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

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

Juan Gomis[,a], Mayara G. Gonçalves[b], Rosa F. Vercher[a], María C. Sabater[c], María A. Castillo[c], Alessandra Bianco Prevot[d], Ana M. Amat[a], Antonio Arques[a*].

[a] Grupo de Procesos de Oxidación Avanzada. Universitat Politècnica de Valéncia, Plaza Ferrándiz y Carbonell (s/n), E-03801, Alcoy, Spain,

[b] U. Tecnológica Federal do Paraná, Rua Deputado Heitor Alencar Furtado, 4900, Curitiba, Brasil.

[c] Dpto. Biotecnología. Univ. Politècnica de València. Camino de Vera, s/ n. 46022 – Valencia, Spain

[d] Università. di Torino, Dipartimento di Chimica Via Giuria 7, Torino, Italy

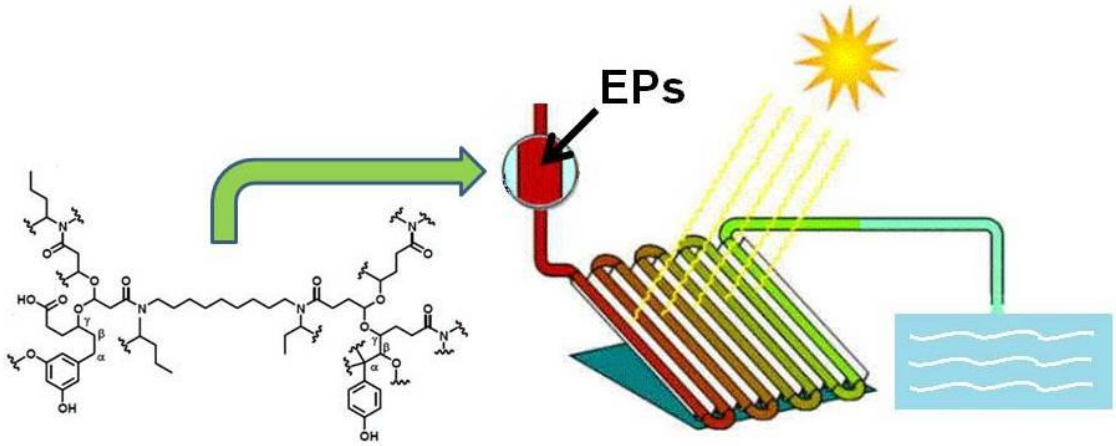
*Corresponding author

E-mail address: aarques@txp.upv.es (A. Arques)

Phone number: ++34 966528417

Fax: ++34 966528438

Graphical abstract



Highlights

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

Keywords: SBO, photostability, photo-Fenton, biocompatibility

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

1. Introduction

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

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

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

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

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

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

2. Experimental

2.1. Materials

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

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

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

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

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

2.2. Reactions

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

to the desired value by adding diluted sulphuric acid. Eventually, the stoichiometric amount of hydrogen peroxide required to oxidize completely each SBO was added, and irradiation was kept until the solution was free of H_2O_2. The amount of H_2O_2 was obtained from the initial chemical oxygen demand (COD) of the SBO, as COD indicates the amount of O_2 required to oxidize completely the sample.

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

2.3. Chemical analysis

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

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

2.4. Bioassays

In order to check the biodegradability of all three substances, biological oxygen demand (BOD_5) assays were carried out according to the standard manometric method (OECD 301 B, CO_2 evolution test), using an OxiTop© (WTW) to seal the bottle and determine the pressure inside [18]. The BOD_5 values were determined for SBO concentrations of 100 mg/L and 1000 mg/L.

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

3. Results

3.1. Chemical and physical characterization of the SBO

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

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

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

species (43 %), and although this is also true for the other SBOs, the proportion is lower (31-37%); on the other hand aromatic carbon is more abundant in CVDFT110 and CVT230. Consequently, the aliphatic/aromatic ratio obtained was clearly higher for FORSUD than for the other two SBOs. It is interesting to note that, again in this case, similar composition was obtained for CFDFT110 and CVT230.

