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1   **Effective heterogeneous electro-Fenton of m-cresol with iron loaded**

2   **active carbon**

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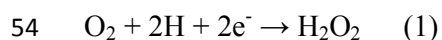
13   **ABSTRACT**

14   The degradation of m-cresol (MC) has been investigated by heterogeneous electro-

15   Fenton using iron loaded activated carbon (Fe-AC) as heterogeneous electro-Fenton

16   catalyst. Experimental results demonstrated that MC was effectively removed through

17   electro-Fenton. Calculated TOC removal and overall energy consumption showed that

18   the use of low iron concentration (28 mg/L) increases the efficiency of the process. The

19   reactions followed a pseudo-first order kinetic equation and kinetic coefficients confirm

20   that the MC reduction, when it is alone, is faster than in presence of a similar

21   compound, tert-butylhydroquinone (TBHQ) (from 0.0935 to 0.0692 min^{-1}); therefore

22   TBHQ exerts an antioxidative protection effect. In all cases, it is concluded that

23   heterogeneous electro-Fenton treatment with Fe-AC follows a process in two steps:

24   adsorption and oxidation; allowing removal rates higher than in the literature. In

25   addition, the reusability of this catalyst was showed operating in continuous mode.

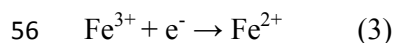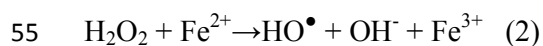26   Finally, LC-MS analysis allowed the development of a plausible degradation route.

27

28   **Keywords**: m-cresol, tert-butylhydroquinone, continuous reactor, electro-Fenton, iron

29   loaded activated carbon.

30   **Introduction**

31   Cresols are an important sub-class of phenols reported by the United States

32   Environmental Protection Agency and the International Program on Chemical Safety as

33   priority pollutants due to their potential toxicity and their low biodegradation.[1-4] In

34   addition, cresols are extensively used in resin manufacturing, pharmaceuticals,

35   pesticides, tri-cresylic acid and surfactants, therefore it is released on the wastewaters

36   from those industries.[1] Thus, there is a great need for the development of a suitable

37   technology able to destroy efficiently these undesirable compounds. Several processes

38   have been developed on the treatment of phenol polluted wastewaters: biodegradation,[5,

39   [6] conventional physico-chemical methods such as adsorption,[7, 8] and conventional

40   advanced oxidation processes (AOPs) such as photodegradation,[9, 10] Fenton oxidation[1,

41   [11] and their combinations.[12] However, some of these techniques require a low pollutant

42   concentration for an efficient pollutant removal or require the transportation, storage

43   and handling of hazardous reactants.[5, 13]

44   Nowadays, electrochemical advanced oxidation processes (EAOPs) provide an

45   alternative that do not require the addition of reagent due to its generation from redox

46   reactions.[14] Electro-Fenton has been reported as the most economic and promising

47   EAOP for the treatment of a wide variety of organic pollutants.[15-19] The performance of

48   this process is based on the electrochemical *in situ* generation of H_2O_2 from the

49   continuous aeration on the cathode (eqn. (1)). Fe^{2+} present on the media catalyst the *in*

50   *situ* generation of highly oxidant hydroxyl radicals from H_2O_2 (eqn. (2)), furthermore

51   Fe^{2+} is continuously recycled by a direct cathodic reaction as shows eqn. (3). The

52   hydroxyl radicals produced are highly oxidative and non-selective molecules that

53   degrade the organic matter.[20-22]

54    $O_2 + 2H + 2e^- \rightarrow H_2O_2$ (1)

55   $H_2O_2 + Fe^{2+} \rightarrow HO^\bullet + OH^- + Fe^{3+}$ (2)

56 $Fe^{3+} + e^- \rightarrow Fe^{2+}$ (3)

57   A crucial parameter for ensuring the appropriate performance of the electro-Fenton

58   process is the electrode material. Several articles reported the removal of m-cresol by

59   electro-Fenton process using GDE, $Ti/SnO_2-Sb_2O_5-IrO_2$ and PbO_2 electrodes.[2, 23]

60   However, the last reports determined that boron-doped diamond electrodes (BDD) are

61   the most promising anode for EAOPs because they have significant characteristics, such

62   as corrosion stability, low adsorption properties and great oxidizing power to remove

63   organic pollutants.[24-26] It can be ascribed to its high O_2-overpotential, which allows the

64   generation of high yields of the strong oxidant hydroxyl radical (BDD-HO$^\bullet$) adsorbed

65   on its surface from water oxidation (eqn. (4)).[25, 27, 28]

66   $BDD(H_2O) \rightarrow BDD-HO^\bullet + H^+ + e^-$ (4)

67   Cathode material should optimize the generation of H_2O_2 among other reduction

68   reactions. Among the different materials that can be used as cathode, foam materials

69   have higher reaction surface, thus the use of nickel foam as cathode can improve the

70   production of hydroxyl radicals; furthermore the presence of nickel produces an

71   additional H_2O_2 generation from the superoxide radical (eqn. (5) (6)).[29]

72   $Ni + 2O_2 \rightarrow Ni^{2+} + 2\ ^\bullet O_2^-$ (5)

73   $^\bullet O_2^- + e^- + 2H^+ \rightarrow H_2O_2$ (6)
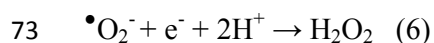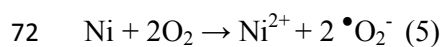
74   Industrial activities constantly produce wastewaters that need a treatment. Therefore, it

75   is necessary to validate an adequate technique to continuously remediate polluted

76   streams. In electro-Fenton process iron on solution gets away on the outflow. Therefore,

77   it is further necessary to improve the electro-Fenton technology in order to reduce this

78   problem and reduce the investment and operation costs. Several studies have focused on

79   the immobilization of iron on supports with physical characteristics that avoid its lost.[15,]

3

80   [30] Activated carbon (AC) is characterized by its great absorption capacity and it has

81   already been used as iron support with different environmental applications.[31-33] In order

82   to overcome the main drawback of the electro-Fenton process operating in continuous

83   mode in this study the use of iron loaded in AC (Fe-AC) is considered a workable

84   solution.

