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# Waste sourced bio-based substances for solar-driven wastewater remediation: Photodegradation of emerging pollutants

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## HIGHLIGHTS

- Bio-based organic substances (SBO) have been used in photochemical processes.
- A mixture of six emerging pollutants has been used as target effluent.
- SBO-mediated reactive species generation cannot compensate for the screen effect.
- SBO have been demonstrated to enhance mild photo-Fenton (pH = 5.2).

## GRAPHICAL ABSTRACT
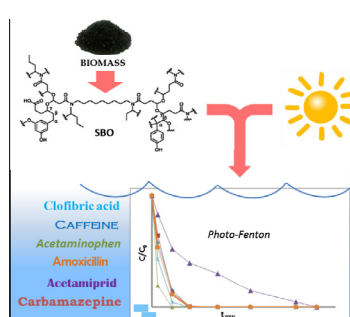


## ARTICLE INFO

## ABSTRACT

The effect of soluble bio-based organic substances (SBO) isolated from urban wastes on photochemical wastewater treatments was investigated using a mixture of six emerging pollutants (EPs), namely acetaminophen, caffeine, acetamiprid, clofibric acid, carbamazepine and amoxicillin. Solar simulated experiments showed that although SBO were able to enhance the indirect photolysis of the EPs, they could not compensate for the light screening effect produced by these colored materials. In contrast, SBO were able to enhance photo-Fenton at slightly acidic conditions (pH = 5.2), most probably increasing iron availability. In the later case, the order of reactivity (amoxicillin $\geqslant$ carbamazepine $\geqslant$ clofibric acid > caffeine > acetaminophen > acetamiprid) was similar to that of the rate constants determined for all six EPs with ·OH. Finally, experiments performed at pilot plant scale with real sunlight at pH = 5.2 and SBO showed that 5 of the EPs were removed in only 25 min and only acetamiprid was more resistant to the process. The overall results show not only how we can use waste to clean out wastes, but also contribute to the studies which show how wastes can become a source of revenue through the industrial exploitation of their chemical value.

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## 1. Introduction

Solar photochemical processes are receiving increasing attention because of their ability to remove toxic or non-biodegradable compounds from the environment. They are relevant from two different points of view: (a) photochemical processes are among the most important pathways for the removal of pollutants in natural aquatic systems [1] and (b) solar photocatalytic processes have been demonstrated as an emerging green technology for wastewater treatment [2]. In both approaches, the influence of natural dissolved organic matter (DOM), particularly humic substances (HS), seems to play a relevant role.

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In the case of natural aquatic ecosystems, two different mechanisms have been proposed for sunlight mediated reactions: direct substrate photolysis or indirect reactions promoted by reactive species generated by natural photosensitizers like nitrate or DOM [1,3]. In particular, HS contribute to the photochemical removal of pollutants [4], as upon irradiation they generate species such as hydroxyl radical (HO·), singlet oxygen ($O_2(a^1\Delta g)$), superoxide, or triplet-excited states of HS [5–9], which can potentially react with pollutants. However, HS may also negatively affect the process by screening sunlight due to their capacity to absorb in a wide range of wavelengths [10].

The applicability of HS in photochemical processes for wastewater treatment has also been investigated. They can be potentially used as photocatalysts; in fact, there is some information reporting on the use of some photochemically active organic compounds in wastewater treatment [11]. However, its major application is as complexing agent for iron in a photo-Fenton process at neutral or mild acidic conditions. This is an efficient photo-oxidative method in which a mixture of catalytic iron salts and sacrificial amounts of hydrogen peroxide are able to generate highly oxidizing species, such as hydroxyl radical [12]. One major drawback of this process is the highly acidic condition required to prevent the precipitation of iron as non-active oxide or hydroxide. Some recent papers have indicated that HS can form photochemically active iron complexes at circumneutral pH [13,14], thus allowing implementation of photo-Fenton-like processes at milder conditions. Unfortunately, in spite of these interesting properties, exploitation of HS as auxiliaries for the photoremediation of contaminated waters at commercial scale is not feasible due to their rather low concentration in natural ecosystems.

