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Additional Information

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

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Graphical abstract

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Highlights

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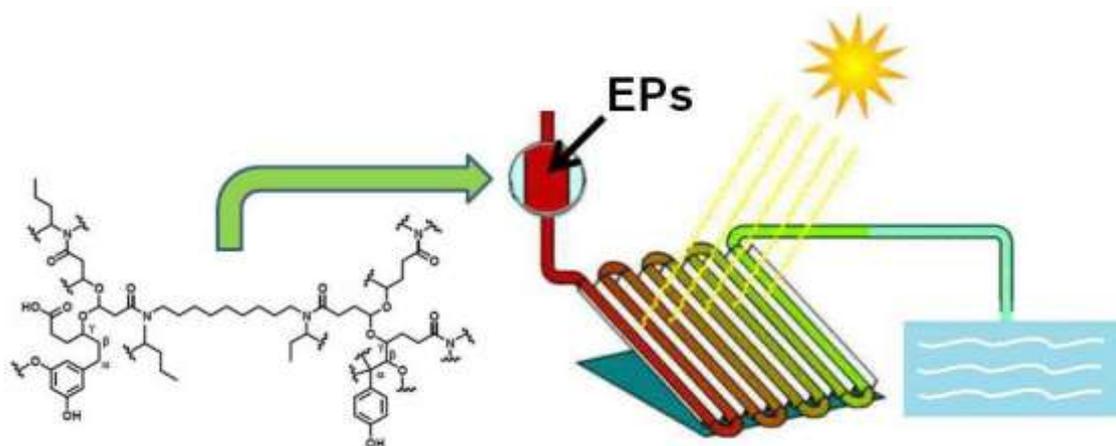
Soluble bio-based substances (SBO) have been employed to drive a mild photo-Fenton

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

The SBO composition is related with their performance in photochemical processes

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Keywords: SBO, photostability, photo-Fenton, biocompatibility

30

Abstract

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

water soluble bio-based substances (SBO) in photo-oxidative processes for wastewater

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

Differences in the functional groups present in these substances can explain major trends

in their physical/chemical properties. Bioassays have proven those materials to be non-

toxic but to show poor biodegradability. Their ability to enhance a photo-Fenton process

at milder pH (5.2) has been investigated using a mixture of emerging compounds in

wastewaters. All the tested SBO were able to remove all pollutants in less than one hour

irradiation, and the best results were obtained with those substances showing higher

41 hydrophilic/hydrophobic ratio. Moreover, although SBOs themselves undergo a slight

42 oxidation, no relevant negative effect has been observed for their use in wastewater

43 treatment.

44

45 **1. Introduction**

46

47 Generation of increasing amount of wastes from human activities has become a serious

48 environmental concern. Developing technologies and processes able to minimize their

49 production should be a priority; however, this is not always possible and alternative

50 approaches are required to deal with this problem, such valorization through their re-use

51 in other processes. In this context, much effort has been devoted in recent years to obtain

52 valuable products from urban bio-wastes (UBW) (see [1] and references therein cited).

53

54 UBW have become a sustainable source of valuable materials, such as water soluble bio-

55 organic substances (SBO). They have been isolated from organic wastes submitted to

56 anaerobic and/or aerobic treatment, yielding biomasses successively hydrolyzed at

57 alkaline pH, the obtained solutions submitted to ultrafiltration, then the retentate is dried

58 and soluble bio-based products obtained as potassium salts [2]. Depending on the origin

59 and treatment of the sourcing UBW, different batches of SBO can be obtained, showing

60 a wide range of chemical composition and properties [3]. In general, SBO are constituted

61 by a mixture of macromolecules which average molecular weight ranges from 67 to 463

62 kg mol^{-1}. These supramolecular assemblies contain long aliphatic chains, aromatic rings

63 and several functional groups as carboxyl, primary and substituted amine and amide,

64 carbonyl, hydroxyl, phenol, ether or esther. Previous papers studied the potential

65   applications of SBO as surfactants [4], in materials chemistry [5], in soil-washing

66   treatments [6], in agriculture [7] or animal husbandry [8].

67

68   SBO chemical composition shows high similarity with that of dissolved organic matter

69   (DOM, e.g. humic or fulvic acids), which is known to generate, upon solar irradiation,

70   highly reactive species able to oxidize pollutants, thus contributing to the abiotic self-

71   remediation of natural ecosystems [9-11]. For this reason, SBO might also be employed

72   in solar photochemical processes for wastewater treatment. Some works have been

73   published reporting on the use SBO as photosensitizer for the degradation of aromatic

74   sulphonic acids [12], phenols [13] or dyes [14, 15]. In addition, SBO might be used to

75   drive a photo-Fenton process under milder conditions. Photo-Fenton is based on the

76   ability of iron salts to decompose hydrogen peroxide into highly reactive species, and the

77   process is greatly enhanced upon irradiation [16]. One major drawback is the highly

78   acidic pH which is required to avoid the formation of photochemically inactive iron

79   oxides and hydroxides; in this context the ability of SBO to complex metal cations, such

80   as iron, is useful for the development of photo-Fenton at circumneutral media [17].

81

82   However, some important issues still remain unexplored. For instance, SBO could only

83   be employed for wastewater detoxification if they show a good biocompatibility, namely

84   low toxicity and high biodegradability. Furthermore, SBO are mainly formed of organic

85   molecules, and can in turn be attacked by reactive species generated in the photo-

86   oxidative processes, with possible changes in their biological or chemical properties. Any

87   modification in SBO composition might result in different performance of these materials

88   and hence, comparison of different batches of SBO is meaningful. With this background

89   the aim of this paper is to gain further insight into the performance, photo-stability and

90 biocompatibility of three types of SBO obtained from different sources. A battery of

91 bioassays have been employed for toxicity and biodegradability determination; SBO

92 performance before and after irradiation has been tested in the degradation of a mixture

93 of emerging pollutants (EPs), namely acetaminophen, caffeine, amoxicillin, clofibric

94 acid, carbamazepine and acetamiprid. These chemicals have been chosen because they

95 are examples of xenobiotics commonly employed in the literature and they have

96 previously employed as target pollutants in works involving SBO in the photo-Fenton

97 process [17].

