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7 **BORON-DOPED DIAMOND ANODIC TREATMENT OF OLIVE MILL WASTEWATERS:**
8 **STATISTICAL ANALYSIS, KINETIC MODELING AND BIODEGRADABILITY**

9
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18
19 **ABSTRACT**

20 The electrochemical treatment of olive mill wastewaters (OMW) over boron-doped diamond (BDD)
21 electrodes was investigated. A factorial design methodology was implemented to evaluate the
22 statistically important operating parameters, amongst initial COD load (1000-5000 mg/L), treatment
23 time (1-4 h), current intensity (10-20 A), initial pH (4-6) and the use of 500 mg/L H₂O₂ as an
24 additional oxidant, on treatment efficiency; the latter was assessed in terms of COD, phenols,
25 aromatics and color removal. Of the five parameters tested, the first two had a considerable effect
26 on COD removal. Hence, analysis was repeated at more intense conditions, i.e. initial COD values
27 up to 10000 mg/L and reaction times up to 7 h and a simple model was developed and validated to
28 predict COD evolution profiles. The model suggests that the rate of COD degradation is zero order

29 regarding its concentration and agrees well with an electrochemical model for the anodic oxidation
30 of organics over BDD developed elsewhere. The treatability of the undiluted effluent (40000 mg/L
31 COD) was tested at 20 A for 15 h yielding 19% COD and 36% phenols removal respectively with a
32 specific energy consumption of 96 kWh/kg COD removed. Aerobic biodegradability and
33 ecotoxicity assays were also performed to assess the respective effects of electrochemical treatment.
34 *Keywords:* boron-doped diamond; electrolysis; factorial design; olive mill wastewater;
35 biodegradability

36

37 **INTRODUCTION**

38 The foodstuff processing industry based on olive oil extraction is an economically important
39 activity for many regions of the Mediterranean Sea area. This process results in large quantities of
40 bio-recalcitrant effluents, that comes from the vegetation water and the soft tissues of the olive
41 fruits mixed with the water used in the different stages of oil production. All these wastewaters
42 together with the industry wash-waters, make up the so-called olive mill wastewaters (OMW).
43 Essentially, OMW consist of water (80-83%), organic compounds (15-18%), and inorganic
44 compounds (2%), and the composition varies broadly depending on many parameters such as the
45 olive variety, harvesting time, climatic conditions and the oil extraction process.

46 The phytotoxicity and strong antibacterial action of OMW has been attributed mainly to its phenolic
47 content; so far, more than thirty phenolic compounds have been identified in OMW at
48 concentrations ranging from 0.5-24 g/L (Niaounakis and Halvadakis, 2006). The presence of these
49 recalcitrant organic compounds constitutes one of the major obstacles in the detoxification of
50 OMW.

51 In this perspective, increasing concern has been expressed about the effective treatment and safe
52 disposal of OMW in the environment. Research efforts have been directed towards the development
53 of efficient treatment technologies including several physical, chemical and biological processes as
54 well as various combinations of them (Mantzavinos and Kalogerakis, 2005). Advanced oxidation

55 processes (AOPs) have been employed as alternative pretreatment methods aiming at reducing the
56 organic load and bio-recalcitrance of these wastewaters. More specifically, electrochemical methods
57 have attracted a great deal of attention basically due to the control simplicity and the increased
58 efficiencies provided by the use of compact bipolar electrochemical reactors. In the case of OMW,
59 electrochemical oxidation over many traditional anodes such as Ti/RuO₂ (Panizza and Cerisola,
60 2006; Un et al., 2008), Ti/IrO₂ (Chatzisyneon et al., 2008), Ti/Pt (Israilides et al., 1997), Ti-Ta/Pt/Ir
61 (Gotsi et al., 2005; Giannis et al., 2007), iron and aluminium electrodes (Inan et al., 2004; Khoufi et
62 al., 2004; Adhoum and Monser, 2004; Un et al., 2006; Khoufi et al., 2007) have been widely
63 investigated.

64 In recent years though, electrochemical oxidation over boron-doped diamond (BDD) anodes is one
65 of the more promising technologies for the treatment of industrial wastewaters. BDD is considered
66 an ideal anode for wastewater treatment since it is characterized by high reactivity towards organics
67 oxidation and efficient use of electrical energy (Comninellis et al., 2008). Several studies report the
68 use of BDD electrodes for the oxidation of model aqueous solutions including phenol (Iniesta et al.,
69 2001; Polcaro et al., 2003) and synthetic wastewaters containing various polyphenolic compounds
70 typically found in OMW (Canizares et al., 2005; Canizares et al., 2006a). Despite the relatively
71 large number of papers dealing with the electrochemical degradation of model aqueous solutions of
72 polyphenolic compounds, reports regarding the anodic oxidation of actual OMW over BDD
73 electrodes are scarce. In particular, Canizares et al. (2006b) investigated the BDD electro-oxidation
74 of OMW that had already been subjected to physicochemical treatment. In their work, the
75 wastewater was the effluent of a treatment plant comprising sequential Fenton oxidation, settling
76 and sand filtration, containing about 700 mg/L of residual COD that could not be oxidized further
77 by the Fenton process. Electrolysis was carried out at 30 mA/cm² and, after 20 Ah/L of charge
78 passed, complete mineralization was achieved with an energy consumption of 100 kWh/kg COD
79 removed.

80 The aim of this work was to study the oxidation of actual OMW over a BDD anode regarding the
81 effect of various operating conditions such as initial organic load, applied current, initial pH,
82 treatment time and the addition of hydrogen peroxide on the conversion of COD, total phenols
83 (TPh) and aromatics, as well as decolorization. A factorial design methodology was adopted to
84 determine the statistical significance of each parameter. Biodegradability of the effluent prior to and
85 after treatment was assessed by the Zahn-Wellens test and ecotoxicity measurements. Moreover, an
86 estimate of energy consumption of the process was attempted.

87

88 **MATERIALS AND METHODS**

89 *OMW*

90 The OMW was provided by a three-phase olive oil mill company, located in Chania, Western Crete,
91 Greece. The effluent was subjected to filtration to remove most of the total solids (TS). The effluent
92 has a strong olive oil smell and a dark black-brown color with maximum absorbance in the visible
93 region at 550 nm. Its main properties prior to and after filtration are given in Table 1.

94

95 *Electrochemical experiments*

96 Experiments were conducted in a DiaCell[®] (type 100) single-compartment electrolytic flow-cell
97 manufactured by Adamant Technologies (Switzerland). Two circular electrodes made of BDD on
98 silicon were used as the anode and cathode; each electrode area was 70 cm² and the distance
99 between them was 0.01 m.

100 In a typical run, the effluent was diluted with tap water to achieve the desirable initial COD
101 concentration, mixed with the electrolyte (1% w/v Na₂SO₄ resulting in 25 mS/cm conductivity) and
102 batch loaded in a vessel. In all cases, the working volume was 10 L which were continuously
103 recirculated in the cell through a peristaltic pump operating at a flowrate of 600 L/h. A spiral coil
104 immersed in the effluent vessel and connected to tap water supply was used to remove the heat
105 released from the electrolytic process. Consequently, all experiments were conducted at constant

106 temperature of $30\pm 2^{\circ}\text{C}$. It should be noted that effective temperature control could not be easily
107 achieved at current intensities greater than 20 A since temperature gradually increased overcoming
108 the maximum permissible temperature recommended by the electrode manufacturer (35°C). For
109 those experiments where the diluted effluent's inherent pH (which was 6 at $\text{COD}_0 \leq 5000 \text{ mg/L}$) was
110 adjusted to acidic conditions, the appropriate amount of 98% w/w H_2SO_4 was added. In those cases
111 where hydrogen peroxide was used as an extra oxidant, the appropriate amount of a 35% w/w
112 solution was added to achieve a 500 mg/L H_2O_2 initial concentration.