Recently, urban bio-wastes have been shown as a potential cost-effective renewable source of soluble bio-based substances [15]; these materials have similar chemical nature and properties as HS present in natural waters and soils [16,17]. SBO have been produced in relatively large scale by alkaline hydrolysis of urban bio-wastes sampled from various process streams and they have been shown rather effective in a wide number of applications, such as polluted soil washing [18], agriculture [19], animal husbandry [20] and material chemistry [21]. At laboratory scale, successful results have been obtained in the SBO-mediated photodegradation of aromatic sulfonic acids [22], phenols [23], as well as azo [24] and cationic dyes [25] dyes. Proving the performance of these substances as auxiliary for larger scale direct solar light photoremediation of a wide number of pollutants is needed to assess the actual viability of SBO assisted photoremediation processes.

With this background, the aim of this work is to assess the applicability of SBO as sensitizers, both, enhancing the degradation of pollutants by photolysis and in mild photo-Fenton process. Degradation of environmentally relevant target compounds, namely emerging pollutants (EPs), will be investigated. These are a group of chemical substances that have been recently detected in fresh waters as a result of human activities. Among EPs can be included pharmaceuticals, hormones, preservatives and bactericides, sunscreens, plasticizers and flame retardants or illicit drugs [26,27]. They are commonly present in natural ecosystems or wastewater treatment plant effluents at concentrations of a few $\mu g\,L^{-1}$ or $ng\,L^{-1}$ and photochemical processes have been demonstrated to be useful for their elimination from the natural waters [28]. For this purpose, a mixture of six EPs belonging to different families has been chosen to test the performance of SBO in their photodegradation. These were acetaminophen (analgesic), caffeine (stimulating agent), acetemiprid (insecticide), clofibric acid (metabolite of clofibrate, also employed as herbicide), carbamazepine (psychiatric drug) and amoxycillin (antibiotic) (see Scheme 1 for structures). They have been chosen because information on their photodegradation is available [10] and the role of HS on their
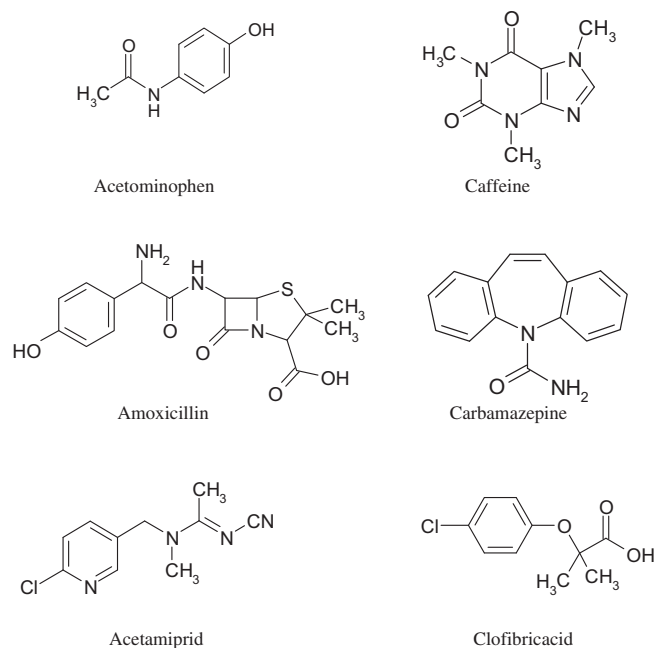


Scheme 1. Chemical structures of EPs employed in this work.

photolysis and in a neutral solar photo-Fenton process is also well established [10,29]. Herein, the photolysis and mild photo-Fenton in the presence of SBOs is studied at laboratory scale. In addition, in order to better evaluate the feasibility of the process, selected experiments have also been performed in a pilot plant for wastewater detoxification under solar irradiation.