98

99 **2. Experimental**

100

101 2.1. Materials

102

103 The following types of SBO were employed: a) FORSUD, isolated from the urban waste

104 organic humid fraction (UWOHF) obtained from separate source collection, mixed with

105 the digestate from an anaerobic reactor fed with UWOHF; b) CVT230, obtained from

106 home gardening and park trimming residues (GR) piles aerated for 230 days; c)

107 CVDFT110, isolated from a mixture 35/55/10 (w/w/w) of FORSUD, GR and urban

108 sewage sludge mix, aerated for 110 days. Chemical composition for sourcing bio-wastes

109 (BW) has been reported in detail in the previously published paper [3].

110

111 The SBO isolation was performed in a pilot plant at the Studio Chiono & Associati in

112 Rivarolo Canavese, Italy [2]. Briefly, it consisted in an electrically heated and

113 mechanically stirred 500 L reactor, a 102 cm long x 10.1 cm diameter polysulfone

114 ultrafiltration (UF) membrane with 5 kDa molecular weight cut-off, and a forced

115 ventilation drying oven. A stirred stainless steel reactor was loaded with 300 L of aqueous

116   solution of KOH and 75 kg of solid biomass at 65 °C and a pH value of ca. 13. After 4

117   hours, the reactor turned off automatically and the mixture was settled down overnight.

118   The supernatant was pumped to a centrifuge (9000 rpm) to remove the small insoluble

119   fraction (mainly silicoaluminates) that was still present after the treatment. The recovered

120   liquid phase was flown at 40 L/h through an UF membrane operating with tangential flow

121   at 7 bar inlet and 4.5 bar outlet pressure to yield a retentate containing 5-10 % of dry

122   matter, which was finally dried at 60 °C. Solid SBO products were obtained in 15-30 %

123   w/w yield, relatively to the starting UBW dry matter. The analytical procedures used to

124   measure the elemental composition and functional groups of SBO were ^{13}C NMR,

125   microanalysis and potentiometric titration, and have been described in detail in previous

126   papers [18, 19].

127

128   Acetaminophen, caffeine, amoxicillin, clofibric acid, carbamazepine and acetamiprid,

129   employed as target pollutants, were purchased from Sigma-Aldrich. Hydrogen peroxide

130   (30% v/v) and ferrous sulphate were supplied by Panreac. Water employed in all the

131   experiments was Milli-Q grade.

132

133   The bioluminescent bacteria *Vibrio fischeri* (strain NRRL-B-11177) were purchased by

134   Macherey-Nagel GmbH & Co. (Düren, Germany). *P. subcapitata*, and ephippia (dormant

135   eggs) of crustacean *Daphnia magna* were supplied by ECOtest S.L. (Valencia, Spain)

136

137   2.2. Reactions

138

139   Experiments devoted to check the SBO photo-stability were performed in cylindrical

140   Pyrex vessel (55 mm i.d.). A solar simulator (Sun 2000, ABET Technologies) equipped

141 with a 550 W Xenon Short Arc Lamp was used as irradiation source (see [20] for the

142 spectrum, which closely matches the solar one). For each experiment, the reactor was

143 loaded with 250 mL of solution containing the SBO (100 mg/L). The pH was adjusted to

144 the desired value by adding diluted sulphuric acid. Eventually, the stoichiometric amount

145 of hydrogen peroxide required to oxidize completely each SBO was added, and irradiation

146 was kept until the solution was free of H_2O_2. The amount of H_2O_2 was obtained from the

147 initial chemical oxygen demand (COD) of the SBO, as COD indicates the amount of O_2

148 required to oxidize completely the sample.

149

150 The same experimental device was employed to check the performance of SBO in a mild

151 photo-Fenton process. In this case, the mixture of all six EPs was employed at an initial

152 concentration of each pollutant of 5 mg/L. All three types of SBO (10 mg/L) were used

153 in parallel experiments. The initial concentration of iron(II) was 5 mg/L (added as sulfate

154 salt) and half the stoichiometric amount of hydrogen peroxide to mineralize the pollutants

155 present in the solution was added. The pH was adjusted to 5.2.

156

157 2.3. Chemical analysis

158

159 The EPs concentration was determined by chromatography (Perkin Elmer model Flexar

160 UPLC FX-10) equipped with a UV-vis detector. A DB-C18 Brownlee Analytical column

161 was used and the eluent was a mixture of acetonitrile (A) and a 0.1% formic acid aqueous

162 solution (B); its composition was changed in a linear gradient, from 3% A to 70% A in 8

163 min with a flow rate of 0.3 mL/min. Wavelengths employed for detection were: 205 nm

164 (acetaminophen, amoxicillin, caffeine and carbamazepine), 225 nm (clofibric acid) and

7

165 245 nm (acetamiprid). Samples were filtered through polypropylene filters (VWR, 0.45

166 µm) before analysis.

167

168 Dissolved organic carbon (DOC) was determined with a Shimadzu model TOC-V CSH

169 apparatus. Chemical oxygen demand (COD) was determined according to the dichromate

170 method [21]: sample digestions were performed at 148ºC in a Thermoreaktor TR300

171 (Merck) and a Spectroquant NOVA 60 (Merck) was used for the photometric

172 determination.   The surface tension of samples was determined by a Krüss K-9

173 tensiometer.

