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Determination of photostability, biocompatibility and efficiency as photo-Fenton auxiliaries of three different types of soluble bio-based substances (SBO)

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15 **Determination of photostability, biocompatibility and**
16 **efficiency as photo-Fenton auxiliaries of three different types**
17 **of soluble bio-based substances (SBO)**

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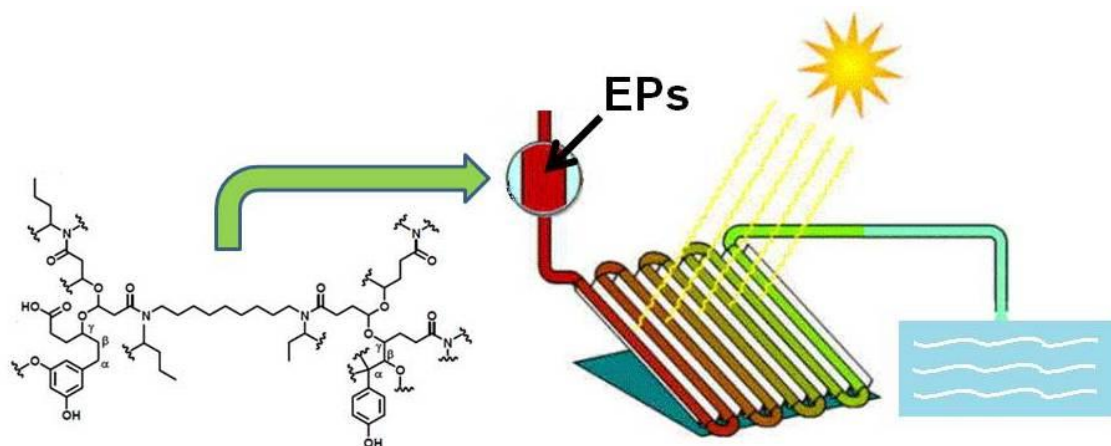
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34 **Graphical abstract**



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36

37 **Highlights**

38

39 Soluble bio-based substances (SBO) have been employed to drive a mild photo-Fenton

40 SBO are non-toxic, show poor degradability and are relatively photostable

41 **The SBO composition is related with their performance in photochemical processes**

42

43 **Keywords:** SBO, photostability, photo-Fenton, biocompatibility

44

45 **Abstract**

46 The aim of this work is to determine the photostability biocompatibility and efficiency

47 of **water** soluble bio-based substances (SBO) in photo-oxidative processes for

48 wastewater treatment. Three batches of SBO, isolated from different sources, have been

49 investigated. Differences in the functional groups present in these substances can

50 explain major trends in their physical/chemical properties. Bioassays have proven those

51 materials to be non-toxic but to show poor biodegradability. Their ability to enhance a

52 photo-Fenton process at milder pH (5.2) has been investigated using a mixture of

53 emerging compounds in wastewaters. All the tested SBO were able to remove all

54 pollutants in less than one hour irradiation, and the best results were obtained with those

55 substances showing higher hydrophilic/hydrophobic ratio. Moreover, although SBOs
56 themselves undergo a slight oxidation, no relevant negative effect has been observed for
57 their use in wastewater treatment.

58

59 **1. Introduction**

60

61 Generation of increasing amount of wastes from human activities has become a serious
62 environmental concern. Developing technologies and processes able to minimize their
63 production should be a priority; however, this is not always possible and alternative
64 approaches are required to deal with this problem, such valorization through their re-use
65 in other processes. In this context, much effort has been devoted in recent years to
66 obtain valuable products from urban bio-wastes (UBW) (see [1] and references therein
67 cited).

68

69 UBW have become a sustainable source of valuable materials, such as water soluble
70 bio-organic substances (SBO). They have been isolated from organic wastes submitted
71 to anaerobic and/or aerobic treatment, yielding biomasses successively hydrolyzed at
72 alkaline pH, the obtained solutions submitted to ultrafiltration, then the retentate is dried
73 and soluble bio-based products obtained as potassium salts [2]. Depending on the origin
74 and treatment of the sourcing UBW, different batches of SBO can be obtained, showing
75 a wide range of chemical composition and properties [3]. In general, SBO are
76 constituted by a mixture of macromolecules which average molecular weight ranges
77 from 67 to 463 kg mol⁻¹. These supramolecular assemblies contain long aliphatic
78 chains, aromatic rings and several functional groups as carboxyl, primary and
79 substituted amine and amide, carbonyl, hydroxyl, phenol, ether or ester. Previous

80 papers studied the potential applications of SBO as surfactants [4], in materials
81 chemistry [5], in soil-washing treatments [6], in agriculture [7] or animal husbandry [8].

82

83 SBO chemical composition shows high similarity with that of dissolved organic matter
84 (DOM, e.g. humic or fulvic acids), which is known to generate, upon solar irradiation,
85 highly reactive species able to oxidize pollutants, thus contributing to the abiotic self-
86 remediation of natural ecosystems [9-11]. For this reason, SBO might also be employed
87 in solar photochemical processes for wastewater treatment. Some works have been
88 published reporting on the use SBO as photosensitizer for the degradation of aromatic
89 sulphonic acids [12], phenols [13] or dyes [14, 15]. In addition, SBO might be used to
90 drive a photo-Fenton process under milder conditions. Photo-Fenton is based on the
91 ability of iron salts to decompose hydrogen peroxide into highly reactive species, and
92 the process is greatly enhanced upon irradiation [16]. One major drawback is the highly
93 acidic pH which is required to avoid the formation of photochemically inactive iron
94 oxides and hydroxides; in this context the ability of SBO to complex metal cations, such
95 as iron, is useful for the development of photo-Fenton at circumneutral media [17].

96

97 However, some important issues still remain unexplored. For instance, SBO could only
98 be employed for wastewater detoxification if they show a good biocompatibility,
99 namely low toxicity and high biodegradability. Furthermore, SBO are mainly formed of
100 organic molecules, and can in turn be attacked by reactive species generated in the
101 photo-oxidative processes, with possible changes in their biological or chemical
102 properties. Any modification in SBO composition might result in different performance
103 of these materials and hence, comparison of different batches of SBO is meaningful.
104 With this background the aim of this paper is to gain further insight into the

105 performance, photo-stability and biocompatibility of three types of SBO obtained from
106 different sources. A battery of bioassays have been employed for toxicity and
107 biodegradability determination; SBO performance before and after irradiation has been
108 tested in the degradation of a mixture of emerging pollutants (EPs), namely
109 acetaminophen, caffeine, amoxicillin, clofibric acid, carbamazepine and acetamiprid.
110 These chemicals have been chosen because they are examples of xenobiotics commonly
111 employed in the literature and they have previously employed as target pollutants in
112 works involving SBO in the photo-Fenton process [17].