## 2. Materials and methods

### 2.1. Reagents

Acetaminophen, caffeine, amoxicillin, clofibric acid, carbamazepine and acetamiprid were purchased from Sigma–Aldrich. Hydrogen peroxide (30% v/v) and ferrous sulfate, used in the photo-Fenton reactions, were supplied by Panreac. Water employed in all the experiments was Milli-Q grade.

The SBO employed in this study, namely CVT230, was obtained from urban bio-wastes sampled from the process lines of ACEA Pinerolese waste treatment plant in Pinerolo (Italy), as described elsewhere [25]. Briefly, the starting refuse was mature compost obtained from gardening-park trimming residues. The collected refuse sample after 230 days of composting was digested 4 h at 60 °C, pH 13 and 4 V/w water/solid ratio. The resulting suspension was centrifuged for 20 min and the supernatant liquid phase filtered through the ultrafiltration membrane (5 kD molecular weight cut-off). The concentrated retentate was then dried at 60 °C to yield the final SBO product. The chemical composition of this material is given in Table 1.

### 2.2. Reactions

Laboratory scale experiments were performed by irradiating aqueous solution containing the six EP at an initial concentration of each pollutant of $5\,mg\,L^{-1}$. Eventually, SBO in the range $1–200\,mg\,L^{-1}$ and $5\,mg\,L^{-1}$ of iron ion were added (as iron(II) sulfate); this is a concentration of iron commonly used in photo-Fenton experiments at mild conditions, as at higher amounts it cannot be easily kept in solution and fast precipitation occurs [29–31]. In experiments involving $H_2O_2$, the stoichiometric

amount of this reagent required to mineralize all the EPs present in the solution was added at the beginning of the experiment (75 mg L$^{-1}$). The pH was adjusted to the desired value by dropwise addition of either 0.1 M NaOH and/or 0.1 M H$_2$SO$_4$. Irradiations were performed in a 250 mL cylindrical Pyrex vessel (55 mm i.d., containing 200 mL solution) at 30–35 °C. A solar simulator (Sun 2000, ABET Technologies) equipped with a 550 W Xenon Short Arc Lamp was used as irradiation source. The incident photon rate over the 280–550 nm range ($P_0 = 3.32 \times 10^{-5}$ Eins L$^{-1}$ s$^{-1}$) was determined using potassium ferrioxalate as actinometer [32]. The system was irradiated for three hours; the solution was magnetically stirred during the experiment and water was eventually added to compensate for evaporation loss. Samples were periodically taken with a syringe, filtered through polypropylene (0.45 µm) and diluted 1:1 with methanol.

Experiments were then scaled-up using natural solar light. A solar photoreactor Solardetox Acadus-2001 (Ecosystem) based on compound parabolic collector technology (CPC) was used. A detailed description of the experimental set-up can be found elsewhere [33]. Briefly, it consisted of 4 borosilicate tubes through which the solution to be treated was flown. Two aluminum parabolic surfaces concentrated the sunlight in the axis of each tube. The total surface of the photoreactor was 0.26 m$^2$, and the irradiated volume, 1.83 L. A reservoir contained the mixture to be treated and from there, it was continuously recirculated to the CPCs with a flow rate that ensures a turbulent flow. The plant, equipped with a radiometer (Acadus 85) to measure UV-A radiation, was left in a sunny place in Alcoy (Eastern Spain), tilted 30° with the horizon. The plant was loaded with 4 L of the solution to be treated (5 mg L$^{-1}$ each EP, and eventually SBO (10 mg L$^{-1}$), and iron (5 mg L$^{-1}$) at the pH of 2.8, 5.2 or 7. In this case, hydrogen peroxide was dosified throughout the experiment, keeping a concentration of ca. 5 mg L$^{-1}$ by means of successive additions of this reagent. Samples were taken from the reservoir and treated as described for lab scale experiments.

