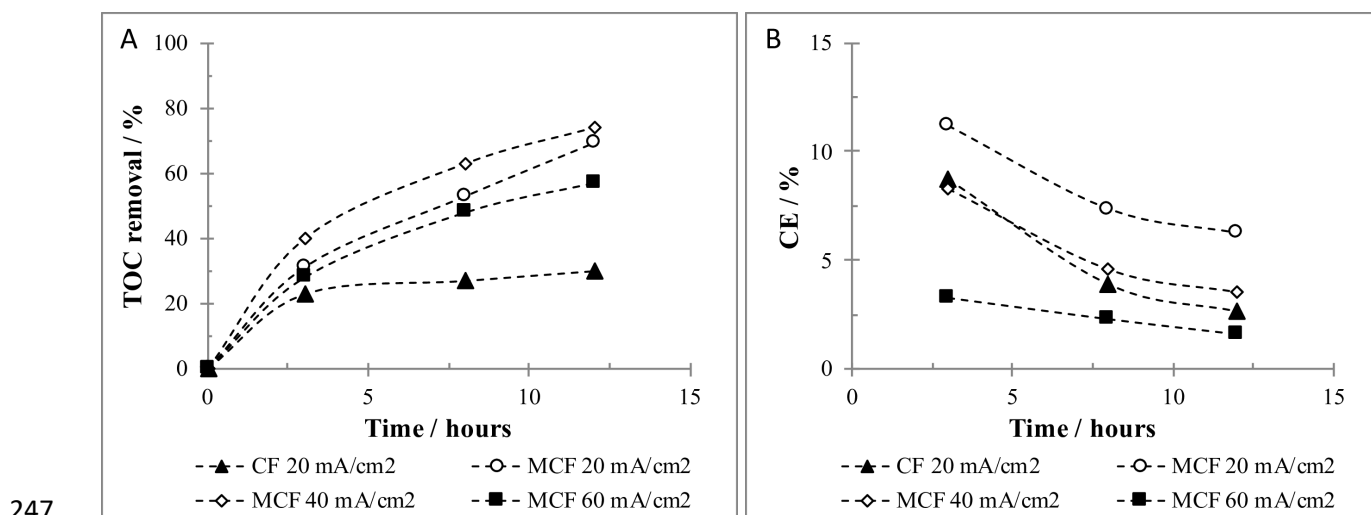
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226 3.2.4 Effect of treatment duration

227 In the previous paragraph, it has been shown that the adoption of BDD anode is necessary in order to
 228 enhance TOC removal for the investigated real wastewater in a limited time (such as 5 h). However,
 229 the utilization of BDD anode results in a dramatic increase of investment cost, due the very high cost
 230 of BDD, and in significant enhancements of operative costs, due to the high cell potentials caused by
 231 the very high anodic potentials required by BDD anode for the mineralization of organics [38, 39].
 232 Hence, in the following, the possible utilization of EF process with cheap anodes such as DSA[®] will
 233 be investigated in order to obtain high the bases of the results presented in the previous TOC removals
 234 by working with cheap DSA[®] anode and focusing on other operating parameters such as the time
 235 passed, the pressure and the possible addition of NaCl.

236 First, a series of electrolyses was performed increasing treatment time up to 12-16 h using both CF
 237 and MCF cathodes at 20 mA cm⁻². As shown in Fig. 5A, for CF a removal of TOC of about 50 % was
 238 achieved after 16 h. However, for MCF a quite good removal of 70 % was achieved after 12 h, thus

239 showing that EF can be effectively used for the treatment of investigated paper mill wastewater, if
 240 enough reaction time is allowed. In particular, the CE after 12 h was about 3 and 6 % at CF and MCF
 241 (Fig. 5B), thus showing that a large part of the charge passed is dissipated for side-processes because
 242 of the high resistance of the residual organics. Experiments at MCF were repeated at 40 and 60 mA
 243 cm^{-2} . At 40 mA cm^{-2} , a slight increase of the TOC removal was achieved, while at 60 mA cm^{-2} a
 244 decrease of the TOC abatement was observed as a result of the higher impact of the cathodic reduction
 245 of hydrogen peroxide to water (see eq. 6) expected at these high current densities (and cathode
 246 potential), as discussed above.



248 Figure 5. Effect of time on the removal of TOC from paper-mill wastewater with DSA[®] anode at CF
 249 and MCF (Fig. 5A) and on the current efficiency (Fig. 5B). Anode: DSA[®]; V = 50 mL; pH = 3;
 250 stirring rate = 600 rpm; [Fe²⁺] = 0.5 mM.

251

252 On overall, the increase of current density resulted in lower final current efficiencies: while at 20 mA
 253 cm^{-2} , after 12 h the CE was about 6 %, it decreased to 3.5 and 1.5 % at 40 and 60 mA cm^{-2} ,
 254 respectively.