113

114 **2. Experimental**

115

116 2.1. Materials

117

118 The following types of SBO were employed: a) FORSUD, isolated from the urban
119 waste organic humid fraction (UWOHF) obtained from separate source collection,
120 mixed with the digestate from an anaerobic reactor fed with UWOHF; b) CVT230,
121 obtained from home gardening and park trimming residues (GR) piles aerated for 230
122 days; c) CVDFT110, isolated from a mixture 35/55/10 (w/w/w) of FORSUD, GR and
123 urban sewage sludge mix, aerated for 110 days.

124

125 The SBO isolation was performed in a pilot plant at the Studio Chiono & Associati in
126 Rivarolo Canavese, Italy [2]. Briefly, it consisted in an electrically heated and
127 mechanically stirred 500 L reactor, a 102 cm long x 10.1 cm diameter polysulfone
128 ultrafiltration (UF) membrane with 5 kDa molecular weight cut-off, and a forced
129 ventilation drying oven. A stirred stainless steel reactor was loaded with 300 L of
130 aqueous solution of KOH and 75 kg of solid biomass at 65 °C and a pH value of ca. 13.

131 After 4 hours, the reactor turned off automatically and the mixture was settled down
132 overnight. The supernatant was pumped to a centrifuge (9000 rpm) to remove the small
133 insoluble fraction (mainly silicoaluminates) that was still present after the treatment.
134 The recovered liquid phase was flown at 40 L/h through an UF membrane operating
135 with tangential flow at 7 bar inlet and 4.5 bar outlet pressure to yield a retentate
136 containing 5-10 % of dry matter, which was finally dried at 60 °C. Solid SBO products
137 were obtained in 15-30 % w/w yield, relatively to the starting UBW dry matter.

138

139 Acetaminophen, caffeine, amoxicillin, clofibric acid, carbamazepine and acetamidrid,
140 employed as target pollutants, were purchased from Sigma-Aldrich. Hydrogen peroxide
141 (30% v/v) and ferrous sulphate were supplied by Panreac. Water employed in all the
142 experiments was Milli-Q grade.

143

144 The bioluminescent bacteria *Vibrio fischeri* (strain NRRL-B-11177) were purchased by
145 Macherey-Nagel GmbH & Co. (Düren, Germany). *P. subcapitata*, and ehippia
146 (dormant eggs) of crustacean *Daphnia magna* were supplied by ECOTest S.L. (Valencia,
147 Spain)

148

149 2.2. Reactions

150

151 Experiments devoted to check the SBO photo-stability were performed in cylindrical
152 Pyrex vessel (55 mm i.d.). A solar simulator (Sun 2000, ABET Technologies) equipped
153 with a 550 W Xenon Short Arc Lamp was used as irradiation source (see [18] for the
154 spectrum, which closely matches the solar one). For each experiment, the reactor was
155 loaded with 250 mL of solution containing the SBO (100 mg/L). The pH was adjusted

156 to the desired value by adding diluted sulphuric acid. Eventually, the stoichiometric
157 amount of hydrogen peroxide required to oxidize completely each SBO was added, and
158 irradiation was kept until the solution was free of H₂O₂. The amount of H₂O₂ was
159 obtained from the initial chemical oxygen demand (COD) of the SBO, as COD
160 indicates the amount of O₂ required to oxidize completely the sample.

161

162 The same experimental device was employed to check the performance of SBO in a
163 mild photo-Fenton process. In this case, the mixture of all six EPs was employed at an
164 initial concentration of each pollutant of 5 mg/L. All three types of SBO (10 mg/L)
165 were used in parallel experiments. The initial concentration of iron(II) was 5 mg/L
166 (added as sulfate salt) and half the stoichiometric amount of hydrogen peroxide to
167 mineralize the pollutants present in the solution was added. The pH was adjusted to 5.2.

168

169 2.3. Chemical analysis

170

171 The EPs concentration was determined by chromatography (Perkin Elmer model Flexar
172 UPLC FX-10) equipped with a UV-vis detector. A DB-C18 Brownlee Analytical
173 column was used and the eluent was a mixture of acetonitrile (A) and a 0.1% formic
174 acid aqueous solution (B); its composition was changed in a linear gradient, from 3% A
175 to 70% A in 8 min with a flow rate of 0.3 mL/min. Wavelengths employed for detection
176 were: 205 nm (acetaminophen, amoxicillin, caffeine and carbamazepine), 225 nm
177 (clofibric acid) and 245 nm (acetamiprid). Samples were filtered through polypropylene
178 filters (VWR, 0.45 µm) before analysis.

179

180 Dissolved organic carbon (DOC) was determined with a Shimadzu model TOC-V CSH
181 apparatus. Chemical oxygen demand (COD) was determined according to the
182 dichromate method [18]: sample digestions were performed at 148°C in a
183 Thermoreaktor TR300 (Merck) and a Spectroquant NOVA 60 (Merck) was used for the
184 photometric determination. The surface tension of samples was determined by a Krüss
185 K-9 tensiometer.

186

187 2.4. Bioassays

188

189 In order to check the biodegradability of all three substances, biological oxygen demand
190 (BOD₅) assays were carried out according to the standard manometric method (OECD
191 301 B, CO₂ evolution test), using an OxiTop[®] (WTW) to seal the bottle and determine
192 the pressure inside [18]. The BOD₅ values were determined for SBO concentrations of
193 100 mg/L and 1000 mg/L.

194

195 Toxicity assays based on *V. fischeri* bacteria were performed based on ISO 11348-
196 3:2007 standardized test; algae growth inhibition assay was performed according to an
197 adaptation of ISO 8692:2004 test, using the chlorophyceae algae *Pseudokirchneriella*
198 *subcapitata*; bioassays based on the inhibition of the mobility of *D. magna* were
199 performed according to the standard ISO 6341:199632 procedure. A detailed
200 description of the experimental procedure followed in all three cases can be found as
201 Supplementary Data (S1). They were chosen as examples of bioassays commonly
202 employed to detect toxicity in water involving different micro-organisms, namely
203 bacteria, algae and crustaceans, in order to better assess the toxicity of these substances
204 in water.