In experiments involving real sunlight, accumulated UV radiation was expressed as $t_{30W}$, which is a parameter commonly used to normalize the intrinsically changing irradiation conditions [2]. It was calculated by Eq. (1), where UV$_{ac}$ is the accumulated solar radiation (J/m$^2$); $V_i$ and $V_t$ are, respectively, the irradiated and total volume (L), and $I$ the average UV irradiance, typically 30 W/m$^2$ in the East of Spain.

$$t_{30W} = \frac{UV_{ac} \times V_i}{I \times V_t} \qquad (1)$$

### 2.3. Analysis

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

UV–Vis absorption spectra were recorded on a Helios γ spectrophotometer (Thermo Scientific) using quartz cells of 1.0 cm optical path length.

The bioluminescence of V. fisheri was used to assess the toxicity of the samples. The assays were carried out according to the standardized methodology (ISO 11348-3 norm), using lyophilized bacteria (V. fischeri, NRRL B-11177, Macherey–Nagel). The standard procedure was employed for reconstitution of the bacteria, using a salty solution. The luminescence was determined by means of a Luminometer Lumifix-Bio-10 (Macherey–Nagel). Toxicity was determined after 15 min incubation. As solutions were slightly colored, toxicity was corrected considering their absorbances at 490 nm [34].

### 2.4. Determination of rate constants of the reactions of the EP with hydroxyl radicals

The second-order rate constant between the EP and HO· ($k_{HO·,EP}$) was determined by a competition kinetics method using the Fenton's reagent [35]. 4-Chlorobenzoic acid (pCBA) was used as reference ($k_{HO·,pCBA} = 5 \times 10^9$ M$^{-1}$ s$^{-1}$) [36]. The reactions were carried out in a foil-wrapped vessel. The initial solution contained 0.35 mM FeSO$_4$ and 0.1 mM of both pCBA and the corresponding EP at pH 2.8. The reaction was initiated by addition of 5 mM H$_2$O$_2$ to the vessel. Samples (1.5 mL) were withdrawn at different reaction times; 0.5 mL methanol were added to prevent further reaction between sampling and analysis. The bimolecular rate constant for the reaction between each EP and HO· radical ($k_{HO·,EP}$) was calculated according to the following equation:

$$k_{HO·,EP} = \left( \frac{\ln([EP]/[EP]_0)}{\ln([pCBA]/[pCBA]_0)} \right) \times k_{HO·,pCBA} \qquad (2)$$

where [EP]$_0$ is the initial concentration of each emerging pollutant, [EP] is the concentration at the sampling time and [pCBA]$_0$ and [pCBA] the corresponding values for pCBA.

## 3. Results and discussion

### 3.1. Photolysis of the mixture of EP in the presence of SBO

A solution containing a mixture of the six investigated emerging pollutants (5 mg L$^{-1}$ of each EP) was irradiated in a solar simulator in the presence of different amounts of SBO (20 and 200 mg L$^{-1}$) at neutral pH. The relative concentration of the pollutants ($C/C_o$, were $C_o$ is the initial concentration and $C$ the concentration at the sampling time) vs. time were fitted in all cases to a semilogarithmic plot and the pseudo-first order rate constant ($k_{obs}$) was calculated from the slope of the obtained line. Fig. 1A shows that the presence of the SBO resulted in a significant decrease in the photolysis rate of the pollutants, as shown by the $k_{obs}$ which were reduced up to 50% in the presence of 20 mg L$^{-1}$ of SBO and even 80% with 200 mg L$^{-1}$. This behavior can be attributed to a light screening

**Table 1**
Chemical composition of the SBO employed in this work: elemental analysis and relative amount of organic functional groups present in the material.