174

175 2.4. Bioassays

176

177 In order to check the biodegradability of all three substances, biological oxygen demand

178 (BOD_5) assays were carried out according to the standard manometric method (OECD

179 301 B, CO_2 evolution test), using an OxiTop[©] (WTW) to seal the bottle and determine

180 the pressure inside [21]. The BOD_5 values were determined for SBO concentrations of

181 100 mg/L and 1000 mg/L.

182

183 Toxicity assays based on V. *fischeri* bacteria were performed based on ISO 11348-3:2007

184 standardized test; algae growth inhibition assay was performed according to an adaptation

185 of ISO 8692:2004 test, using the chlorophyceae algae *Pseudokirchneriella subcapitata*;

186 bioassays based on the inhibition of the mobility of D. magna were performed according

187 to the standard ISO 6341:199632 procedure. A detailed description of the experimental

188 procedure followed in all three cases can be found as Suplementary Data (S1). They were

189 chosen as examples of bioassays commonly employed to detect toxicity in water

190 involving different micro-organisms, namely bacteria, algae and crustaceans, in order to

191 better assess the toxicity of these substances in water.

192

193 **3. Results**

194

195 3.1. Chemical and physical characterization of the SBO

196

197 A chemical characterization of FORSUD, CVT230 and CVDFT110 is summarized in

198 Table 1. Data show that FORSUD has the highest organic content, as indicated by the

199 percentages of volatile solids and carbon; on the other hand, scarce differences can be

200 found between CVT230 and CVDFT110 regarding this parameter. It is interesting to

201 notice that a significant amount of metals can be found in all three materials; this can be

202 due either to metal already present in the starting materials or added in the isolation

203 process (e.g. potassium). The presence of metals, in particular iron, might be of interest,

204 as the ability of complexed iron to drive a photo-Fenton process at mild conditions has

205 been recently described [17]; on the other hand, heavy metals, although found at very low

206 amounts, might be a concern, and hence, bioassays to determine SBO biocompatibility

207 are required.

208

209 The gross amount of ions released into the aqueous medium might be important for the

210 performance of a photo-oxidative reaction and can be related to the conductivity of

211 solutions of these substances. Although values are not very different, higher conductivity

212 was measured for FORSUD (29 mS/cm for 1 g/L concentration, 9 mS/cm for 50 mg/L)

213 while lower values were obtained for the other two studied materials (8-12 mS/cm for 1

214 g/L and 0.3-0.5 mS/cm for 50 mg/L).

215

216 In addition, the relative amount of some functional groups present in all three SBOs is

217 shown in Table 2. In the case of FORSUD, aliphatic carbon is the predominating species

218 (43 %), and although this is also true for the other SBOs, the proportion is lower (31-

219 37%); on the other hand aromatic carbon is more abundant in CVDFT110 and CVT230.

220 Consequently, the aliphatic/aromatic ratio obtained was clearly higher for FORSUD than

221 for the other two SBOs. It is interesting to note that, again in this case, similar composition

222 was obtained for CFDFT110 and CVT230.

223

224 Another useful gross parameter employed in characterization of natural organic matter is

225 the E_2/E_3 ratio [22], where E_2 and E_3 are the absorbances at 250 nm and 365 nm

226 respectively; this ratio has been related with the average molecular weight of the

227 macromolecules, as well as its aromaticity (the higher ratio, the lower aromaticity and

228 molecular weight). The application to the E2/E3 ratio to SBO gave results consistent with

229 theier composition: higher values for E_2/E_3 were indeed obtained for FORSUD (3.83)

230 that, as stated above, shows the minor proportion of aromatic groups; lower values were

231 obtained for the other two SBO (ca. 2.3)

232

233 The structure of the SBO can be also related their surfactant activity. In order to gain

234 further insight into this behavior, surface tension of water was measured in the presence

235 of four different concentrations of these materials. Results given in Figure 1 shows that

236 higher decreases in surface tension were observed for FORSUD, as 1 g/L of this material

237 was able to decrease the surface tension to 46 mN/m (the value for distilled water is ca.

238 73 mN/m); although the other SBO also behave as surfactants, significantly lower

239 decreases in surface tension were measured. This different behavior can be explained by

240 considering the hydrophilic/hydrophobic ratio of these materials; this parameter was

241 calculated as a ratio between the carbon atoms present at hydrophobic functional groups

242 (aliphatic, aromatic, methoxy, amide, amine, alkoxy, phenoxy, and anomeric) and those

243 present in hydrophilic moieties (carboxylic, phenol or ketones). By comparing data of

244 Table 2 and Figure 1, it can be observed that the percentage of aliphatic carbon follows

245 the same trend as the decrease in the surface tension: FORSUD $\gg$ CVT230 $>$

246 CVDFT110.

247

248 3.2. Biocompatibility of the SBO

249

250 BOD_5 was used to check the biodegradability of these materials in two different

251 concentrations, 100 mg/L and 1000 mg/L. Table 3 shows that low BOD_5 values were

252 obtained in all cases. As this parameter is highly influenced by the amount of organics

253 present in the solution, the BOD/COD ratio has been employed as a better indicator for

254 biodegradability [23]. This ratio was systematically below 0.1 (Table 3), what can be

255 associated with a poor biodegradability of SBOs. This could be attributed to the fact that

256 these materials have been submitted, for a long time, to the action of microorganisms and

257 hence, only the fraction refractory to biological degradation remains. Other organic

258 materials which are the result of the action of microbiological activity for long periods of

259 time also show poor biodegradability; examples of such substances are humic and fulvic

260 substances [24, 25] or landfill leachates [26].