85   The aim of this work is to design an electro-Fenton continuous reactor with BDD as

86   anode and nickel foam as cathode to treat polluted effluents in a continuous mode at the

87   bench scale using Fe-AC as Fenton catalyst. To analyse the technique's capacity, m-

88   cresol and tert-butylhydroquinone were used as model pollutants.

89   **Experimental**

90   **Materials**

91   In this study, solutions of m-cresol (MC) (100 mg/L) and tert-butylhydroquinone

92   (TBHQ) were provided by Sigma-Aldrich (Barcelona, Spain) and used in order to

93   evaluate the electro-Fenton treatments. Their structure and properties are shown in

94   Table 1.

95   **Catalyst preparation and characterization**

96   Iron load on activated carbon (Fe-AC) was carried out by mixing a constant volume

97   (0.15 L) of iron aqueous solution at 1000 mg/L of Fe^{3+} (Fe_2SO_3; Sigma-Aldrich, Spain)

98   with 3 g of Activated Carbon (AC) (Granulated n°2 QP Panreac Spain) in 0.25 L

99   Erlenmeyer flasks. The flasks were agitated in an incubator (Thermo Forma 420) at 150

100   rpm and 20°C for 30 minutes. The phenantroline method 3500 D (Standard Methods- 18

101   Ed. 1992) was used to measure the iron that remained unabsorbed in the supernatant

102   liquid. Finally, the resulting Fe-AC composite was dried in an oven at 105°C and stored

103   at room temperature.

104   Fe-AC was characterized by Scanning Electron Microscopy (SEM) performed on a

105   JEOL JSM-6700F equipped with an Energy Dispersive Microanalysis (EDS) Oxford

106   Inca Energy 300 SEM using an accelerating voltage of 20 kV (Electron Microscopy

107   Service, C.A.C.T.I., University of Vigo).

108   **Electro-Fenton reactor set-up**

109   The heterogeneous electro-Fenton with Fe-AC was performed in a cylindrical glass

110   reactor with a working volume of 0.15 L. The electric field (5 V) was applied by a 1.6

111   mm thick nickel foam cathode (Goodfellow Cambridge Ltd, United Kingdom) and a

112   BDD anode (DIACHEM®, Germany) connected to a direct current power supply (HP

113   model 3662, Agilent Technologies Spain, S.L.). The electrodes (surface 15 cm^2) were

114   placed opposite to each other at 1 cm above the bottom of the cell and with an electrode

115   gap of 6 cm. Current intensity was monitored with a multimeter (Fluke 175). H_2O_2 was

116   continuously electrogenerated *via* oxygen reduction on the cathode, by bubbling 1

117   L/min of compressed air. Reaction mixture contains 150 ml of solution Na_2SO_4 (0.01

118   M) as electrolyte, 100 mg/L of phenolic compound and 3 g of Fe-AC at different iron

119   concentrations (46 mg/L and 28 mg/L). The pH was adjusted to 2 by the addition of

120   sulphuric acid (Sigma Aldrich, Spain). The medium was maintained in suspension by

121   magnetic stirring avoiding concentration gradients in the cell.

122   **Sample preparation and preservation**

123   For all experiments, 1 mL samples were taken periodically from the reactor,

124   centrifugued (Sigma 3K-18) for 10 minutes at 7000 rpm to remove solid and stored at

125   4°C until chemical analysis.

126 **Analytical procedures**

127 A survey of literature describes the analytical methods available for quantifying,

128 monitoring and detecting phenolic compounds.[34] In this work, HPLC, LC-MS and TOC

129 analysis were performed.

130 The concentrations of MC and TBHQ were quantified by means of HPLC (Agilent

131 1100) equipment with an XDF-C8 reverse-phase column (150 x 4.6 mm i.d., 5 µm).

132 Prior to injection, the samples were filtered through a 0.45 µm Teflon filter. The

133 injection volume was set at 10 µL, and the gradient of eluent (acetonitrile/water with a

134 1.5 % of acetic acid) was pumped at a rate of 1 mL/min for 20 minutes. Detection was

135 performed with a diode array detector at 274 nm for MC and 292 nm for TBHQ, and the

136 column was maintained at room temperature.

137 In order to identify the transformation products obtained in the MC degradation several

138 samples were analyzed with an LC-MS (Agilent 1100) equipment with a LC column

139 ZORBAX. Filtration through a 0.45 µm Teflon filter was done before the injection. In

140 this case the isocratic eluent was 90 (water):10 (acetonitrile) that was pumped at a rate

141 of 0.5 mL/min for 40 minutes. Detection was carried out with a diode array detector at

142 218 nm and the column temperature was maintained at 23ºC. The coupled mass

143 spectrometer employed was a Hewlett-Packard 5989B with a detection range from 10 to

144 2000 Da.