| Characteristic | Value | Characteristic | Value (%) |
|---|---|---|---|
| Volatile solids (%, w/w) | 72.1 | Aliphatic carbon | 72.1 |
| Carbon (%, w/w) | 38.2 | Amine | 38.2 |
| Nitrogen (%, w/w) | 4.0 | Methoxy | 4.0 |
| Si (%, w/w) | 2.55 | Alkoxy | 2.55 |
| Fe (%, w/w) | 0.77 | Anomeric carbon | 0.77 |
| Al (%, w/w) | 0.49 | Aromatic | 0.49 |
| Mg (%, w/w) | 1.13 | Phenolic carbon | 1.13 |
| Ca (%, w/w) | 6.07 | Phenoxy | 6.07 |
| K (%, w/w) | 3.6 | Carboxylic | 3.6 |
| Na (%, w/w) | 0.16 | Amide | 0.16 |
| Cu (mg/l) | 202 | Carbonilic | 202 |
| Ni (mg/l) | 92 | Lipophilic/hydrophilic ratio | 92 |
| Zn (mg/l) | 256 | Aliphatic/aromatic ratio | 256 |
| Cr (mg/l) | 19 | | |
| Pb (mg/l) | 85 | | |
| Hg (mg/l) | 0.2 | | |

effect of the highly colored organics SBO that affected the penetration of light into the system. This is a rather common behavior in photochemical processes; for instance, when the same mixture of EPs was irradiated in the presence of 20 mg L$^{-1}$ of humic substances, a decrease in the pseudo-first order rate constants in the range 10–40% was observed [10].

Despite these results, SBO-mediated photogeneration of reactive species that contribute to the indirect photolysis of the EP should not be ruled out. In order to clarify this point, the effect of light attenuation by the presence of SBO on the direct photolysis of each EP in the mixture was estimated by means of the light screening factor, $\widetilde{S}_{\Delta\lambda}$ [37]. This parameter is defined as the ratio of the intensity of light absorbed by the target compound with and without the presence of the attenuator ($I_{a\text{-with SBO}}$ and $I_{a\text{-without SBO}}$, respectively)

$$\widehat{S}_{\Delta\lambda} = \frac{I_{a\text{-with SBO}}}{I_{a\text{-without SBO}}} \tag{3}$$

$$I_{a\text{-with SBO}} = P_0 \sum_\lambda p_\lambda (1 - 10^{-(A+A_{SBO})}) \frac{A_{EP}}{(A+A_{SBO})} \tag{4}$$

$$I_{a\text{-without SBO}} = P_0 \sum_\lambda p_\lambda (1 - 10^{-A}) \frac{A_{EP}}{A} \tag{5}$$
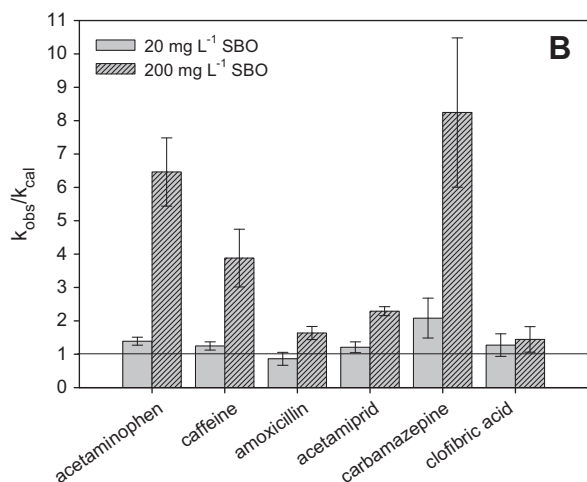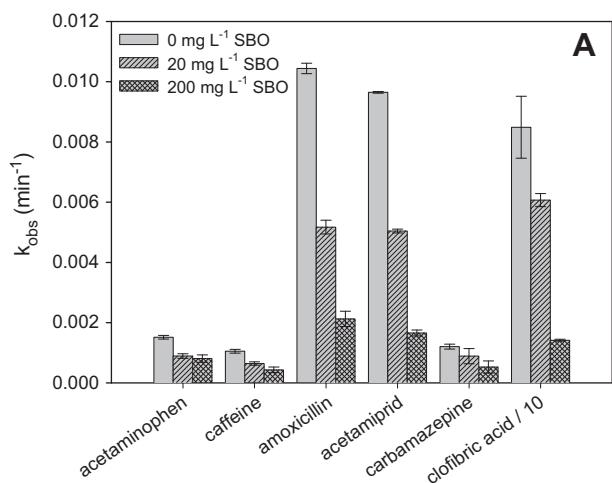