205

206 **3. Results**

207

208 3.1. Chemical and physical characterization of the SBO

209

210 A chemical characterization of FORSUD, CVT230 and CVDFT110 is summarized in
211 Table 1. Data show that FORSUD has the highest organic content, as indicated by the
212 percentages of volatile solids and carbon; on the other hand, scarce differences can be
213 found between CVT230 and CVDFT110 regarding this parameter. It is interesting to
214 notice that a significant amount of metals can be found in all three materials; this can be
215 due either to metal already present in the starting materials or added in the isolation
216 process (e.g. potassium). The presence of metals, in particular iron, might be of interest,
217 as the ability of complexed iron to drive a photo-Fenton process at mild conditions has
218 been recently described [17]; on the other hand, heavy metals, although found at very
219 low amounts, might be a concern, and hence, bioassays to determine SBO
220 biocompatibility are required.

221

222 The gross amount of ions released into the aqueous medium might be important for the
223 performance of a photo-oxidative reaction and can be related to the conductivity of
224 solutions of these substances. Although values are not very different, higher
225 conductivity was measured for FORSUD (29 mS/cm for 1 g/L concentration, 9 mS/cm
226 for 50 mg/L) while lower values were obtained for the other two studied materials (8-12
227 mS/cm for 1 g/L and 0.3-0.5 mS/cm for 50 mg/L).

228

229 In addition, the relative amount of some functional groups present in all three SBOs is
230 shown in Table 2. In the case of FORSUD, aliphatic carbon is the predominating

231 species (43 %), and although this is also true for the other SBOs, the proportion is lower
232 (31-37%); on the other hand aromatic carbon is more abundant in CVDF110 and
233 CVT230. Consequently, the aliphatic/aromatic ratio obtained was clearly higher for
234 FORSUD than for the other two SBOs. It is interesting to note that, again in this case,
235 similar composition was obtained for CFDFT110 and CVT230.

236

237 Another useful gross parameter employed in characterization of natural organic matter
238 is the E_2/E_3 ratio [19], where E_2 and E_3 are the absorbances at 250 nm and 365 nm
239 respectively; this ratio has been related with the average molecular weight of the
240 macromolecules, as well as its aromaticity (the higher ratio, the lower aromaticity and
241 molecular weight). The application to the E_2/E_3 ratio to SBO gave results consistent
242 with their composition: higher values for E_2/E_3 were indeed obtained for FORSUD
243 (3.83) that, as stated above, shows the minor proportion of aromatic groups; lower
244 values were obtained for the other two SBO (ca. 2.3)

245

246 The structure of the SBO can be also related their surfactant activity. In order to gain
247 further insight into this behavior, surface tension of water was measured in the presence
248 of four different concentrations of these materials. Results given in Figure 1 shows that
249 higher decreases in surface tension were observed for FORSUD, as 1 g/L of this
250 material was able to decrease the surface tension to 46 mN/m (the value for distilled
251 water is ca. 73 mN/m); although the other SBO also behave as surfactants, significantly
252 lower decreases in surface tension were measured. This different behavior can be
253 explained by considering the hydrophilic/hydrophobic ratio of these materials; **this**
254 **parameter was calculated as a ratio between the carbon atoms present at hydrophobic**
255 **functional groups (e.g. aliphatic or aromatic) and those present in hydrophilic moieties,**

256 such as carboxylic, hydroxylic, phenolic or amines. By comparing data of Table 2 and
257 Figure 1, it can be observed that the percentage of aliphatic carbon follows the same
258 trend as the decrease in the surface tension: FORSUD >> CVT230 > CVDFT110.

259

260 3.2. Biocompatibility of the SBO

261

262 BOD₅ was used to check the biodegradability of these materials in two different
263 concentrations, 100 mg/L and 1000 mg/L. Table 3 shows that low BOD₅ values were
264 obtained in all cases. As this parameter is highly influenced by the amount of organics
265 present in the solution, the BOD/COD ratio has been employed as a better indicator for
266 biodegradability [20]. This ratio was systematically below 0.1 (Table 3), what can be
267 associated with a poor biodegradability of SBOs. This could be attributed to the fact that
268 these materials have been submitted, for a long time, to the action of microorganisms
269 and hence, only the fraction refractory to biological degradation remains. Other organic
270 materials which are the result of the action of microbiological activity for long periods
271 of time also show poor biodegradability; examples of such substances are humic and
272 fulvic substances [21, 22] or landfill leachates [23].

273

274 However, low biodegradability should not be a major concern if it is not associated to
275 toxicity, as concentrations employed in wastewater treatment are systematically well
276 below 100 mg/L [15, 17, 24]. Results shown in Figure 2 indicate that the toxicity of
277 these materials is rather low in the range of concentrations tested (0-50 mg/L), as
278 toxicity values were lower than 30% in all the bioassays employed (based on *V. fischeri*,
279 *P. subcapitata* and *D. magna*), and even they were below 5% in most of the assays. This

280 implies that SBO can be classified as non-toxic materials showing very poor
281 biodegradability.

282

283 3.3. SBO as auxiliaries in photochemical methods for wastewater treatment

284

285 The role of SBO in photochemical methods for wastewater treatment has been
286 investigated in a series of previous papers, using CVT230. Briefly, results show that the
287 use of this material as photocatalyst under UV-visible light irradiation is not attractive,
288 as the screen effect of the strongly coloured SBO solutions compensate their capability
289 to generate reactive species [15, 17]. On the contrary, the use of SBO as iron
290 complexing agent to implement photo-Fenton process at mild conditions seems more
291 promising, as the reaction could be implemented at pH = 5 without a significant loss of
292 efficiency [24].

293

294 However, only results using CVT230 are available and the different composition of the
295 other SBO might influence their performances. Hence, photodegradation of a mixture of
296 six emerging pollutants (acetaminophen, caffeine, acetemiprid, clofibric acid,
297 carbamazepine and amoxicillin) was studied with all three substances, FORSUD,
298 CVT230 and CVDFT110. As happened with CVT230 [17], none of the SBO was able
299 to enhance the photolysis of the studied pollutants under visible light irradiation (data
300 not shown). On the other hand, Figure 3 shows the all three material were able to drive a
301 photo-Fenton process at mild conditions (pH = 5.2), as most pollutants were removed in
302 less than 30 min of irradiation and only acetamiprid required longer treatment times to
303 be completely eliminated (30-60 min). However some slight differences could be found
304 in the efficiency of all three materials, which followed the trend CVDFT110 \geq CVT230

305 > FORSUD. This could be attributed to differences in the functional groups present in
306 all three materials: CVDFT110 and CVT230 show relatively similar composition, with
307 lower amounts of aliphatic carbon, which is expected to be photochemically non active
308 and unable to complex iron; these functional groups are present in more extent in
309 FORSUD, showing the worst performance.