255

256 3.2.5 Effect of the pressure and of the addition of sodium chloride

257 It has been recently shown that the utilization of pressurized air or oxygen can allow to enhance
 258 dramatically the generation of hydrogen peroxide at carbonaceous cathodes and accelerate the EF
 259 process [29, 33]. As an example, a maximum concentration of about 0.8 and 30 mM of H₂O₂ was
 260 achieved at carbon felt with air fed at room pressure and 30 relative bar, respectively [30]. The
 261 generation of hydrogen peroxide was, further, improved using both MCF cathode and pressurized air
 262 [33]. For EF, it was shown that the treatment of water contaminated by model organic pollutant such
 263 as Acid Orange 7 and maleic acid is accelerated using pressurized air [30]. Ltaïef and co-authors have
 264 also shown that the EF treatment of water solutions of caffeic acid strongly improved using
 265 pressurized oxygen both in the presence of homogeneous and heterogeneous catalysts [40]. However,
 266 in the case of water solutions of a very resistant organic pollutant such as 3-chlorophenol the removal
 267 of COD was very low also using pressurized oxygen [40]. Here, the effect of the pressure was
 268 evaluated for a real wastewater coming from a paper mill industry using system (II), 1 and 10 bar and
 269 both CF and MCF cathodes for 16 h at 20 mA cm⁻².

270 As shown in table 2, at CF cathode the utilization of 10 bar allowed to increase the final removal of
 271 TOC from 48 (entry 1) to 58 % (entry 2). However, at MCF cathode a very small effect of the pressure
 272 was observed at 20 mA cm⁻² (entries 3 and 4), while at 60 mA cm⁻², a higher final removal was
 273 obtained at 10 bar. Hence, it can be assumed that for the organics present in the investigated
 274 wastewater, at least at MCF and at adopted operating conditions, the mineralization of organics seems
 275 not to be limited in a relevant way by the cathodic step of H₂O₂ generation.

276

277 Table 2. Effect of pressure and NaCl addition on the removal of TOC of paper-mill wastewater with
 278 DSA[®] anode at CF or MCF cathode.^a

Entry	Cathode	Current density (mA cm ⁻²)	Pressure (bar)	TOC removal (%)
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1	CF	20	1	48
2	CF	20	10	58
3	MCF	20	1	83
4	MCF	20	10	81
5	MCF	60	1	72
6	MCF	60	10	84
7*	MCF	20	1	91

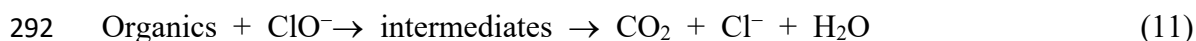
279 * addition of 1 g L⁻¹ of NaCl.

280 ^aAnode: DSA[®]; V = 50 mL; pH = 3; stirring rate = 600 rpm; [Fe²⁺] = 0.5 mM.

281

282 A widely adopted electrochemical route for the treatment of wastewater contaminated by organic
283 pollutants is the indirect oxidation by active-chlorine electrogenerated by anodic oxidation of
284 chlorides (eq. 8). In this process, the anodic oxidation of chlorides at suitable anodes gives rise to the
285 formation of chlorine, hypochlorous acid and/or hypochlorite, depending on pH (eqs. 9 to 11), which
286 can oxidize the organics near the anode and/or in the bulk (see eq. 11 in the case of alkaline medium)
287 [11, 21].

288



293 Here, the indirect oxidation of EF coupled with electro-generated active chlorine was studied with a
294 series of test in the presence of NaCl (1 g L⁻¹) performed at Ti/IrO₂-Ta₂O₅ anode and MCF cathode.
295 As shown in table 2, the addition of NaCl allowed to increase significantly the removal of TOC (see

296 entries 3 and 7), thus showing that this kind of wastewater can be effectively treated by a coupled
297 approach consisting in EF and oxidation by electro-generated active chlorine.

298

299

300

301 **4. Conclusions**

302 The treatment of a real paper mill wastewater by EF process was widely investigated. It was found
303 that the performances of the process, in terms of removal of TOC and of current efficiency (CE),
304 dramatically depends on the adopted operative conditions:

- 305 • quite high abatements of TOC were achieved by long electrolyses using proper cathodes;
- 306 • the performances of the process are improved using MCF or GDE cathodes with respect to
307 that achieved at carbon felt;
- 308 • the removal of TOC can be drastically improved coupling the EF with a suitable anodic
309 process such as the direct anodic oxidation at BDD anode or the electro-generation of active
310 chlorine in the presence of NaCl;
- 311 • at MCF cathode, the utilization of pressure at low current densities does not give important
312 improvements of TOC removal or CE;
- 313 • the optimal current density depends on the adopted cathode.

314 In conclusion, this work has shown that EF process can be effectively used for the removal of organics
315 by real paper mill wastewater at suitable operating conditions and sufficient treatment duration.

316

317 **Acknowledgments**

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320

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