113

114 *Analytical measurements*

115 COD was determined by the dichromate method. The appropriate amount of sample was introduced
116 into commercially available digestion solution (0-1500 mg/L) containing potassium dichromate,
117 sulfuric acid and mercuric sulfate (Hach Europe, Belgium) and the mixture was then incubated for
118 120 min at 150°C in a COD reactor (Model 45600-Hach Company, USA). COD concentration was
119 measured colorimetrically using a DR/2010 spectrophotometer (Hach Company, USA).

120 The total phenolic content was determined colorimetrically at 765 nm on a Shimadzu UV 1240
121 spectrophotometer using the Folin-Ciocalteu reagent according to the procedures described in
122 detail elsewhere (Singleton et al., 1999). Gallic acid monohydrate was used as standard to quantify
123 the concentration of phenols in OMW.

124 Sample absorbance was scanned in the 200-800 nm wavelength band on a Shimadzu UV 1240
125 spectrophotometer. Color and aromatics were measured at 550 and 254 nm respectively. Residual
126 H_2O_2 concentration was monitored using Merck peroxide test strips in the range 0-25 and 0-100
127 mg/L. Changes in effluent pH and conductivity during electrolytic treatment were checked using a
128 Toledo 225 pH meter and a Toledo conductivity meter respectively.

129 Biodegradability tests were carried out according to the Zahn-Wellens protocol (OECD, 1996) for
130 representative OMW samples prior to and after electrochemical treatment. The purpose of this
131 method is to evaluate the potential ultimate biodegradability of water soluble, non-volatile organic

132 substances when exposed to relatively high concentrations of microorganisms in a static test.
133 Activated sludge was taken from the municipal wastewater treatment plant of Chania, W. Crete,
134 Greece and 1 g/L of non-adapted, dry biomass was added to each sample, whose concentration was
135 1000 mg/L COD.

136 The luminescent marine bacteria *V. fischeri* was used to assess the acute ecotoxicity of OMW
137 samples prior to and after treatment. The inhibition of bioluminescence of *V. fischeri* was measured
138 using a LUMISTox analyzer (Dr. Lange, Germany). Toxicity is expressed as EC₅₀, which is the
139 effective concentration of a toxicant causing 50% reduction of light output after 15 min at 15°C.

140

141 *Determination of mass transfer coefficient*

142 Mass transfer coefficient in the electrolytic cell at 600 L/h flowrate was evaluated according to the
143 diffusion limiting current technique (Wragg et al., 1980) focusing on the anodic oxidation reaction
144 of potassium ferro-cyanide to ferri-cyanide. A 2:1 mixture of potassium ferro-cyanide and ferri-
145 cyanide in 0.5 M NaOH aqueous solution at various mixture concentrations in the range 6-36 mM is
146 employed to generate polarization curves and the mass transfer coefficient can then be computed as
147 follows:

148

$$149 \quad I_{\text{lim}} = (nFk_m)C_b \quad (1)$$

150 where k_m : Mass transfer coefficient (m/s),

151 I_{lim} : Limiting current (A),

152 A: Electrode surface area (m²),

153 F: Faraday constant (96487 C/mol),

154 C_b : Bulk concentration of ferro-cyanide (mol/m³),

155 n: Number of electrons exchanged in the anodic reaction, e.g. n=1 for the ferro/ferri couple.

156

157 **RESULTS AND DISCUSSION**

158 *COD degradation*

159 There are two ways one can investigate the effect of a large number of variables. The most
160 commonly used method involves the variation of one variable while keeping the other variables
161 constant, until all variables have been studied. This methodology has two disadvantages: Firstly, a
162 large number of experiments is required, and secondly it is likely that the combined effect of two or
163 more variables may not be identified.

164 In this work, a statistical approach was chosen based on a factorial experimental design that would
165 allow us to infer about the effect of the variables with a relatively small number of experiments. The
166 independent variables of the experimental design are presented in Table 2. Each one of the five
167 variables received two values, a high value (indicated by the + sign) and a low value (indicated by
168 the – sign). Five independent variables that would affect treatment efficiency were taken into
169 account, namely applied current, initial COD concentration, treatment time, initial solution pH and
170 H₂O₂ concentration. Initial COD, treatment time and initial solution pH were chosen as they
171 typically play a key role in dictating the performance (in terms of rates and costs) of industrial
172 wastewater treatment by advanced oxidation, while the applied current is a determining factor in
173 electrochemical reactions. Treatment for 1-4 h is a reasonable timescale for most applications of
174 AOPs, while it was decided to operate in the range 10-20 A to safeguard efficient treatment (since
175 electrochemical performance deteriorates at reduced currents) without compromising safety issues.
176 Acidic or near neutral conditions were chosen as they correspond to the raw and diluted effluent's
177 inherent pH respectively. The rationale for the use of H₂O₂ was the extra oxidizing capacity
178 associated with the generation of hydroxyl radicals and other reactive moieties from the dissociation
179 of peroxide. The experimental design followed in this work was a full 2⁵ experimental set, which
180 required 32 experiments.

181 The design matrix of the experiments and the statistical analysis of these were made by means of
182 the software package Minitab 14. The results obtained in terms of two measured response factors
183 (dependent variables), namely concentration of COD oxidized in mg/L (response factor Y₁) and

184 concentration of TPh removed in mg/L (response factor Y_2) are presented in Table 3. Table 3 also
185 shows the percent removal of COD, TPh, color and aromatics.

186 In general, moderate to high levels of TPh removal and decolorization can be achieved at relatively
187 intense treatment conditions, i.e. long treatment times and/or high applied current intensities. At the
188 same time, the extent of COD degradation and aromatics removal is lower suggesting the presence
189 of compounds that are resistant to oxidation. In certain cases though, an increase in the
190 concentration of COD, TPh and aromatics, as well as in sample color has been observed; this
191 phenomenon usually occurs at the early stages of the reaction (1 h) and may be due to several
192 reasons, namely: (i) oxidative polymerization of certain OMW constituents like phenols and tannins
193 which would result in color and COD increase in the effluent as has also been observed by other
194 researchers (Gotsi et al., 2005; Khoufi et al., 2006), (ii) dissolution of unfiltered solids upon
195 electrochemical oxidation, thus releasing organic matter in the liquid phase as has also been
196 reported by Kotta et al. (2007). Nonetheless, such dissolution is not expected to contribute
197 substantially to the increased concentrations since most of the solids had already been removed
198 from the effluent, and (iii) interference of residual, unreacted H_2O_2 with the COD test as this has
199 originally been demonstrated by Talinli and Anderson (1992). To estimate the extent of such
200 interference, solutions containing H_2O_2 at concentrations up to 250 mg/L (this corresponds to the
201 maximum concentration of residual peroxide according to Table 3) were measured with respect to
202 their COD content; in all cases, the contribution due to the presence of H_2O_2 did not exceed 80
203 mg/L. (It should be pointed out, though, that increased concentrations of the pollution indices were
204 also recorded in runs performed without H_2O_2 .)

205 Statistical analysis of the response factors Y_1 and Y_2 according to the factorial design technique
206 involves the estimation of the average effect, the main effects of each individual variable as well as
207 their two and higher order interaction effects (Daniel, 1976; Box et al., 1978). The average effect is
208 the mean value of each response factor, while the main and interaction effects are the difference
209 between two averages: main effect = $\bar{Y}_+ - \bar{Y}_-$, where \bar{Y}_+ and \bar{Y}_- are the average response factors at

210 the high and low level respectively of the independent variables or their interactions. Estimation of
211 the average effect, as well as the main and interaction effects was made by means of the statistical
212 package Minitab 14 and the results are summarized in Table 4.