Another useful gross parameter employed in characterization of natural organic matter is the E_2/E_3 ratio [19], where E_2 and E_3 are the absorbances at 250 nm and 365 nm respectively; this ratio has been related with the average molecular weight of the macromolecules, as well as its aromaticity (the higher ratio, the lower aromaticity and molecular weight). The application to the E2/E3 ratio to SBO gave results consistent with theier composition: higher values for E_2/E_3 were indeed obtained for FORSUD (3.83) that, as stated above, shows the minor proportion of aromatic groups; lower values were obtained for the other two SBO (ca. 2.3)

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

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

3.2. Biocompatibility of the SBO

BOD_5 was used to check the biodegradability of these materials in two different concentrations, 100 mg/L and 1000 mg/L. Table 3 shows that low BOD_5 values were obtained in all cases. As this parameter is highly influenced by the amount of organics present in the solution, the BOD/COD ratio has been employed as a better indicator for biodegradability [20]. This ratio was systematically below 0.1 (Table 3), what can be associated with a poor biodegradability of SBOs. This could be attributed to the fact that these materials have been submitted, for a long time, to the action of microorganisms and hence, only the fraction refractory to biological degradation remains. Other organic materials which are the result of the action of microbiological activity for long periods of time also show poor biodegradability; examples of such substances are humic and fulvic substances [21, 22] or landfill leachates [23].

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

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

3.3. SBO as auxiliaries in photochemical methods for wastewater treatment

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

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

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

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

3.4 Photostability of SBOs

It is interesting to study the photostability of the SBOs as in the wastewater treatment processes they are also submitted to chemical photo-oxidation; furthermore, this information might be valuable for studies on the behavior of anthropogenic organic matter in the environment. For this purpose, they were irradiated (100 mg/L) for 24 hours with a solar simulator; DOC, COD and BOD_5 were determined at selected sampling times. Figure 4 shows that there was a slow decrease in DOC and COD values

for CVT230, (ca. 25 % after 1 day of irradiation) indicating that some oxidation of SBO occurred; this can be more easily appreciated by the chemical oxidation state (COS), which is a parameter which relates the COD at the sampling with the initial DOC and a COS value of +4 is assigned for CO_2 (the most oxidized species of carbon) and -4 for CH_4 (the most reduced) [25]. During the process, the COS was increased from -0.9 to +0.2, and it should be associated with an oxidation of the organics present in the sample; a similar behavior was observed for CVDFT110 and FORSUD (data not shown). On the other hand, average oxidation state, which only refers to the organics remaining in solution (CO_2 is excluded from calculations by employing the DOC at the sampling time) did not suffer significant changes oscillating between -1 and -0.6 throughout the process; hence, no dramatic changes in the composition of the remaining organics might be expectable. Regarding to biocompatibility, the BOD_5/COD ratio was calculated after 24 hours of irradiation and the obtained values were 0.24 for CVDFT110, 0.08 for CVT230 and 0.14 for FORSUD; this ratio was in all cases slightly above that calculated for the same SBO before irradiation; finally, toxicity values did not vary significantly throughout the process (data not shown). A possible explanation to the above described trends is that the SBO molecules are partly oxidized into smaller and more hydrophilic ones which can be more easily metabolized by micro-organisms. A decrease of the molecular weight of macromolecules under irradiation is a well-known behaviour for macromolecules, for instance it has been observed for humic and fulvic substances when they were irradiated [26].