**Fig. 1.** Photodegradation of the mixture of EPs at different SBO amounts. [EP]$_0$ = 5 mg L$^{-1}$; pH = 7. (A) Pseudo-first order rate constants ($k_{obs}$), for clofibric acid, the $k_{obs}$ values reported are divided by ten; (B) Ratio of rate constants $k_{obs}/k_{cal}$. Error bars represent standard deviations.
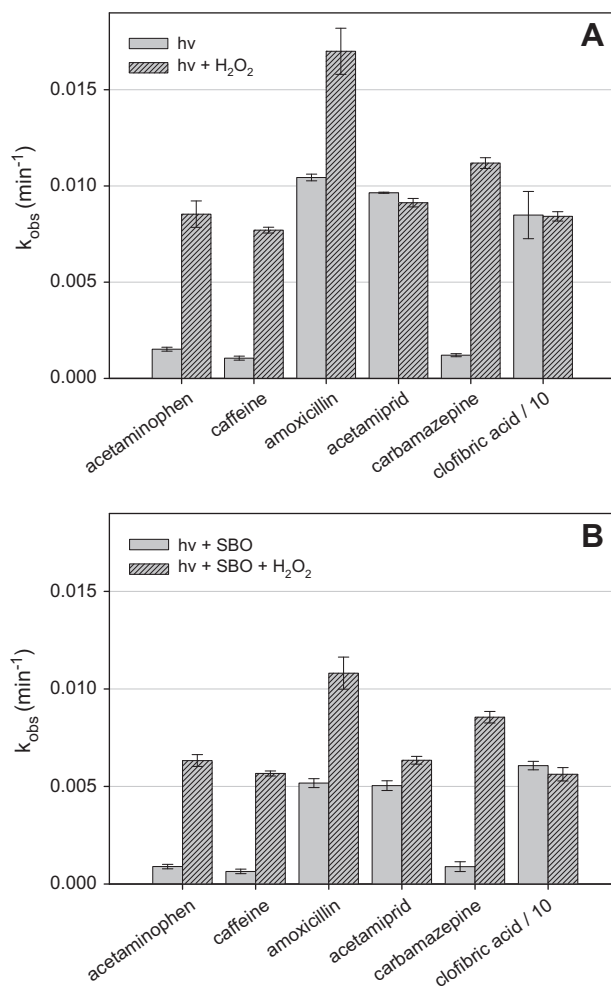




**Fig. 2.** Photodegradation of the mixture of EPs (5 mg L$^{-1}$ of each EP) without and with H$_2$O$_2$ (2.2 mM) at pH 7: (A) in the absence of SBO and (B) with SBO (20 mg L$^{-1}$). For clofibric acid, the $k_{obs}$ values reported are divided by ten. Error bars represent standard deviations.

where $P_0$ is the incident photon rate, $p_\lambda$ is the fraction of photons emitted by the lamp in a small finite wavelength interval. $A_{EP}$ represents the absorbance of the EP, and A stands for the absorbance of the solution of the EPs mixture without SBO and $A_{SBO}$ represents the absorbance of SBO. Dividing Eq. (4) by Eq. (5) the following expression for $\widetilde{S}_{\Delta\lambda}$ can be obtained:

$$\widehat{S}_{\Delta\lambda} = \frac{\sum_\lambda p_\lambda (1 - 10^{-(A_\lambda+A_{\lambda,SBO})}) \frac{A_{\lambda,EP}}{(A_\lambda+A_{\lambda,SBO})}}{\sum_\lambda p_\lambda (1 - 10^{-A_\lambda}) \frac{A_{\lambda,EP}}{A_\lambda}} \tag{6}$$