213 A key element in the factorial design statistical procedure is the determination of the significance of
214 the estimated effects. Lenth's method was used for the assessment of the significance of the main
215 and interaction effects in un-replicated factorial designs (Lenth, 1989). Lenth's method assumes that
216 there are m independent effects, and that they all have the same variance. According to this method
217 the pseudo-standard error (PSE) is estimated. First, the median of the absolute values of the effects
218 is determined and then $s_0=1.5 \times \text{median}$. Subsequently, any estimated effect exceeding $2.5 \times s_0$ is
219 excluded and the new median and $\text{PSE}=1.5 \times \text{median}$ are calculated.

220 Once PSE has been obtained, it is multiplied by a factor $t_{0.95;d}$, that is obtained from tables of
221 quantiles of the t-distribution for common values of m and degrees of freedom, $d=m/3$, to estimate a
222 margin of error (ME) for the effects.

223 An important concern is that several inferences are being made simultaneously. With a large
224 number, m , of effects, it is expected that one or two estimates of inactive effects will exceed the
225 margin of error (ME) leading to false conclusions. To account for this possibility, a simultaneous
226 margin of error (SME) equal to $t_{\gamma;d} \times \text{PSE}$ has been also defined with $\gamma= (1+0.95^{1/m})/2$. The present
227 study was done for a confidence interval of 95%.

228 All estimated effects greater than the ME, in absolute values, are deemed significant. On the other
229 hand, all other effects whose values are lower than the ME can be attributed to random statistical
230 error. Moreover, an effect that exceeds the ME but not the SME should be viewed with some
231 caution, as it may be an artifact of testing several effects. In other words there is at most a 5%
232 chance that one individual inactive effect will exceed the ME, while there is at most a 5% chance
233 that any inactive effect will exceed the SME (Lenth, 2006).

234 A very useful pictorial presentation of the estimated effects and their statistical importance can be
235 accomplished using the Pareto chart of the effects. The Pareto chart displays the absolute values of

236 the effects in a bar chart, as well as the decision lines for the ME and SME. The Pareto chart of the
237 effects for the COD oxidation is shown in Fig. 1a. There are seven effects that are greater than the
238 SME decision threshold. Among them, the two most significant ones are the influent COD (X_1) and
239 treatment time (X_5), revealing a positive effect on treatment efficiency. This means that an increase
240 in their level brings about an increase in the amount of COD oxidized. It can be also observed that
241 their effects on COD removal are about the same in absolute values. Moreover, the interaction of
242 these two effects yields a positive effect on treatment performance. However, solution pH yields a
243 negative effect regarding COD both as individual effect and through its interaction with influent
244 COD, indicating that a decrease in its level brings about an increase in the amount of COD
245 oxidized. In other words, treatment efficiency in terms of COD removal appears to be enhanced at
246 acidic conditions. It should be also noted that there are two other significant interactions of effects
247 that positively affect electrolytic treatment and these involve influent COD, current and initial pH.
248 It was then decided to proceed with a new factorial design to further investigate the effects of the
249 two most significant variables, i.e. influent COD and treatment time. The experimental design
250 followed in this case was a full 2^2 experimental set which required 4 experiments. The values
251 chosen for the independent variables and the obtained results in terms of mg/L of COD and TPh
252 oxidized, as well as the extent of decolorization and COD and TPh removal are presented in Table
253 5. For this set of runs (i.e. $COD_0 \geq 5000$ mg/L), initial solution pH was about 4.5 and it was left
254 unchanged as acidic conditions were found to promote degradation. Moreover, the applied current
255 was 20 A to ensure high potentials at the electrolytic cell, while complying with safety regulations.
256 No hydrogen peroxide was added since it had no significant effect on COD removal.
257 Estimation of the average effect, the main effects of the two variables and their interaction appear in
258 Table 6. An estimate of the standard error was obtained by performing repeat runs at the center
259 point of the factorial design, i.e. the variables receive mean values between their high and low
260 levels. To identify important effects when replicated experiments are carried out, the corresponding
261 p-values are computed. If the p-value is ≥ 0.05 that effect is not statistically significant at the $\geq 95\%$

262 confidence level. Hence, it is evident from Table 6 that both treatment time and influent COD affect
 263 positively electrolytic treatment, indicating that an increase in their level brings an increase in the
 264 amount of COD removed. The reaction time is the most significant variable, since its effect is
 265 higher than the effect which corresponds to the influent COD. Based on the variables and
 266 interactions which are statistically significant, a model describing the experimental response for
 267 COD removal was constructed as follows:

268

$$269 \quad Y_1 = 2153.6 + \frac{845}{2} X_1 + \frac{1335}{2} X_5 \quad (2)$$

270 where Y_1 is the mass of COD oxidized (mg/L), X_i are the transformed forms of the independent
 271 variables according to:

272

$$273 \quad X_i = \frac{Z_i - \frac{Z_{high} + Z_{low}}{2}}{\frac{Z_{high} - Z_{low}}{2}} \quad (3)$$

274 and Z_i are the original (untransformed) values of the variables.

275 The coefficients that appear in equation (2) are half the calculated effects, since a change of $X=-1$ to
 276 $X=1$ is a change of two units along the X axis. The model predicts a linear dependency of the mass
 277 of COD oxidized on the operating variables. Therefore, eqn (2) can be transformed to give COD
 278 profile as follows:

279

$$280 \quad COD = 1561.4 + 0.831COD_0 - 445t \quad (4)$$

281 Inferring from the two factorial designs in terms of COD removal, it could be argued that for
 282 $COD < 5000$ mg/L, both treatment time and influent COD affect positively and equally COD
 283 removal (effects X_1 and X_5 in Table 4). On the other hand and for $COD > 5000$ mg/L, the removal is
 284 mainly affected by the treatment time and to a lesser extent by influent COD, i.e. the reaction is
 285 near zero order regarding COD concentration.

286

287 *Model validation and comparison to other models*

288 The validation of the factorial design model was based on the calculation of the residuals which are
289 the observed minus the predicted values. The normal probability plot of the residuals for COD is
290 shown in Fig. 2. All data points lie close to a straight line and within the 95% confidence interval
291 lines. These results indicate that the calculated residuals follow a normal distribution with mean
292 values near zero. According to the above observations, it can be concluded that there is a good
293 agreement between the experimental values and the mathematical model developed and the
294 observed differences (i.e. the residuals) may be readily explained as random noise. This is also
295 demonstrated in Fig. 3 where the experimental data of Run 5 in Table 5 are compared to the COD
296 profile obtained from eqn (4); profiles, as would be expected, are in very good agreement.

297 Panizza et al. (2001) developed a mathematical model to predict COD evolution during the
298 electrochemical mineralization of organics over BDD anodes. In particular, when the process
299 operates under current control (i.e. $j < j_{lim}$), the following equation applies:

300

301
$$COD = COD_0 \left(1 - \frac{j A k_m t}{j_{lim}^0 V_R} \right) \quad (5)$$

302 where V_R : Liquid volume (m^3),

303 $j_{lim}^0 = 4Fk_m COD_0$: Initial limiting current density (A/m^2),

304 j : Applied current density (A/m^2).

305 For the conditions of Run 5 in Table 5, the process operates under current control and eqn (5) can
306 be applied. Linear regression of the experimental data gives a k_m value of $2.2 \cdot 10^{-5}$ m/s and the
307 respective profile is also presented in Fig. 3. The research group who developed the above model
308 reported a k_m value of about $1.5 \cdot 10^{-5}$ m/s for a similar, single-compartment electrolytic reactor
309 operating at 200 L/h recirculation rate (Gherardini et al., 2001; Bellagamba et al., 2002; Montilla et
310 al., 2002).