145 Total Organic Carbon (TOC) in aqueous solutions was determined by using a Lange

146 curette test (LCK 380) in a Hanch Lange DR 2800, according to stand method DIN

147 38409-H3. The sample was introduced in the Lange cuvette. Under the conditions of the

148 test, the carbon forms carbon dioxide, which diffuses through a membrane into an

149   indicator solution. The change of color of the indicator solution is evaluated

150   photometrically.

151   H_2O_2 concentration was determined by the titanium oxalate method.[35] The method is

152   based on the generation of a yellow-orange titanium (IV) peroxide complex with a

153   maximum absorbance at 400 nm. Thus, 2 mL of sample are mixed with 0.25 mL of

154   sulphuric acid (0.5 mmol/L), 0.2 mL of potassium titanium oxide oxalate dehydrate

155   (0.14 mol/L) and 0.05 mL of distilled water for a final volume of 2.5 mL, after 5

156   minutes the absorbance was measured spectrophotometrically. All reagents were

157   provided by Sigma-Aldrich (Barcelona, Spain).

158   **Kinetic studies**

159   Kinetic studies were done in order to model the behavior of the heterogeneous EF-Fe-

160   AC. The concentration profiles of selected degradation compounds were fitted by a

161   suitable kinetic equation and the rate constants were calculated by using SigmaPlot 4.00

162   (1997) software. The SigmaPlot curve fitter uses an iterative procedure, based on the

163   Marquardt-Levenberg algorithm, which seeks the values of the parameters that

164   minimize the sum of the squared differences between the observed and predicted values

165   of the dependent variable.

166   **Measurement of process efficiency**

167   In addition to analyzing compounds concentration and therefore their removal during

168   the experiments, other specific energetic parameter is useful such as energy

169   consumption per amount of TOC destroyed (eqn. (7)) were evaluated.

170    $$Energy\ consumption\ (kWh/kg_{TOC}) = \frac{I \cdot V \cdot t}{(\Delta m_{TOC}) V_s} \qquad (7)$$

171   where I is the average applied current (A), V is the cell voltage (V), t is the treatment

172   time (h), Vs is the solution volume (L) and Δm_{TOC} is the decay in TOC concentration

173   (g/L)

174   **Continuous EF-FeAC process set-up**

175   An electrochemical cell with the same characteristics than the one used for the batch

176   experiments was selected (Fig. 1). The electro-Fenton reactor had a working volume of

177   0.15 L with 3 g of FeAC at an iron concentration of 28 mg/L and pH 2. H_2O_2 was

178   produced electrochemically by bubbling compressed air near the cathode at

179   approximately 1 L/min. The polluted solution was homogenized by a magnetic stirrer.

180   A dual-headed peristaltic pump was used to maintain a continuous flow of MC solution

181   through the reactor. Samples from the outlet flow were frequently taken to measure pH

182   and analyze MC concentration. The reactor operated in continuous mode at residence

183   times of 45 and 60 minutes. In all cases, each steady-state was maintained for at least

184   three times the residence time.

185   **Results and Discussion**

186   **Heterogeneous electro-Fenton treatment of MC**

187   Initially, the preparation of Fe-AC was carried out by adsorption technique. Due to

188   precipitation of the Fe^{3+} as iron hydroxide, it is not possible to carry out adsorption

189   experiments with iron at pH>4.0. For this reason, in these experiments, the natural pH

190   of the iron solution was used. The kinetic of iron adsorption can provide valuable

191   insights about the reaction pathways and mechanisms of the reaction. The kinetic and

192   thermodynamic behaviour of the adsorption reaction fitted very well to a pseudo-

193   second-order model and the adsorption is endothermic in nature and mainly physical.[36-

194   38]

195   In order to verify the adsorption of iron onto AC a Scanning Electron Microscopy and

196   Energy Dispersive Spectrometry (SEM/EDS) was performed. EDS is an analytical

197   technique used for the elemental analysis or chemical characterization of a sample. As

198   can be seen in the SEM images (Fig. 2), AC has high porosity and consequently a good

199   adsorption capacity. In addition, EDS spectral analysis confirms the increasing of iron

200   onto the Fe-AC after the adsorption process. The elementary composition of the AC

201   indicates that there is not iron with a carbon content of 89.19%, however this value

202   change after the adsorption and the composition of Fe-AC is 84.61% of carbon and the

203   iron concentration increased up to 2.53%. These results reflected that iron specie

204   remained homogeneously onto the AC structure (Fig 2B).

205   The electro-Fenton process with Fe-AC was conducted in batch mode with two initial

206   iron concentrations 46 mg/L and 28 mg/L on Fe-AC. Fig. 3 shows the profile of MC

207   reduction along the treatment time. As can be observed, the heterogeneous electro-

208   Fenton with a lower iron concentration on Fe-AC improves the rate of MC reduction.

209   Thus, it was determined that the best iron concentration is 28 mg/L in order to carry out

210   the electro-Fenton reactions with Fe-AC for the treatment of MC. This result is in

211   agreement with several other studies such as the cresol degradation by Fenton process

212   and phenol degradation by electro-Fenton and sono-electro-Fenton processes.[1, 39] In

213   these studies, it was reported that a further increase in Fe^{2+} ion concentration did not

214   correspondingly increase its reactivity, probably due to direct reaction of hydroxyl

215   radical with metal ions. In addition, our results are in concordance with other previous

216   results in which it is postulated that AC is able to decompose hydrogen peroxide and,

217   therefore, to generate hydroxyl radical. For this reason, it is not necessary the presence

218   of a high iron concentration into AC.[40]

219   In this experiments the H_2O_2 was generated and transformed in Fenton´s reactions and

220   the H_2O_2 concentration was around 0.3-0.4 mmol/L. This fact is due to air and nickel

221   react to generate H_2O_2 as described in equation 5 and 6, this results are in accordance

222   with those obtained by Liu[29] who reported the improvement on the H_2O_2 generation and

223   consequently the hydroxyl radical generation. Moreover, the regeneration of Ni^{2+} due to

224   the electric field avoids the nickel ions leaching and the electrode keeps its structure and

225   composition along the treatment.