310

311 The toxicity of the sample was followed along the process according to the inhibition of
312 the luminescence of *V. fischeri*. It can be observed in Figure 4, that although a very
313 slight increase in the toxicity was observed, most probably due to the release of toxic
314 by-products at the early stages of the photochemical process, as reported before
315 elsewhere [26']; however, these values were very low (systematically below 15%) and
316 then decreased to reach final values below 5%. As the concentration of pharmaceuticals
317 in the environment is significantly lower than that employed in this work, and that SBO
318 amount should not be above 20 mg/L, this might indicate that the risk associated with
319 the release of toxic chemical during the process is acceptable, although further research
320 on this issue is still necessary.

321

322 3.4 Photostability of SBOs

323

324 It is interesting to study the photostability of the SBOs as in the wastewater treatment
325 processes they are also submitted to chemical photo-oxidation; furthermore, this
326 information might be valuable for studies on the behavior of anthropogenic organic
327 matter in the environment. For this purpose, they were irradiated (100 mg/L) for 24
328 hours with a solar simulator; DOC, COD and BOD₅ were determined at selected
329 sampling times. Figure 4 shows that there was a slow decrease in DOC and COD values

330 for CVT230, (ca. 25 % after 1 day of irradiation) indicating that some oxidation of SBO
331 occurred; this can be more easily appreciated by the chemical oxidation state (COS),
332 which is a parameter which relates the COD at the sampling with the initial DOC and a
333 COS value of +4 is assigned for CO₂ (the most oxidized species of carbon) and -4 for
334 CH₄ (the most reduced) [25]. During the process, the COS was increased from -0.9 to
335 +0.2, and it should be associated with an oxidation of the organics present in the
336 sample; a similar behavior was observed for CVDF110 and FORSUD (data not
337 shown). On the other hand, average oxidation state, which only refers to the organics
338 remaining in solution (CO₂ is excluded from calculations by employing the DOC at the
339 sampling time) did not suffer significant changes oscillating between -1 and -0.6
340 throughout the process; hence, no dramatic changes in the composition of the remaining
341 organics might be expectable. Regarding to biocompatibility, the BOD₅/COD ratio was
342 calculated after 24 hours of irradiation and the obtained values were 0.24 for
343 CVDF110, 0.08 for CVT230 and 0.14 for FORSUD; this ratio was in all cases slightly
344 above that calculated for the same SBO before irradiation; finally, toxicity values did
345 not vary significantly throughout the process (data not shown). A possible explanation
346 to the above described trends is that the SBO molecules are partly oxidized into smaller
347 and more hydrophilic ones which can be more easily metabolized by micro-organisms.
348 A decrease of the molecular weight of macromolecules under irradiation is a well-
349 known behaviour for macromolecules, for instance it has been observed for humic and
350 fulvic substances when they were irradiated [26].

351

352 The same procedure was followed in the presence of hydrogen peroxide, as it has been
353 described that the amounts of iron present in the SBO composition can drive a photo-
354 Fenton like process. For this purpose, the stoichiometric amount of peroxide required to

355 oxidize completely each SBO was added and it was irradiated until the solution was free
356 of H₂O₂. Table 4 shows variations in significant parameters. In all cases, similar trends
357 were obtained, only diverging in the numerical values, which should not be
358 overemphasized: a) there was a moderate mineralization of the samples, in the range 20-
359 30%, b) COD also decreased with a concomitant increase in COS, what indicates that
360 stronger oxidation than for photolysis was obtained, c) AOS also increased, although
361 variation was lower than for COS what might indicate that severe modification of
362 organics remaining in solution should be ruled out, d) there was some increase in
363 biodegradability as shown by higher BOD₅ values, and more clearly by the BOD/COD
364 ratio, although these changes were not very acute, e) surface tension increased to reach
365 values close to that of distilled water, f) the E₂/E₃ ratio significantly increased. All these
366 data are again in agreement with a cleavage of the starting SBO to generate smaller,
367 more oxidized and more hydrophilic substances. In fact, similar trends have been
368 observed for landfill leachates [27].

369

370 It was also interesting to determine the effect of mild photo-Fenton on SBOs oxidation
371 For this purpose the three different SBOs (100 mg/L) were submitted to a photo-Fenton
372 at pH = 5.2 with the stoichiometric amount of hydrogen peroxide and 5 mg/L of
373 iron(II). Data obtained after 4 hours of irradiation showed very similar trends to that
374 irradiated for one day, with DOC and COD decreases systematically above 50% (in
375 some cases up to 75%) and the E₂/E₃ was between 4 and 5 for CVT230 and CVDFT110
376 while it reached 15 in the case of FORSUD.

377

378 Finally, the effect of oxidation on SBO performance was also analyzed. For this
379 purpose, samples containing 100 mg/L of each SBO were irradiated in the presence of

380 the stoichiometric amount of hydrogen peroxide; once they were free of hydrogen
381 peroxide, 25 mL of this solution was diluted to 250 mL (to reach an initial SBO
382 concentration of 10 mg/L); the emerging pollutants (acetaminophen, caffeine,
383 acetamiprid, clofibrac acid, carbamazepine and amoxicillin) were added (5 mg/L of
384 each), as well as hydrogen peroxide (half the stoichiometric amount required to oxidize
385 the pollutants) and iron (5 mg/L); finally the pH adjusted to 5.2 and the mixture was
386 irradiated. A plot of the relative concentration of each pollutant vs. time can be found in
387 Figure 5. When comparing with Figure 2, it can be observed that all three photo-
388 oxidized materials were still able to drive a mild photo-Fenton. Nonetheless differences
389 among them can be appreciated: while photo-treated FORSUD showed better
390 performance than the original material, the reverse was true for the others. This might
391 be due to differences in the functional groups present in those substances: oxidation of
392 FORSUD, where aliphatic carbon has predominance, might result in an increase in the
393 number of hydrophilic groups able to complex iron; on the other hand, in CVDFT110
394 and CVT230, oxidation might result in a stronger degradation of the molecules and
395 some loss of photochemical activity.

396

397 **4. Conclusions**

398 The obtained results underline the importance of SBO characterization and of
399 establishing structure-properties relationship in order to optimize the choice of the
400 product to be used depending on the specific application. With particular attention to
401 mild photo-Fenton processes, this work shows the importance of carefully considering
402 the effect of irradiation not only on the target pollutant to be degraded but also on the
403 SBO used to promote the pollutant degradation, in order to choose the most efficient for
404 longer times.

405

406 Despite their low biodegradability, SBO do not show relevant toxicity, thus encouraging
407 further investigation on their use in mild photo-Fenton processes.

408

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414

415 **References**

416 [1] A. Demirbas, *Energy Convers. Manage.* 50 (2009) 2782-2801.

417 [2] E. Montoneri, D. Mainero, V. Boffa, D.G. Perrone, C. Montoneri, C. *Int. J. Global*
418 *Environ. Issues* 11 (2011) 170-196.