Since the irradiation source emits light with wavelength higher than 280 nm and the EPs absorbs light up to $\lambda \sim 350$ nm, the $S_{\Delta\lambda}$ values were calculated in the 280–350 nm wavelength range. The emission spectrum of the lamp and the absorbance spectra of the EPs and SBO used for estimating the $\widetilde{S}_{\Delta\lambda}$ are shown in Figs. S1 and S2 in the Supplementary data. The direct photolysis rate constants in the presence of SBO ($k_{cal}$) were calculated from the equation, $k_{cal} = \widehat{S}_{\Delta\lambda} \times k_d$, where $k_d$ is the direct photolysis pseudo-first order rate constant of each EP measured in absence of SBO. The values of $k_d$ obtained for the different experimental conditions are reported in Table S1 in the Supplementary data. Therefore, the contribution of the indirect photoprocesses induced by the photolysis of SBO to the degradation of the EPs can be evaluated through the ratio of $k_{obs}/k_{cal}$. If SBO were only responsible for a

screen effect, then $k_{cal}$ would be coincident with $k_{obs}$ and hence a $k_{obs}/k_{cal} = 1$ would be obtained. However, irradiation of the EPs mixture with SBO at pH = 7 results in $k_{obs}/k_{cal}$ values higher than 1 (Fig. 1B), i.e., a contribution of indirect processes is needed to explain the difference between $k_{obs}$ and $k_{cal}$. This contribution is of higher relevance at larger concentrations of SBO. Similar results were obtained at pH = 2.8 and 10 (Figs. S3 and S4, Supplementary Data). In all cases, higher involvement of indirect photoprocesses was observed for the EPs more reluctant to direct photolysis (e.g. acetaminophen, caffeine and carbamazepine). This trend is analogous to that obtained using HS [10].

### 3.2. Effect of $H_2O_2$

Addition of $H_2O_2$ at pH 7 resulted in a faster photolysis of the EPs in the absence of SBO as shown by the higher $k_{obs}$ obtained for almost all the EPs (except for clofibric acid and acetamiprid, Fig. 2A). Moreover, the effect of $H_2O_2$ addition is more significant for those EPs more reluctant to direct photolysis. This can be explained by considering two competitive photodegradation routes: direct photolysis and reaction with HO· radicals generated from the photolysis of $H_2O_2$. Since a low rate of production of HO· radicals is expected from the absorption coefficients of $H_2O_2$ above 280 nm [32], the contribution of indirect mechanisms to the overall degradation process is less significant for those EPs which show faster direct photolysis (amoxicillin, acetamiprid and clofibric acid). A similar trend was observed in the presence of 20 mg L$^{-1}$ of SBO (Fig. 2B), although lower $k_{obs}$ values were obtained for each EP, most probably due to the light screening effect and scavenging of HO· radicals by SBO.

Again in this case, the contribution of indirect photolysis due to SBO was estimated by the $k_{obs}/k_{cal}$ ratio, with $k_{cal}$ calculated using the pseudo-first order rate constant obtained from the photolysis of the EPs mixture in the presence of $H_2O_2$ ($k_{d,H2O2}$). The values of $k_{obs}/k_{cal}$ (all above 1) were found to increase with the concentration of SBO (Fig. 3A) except for amoxicillin, for which a maximum at 5 mg L$^{-1}$ of SBO was observed. The comparison between the $k_{obs}/k_{cal}$ values obtained with 20 mg L$^{-1}$ of SBO in the presence and absence of $H_2O_2$ (Figs. 3A and 1B), shows a slight enhancement of the indirect photo-processes for almost all the EPs when $H_2O_2$ is added. This effect, which has already been observed when studying the decoloration of crystal violet in the presence of SBO [25], could be attributed to a photo-Fenton reaction. This process requires the presence of iron to decompose hydrogen peroxide into HO· radical and significant amounts of iron (0.77% w/w on dry SBO matter basis) have been detected in the SBO employed here, as shown in Table 1.