226   The MC concentration profiles allow the evaluation of the kinetic behavior of this

227   reaction. The obtained data were adjusted to several orders and the best fit was obtained

228   when a pseudo-first-order kinetic expression was used (eqn. (8)).

$$\frac{dC}{dt} = -kC \qquad\qquad (8)$$

229   where C is concentration of MC (mg/L); t is reaction time (min) and k is kinetic

230   coefficient for the pseudo-first order reaction (min^{-1}).

231   This result is in accordance with the postulated by Lucas & Peres[41] for the Fenton

232   treatment of olive mill wastewater and the electro-Fenton treatment of MC. They

233   concluded that the reaction kinetic behavior could be represented by a simple

234   irreversible reaction of pseudo-first-order kinetics with respect to MC concentration.

235   This behavior was also corroborated by Chu[42].

236   The rate constants values and the statistical correlation parameters are shown in Fig. 4.

237   As expected from the degradation profiles, the highest kinetic parameter value was

238   k=0.0935 min^{-1} to lower iron concentration (28 mg/L). Chu[42] surveyed the effect of iron

239   and initial MC concentration on the decay kinetics of electrochemical degradation of

240   MC using porous carbon-nanotube-containing cathode and Ti/SnO_2–Sb_2O_5–IrO_2 anode.

241   They observed that the kinetic parameter value (0.0239 min^{-1}) obtained with 33.6 mg/L

242   of iron was evidently lower than the value (0.0276 min^{-1}) obtained at an iron

243   concentration of 22.4 mg/L. Although the effect of iron was similar, the kinetic values

244   and the reaction rate were higher around 4-fold than reported in the literature[37].

245   This fact could be due to the use of this catalyst Fe-AC. It is known that AC has a high

246   adsorption capacity, which has been widely studied for the treatment of different

247   polluted wastewaters.[31, 43, 44] Detailed explanation of the application of AC to phenolic

248   adsorption has been given by Busca.[45] As it is mentioned in previous papers the

249   heterogeneous electro-Fenton treatment is a process that takes place in two steps.[15, 46]

250   Initially, the pollutant is adsorbed on the catalyst and after it is degraded by oxidation

251   reactions.

252   For testing this hypothesis, the adsorption on Fe-AC of MC and MC desorption after

253   electro-Fenton treatment was evaluated. As it can be seen in Fig. 5 a high adsorption

254   rate was detected, reaching a total MC reduction by adsorption after 120 minutes.

255   However, in the heterogeneous electro-Fenton process, near complete reduction is

256   achieved after 45 minutes (Fig. 3). Fe-AC proved to have a very high adsorption

257   capacity that did not reach the saturation after 3 cycles of 0.15 L of MC solution on 3g

258   of Fe-AC at an iron concentration of 28 mg/L.

259   Thus, these results indicate that the electro-Fenton of MC in heterogeneous electro-

260   Fenton with Fe-AC is a process that couples adsorption and degradation, for this reason

261   after 90 minutes of electro-Fenton treatment, the remaining MC adsorbed on the Fe-AC

262   is nearly the 1% of initial concentration. This results prove that adsorption on Fe-AC is

263   followed by a fast degradation on the Fe-AC surface.

264   The TOC measurements show a similar behaviour as the MC reduction, thought they

265   need more treatment time to reach the complete mineralization. Thus, after 120 minutes

266   of treatment, TOC was reduced by 67.3% with 46 mg/L of iron and 83% with 28 mg/L

267   of iron and the energy consumption per TOC reduced was 29.7 and 15.1 kWh/kg_{TOC}

268   operating with initial iron concentrations of 46 mg/L and 28 mg/L, respectively. This

269   study has shown that the energy consumption from the system operating at the lower

270   iron concentration was about 2 folds of magnitude lower than those obtained at initial

271   iron concentrations of 46 mg/L.

272   These TOC values were greater to that found by Isarain-Chávez[47] for mineralization of

273   organic pollutants by combined electrocoagulation and photoelectro-Fenton processes

274   (70% in 180 minutes) and Liu[48] in the catalytic wet peroxide oxidation of MC; in which

275   the TOC removal reached 51.0% after 120 minutes of treatment. These results

276   demonstrate the efficiency of the heterogeneous electro-Fenton with Fe-AC, which

277   quantitatively reduces the organic load.

278   **Heterogeneous electro-Fenton treatment of TBHQ alone and in combination of**

279   **MC**

280   TBHQ is an antioxidant used on biodiesel to prevent its spoiling.[49] This molecule was

281   selected to evaluate its effect on the treatment of MC due to its similar structure and

282   composition. For this reason, the electro-Fenton process was carried out at the optimal

283   conditions (pH 2, 0.01 M of Na_2SO_4 and 28 mg/L of iron concentration) to degrade a

284   TBHQ solution and its combination with MC (Fig. 6).

285   Fig. 6 shows that the reduction of MC when TBHQ is present on the solution is lower

286   than alone. In all cases, TBHQ is reduced faster than MC. The reduction of TBHQ is so

287   fast that it is not modified in presence of MC. The kinetic study of the different

288   treatments shows a pseudo-first order and the values of their kinetic coefficient confirm

289   the aforementioned tendency, with a faster reduction of MC, when it is alone, than in

290   presence of TBHQ (from 0.0935 to 0.0692 min^{-1}) (Fig. 4). Therefore TBHQ seem to

291   have an antioxidative protection of MC reducing its decomposition.