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

oxidize completely each SBO was added and it was irradiated until the solution was free of H_2O_2. Table 4 shows variations in significant parameters. In all cases, similar trends were obtained, only diverging in the numerical values, which should not be overemphasized: a) there was a moderate mineralization of the samples, in the range 20-30%, b) COD also decreased with a concomitant increase in COS, what indicates that stronger oxidation than for photolysis was obtained, c) AOS also increased, although variation was lower than for COS what might indicate that severe modification of organics remaining in solution should be ruled out, d) there was some increase in biodegradability as shown by higher BOD_5 values, and more clearly by the BOD/COD ratio, although these changes were not very acute, e) surface tension increased to reach values close to that of distilled water, f) the E_2/E_3 ratio significantly increased. All these data are again in agreement with a cleavage of the starting SBO to generate smaller, more oxidized and more hydrophilic substancess. In fact, similar trends have been observed for landfill leachates [27].

It was also interesting to determine the effect of mild photo-Fenton on SBOs oxidation For this purpose the three different SBOs (100 mg/L) were submitted to a photo-Fenton at pH = 5.2 with the stoichiometric amount of hydrogen peroxide and 5 mg/L of iron(II). Data obtained after 4 hours of irradiation showed very similar trends to that irradiated for one day, with DOC and COD decreases systematically above 50% (in some cases up to 75%) and the E_2/E_3 was between 4 and 5 for CVT230 and CVDFT110 while it reached 15 in the case of FORSUD.

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

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

4. Conclusions

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

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

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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

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

Table 3: BOD_5 values and BOD/COD ratio obtained for all three different types of 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

Table 4: Irradiation of all three SBOs in the presence of hydrogen peroxide: main parameters before and after irradiation. The initial SBO concentration was 100 mg/L, the concentration of H_2O_2 was 215 mg/L (the stoichiometric amount required to oxidize completely the SBO) and irradiation time was 6 hours.

	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

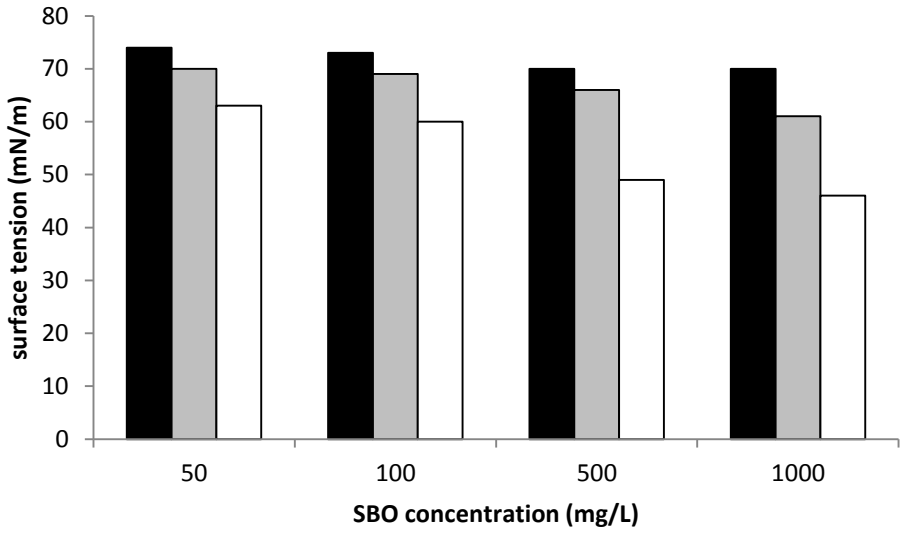

Figure 1: Surface tension of solutions containing different concentrations of three batches of SBOs: CVDFT 110 (black bars) CVT 230 (grey bars), FORSUD (white bars).