261

262 However, low biodegradability should not be a major concern if it is not associated to

263 toxicity, as concentrations employed in wastewater treatment are systematically well

264 below 100 mg/L [15, 17, 27]. Results shown in Figure 2 indicate that the toxicity of these

265 materials is rather low in the range of concentrations tested (0-50 mg/L), as toxicity values

266 were lower than 30% in all the bioassays employed (based on *V. fischeri*, *P. subcapitata*

267 and *D. magna*), and even they were below 5% in most of the assays. This implies that

268 SBO can be classified as non-toxic materials showing very poor biodegradability.

269

270 3.3. SBO as auxiliaries in photochemical methods for wastewater treatment

271

272 The role of SBO in photochemical methods for wastewater treatment has been

273 investigated in a series of previous papers, using CVT230. Briefly, results show that the

274 use of this material as photocatalyst under UV-visible light irradiation is not attractive, as

275 the screen effect of the strongly coloured SBO solutions compensate their capability to

276 generate reactive species [15, 17]. On the contrary, the use of SBO as iron complexing

277 agent to implement photo-Fenton process at mild conditions seems more promising, as

278 the reaction could be implemented at pH = 5 without a significant loss of efficiency [27].

279

280 However, only results using CVT230 are available and the different composition of the

281 other SBO might influence their performances. Hence, photodegradation of a mixture of

282 six emerging pollutants (acetaminophen, caffeine, acetemiprid, clofibric acid,

283 carbamazepine and amoxicillin) was studied with all three substances, FORSUD,

284 CVT230 and CVDFT110. As happened with CVT230 [17], none of the SBO was able to

285 enhance the photolysis of the studied pollutants under visible light irradiation (data not

286 shown). On the other hand, Figure 3 shows the all three material were able to drive a

287 photo-Fenton process at mild conditions (pH = 5.2), as most pollutants were removed in

288 less than 30 min of irradiation and only acetamiprid required longer treatment times to

289 be completely eliminated (30-60 min); this is in sharp contrast with the experiments

290 carried out in the absence of SBO, where five of the pollutants still remained in the

291 solution after 60 min of irradiation, clearly showing the beneficial role of SBO. However

292 some slight differences could be found in the efficiency of all three materials, which

293 followed the trend CVDFT110 ≥ CVT230 > FORSUD. This could be attributed to

294 differences in the functional groups present in all three materials: CVDFT110 and

295 CVT230 show relatively similar composition, with lower amounts of aliphatic carbon,

296 which is expected to be photochemically non active and unable to complex iron; these

297 functional groups are present in more extent in FORSUD, showing the worst

298 performance.

299

300 The toxicity of the sample was followed along the process according to the inhibition of

301 the luminescence of V. fischeri. It can be observed in Figure 4, that although a very slight

302 increase in the toxicity was observed, most probably due to the release of toxic by-

303 products at the early stages of the photochemical process, as reported before elsewhere

304 [28]; however, these values were very low (systematically below 15%) and then

305 decreased to reach final values below 5%. As the concentration of pharmaceuticals in the

306 environment is significantly lower than that employed in this work, and that SBO amount

307 should not be above 20 mg/L, this might indicate that the risk associated with the release

308 of toxic chemical during the process is acceptable, although further research on this issue

309 is still necessary.

310

311 3.4 Photostability of SBOs

312

313 It is interesting to study the photostability of the SBOs as in the wastewater treatment

314 processes they are also submitted to chemical photo-oxidation; furthermore, this

315 information might be valuable for studies on the behavior of anthropogenic organic matter

316 in the environment. For this purpose, they were irradiated (100 mg/L) for 24 hours with

317 a solar simulator; DOC, COD and BOD_5 were determined at selected sampling times.

318 Figure 5 shows that there was a slow decrease in DOC and COD values for CVT230, (ca.

319 25 % after 1 day of irradiation) indicating that some oxidation of SBO occurred; this can

320 be more easily appreciated by the chemical oxidation state (COS), which is a parameter

321 which relates the COD at the sampling with the initial DOC and a COS value of +4 is

322 assigned for CO_2 (the most oxidized species of carbon) and -4 for CH_4 (the most reduced)

323 [29]. During the process, the COS was increased from -0.9 to +0.2, and it should be

324 associated with an oxidation of the organics present in the sample; a similar behavior was

325 observed for CVDFT110 and FORSUD (data not shown). On the other hand, average

326 oxidation state, which only refers to the organics remaining in solution (CO_2 is excluded

327 from calculations by employing the DOC at the sampling time) did not suffer significant

328 changes oscillating between -1 and -0.6 throughout the process; hence, no dramatic

329 changes in the composition of the remaining organics might be expectable. Regarding to

330 biocompatibility, the BOD_5/COD ratio was calculated after 24 hours of irradiation and

331 the obtained values were 0.24 for CVDFT110, 0.08 for CVT230 and 0.14 for FORSUD;

332 this ratio was in all cases slightly above that calculated for the same SBO before

333 irradiation; finally, toxicity values did not vary significantly throughout the process (data

334 not shown). A possible explanation to the above described trends is that the SBO

335 molecules are partly oxidized into smaller and more hydrophilic ones which can be more

336 easily metabolized by micro-organisms. A decrease of the molecular weight of

337 macromolecules under irradiation is a well-known behaviour for macromolecules, for

338 instance it has been observed for humic and fulvic substances when they were irradiated

339 [30].

340

341 The same procedure was followed in the presence of hydrogen peroxide, as it has been

342 described that the amounts of iron present in the SBO composition can drive a photo-

343 Fenton like process. For this purpose, the stoichiometric amount of peroxide required to

344 oxidize completely each SBO was added and it was irradiated until the solution was free

345 of H_2O_2. Table 4 shows variations in significant parameters. In all cases, similar trends

346 were obtained, only diverging in the numerical values, which should not be

347 overemphasized: a) there was a moderate mineralization of the samples, in the range 20-

348 30%, b) COD also decreased with a concomitant increase in COS, what indicates that

349 stronger oxidation than for photolysis was obtained, c) AOS also increased, although

350 variation was lower than for COS what might indicate that severe modification of

351 organics remaining in solution should be ruled out, d) there was some increase in

352 biodegradability as shown by higher BOD_5 values, and more clearly by the BOD/COD

353 ratio, although these changes were not very acute, e) surface tension increased to reach

354 values close to that of distilled water, f) the E_2/E_3 ratio significantly increased, which

355 could be correlated with a decrease in the molecular weight. All these data are again in

356 agreement with a cleavage of the starting SBO to generate smaller, more oxidized and

357 more hydrophilic substancess. In fact, similar trends have been observed for landfill

358 leachates [31].