292   In addition, the adsorption of TBHQ on Fe-AC was studied. It is detected a faster

293   adsorption and all TBHQ is removed from the solution after 30 minutes; however in the

294   electro-Fenton treatment the total reduction was achieved after 20 minutes.

295   Furthermore, after a heterogeneous electro-Fenton with Fe-AC of TBHQ there is not

296   TBHQ adsorbed on Fe-AC, which confirms the efficiency of the treatment. This fact

297   confirms again the hypothesis of a combined process with adsorption in catalyst

298   followed by the degradation action of hydroxyl radical.

299   To verify the efficiency in the organic pollutant degradation by heterogeneous electro-

300   Fenton with Fe-AC, the reduction in TOC was evaluated in all reaction media

301   employed. TOC was not significantly influenced by the presence of several compounds

302   in the reaction media. High TOC reduction 91.2% and 91.3% was detected after 120

303   minutes treatment of TBHQ alone and in combination of MC, respectively. This values

304   are higher that found in the literature. Izaomen[50] studied the degradation of o-cresol and

305   p-cresol by Fenton and photo-Fenton. They found that photo-Fenton process was more

306   efficient than Fenton in the mineralization and 90% of TOC removal was achieved in

307   150 minutes of UV.

308   **Continuous heterogeneous electro-Fenton treatment of MC**

309   In order to evaluate the activity and stability of the catalytic action of the Fe-AC and

310   minimize site requirements for the treatment of large amounts of wastewater, a

311   continuous mode for the electro-Fenton with Fe-AC of MC at different residence times

312   was tested. The process took place in a reactor of similar characteristics than the one

313   used for batch experiments and described in experimental and Fig. 1. Initially the

314   hydrodynamic behaviour of this reactor was studied through the residence time

315   distribution (RTD) curves. These tracer experiments were carried out at different flow

316   rates to confirm that the reactor used in this work closely matches ideal mixing

317   conditions. Thus, the reactor behaved as a continuous stirred-tank reactor (CSTR) and it

318   can be assumed that the concentration everywhere in the reactor is equal to the outlet

319   concentration and the fluid has a mean residence time equal to the reactor volume

320   divided by the volumetric flow rate through the tank.

321   To model this process it is necessary to include the kinetic behaviour determined in the

322   previous batch experiments. An expression that relates the reduction of MC and

323   residence times was obtained on the basis of the CSTR hydrodynamic behabiour and the

324   first order kinetic model. It is shown in eqn. (9).

325    $$R = 100 \cdot \frac{k \cdot \tau}{1 + k \cdot \tau} \quad (9)$$

326   where R is the percentage of MC reduction, k is the previously obtained kinetic

327   coefficient for the first order reaction (min^{-1}) and τ is the residence time (min).

328   Fig. 7 shows the increase of reduction percentage with the residence time, attaining 72%

329   for a residence time of 45 minutes and 80% for a residence time of 1 hour. The value of

330   energy consumption per TOC reduced was found to be 8.2 kW h/kg$_{TOC}$ and

331   corresponding to TOC removal efficiency of 83.4%, demonstrating adequate low energy

332   consumptions.

333   In addition, the theoretical reduction values were calculated using Eq. (9) for the two

334   employed residence times, and they are represented in Fig. 7 as the long dashed line.

335   The proposed model was able to satisfactorily describe the MC reduction data and to

336   serve our goal of properly characterizing the kinetics of the remediation process.

337   **Analysis of MC degradation compounds**

338   In order to identify the transformation products obtained in the MC degradation, several

339   samples were analyzed with LC-MS. The LC-MS study of MC solution treated in the

340   heterogeneous electro-Fenton with Fe-AC was carried out at initial time, after 3 hours

341   and after 24 hours.

342   At initial time several compounds with a phenolic group are found, while its intensity is

343   very low and increases with treatment time. MC is only found at initial time, after 3

344   hours of treatment there are intermediate products that were identified and after 24

345   hours just a few compounds are found and identified. Among the phenolic derivatives

346   found, 2-methylhydroquinone appears at initial degradation times and 2-methyl-p-

347   benzoquinone appears after 3 hours; however none of them appear after 24 hours of

348   treatment time. These compounds were detected by Flox,[2] Flox[12] and Chu[42] as

349   intermediate products in different EAOPs of MC. The degradation pathway is

350   represented in Fig. 8. Similar reaction sequence for the electro-Fenton degradations of

351   MC in acid medium using a BDD anode was proposed by Flox.[12]

352   **Conclusion**

353　In the present work, the heterogeneous electro-Fenton process used Fe-AC as catalyst

354　for the degradation of MC. The performance of this technique is characterized by the

355　following:

356　- AC demonstrated its capacity to absorb iron and to perform as catalyst on the

357　　heterogeneous electro-Fenton treatment.

358　- The evaluation of iron dosage showed that 28 mg/L contains the required

359　　amount to the electro-Fenton reactions to take place, besides AC has been found

360　　in literature as competitor on the hydroxyl radical production.

361　- The heterogeneous electro-Fenton treatment with Fe-AC has proved to be a

362　　process where adsorption is followed by oxidation leading a decontaminated

363　　wastewater and a pollutant free catalyst.

364　- The analysis of antioxidant TBHQ showed the capacity of this compound to

365　　slow down the MC degradation.