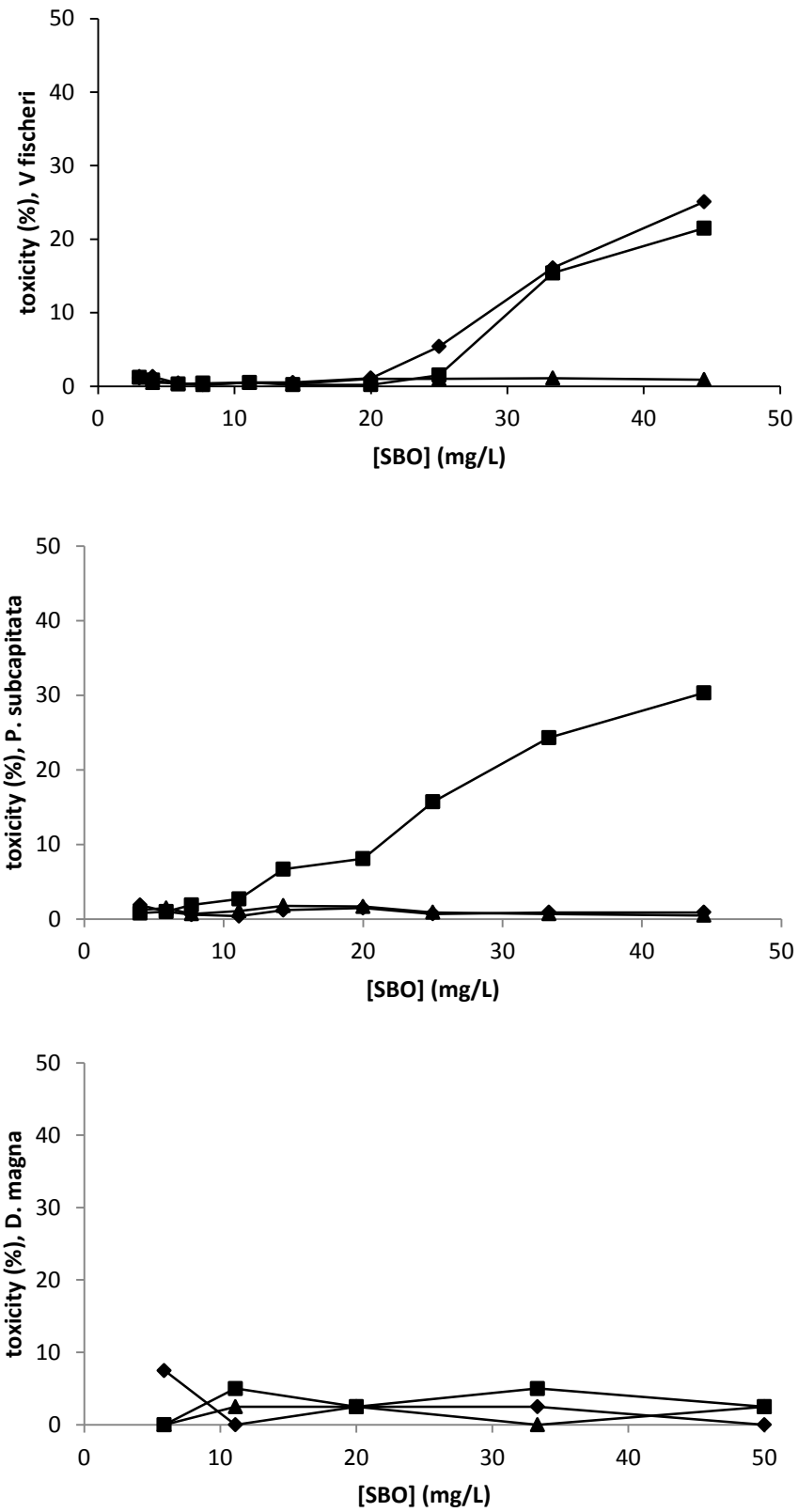

Figure 2: Toxicity of three different batches of SBOs (CVDFT 110 (♦) CVT 230 (■), FORSUD (▲)) measured according to bioassays based on *V. fischeri* (above), *P. subcapitata* (middle) and *D. magna* (below).