359

360 It was also interesting to determine the effect of mild photo-Fenton on SBOs oxidation

361 For this purpose the three different SBOs (100 mg/L) were submitted to a photo-Fenton

362 at pH = 5.2 with the stoichiometric amount of hydrogen peroxide and 5 mg/L of iron(II).

363 Data obtained after 4 hours of irradiation showed very similar trends to that irradiated for

364 one day, with DOC and COD decreases systematically above 50% (in some cases up to

365   75%) and the E_2/E_3 was between 4 and 5 for CVT230 and CVDFT110 while it reached

366   15 in the case of FORSUD.

368   Finally, the effect of oxidation on SBO performance was also analyzed. For this purpose,

369   samples containing 100 mg/L of each SBO were irradiated in the presence of the

370   stoichiometric amount of hydrogen peroxide; once they were free of hydrogen peroxide,

371   25 mL of this solution was diluted to 250 mL (to reach an initial SBO concentration of

372   10 mg/L); the emerging pollutants (acetaminophen, caffeine, acetamiprid, clofibric acid,

373   carbamazepine and amoxicillin) were added (5 mg/L of each), as well as hydrogen

374   peroxide (half the stoichiometric amount required to oxidize the pollutants) and iron (5

375   mg/L); finally the pH adjusted to 5.2 and the mixture was irradiated. A plot of the relative

376   concentration of each pollutant vs. time can be found in Figure 6. When comparing with

377   Figure 2, it can be observed that all three photo-oxidized materials were still able to drive

378   a mild photo-Fenton. Nonetheless differences among them can be appreciated: while

379   photo-treated FORSUD showed better performance than the original material, the reverse

380   was true for the others. This might be due to differences in the functional groups present

381   in those substances: oxidation of FORSUD, where aliphatic carbon mas predomination,

382   might result in an increase in the number of hydrophylic groups able to complex iron; on

383   the other hand, in CVDFT110 and CVT230, oxidation might result in a stronger

384   degradation of the molecules and some loss of photochemical activity.

386   **4. Conclusions**

387   The obtained results underline the importance of SBO characterization and of establishing

388   structure-properties relationship in order to optimize the choice of the product to be used

389   depending on the specific application. With particular attention to mild photo-Fenton

16

390   processes, this work shows the importance of carefully considering the effect of

391   irradiation not only on the target pollutant to be degraded but also on the SBO used to

392   promote the pollutant degradation, in order to choose the most efficient for longer times.

393

394   Despite their low biodegradability, SBO do not show relevant toxicity, thus encouraging

395   further investigation on their use in mild photo-Fenton processes.

396

401

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458

459   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

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461

462   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

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464

465   Table 3: BOD$_5$ values and BOD/COD ratio obtained for all three different types of SBOs

466   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

467
468

469 Table 4: Irradiation of all three SBOs in the presence of hydrogen peroxide: main

470 parameters before and after irradiation. The initial SBO concentration was 100 mg/L, the

471 concentration of H_2O_2 was 215 mg/L (the stoichiometric amount required to oxidize

472 completely the SBO) and irradiation time was 6 hours.

473

	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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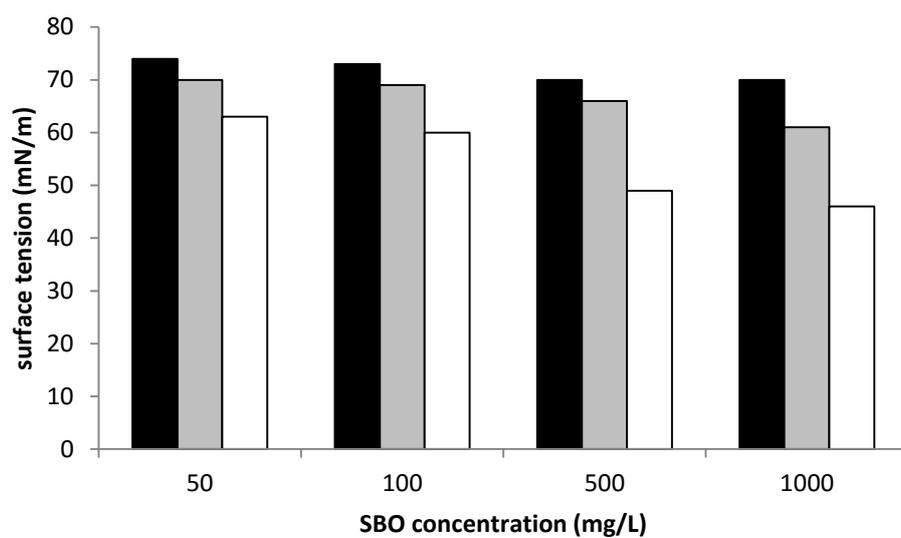
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478   Figure 1: Surface tension of solutions containing different concentrations of three batches

479   of SBOs: CVDFT 110 (black bars) CVT 230 (grey bars), FORSUD (white bars).