366　- Kinetic studies demonstrated that the process follows a pseudo-first-order

367　　kinetic equation which shows that 28 mg/L of iron behaves faster that 46 mg/L

368　　and that the presence of TBHQ diminishes the kinetic constant.

369　- The study of energy consumption and TOC removal further confirmed the

370　　efficiency of the developed process to the degradation of MC.

371　- Finally, the identification of a plausible degradation route eases the

372　　understanding of process oxidation pathways.

373

374　**Acknowledgements**

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385 **Table and figure captions**

386 **Fig. 1.** Schematic diagram of electro-Fenton experimental set-up in continuous

387 processing: (1) Nickel foam acting as cathode, (2) BDD electrode acting as anode, (3)

388 powersupply, (4) air supply, (5) magnetic stirrer, (6) dual-headed peristaltic pump, (7)

389 inlet flow, (8) outlet flow.

390 **Fig. 2.** A. Scaning electron microscopy (SEM) image of Fe-AC and B. Fe maping of

391 energy dispersive scaning spectroscopy (EDS) of Fe-AC.

392 **Fig. 3.** Profiles of MC reduction by heterogeneous electro-Fenton with Fe-AC at an iron

393 concentration of 46 mg/L (black squares) and 28 mg/L (black circles).

394 **Fig. 4.** Pseudo-first-order kinetic equation of heterogeneous electro-Fenton of MC

395 (black circles) working with 28 mg/l of iron, MC in presence of TBHQ (white circles)

396 working with 28 mg/l of iron and MC (black squares) working with 46 mg/l of iron.

397 **Fig. 5.** Batch adsorption profiles of MC on Fe-AC. Each batch contained 100 mg/L of

398 MC at pH 2 and 0.01 M of Na_2SO_4.

399 **Fig. 6.** Profiles of MC and TBHQ reduction by heterogeneous electro-Fenton with Fe-

400 AC at an iron concentration of 28 mg/L in different reaction media: MC alone (black

401 circles), MC in presence of TBHQ (white circles), TBHQ alone (black triangles) and

402 TBHQ in presence of MC (white triangles).

403 **Fig 7.** Continuous electro-Fenton with Fe-AC (28 mg Fe/L) treatment of MC at two

404 residence times (45 and 60 min); dotted lines correspond with the theoretic reduction
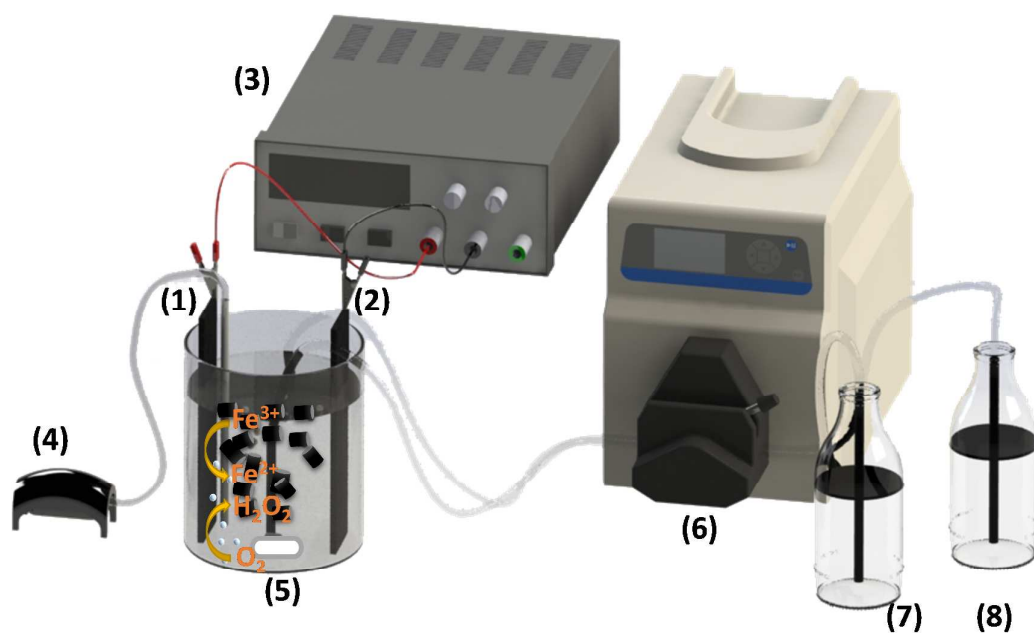
405 from the kinetic behaviour.

406 **Fig. 8.** Proposed reaction sequence on the degradation of m-cresol by the heterogeneous

407 electro-Fenton with Fe-AC.

408 **Table 1.** Chemical formula and structure, CAS number and concentration of studied
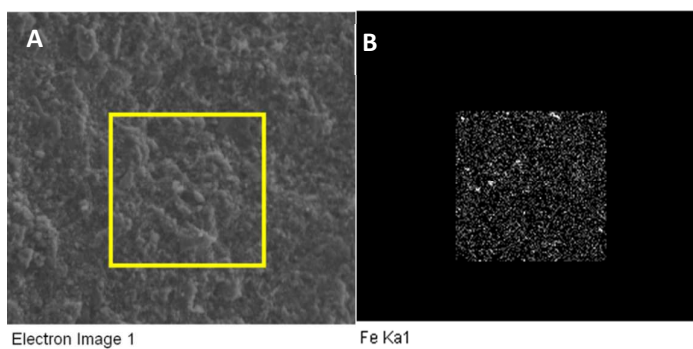
409 compounds.