311 Fig. 4a shows the polarization curves of the ferro/ferri cyanide redox couple at various ferro-
312 cyanide concentrations, from which limiting currents are computed. The latter are plotted in the
313 form of eqn (1) and from the slope of the resulting straight line (Fig. 4b), a k_m value of $1.75 \cdot 10^{-5}$ m/s
314 is computed. This value is then used to obtain the COD profile (Fig. 3) according to eqn (5). The
315 discrepancy between the experimentally determined and fitted k_m values can be attributed to the fact
316 that the matrix (ferro/ferri cyanide) employed to determine the coefficient is substantially different
317 from the actual OMW.

318

319 *TPh degradation*

320 Fig. 1b displays the Pareto chart for TPh removal. There is only one significant effect that is greater
321 than the SME decision threshold and this is the addition of hydrogen peroxide which enhances
322 treatment efficiency. At this point, it should be mentioned that H_2O_2 concentration was monitored
323 during electrolysis and it was found that it was rapidly consumed, i.e. by about 60% within the first
324 30 min. This implies that oxidation in the solution bulk (indirect oxidation) in the presence of
325 hydrogen peroxide plays an important role for the degradation of phenolic compounds. The latter
326 appear to be susceptible to hydroxyl radical attack induced by the relatively high H_2O_2 :TPh
327 concentration ratio.

328 Moreover, the second 2^2 factorial design analysis (Table 6) shows that neither treatment time nor
329 influent COD or their interaction have a significant effect on TPh removal, since none of their p-
330 values are lower than 0.05. This is rather expected since H_2O_2 addition, which was the main
331 significant parameter for TPh removal according to the first 2^5 factorial design, was not included in
332 the second one.

333 On the assumption that TPh are represented by gallic acid (monohydrate), the stoichiometry of its
334 reaction to carbon dioxide and water dictates that 100 mg of gallic acid would require 102 mg
335 oxygen for the complete oxidation; therefore the last column of Table 3 corresponds to the
336 concentration of COD oxidized due to the phenolic fraction of the effluent. It is evident that TPh

337 removal represents only a small fraction of the overall COD removal (in terms of mass of COD
338 oxidized), indicating that electrochemical oxidation reactions are non-selective attacking various
339 compounds that are either originally present in OMW or formed as secondary reaction by-products.
340 The factorial design analysis also showed (data not presented) that treatment time is the single most
341 significant factor affecting positively color and aromatics removal. This can also be clearly seen in
342 Table 3 where the degree of color and aromatics removal is higher for the runs performed at
343 prolonged treatment times.

344

345 *Energy consumption*

346 Electrochemical treatment is undoubtedly an energy-intensive process and its efficiency is usually
347 assessed in terms of specific energy consumption (SEC). This is defined as the amount of energy
348 consumed per unit mass of organic load removed. Representative temporal profiles of cumulative
349 SEC with respect to COD removal are shown in Fig. 5. Obviously, SEC is lower at higher influent
350 COD values and it does not considerably increase upon prolonged treatment times. This comes to
351 boost the argument drawn from the factorial design analysis that treatment is enhanced at high
352 influent COD values.

353 In light of this, a last experiment was performed with the undiluted OMW ($COD_0=40000$ mg/L) to
354 assess the treatability of the effluent with the proposed process; as seen in Fig. 6, treatment for 15 h
355 at 20 A led to 19% COD and 36% TPh degradation respectively with a SEC value (Fig. 5) of 96
356 kWh/kg COD removed. Fig. 6 also shows a comparison between the experimental COD profile and
357 that obtained according to the following equation:

358

$$359 \quad COD = COD_0 - 445t \quad (6)$$

360 Like eqn (4), eqn (6) also predicts that COD decreases linearly with treatment time. The only
361 difference between them is the constant term which, for eqn (4), has been computed for

362 $5000 \leq \text{COD}_0 \leq 10000$ mg/L. For influent COD values well over this range (i.e. $\text{COD}_0 = 40000$ mg/L),
363 eqn (6) must be used denoting that the reaction is zero order with regard to COD concentration.
364 In a recent study (Chatzisymeon et al., 2009), we reported that treatment of the same OMW at 5000
365 mg/L COD_0 by UV-A/ TiO_2 photocatalysis would result in about 20% COD reduction after 4 h of
366 irradiation with a SEC value of 5000 kWh/kg COD removed. Electrochemical treatment at
367 comparable conditions (Run 2 in Table 5) yields a similar performance in terms of COD removal
368 with a SEC value (Fig. 5) of 210 kWh/kg COD removed. Nevertheless, this is still unrealistic for
369 practical applications since the cost of electricity would be 7-10 €/kg COD removed even for the
370 most favorable conditions of Fig. 5. This is about two orders of magnitude greater than the running
371 cost of a combined aerobic-anaerobic treatment process, while the respective cost for lime
372 coagulation alone (a typical OMW treatment process in Greece and elsewhere in the Mediterranean)
373 would be in the order of 0.01 €/kg solids removed (Tzagaroulakis et al., 2005).

374

375 *Biodegradability and toxicity studies*

376 The aerobic biodegradability of OMW samples prior to and after treatment for 7 h at 20 A was
377 assessed according to the Zahn-Wellens test and the results are shown in Fig. 7. As clearly seen, the
378 untreated OMW at COD_0 values of 5000 and 10000 mg/L is susceptible to aerobic biodegradation
379 which levels off at about 80% after 10-13 days of inoculation. This is almost exclusively due to
380 biochemical processes since COD measurements during the early stages of the test showed
381 negligible adsorption of organics onto the biomass. Nevertheless, the original effluent still contains
382 a considerable fraction of organics that cannot be degraded aerobically. Interestingly, the
383 biodegradability of the treated OMW samples has been reduced to about 60-70%, thus implying the
384 formation of reaction by-products that are less readily degradable aerobically than the original
385 OMW constituents. All four samples were highly ecotoxic to *V. fischeri* with EC_{50} values never
386 exceeding 5%. This is possibly due to the combined effect of increased organic concentration and
387 the presence of toxic species in the samples.

388

389 **CONCLUSIONS**

390 Wastewater from the olive oil industry was electrochemically oxidized over boron-doped diamond
391 electrodes with emphasis given on the effect of various operating conditions on treatment efficiency
392 with regard to COD, TPh, color and aromatics removal. To evaluate in a coherent way the
393 importance of the various parameters involved, a factorial design methodology was followed. Major
394 conclusions are as follows:

395 (1) Treatment time and the initial concentration of organic pollutants are two factors that dictate, to
396 a great degree, the efficiency of OMW electrochemical mineralization. In fact, they both become
397 crucial at increased organic loads in terms of both treatment and cost efficacy. Although
398 mineralization of OMW is difficult even at intense conditions, other pollutants such as phenols and
399 color can easily be removed.

400 (2) A simple model for COD removal was developed, validated against experimental data and
401 compared to an electrochemical kinetic model. The development of such empirical models with
402 relatively few experiments is of great importance as they can form the basis for process
403 optimization and scale-up. It should be noticed though that such models can work satisfactorily
404 within the range of conditions from which they have been developed and may be viewed with
405 caution at conditions outside this range.

406 (3) Process integration for the treatment of heavily polluted industrial effluents is becoming
407 common place. In a complex battery of treatments, biological processes are likely to play an
408 important role. In this view, biodegradability and ecotoxicity tests are required to assess effluent
409 biotreatability; at the conditions in question, BDD electrochemical oxidation does not appear to
410 improve the aerobic biodegradability of OMW as assessed by the Zahn-Wellens test. Studies are
411 underway to assess the feasibility of a sequential biological-electrochemical process for OMW
412 treatment.

413

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419

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506

507 **Table 1.** Properties of OMW samples used in this study.

508

Properties	OMW prior to filtration	OMW after filtration
COD, g/L	47	40
Total phenols (TPh), g/L	8.1	3.5
Total solids (TS), g/L	50.3	0.6
pH	4.6	4.4
Conductivity, mS/cm	17	18

509

510

511

512 **Table 2.** Independent variables of the 2⁵ factorial design of experiments.