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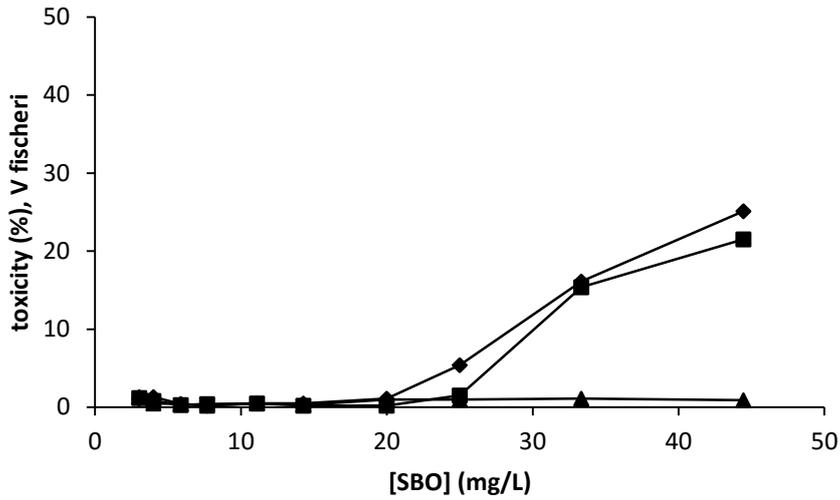
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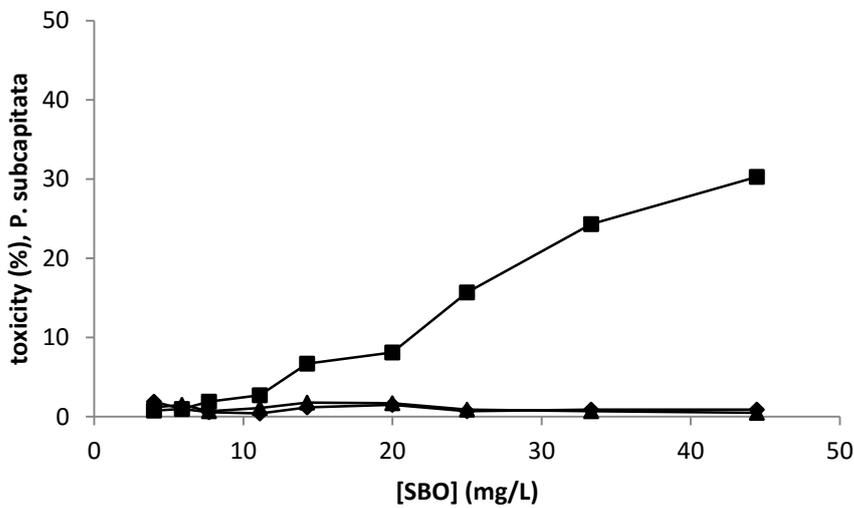
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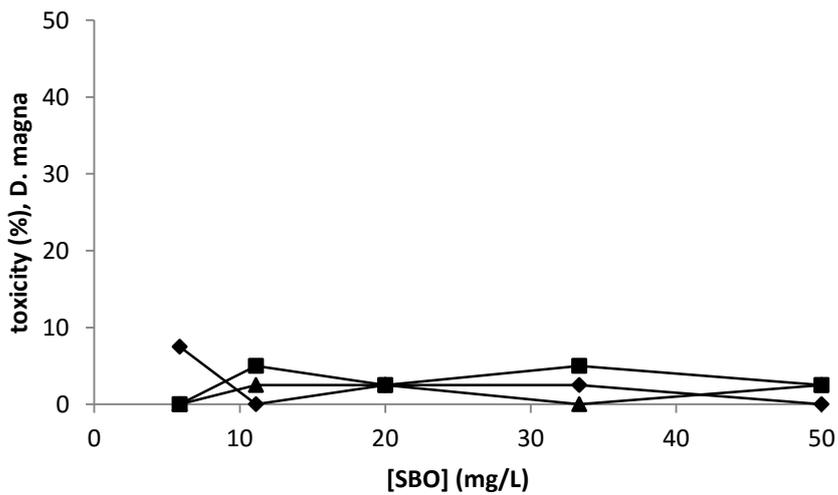
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484   Figure 2: Toxicity of three different batches of SBOs (CVDFT 110 (♦) CVT 230 (■),

485   FORSUD (▲)) measured according to bioassays based on *V. fischeri* (above), *P.*

486   *subcapitata* (middle) and *D. magna* (below).