419 [3] E. Montoneri, V. Boffa, P. Savarino, D.G. Perrone, M. Ghezzi, C. Montoneri, M.
420 Mendichi, *Waste Manage.* 31 (2011) 10-17.

421 [4] P. Quagliotto, E. Montoneri, F. Tambone, F. Adani, R. Goberto, G. Viscardi,
422 *Environ. Sci. Technol.* 40 (2006) 1686-1692.

423 [5] V. Boffa, D.G. Perrone, E. Montoneri, G. Magnacca, L. Bertinetti, L. Garlasco, R.
424 Mendichi, *ChemSusChem* 3 (2010) 445-452.

425 [6] E. Montoneri, L. Tomasso, N. Colajanni, I. Zelano, F. Alberi, G. Cossa, R. Barberis,
426 *Int. J. Environ. Sci. Technol.* 11 (2014) 251-262.

427 [7] O. Sortino, M. Dipasquale, E. Montoneri, L. Tomasso, P. Avetta, A. Bianco Prevot,
428 *Agron. Sustain. Dev.* 33 (2013) 433-441.

- 429 [8] C. Montoneri, E. Montoneri, L. Tomasso, A. Piva, *J. Agriculture Sci.* 13 (2013) 31-
430 44.
- 431 [9] C. Tixier, H.P. Singer, S. Oellers, S.R. Müller, *Environ. Sci. Technol.* 37 (2003)
432 1061-1068.
- 433 [10] J. Peuravuori, K. Pihlaja, *Anal. Bioanal. Chem.* 394 (2009) 1621-1636.
- 434 [11] J.J. Guerard, Y.P. Chin, H. Mash, C.M. Hadad, *Environ. Sci. Technol.* 43 (2009)
435 8587-8592.
- 436 [12] P. Avetta, A. Bianco Prevot, D. Fabbri, E. Montoneri, L. Tomasso, *Chem. Eng. J.*
437 197 (2012) 193-198.
- 438 [13] A. Bianco Prevot, P. Avetta, D. Fabbri, E. Laurenti, T. Marchis, D.G. Perrone,
439 Montoneri, V. Boffa, *ChemSusChem*, 4 (2011) 85-90.
- 440 [14] A. Bianco Prevot, D. Fabbri, E. Pramauro, C. Baiocchi, C. Medana, E. Montoneri,
441 V. Boffa, *J. Photochem. Photobiol. A: Chem.* 209 (2010) 224-231.
- 442 [15] J. Gomis, R.F. Vercher, A.M. Amat, D.O. Mártire, M.C. González, A. Bianco
443 Prevot, E. Montoneri, A. Arques, L. Carlos, *Catal. Today* 209 (2013) 176-180.
- 444 [16] J.J. Pignatello, E. Oliveros, A. MacKay, *Crit. Rev. Environ. Sci. Technol.* 36
445 (2006) 1-84.
- 446 [17] J. Gomis, A. Bianco Prevot, E. Montoneri, M.C. González, A.M. Amat, D.O.
447 Mártire, A. Arques, L. Carlos, *Chem. Eng. J.* 235 (2014) 236-243.
- 448 [18] L. Carlos, D.O. Martire, M.C. Gonzalez, J. Gomis, A. Bernabeu, A.M. Amat, A.
449 *Water Res.* 46 (2012) 4732-4740.
- 450 [18] APHA, AWWA, WPCF, *Standard Methods for the examination of water and*
451 *wastewater*. 20th edition. American Public Health Association, Washington DC, 1998.
- 452 [19] J. Peuravuori, K. Pihlaja, *Anal. Chim. Acta* 337 (1997) 133-149.
- 453 [20] W. Guhl, J. Steber, *Chemosphere* 63 (2006) 9-16.

- 454 [21] R. G. Quails, B. L. Raines, *Soil Sci. Soc. Am. J.* 56 (1992) 578-586.
- 455 [22] Xu, X.Y., Zeng, G.M., Peng, Y.R., Zeng, Z., *Chem. Eng. J.* 200-202 (2012) 25-31.
- 456 [23] J. Lopes de Morais, P. Peralta Zamora, *J. Hazard. Mater. B* 123 (2005) 181-186.
- 457 [24] J. Gomis, L. Carlos, A. Bianco Prevot, A.C.S.C. Teixeira, M. Mora, A.M. Amat, R.
458 Vicente, A. Arques, *Catal Today*, 2014, in press.
- 459 [25] A.M. Amat, A. Arques, F. Galindo, M.A. Miranda, L. Santos-Juanes, R.F. Vercher,
460 R. Vicente, *Appl. Catal. B: Environ.* 73 (2007) 51-57.
- 461 [26'] A. Bernabeu, S. Palacios, R. Vicente, R. Vercher, S. Malato, A. Arques, A.M.
462 Amat, *Chem Eng. J.* 198-199 (2012) 65-72.
- 463 [26] L. Lou, H. Xie, *Chemosphere* 65 (2006) 2333-2342
- 464 [27] R.C. Martins, D.V. Lopes, M.J. Quina, R.M. Quinta-Ferreira, *Chem. Eng. J.* 192
465 (2012) 219-225.

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467

468 Table 1. Elemental composition of the three batches of SBOs employed in this work.

	FORSUD	CVDF	CVT230
Volatile solids (% w/w)	84.6	72.7	72.1
Carbon (% w/w)	45.1	35.5	38.2
Nitrogen (% w/w)	7.8	4.3	4.0
Si (% w/w)	0.36	0.92	2.55
Fe (% w/w)	0.16	0.53	0.77
Al (% w/w)	0.78	0.44	0.49
Mg (% w/w)	0.18	0.49	1.13
Ca (% w/w)	1.32	2.59	6.07
K (% w/w)	9.2	5.4	3.6
Na (% w/w)	0.39	0.15	0.16
Cu (mg/kg)	100	216	202
Ni (mg/kg)	27	71	92
Zn (mg/kg)	185	353	256
Cr (mg/kg)	11	30	19
Pb (mg/kg)	44	75	85
Hg (mg/kg)	0.2	0.4	0.2

469

470

471 Table 2. Main functional groups present in the three batches of SBOs that are studies

	FORSUD	CVDFT110	CVT230
Aliphatic carbon (%)	43	31	37
Amine (%)	10	8	7
Methoxy (%)	4	-	-
Alkoxy (%)	10	20	14
Anomeric carbon (%)	3	7	4
Aromatic (%)	10	16	13
Phenolic carbon (%)	2	6	5
Phenoxy (%)	1	2	2
Carboxylic (%)	7	9	12
Amide (%)	9	1	1
Carbonilic (%)	1	-	5
Lipophilic/hydrophilic ratio	9.3	5.3	3.6
Aliphatic/aromatic ratio	3.3	1.3	1.8
E ₂ /E ₃ ratio	3.83	2.31	2.38