513

Level of value	X ₁ [COD] ₀ , mg/L	X ₂ Current, A	X ₃ [H ₂ O ₂], mg/L	X ₄ pH ₀	X ₅ Treatment time, h
-	1000	10	0	4	1
+	5000	20	500	6	4

Table 3. Design matrix of the 2⁵ factorial experimental design and observed response factors, as well as percent removal of COD, TPh, color and aromatics and residual H₂O₂ concentration.

Run order	X ₁ [COD] ₀ , mg/L	X ₂ Current, A	X ₃ [H ₂ O ₂], mg/L	X ₄ pH ₀	X ₅ Time, h	Y ₁ COD oxidized, mg/L	Y ₂ TPh oxidized, mg/L	% COD removal	% TPh removal	% Color removal	% Aromatics removal	Residual H ₂ O ₂ , mg/L	COD oxidized from TPh, mg/L
1	-	+	+	+	+	288	82	29	100	93	26	150	90
2	-	+	+	-	+	302	78	30	97	94	26	50	88
3	+	+	-	-	+	1260	79	23	23	62	11	0	89
4	-	-	+	-	-	-118	18	-18	31	82	-2	150	20
5	+	-	-	-	+	1570	152	25	32	67	38	0	172
6	-	-	+	+	-	-132	12	-21	23	74	-4	150	14
7	+	-	-	-	-	1030	15	16	3	65	33	0	17
8	+	+	+	-	+	1090	258	21	51	57	2	25	291
9	-	+	-	+	-	22	33	2	37	38	-2	0	37
10	+	-	+	+	-	460	17	8	5	12	-1	150	19
11	+	+	+	-	-	-140	102	-3	20	18	-13	100	115
12	+	+	-	-	-	110	-167	2	-49	55	-6	0	-188
13	+	-	+	+	+	910	71	16	21	24	9	50	80
14	+	-	+	-	+	1870	187	29	41	63	30	50	210
15	-	+	-	+	+	350	83	33	93	91	30	0	94
16	+	-	-	+	+	380	23	7	7	20	7	0	26
17	-	-	+	-	+	136	54	21	92	90	20	100	60
18	-	-	-	-	-	-26	-9	-3	-13	59	-11	0	-10
19	-	+	+	+	-	-62	46	-6	58	54	-6	150	52
20	+	-	-	+	-	-80	-106	-1	-32	-2	-4	0	-120
21	+	+	+	+	-	0	183	0	37	19	-5	150	207
22	+	-	+	-	-	1020	128	16	28	28	15	150	143
23	-	-	-	+	+	286	37	27	72	71	28	0	43
24	+	+	+	+	+	1370	258	25	52	39	17	50	291
25	-	-	-	-	+	256	33	25	45	72	10	0	37
26	-	+	-	-	-	-20	-13	-2	-26	72	-7	0	-15
27	-	+	-	-	+	286	19	33	37	89	20	0	21
28	+	+	-	+	-	-290	-126	-6	-39	-6	-10	0	-143
29	+	+	-	+	+	1100	25	21	8	24	12	0	27
30	-	-	-	+	-	74	-7	7	-15	30	15	0	-8
31	-	+	+	-	-	-80	45	-8	56	82	-1	250	51
32	-	-	+	+	+	84	51	13	97	89	25	150	58

Table 4. Average and main effects of the independent variables and their two and higher order interactions of the 2^5 factorial design on the response factors Y_1 and Y_2 .

Effect	Value of Effect	
	COD removal (Y_1)	TPh removal (Y_2)
<i>Average Effect</i>	415.8	51.91
<i>Main Effects</i>		
X ₁	625.9	33.56
X ₂	-133.4	19.31
X ₃	43.1	94.94
X ₄	-236.6	-18.56
X ₅	610.6	82.44
<i>Two-factor Interactions</i>		
X ₁ X ₂	-199.1	-3.69
X ₁ X ₃	144.4	68.69
X ₁ X ₄	-258.4	-32.56
X ₁ X ₅	319.4	43.44
X ₂ X ₃	-49.4	44.94
X ₂ X ₄	232.9	41.44
X ₂ X ₅	202.6	14.94
X ₃ X ₄	91.4	-0.19
X ₃ X ₅	27.1	-21.44
X ₄ X ₅	-13.6	-10.19
<i>Three-factor Interactions</i>		
X ₁ X ₂ X ₃	-103.1	38.94
X ₁ X ₂ X ₄	227.1	26.69
X ₁ X ₂ X ₅	128.6	14.81
X ₁ X ₃ X ₄	152.4	16.19
X ₁ X ₃ X ₅	17.9	-18.44
X ₁ X ₄ X ₅	1.1	-13.44
X ₂ X ₃ X ₄	18.4	-1.19
X ₂ X ₃ X ₅	-7.4	-0.94
X ₂ X ₄ X ₅	59.9	-9.19
X ₃ X ₄ X ₅	-27.6	0.19
<i>Four-factor Interactions</i>		
X ₁ X ₂ X ₃ X ₄	6.6	10.06
X ₁ X ₂ X ₃ X ₅	-22.6	-0.69
X ₁ X ₂ X ₄ X ₅	47.6	-11.19
X ₁ X ₃ X ₄ X ₅	-24.9	1.94
X ₂ X ₃ X ₄ X ₅	8.4	-0.31
<i>Five-factor Interactions</i>		
X ₁ X ₂ X ₃ X ₄ X ₅	19.1	-1.69
Lenth's PSE	53.1	21.2
ME	109.5	43.7
SME	208.3	83.2

Table 5. Design matrix of the 2^2 factorial experimental design and observed response factors, as well as percent removal of COD, TPh and color. Other conditions: $\text{pH}_0=4.5$, 20 A of current intensity, without H_2O_2 .

Run Order	X_1 [COD] ₀ , mg/L	X_5 Time, h	Y_1 COD oxidized, mg/L	Y_2 TPh oxidized, mg/L	% COD removal	% TPh removal	% Color removal
1	7500	5.5	2115	208	29	40	46
2	5000	4	1220	125	26	37	4
3	7500	5.5	2055	172	29	35	49
4	10000	4	1750	167	19	25	21
5	10000	7	3400	343	28	40	33
6	7500	5.5	2295	98	32	24	46
7	5000	7	2240	217	38	50	68

Table 6. Average and main effects of the independent variables, their two order interaction and respective p-values of the 2^2 factorial design on the response factors Y_1 and Y_2 .

	COD removal (Y_1)		TPh removal (Y_2)	
	Effect	P-value	Effect	P-value
<i>Average</i>	2153.6	0	190	0.004
<i>Main</i>				
X_1	845	0.004	84	0.26
X_5	1335	0.001	134	0.12
<i>Two-factor Interaction</i>				
$X_1 X_5$	315	0.054	42	0.54
SE	51		30.6	

LIST OF FIGURES

Fig. 1. Pareto chart of the effects for (a) COD and (b) TPh removal for the full 2^5 factorial design.

White bars: positive effects; Black bars: negative effects.

Fig. 2. Normal probability plot of the residuals. COD removal model for the full 2^2 factorial design.

Fig. 3. Comparison between experimental and modelled COD profiles. Conditions as in Run 5, Table 5.

Fig. 4. Determination of mass transfer coefficient, k_m . (a) Polarization curves for various ferrocyanide concentrations and (b) plot of eqn (1).

Fig. 5. Specific energy consumption (SEC) during electrolysis at 20 A and various COD_0 values.

Fig. 6. COD and TPh removal (left axis) and experimental and modelled COD profiles (right axis) during electrolysis at 40000 mg/L COD_0 and 20 A.