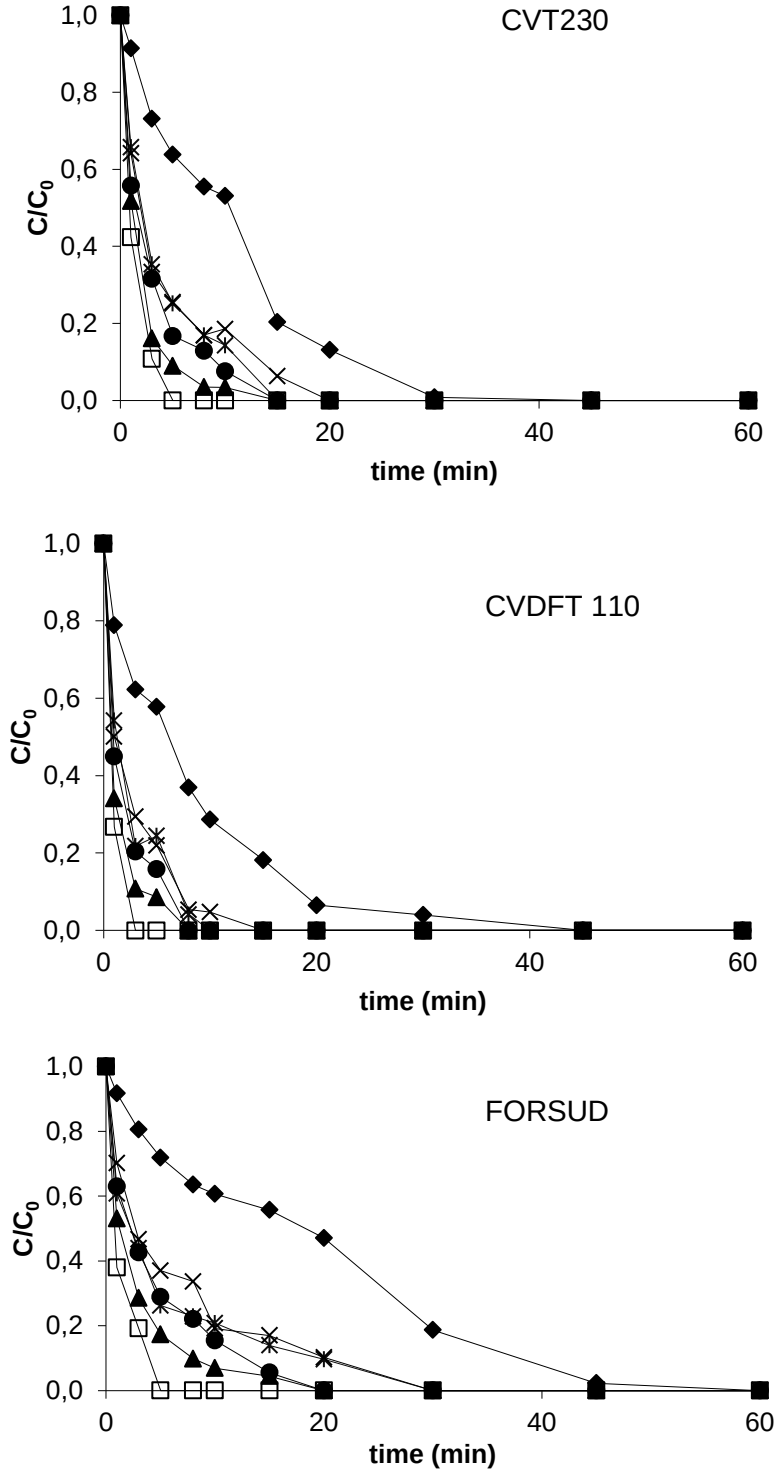

Figure 3. Photo-Fenton process at pH = 5.2 in the presence of three types of SBOs: CVT 230 (above), CVDFT 110 (middle) and FORSUD (below). Plot of the relative concentration of pollutant vs time: amoxycillin (□), acetaminophen (✳), acetemiprid (♦), caffeine (×), clofibric acid (●) and carbamazepine (▲)