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413

Fig. 1. Schematic diagram of electro-Fenton experimental set-up in continuous

processing. Nickel foam acting as cathode (1), BDD electrode acting as anode (2),

powersupply (3), air supply (4), magnetic stirrer (5), dual-headed peristaltic pump (6),
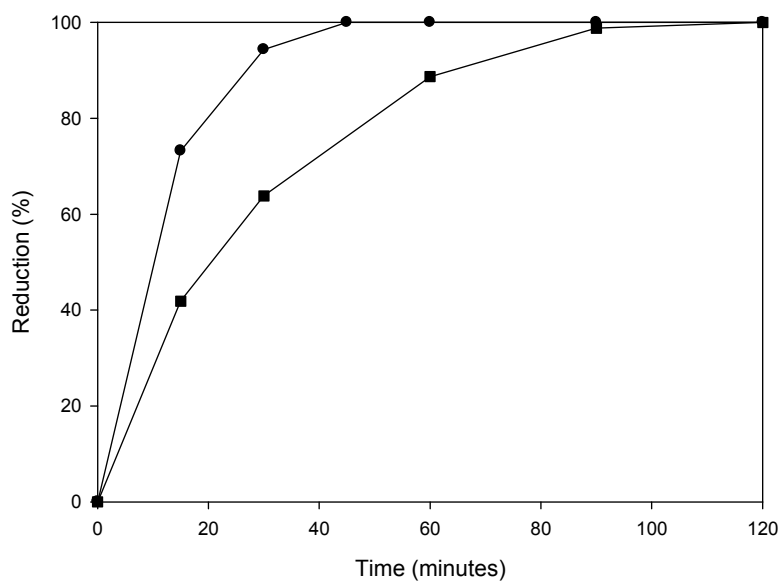
outlet flow (7), inlet flow (8).

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419

Electron Image 1   Fe Ka1

420 **Fig. 2.** A. Scaning electron microscopy (SEM) image of Fe-AC and B. Fe maping of

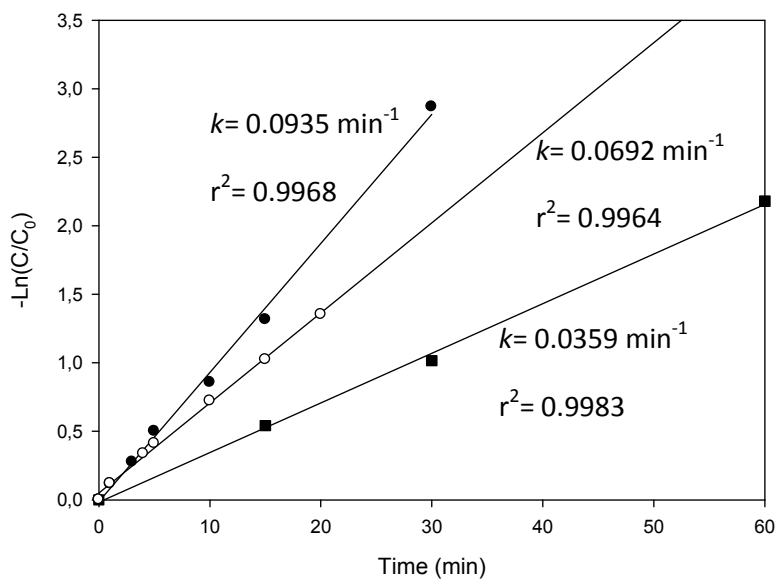421 energy dispersive scaning spectroscopy (EDS) of Fe-AC.

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423

424   **Fig. 3.** Percentage of MC reduction with treatment time in the heterogeneous electro-

425   Fenton with Fe-AC at an iron concentration of 46 mg/L (black squares) and 28 mg/L
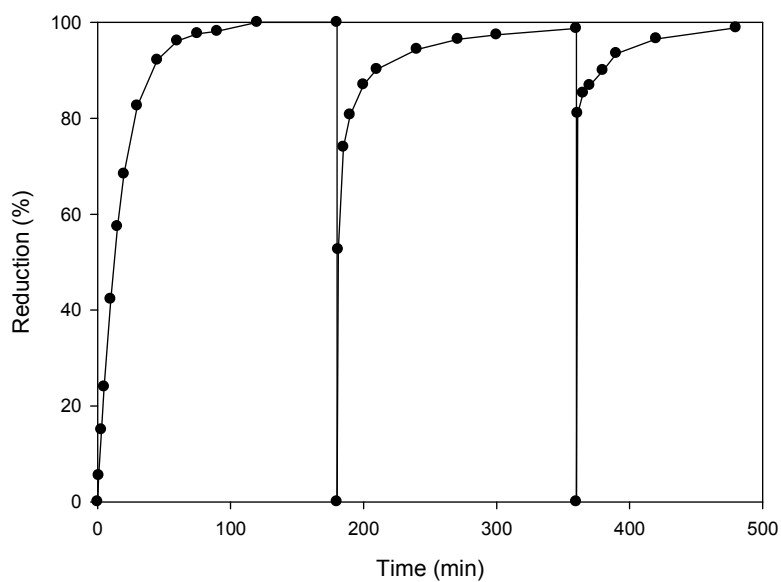
426   (black circles).

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428

Fig. 4. Integrated pseudo-first-order kinetic equation and its constants extracted from the slope, of heterogeneous electro-Fenton of MC (black circles) working with 28 mg/L of iron, MC in presence of TBHQ (white circles) working with 28 mg/L of iron and MC (black squares) working with 46 mg/L of iron.