Fig. 7. Zahn-Wellens biodegradability for OMW samples prior to and after 7 h of electrolytic treatment at 20 A.

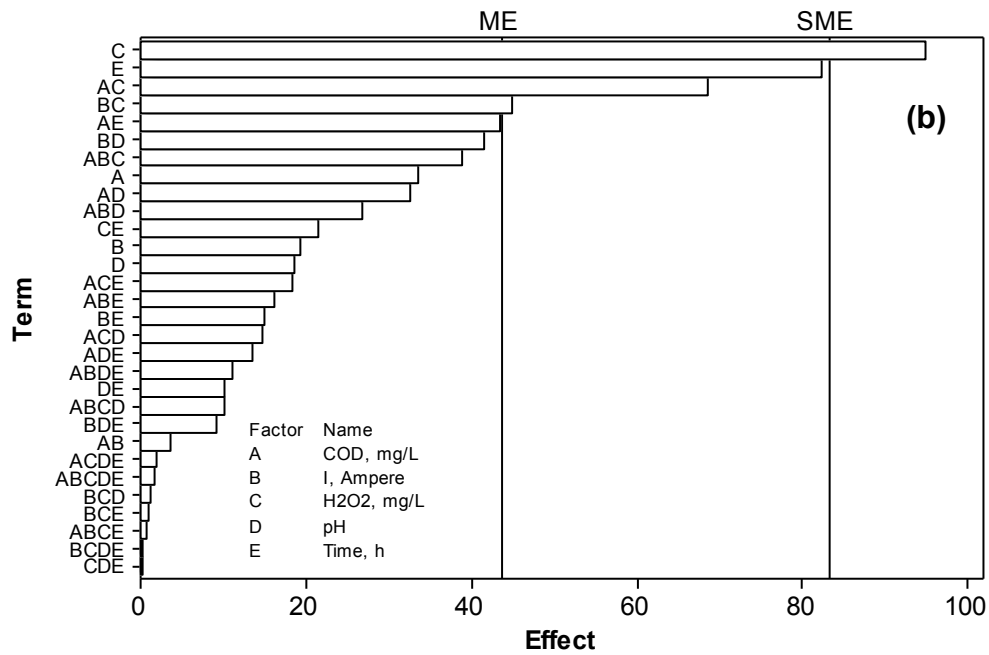
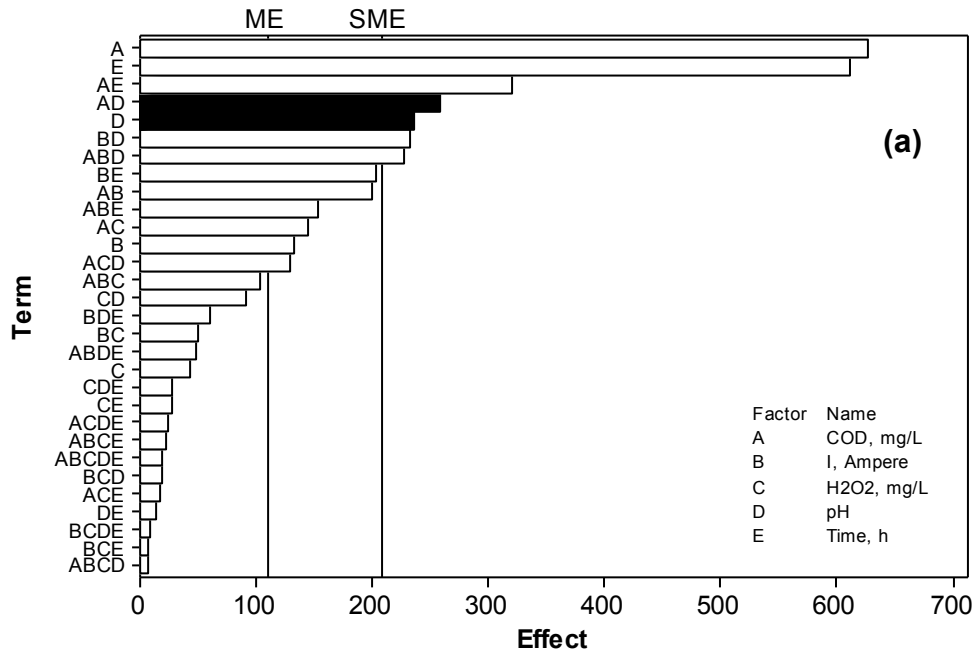


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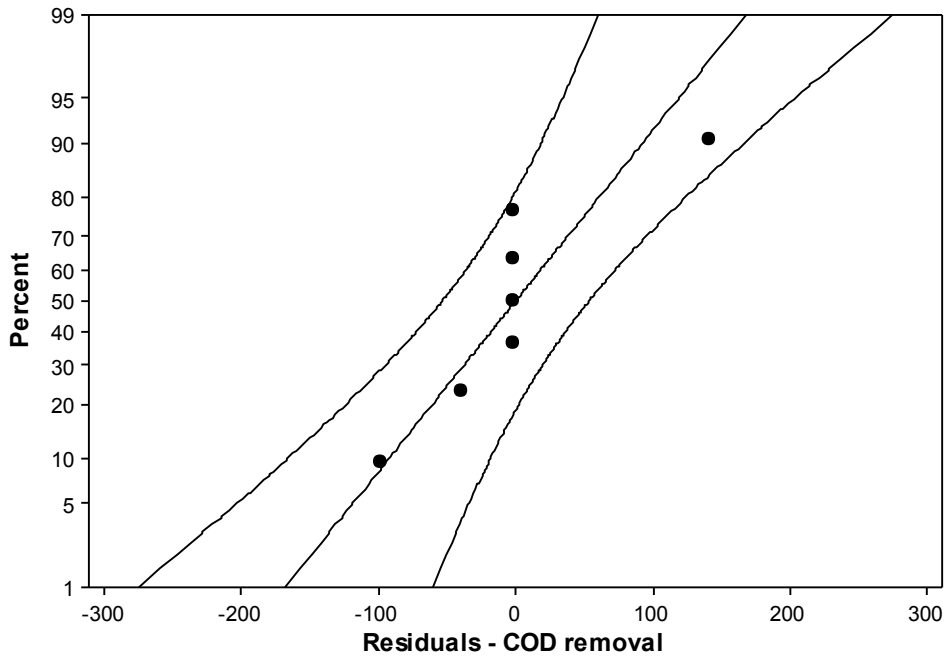


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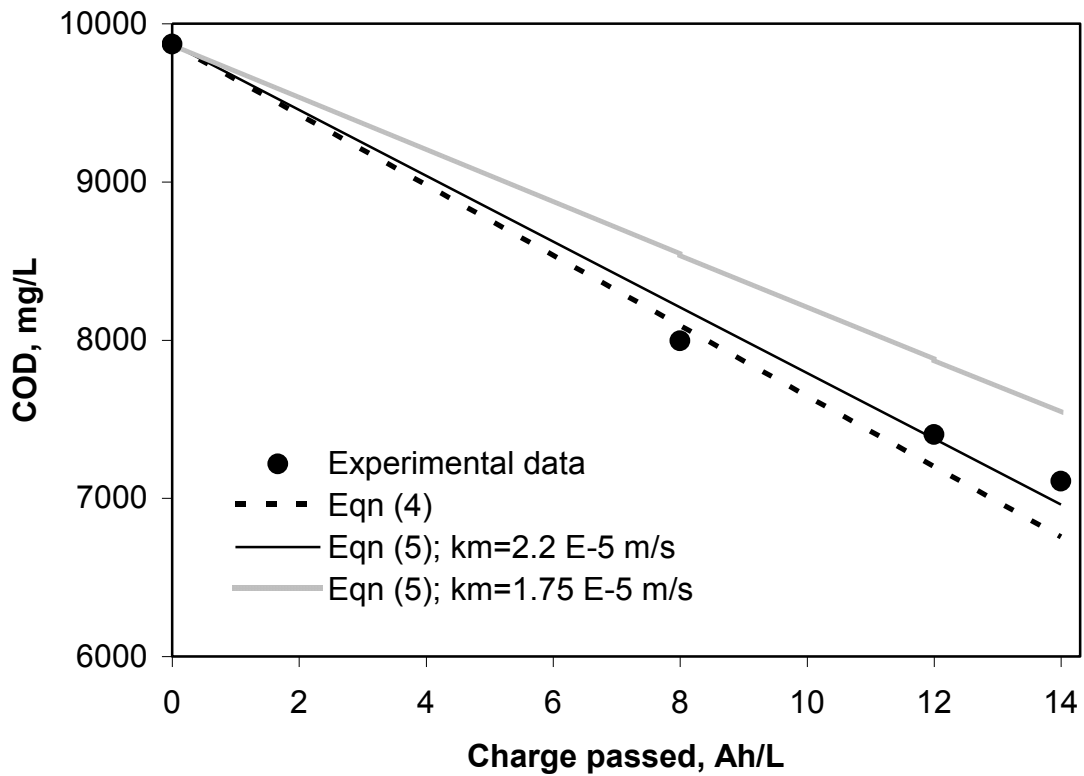