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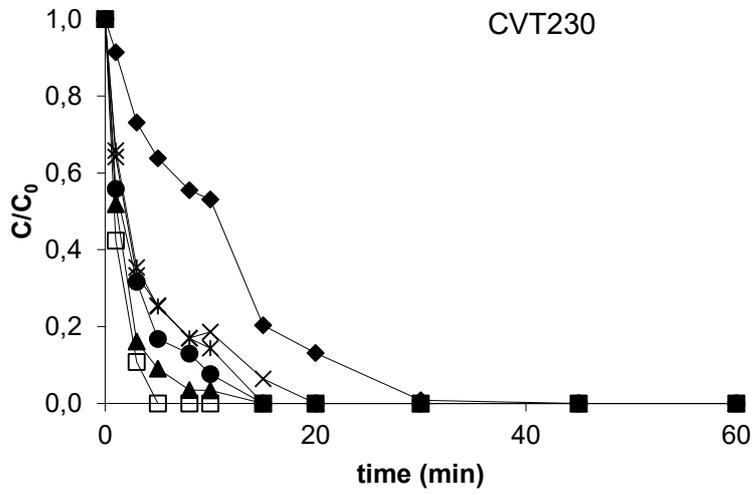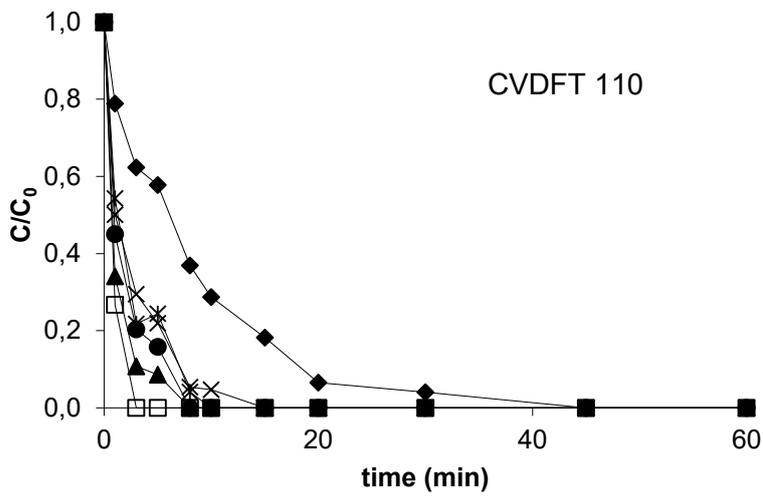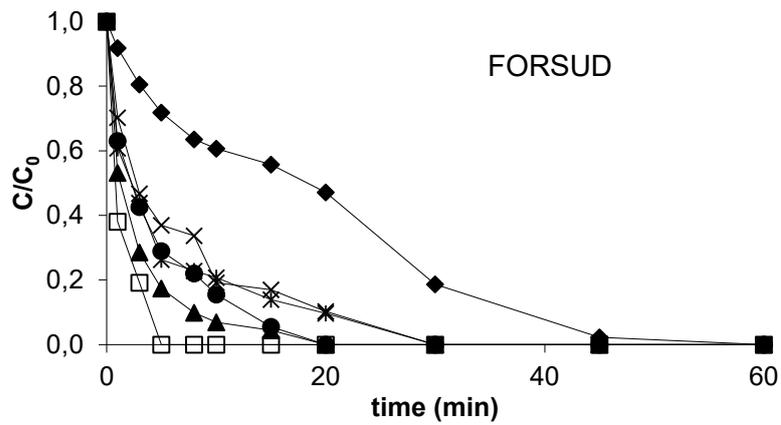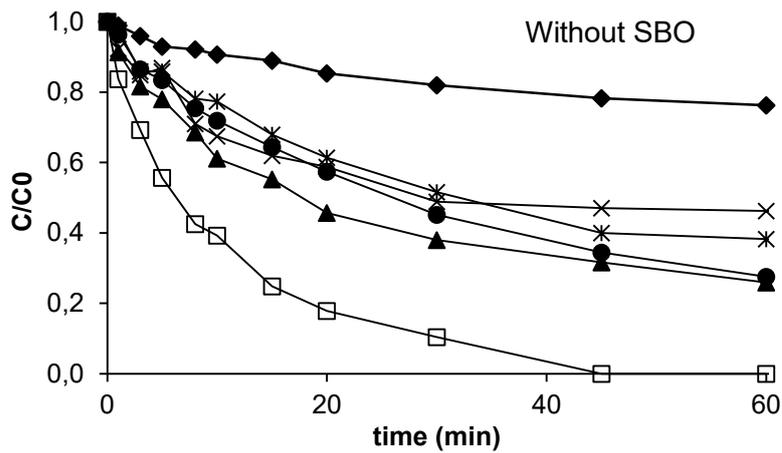
Figure 3. Photo-Fenton process at pH = 5.2 in the presence of three types of SBOs: CVT 230, CVDFT 110 and FORSUD. Plot of the relative concentration of pollutant vs time: amoxycillin (□), acetaminophen (✱), acetemiprid (♦), caffeine (×), clofibric acid (●) and carbamazepine (▲). Data obtained without SBO are also given for the sake of comparison.

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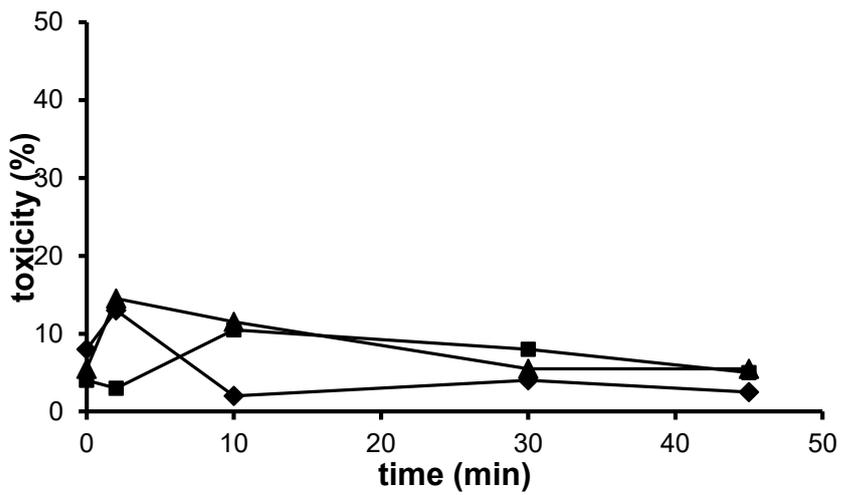
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503 Figure 4: Inhibition of the luminescence of V. fischeri bacteria obtained during a photo-
504 Fenton process at pH = 5.2 of the mixture of six pollutants in the presence of three types
505 of SBOs: CVT 230 (♦), CVDFT 110 (■) and FORSUD (▲).
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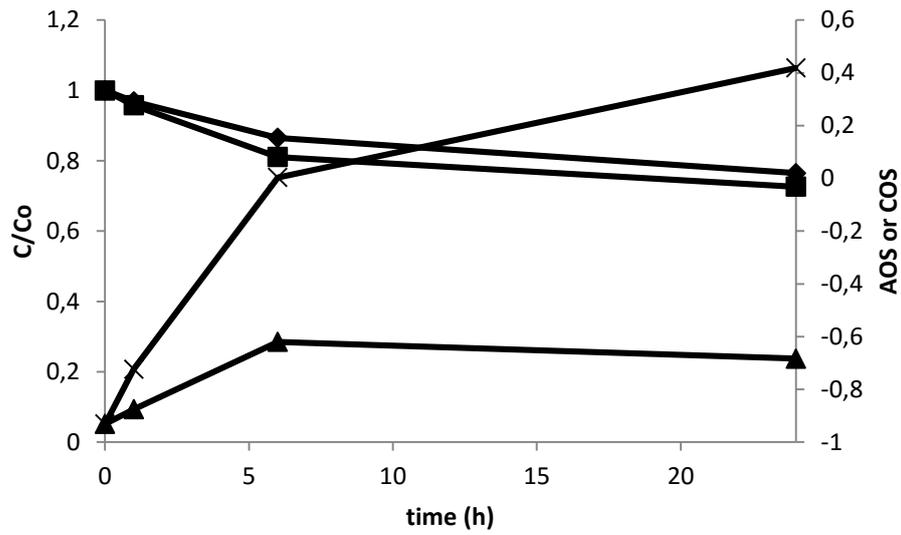
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509   Figure 5: Changes in COD (■), DOC (♦), AOS (▲) and COS (×) vs. irradiation time for