472

473

474 Table 3: BOD₅ values and BOD/COD ratio obtained for all three different types of
475 SBOs at two different concentrations (COD values are shown in Table 4)

	100 mg/l		1 g/l	
	BOD (mg/l)	BOD/COD	BOD (mg/l)	BOD/COD
CVDFT 110	6	0.06	20	0.02
CVT 230	4	0.04	30	0.03
FORSUD	10	0.09	80	0.08

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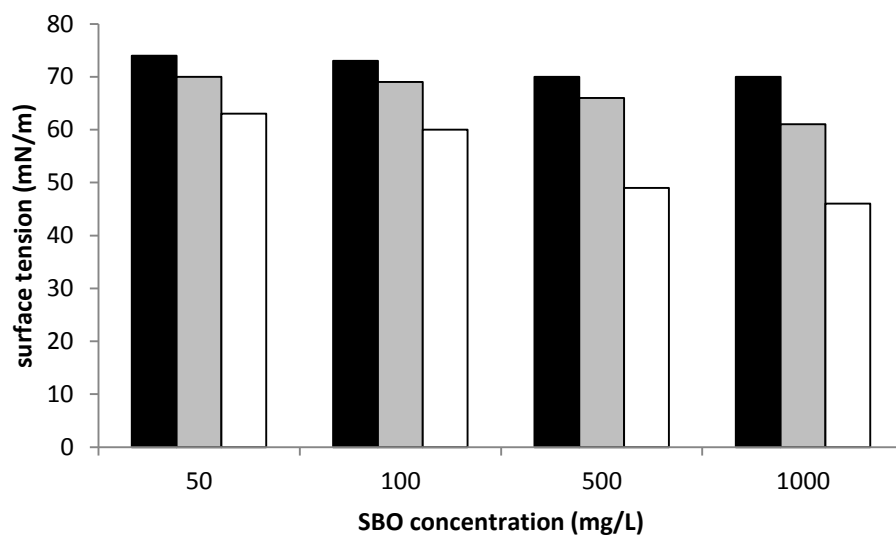
478 Table 4: Irradiation of all three SBOs in the presence of hydrogen peroxide: main
 479 parameters before and after irradiation. The initial SBO concentration was 100 mg/L, the
 480 concentration of H₂O₂ was 215 mg/L (the stoichiometric amount required to oxidize
 481 completely the SBO) and irradiation time was 6 hours.

482

	CVDFT 110		CVT 230		FORSUD	
	Before	Irradiated	Before	Irradiated	Before	Irradiated
DOC (mg/l)	30.2	23.9	28.2	23.5	35.0	25.0
COD (mg/l)	101	76	95	63	111	67
BOD ₅	6	15	4	9	10	15
AOS	-1,01	-0.76	-1.04	0.02	-0.77	0.08
COS	-1,01	0.24	-1.04	0.65	-0.77	1.12
BOD/COD	0.06	0.20	0.04	0.14	0.09	0.22
Surface tension	73	73	69	73	60	66
E ₂ /E ₃ ratio	2.31	3.55	2.38	3.89	3.83	11.1

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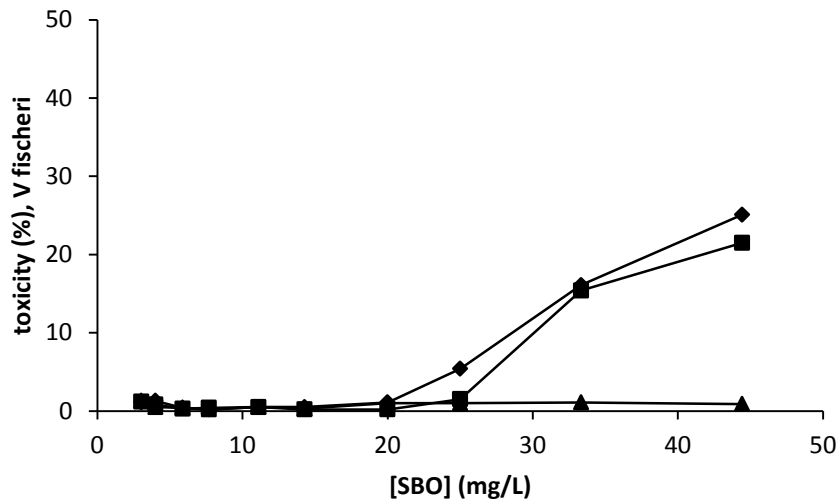


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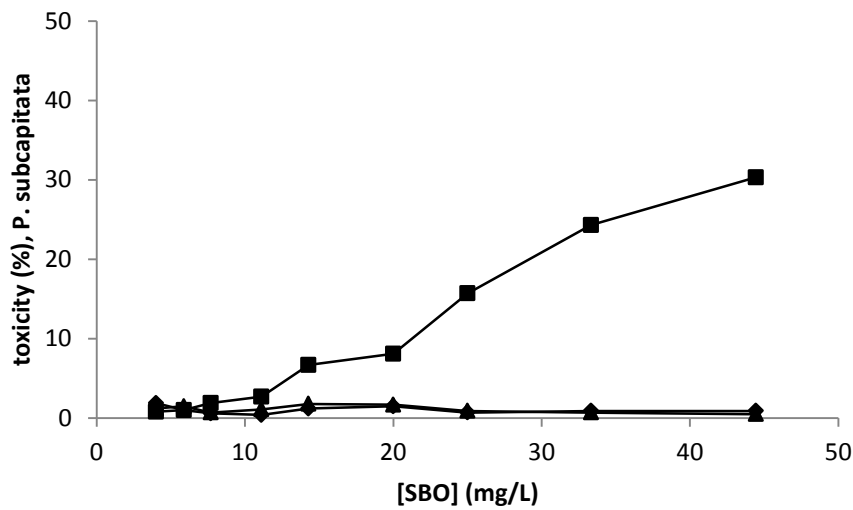
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487 Figure 1: Surface tension of solutions containing different concentrations of three
488 batches of SBOs: CVDFT 110 (black bars) CVT 230 (grey bars), FORSUD (white
489 bars).