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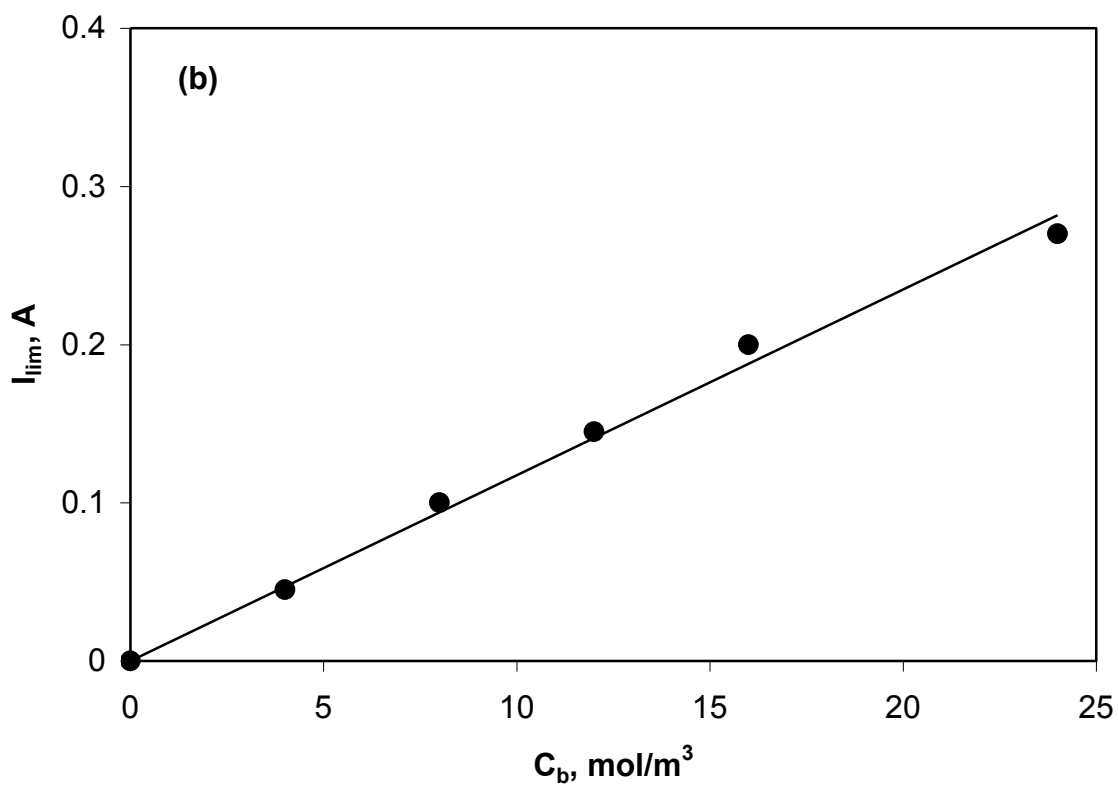
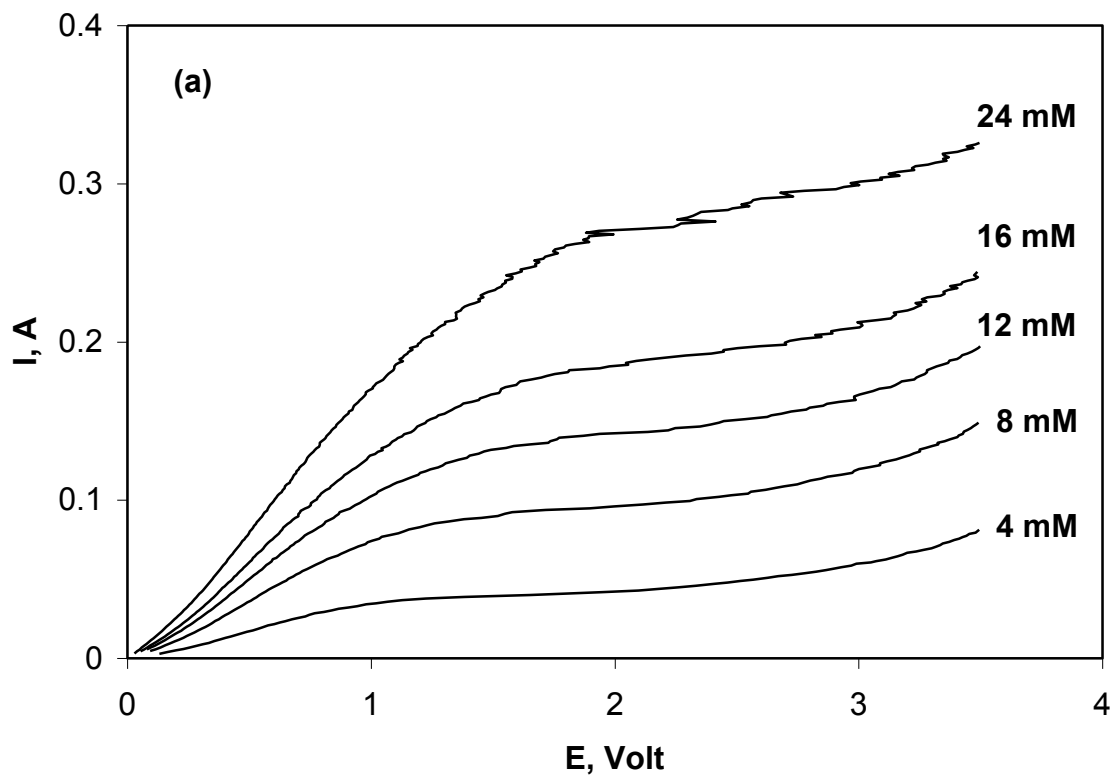