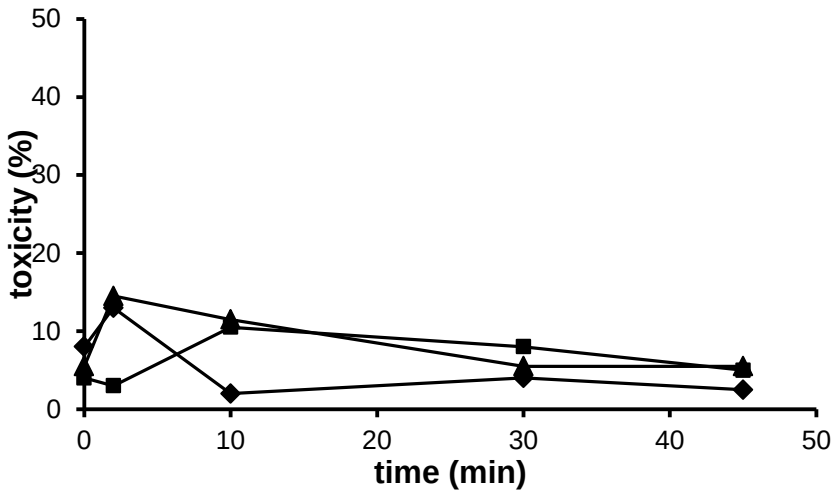

Figure 4: Inhibition of the luminescence of V. fischeri bacteria obtained during a photo-Fenton process at pH = 5.2 of the mixture of six pollutants in the presence of three types of SBOs: CVT 230 (♦), CVDFT 110 (■) and FORSUD (▲).

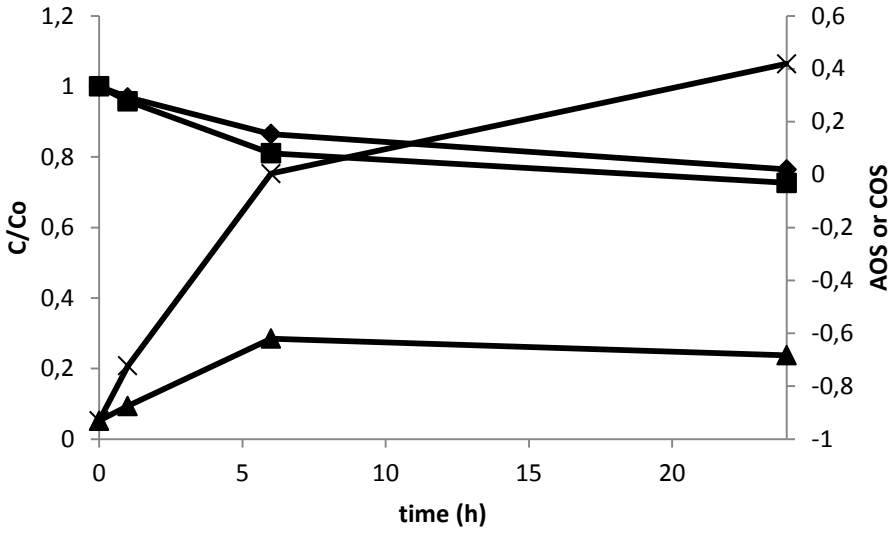

Figure 5: Changes in COD (■), DOC (♦), AOS (▲) and COS (×) vs. irradiation time for CVT 230.