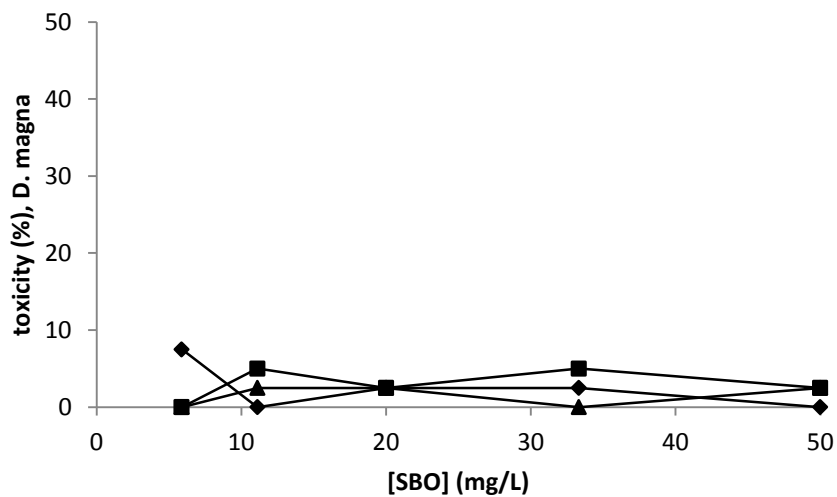
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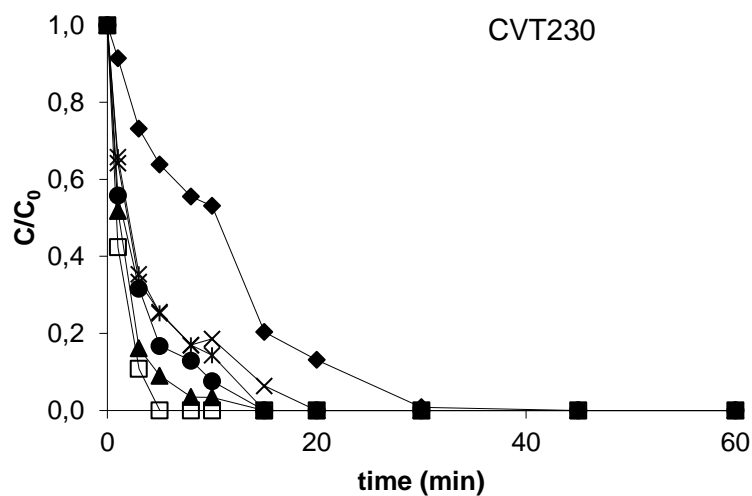
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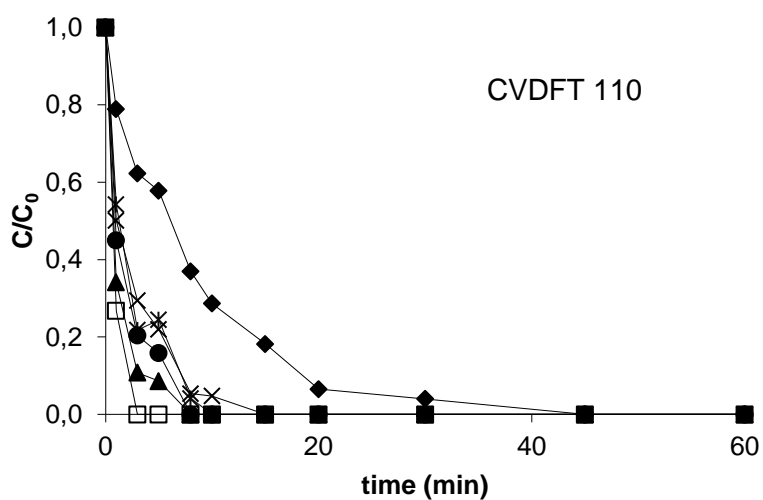
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494 Figure 2: Toxicity of three different batches of SBOs (CVDFT 110 (♦) CVT 230 (■),
 495 FORSUD (▲)) measured according to bioassays based on *V. fischeri* (above), *P.*
 496 *subcapitata* (middle) and *D. magna* (below).

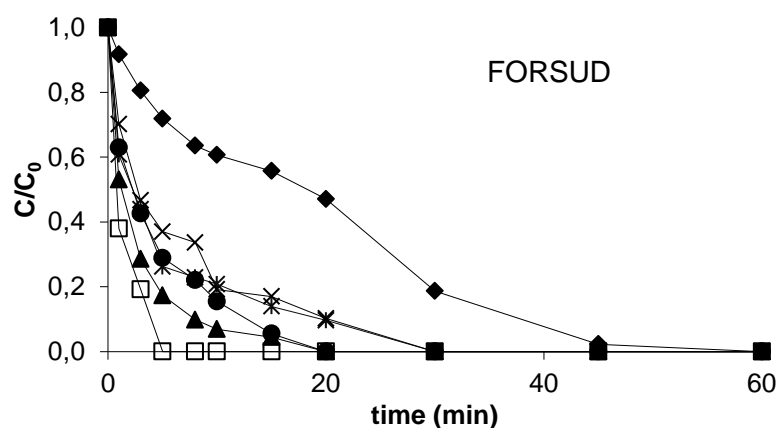
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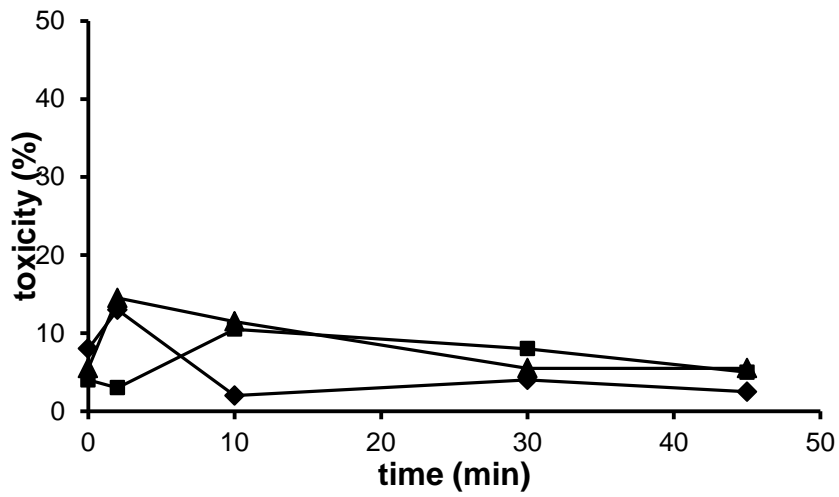


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504 Figure 3. Photo-Fenton process at pH = 5.2 in the presence of three types of SBOs:
505 CVT 230 (above), CVDFT 110 (middle) and FORSUD (below). Plot of the relative
506 concentration of pollutant vs time: amoxicillin (□), acetaminophen (*), acetemiprid
507 (◆), caffeine (×), clofibric acid (●) and carbamazepine (▲)