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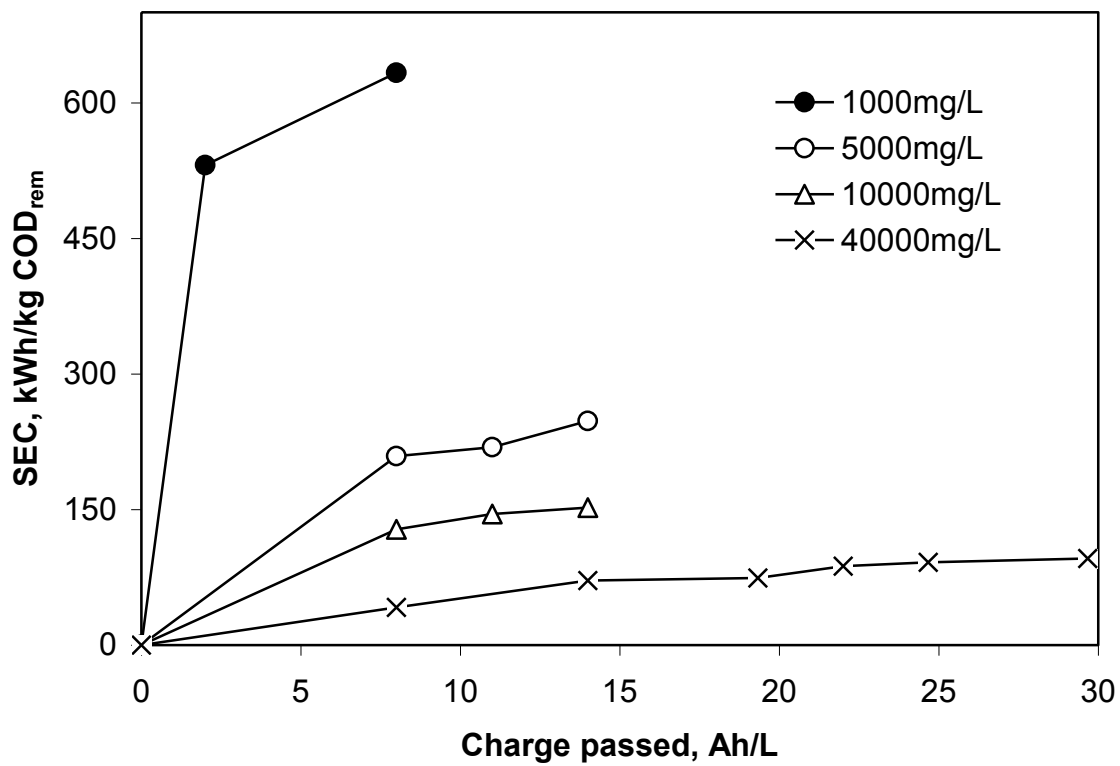


Fig. 5. Specific energy consumption (SEC) during electrolysis at 20 A and various COD₀ values.

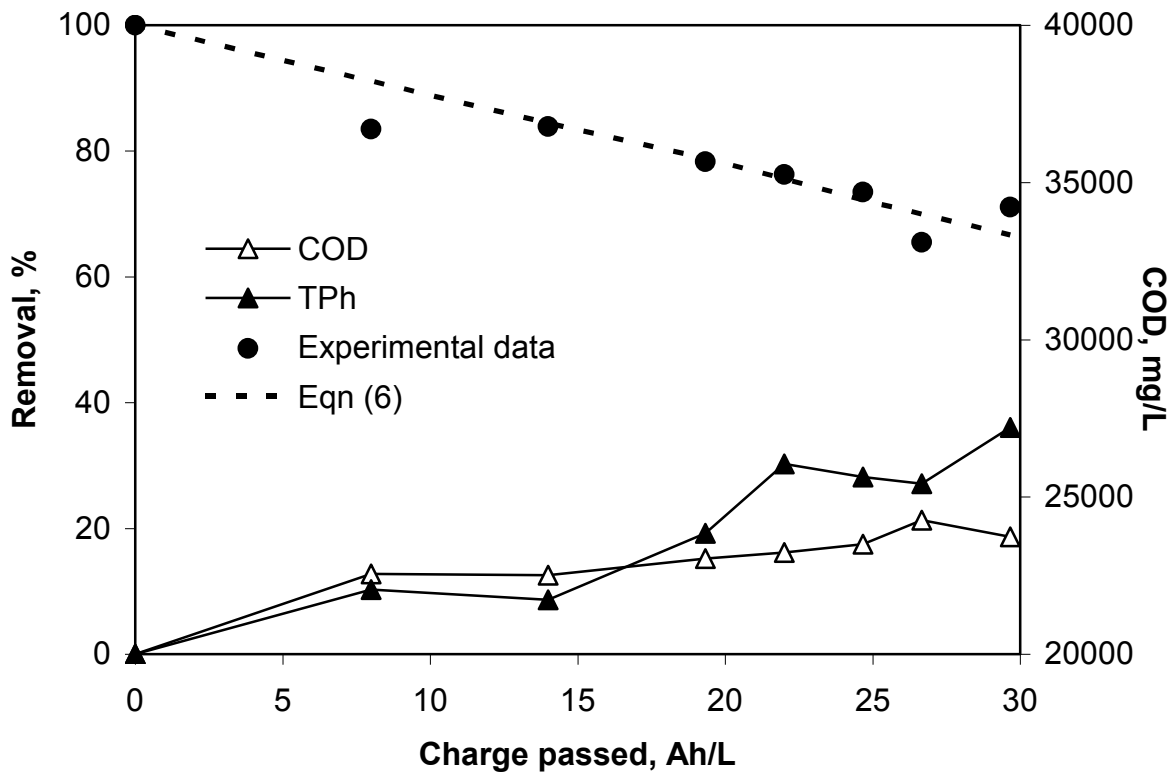


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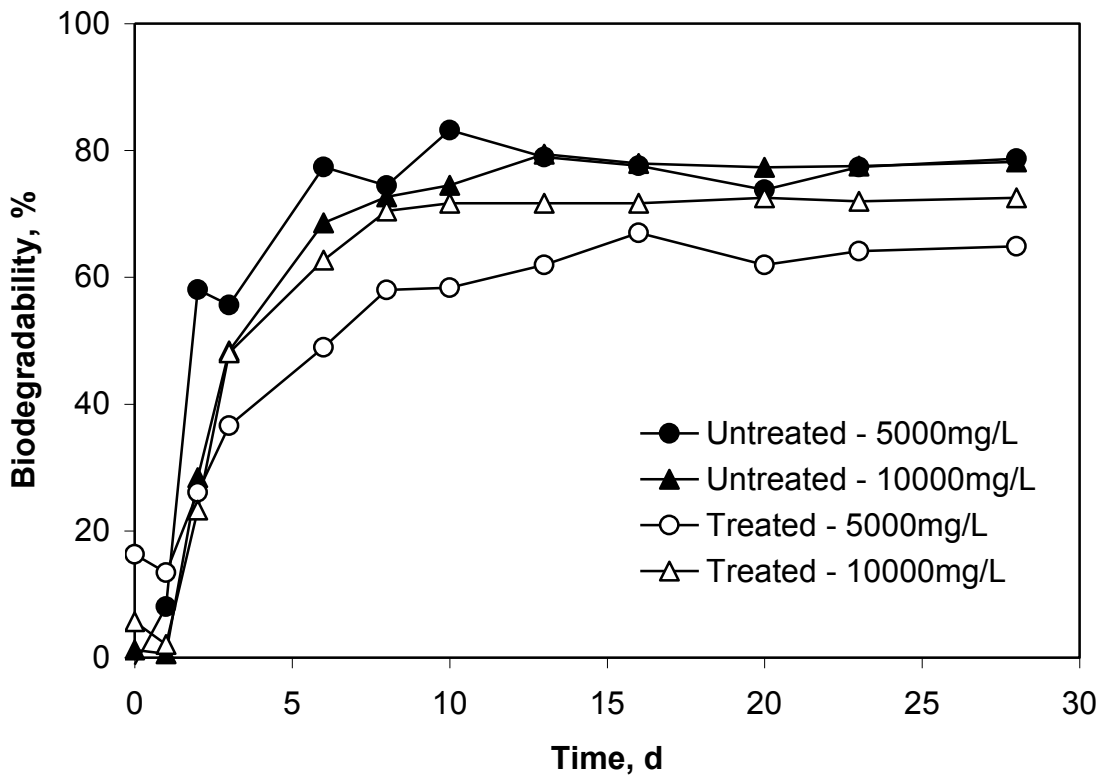


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