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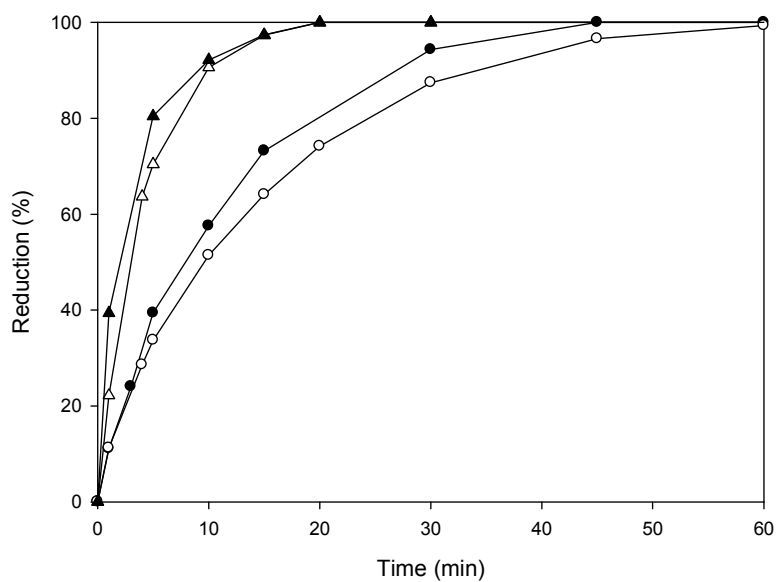
Fig. 5. Batch adsorption profiles of MC on Fe-AC. Each batch contained 100 mg/L of
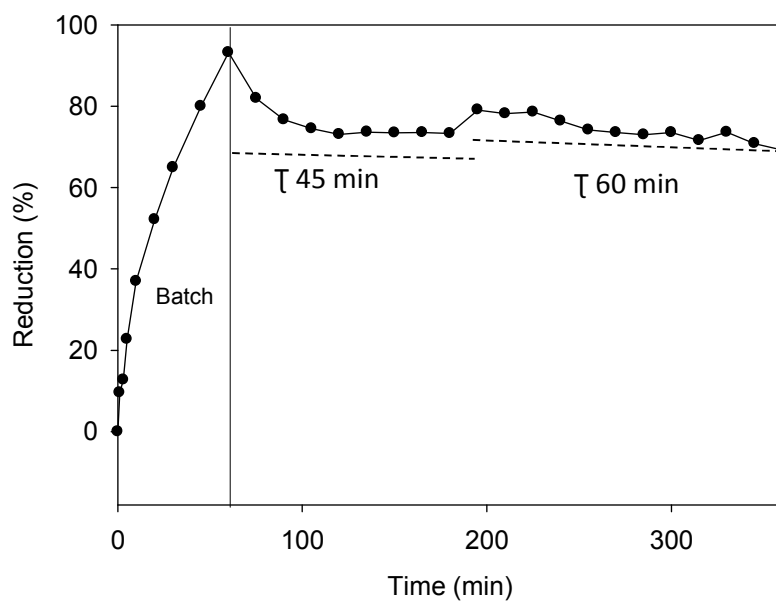
MC at pH 2 and 0.01 M of Na_2SO_4.

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Fig. 6. Profiles of MC and TBHQ reduction by heterogeneous electro-Fenton with Fe-

AC at an iron concentration of 28 mg/L in different reaction media: MC alone (black

circles), MC in presence of TBHQ (white circles), TBHQ alone (black triangles) and

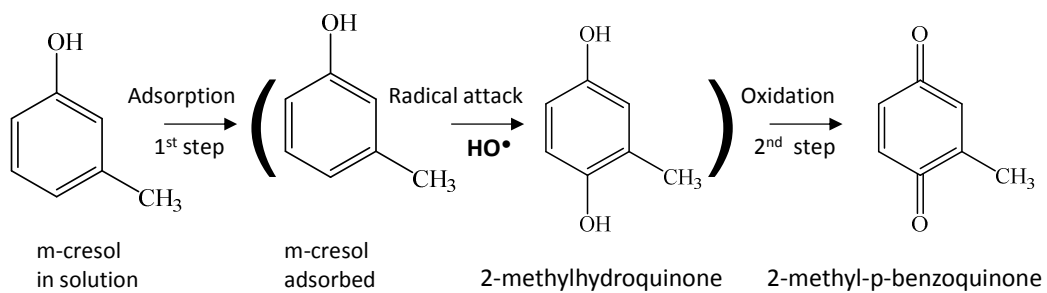TBHQ in presence of MC (white triangles).

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445   **Fig 7.** Continuous electro-Fenton with Fe-AC (28 mg Fe/L) treatment of MC at two

446   residence times (45 and 60 min); dotted lines correspond with the theoretic reduction

447   from the kinetic behaviour.

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450　　**Fig. 8.** Proposed reaction sequence on the degradation of MC by the heterogeneous
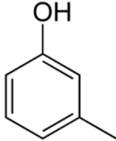
451　　electro-Fenton with Fe-AC.

452

m-cresol in solution → (1st step, Adsorption) m-cresol adsorbed → (Radical attack, HO•) 2-methylhydroquinone → (2nd step, Oxidation) 2-methyl-p-benzoquinone
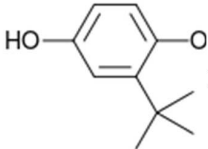
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454

455 **Table 1.** Chemical formula and structure, CAS number and concentration of studied

456 compounds.

Compound	CAS number	Molecular formula	Structure	Concentration (mg/L)
m-cresol (MC)	108-39-4	C_7H_8O		100
Tert-butylhydroquinone (TBHQ)	1948-33-0	$C_{10}H_{14}O_2$		100

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