510   CVT 230.

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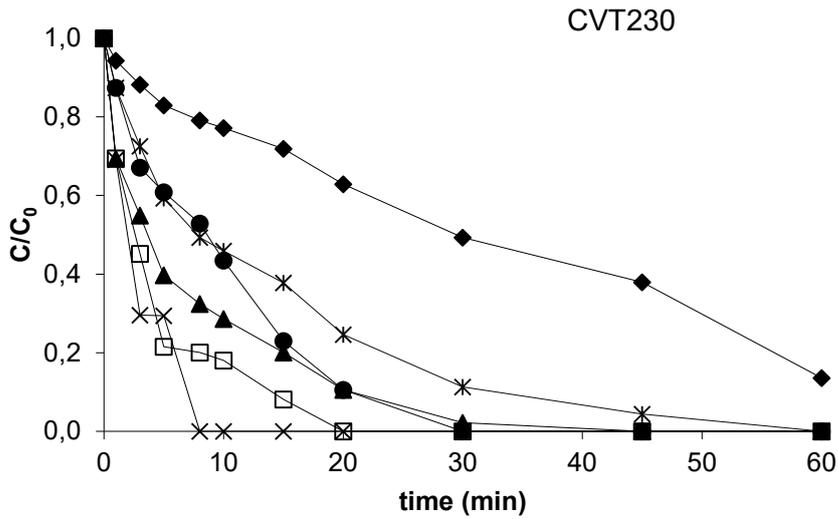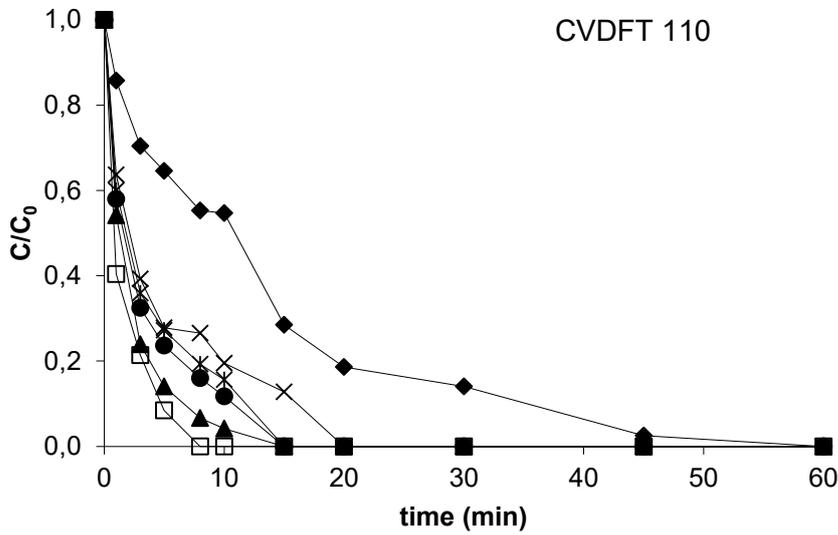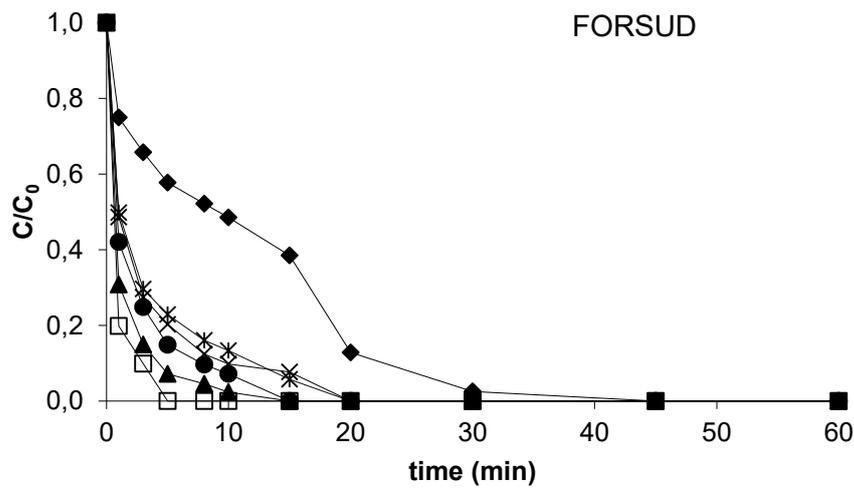
Figure 6. Photo-Fenton process at neutral pH in the presence of three types of irradiated SBOs: CVT 230 (above), CVDFT 110 (middle) and FORSUD (below). Plot of the relative concentration of pollutant vs time: amoxycillin (□), acetaminophen (✳),

519   acetemiprid (♦), caffeine (×), clofibric acid (●) and carbamazepine (▲)

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