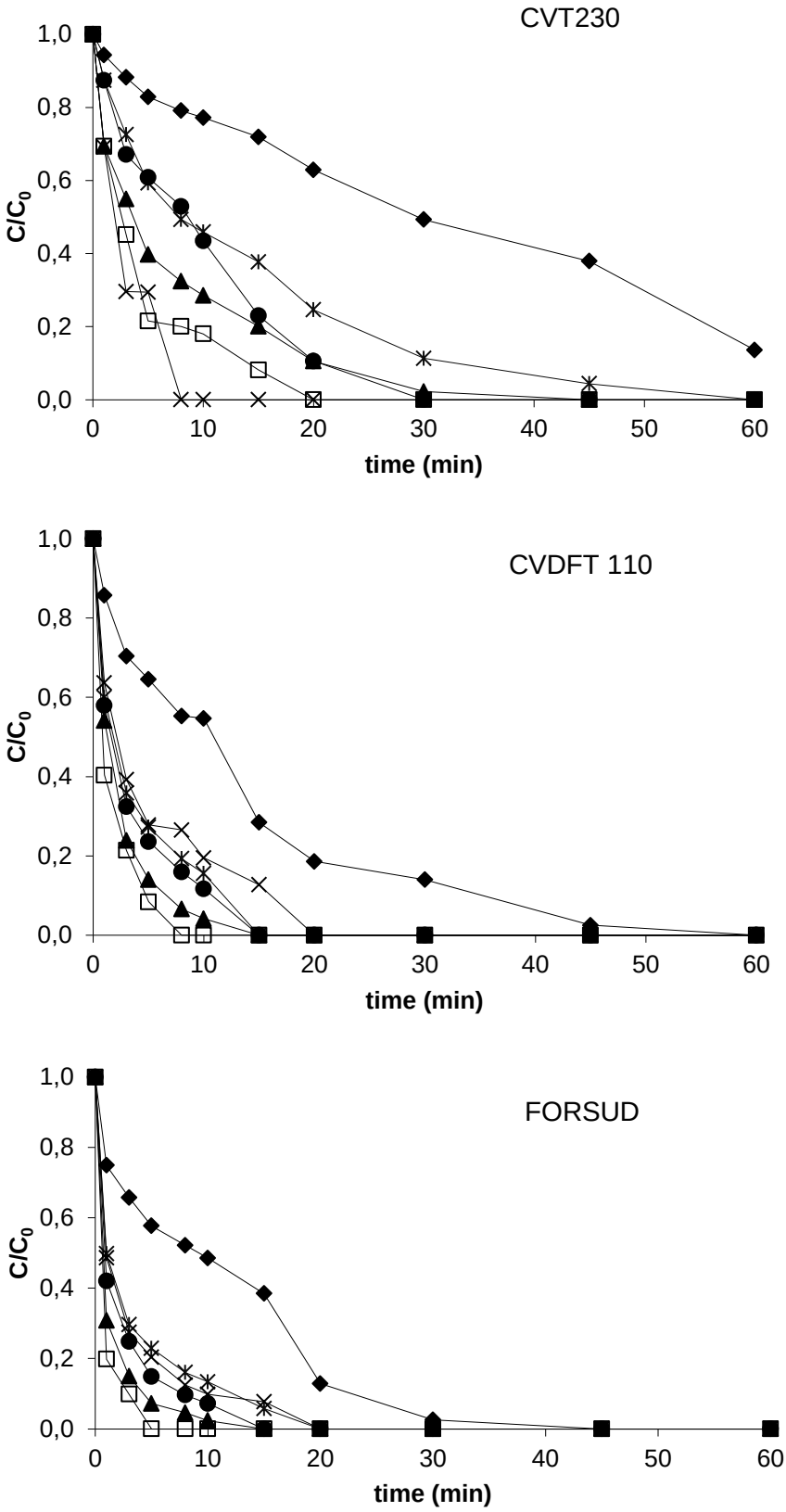

Figure 6. Photo-Fenton process at neutral pH in the presence of three types of irradiated SBOs: CVT 230 (above), CVDFT 110 (middle) and FORSUD (below). Plot of the relative concentration of pollutant vs time: amoxycillin (□), acetaminophen (∗), acetemiprid (♦), caffeine (×), clofibric acid (●) and carbamazepine (▲)

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