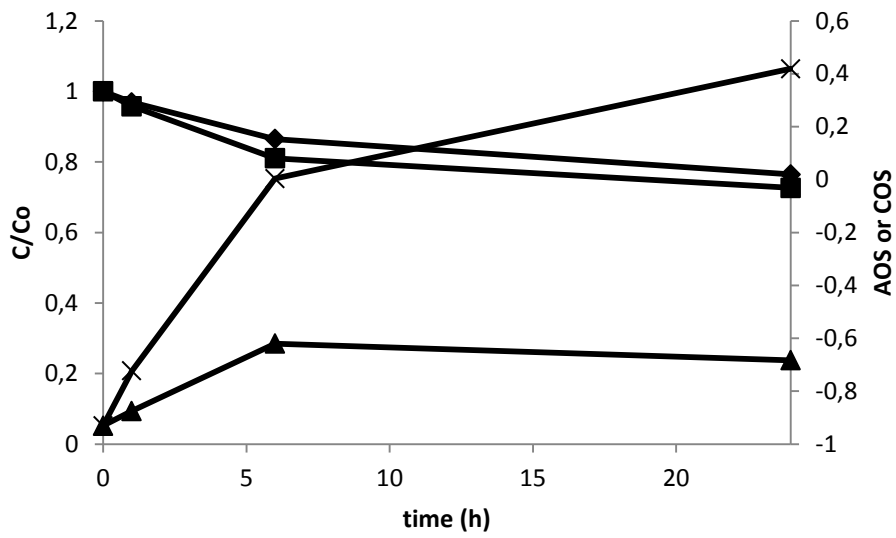


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509 Figure 4: Inhibition of the luminescence of *V. fischeri* bacteria obtained during a photo-
 510 Fenton process at pH = 5.2 of the mixture of six pollutants in the presence of three types
 511 of SBOs: CVT 230 (♦), CVDFT 110 (■) and FORSUD (▲).

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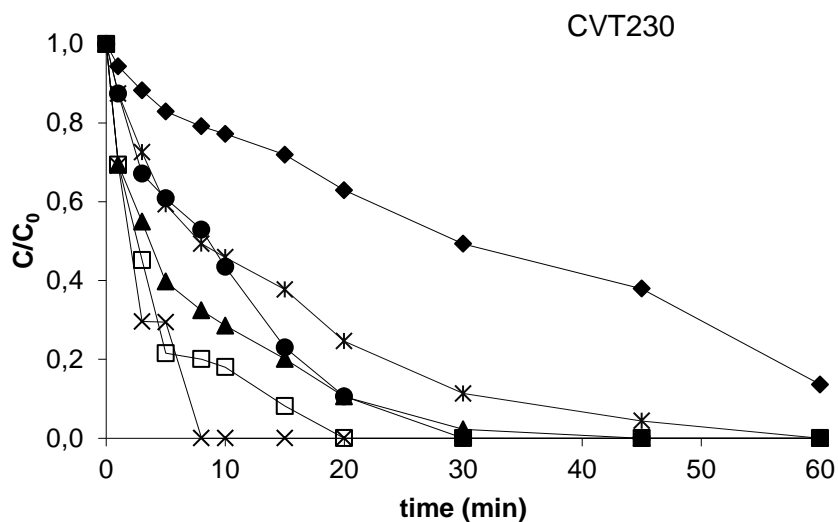


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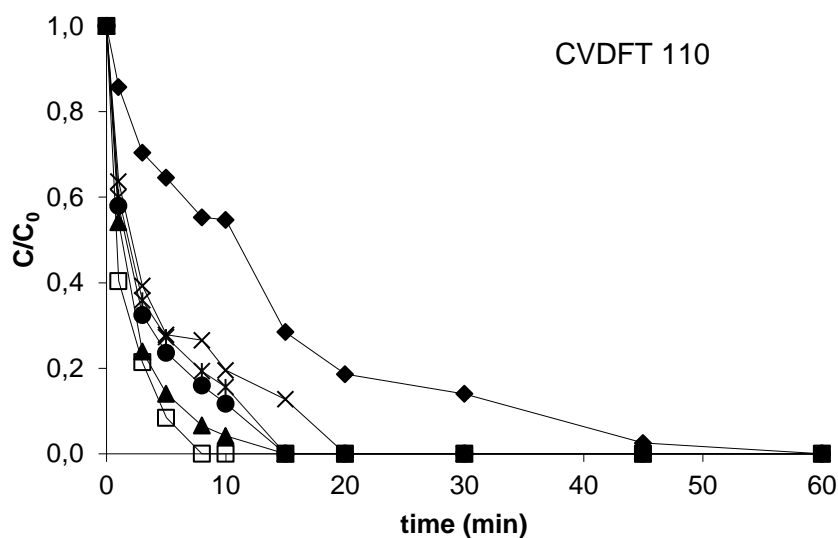
515 Figure 5: Changes in COD (■), DOC (◆), AOS (▲) and COS (×) vs. irradiation time
516 for CVT 230.

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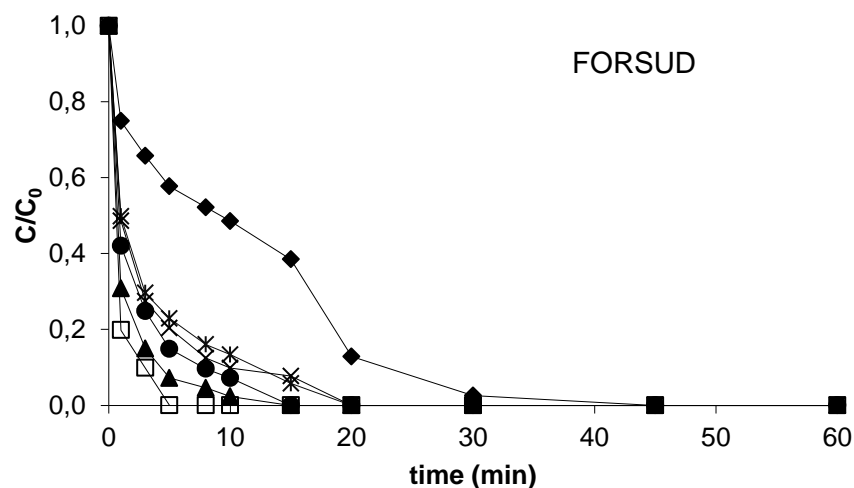
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522 Figure 6. Photo-Fenton process at neutral pH in the presence of three types of irradiated
 523 SBOs: CVT 230 (above), CVDFE 110 (middle) and FORSUD (below). Plot of the
 524 relative concentration of pollutant vs time: amoxicillin (□), acetaminophen (*),
 525 acetemiprid (◆), caffeine (×), clofibric acid (●) and carbamazepine (▲)