In order to clarify the possible involvement of a photo-Fenton process, experiments were performed at pH = 2.8, which is close to the optimal acidity for this treatment [12]. As can be seen in Fig. 3B, the involvement of indirect processes is more significant under these conditions, where $k_{obs}/k_{cal}$ ratios above 2 were reached in most cases, and even values close to 10 were eventually found. Furthermore, the $k_{obs}/k_{cal}$ obtained at pH 2.8 without $H_2O_2$ (Fig. S3, Supplementary data) were much lower than those obtained in the presence of $H_2O_2$ (Fig. 3B), supporting the involvement of the photo-Fenton reaction in the degradation process of the EPs.

### 3.3. Photo-Fenton process at laboratory scale

Further experiments were carried out to explore the possibility of using SBO in photo-Fenton at milder conditions. In order to minimize the effect of photolysis, a glass filter was used to cut off the small fraction of radiation emitted by the simulator below 300 nm. With this experimental set up, the direct photolysis rate constant ($k_d$) for all EPs decreased more than one order of magnitude.
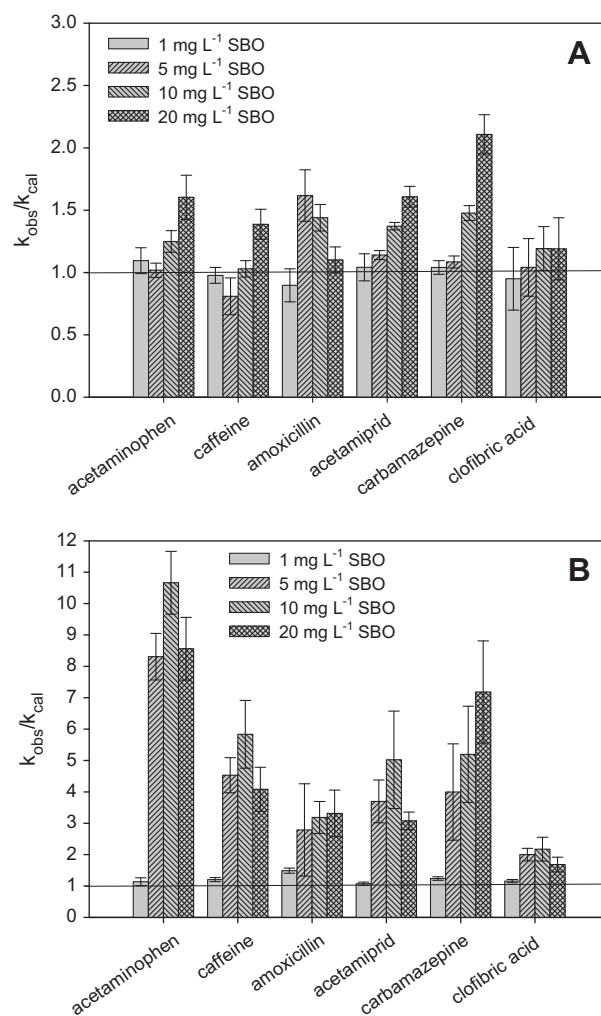


Fig. 3. Photodegradation of the mixture of EPs (5 mg L$^{-1}$ of each EP) in the presence of $H_2O_2$ (2.2 mM) and different amounts of SBO: (A) pH = 7; (B) pH = 2.8. Error bars represent standard deviations.

Degradation of the mixture of EPs with the photo-Fenton process was performed adding 5 mg L$^{-1}$ of iron(II) (using the sulfate salt) and $H_2O_2$ (75 mg L$^{-1}$) in the absence and presence of SBO (10 mg L$^{-1}$) at pH 2.8, which is the optimum for photo-Fenton, and at milder medium, namely 5.2, where precipitation of iron already occurs; experiments were also carried out al pH = 7, but the process was to inefficient to obtain reliable quantitative data. Pseudo-first order rate constants were determined for each EP in the mixture with and without SBO, $k_{SBO}$ and $k_0$ respectively. The ratio $k_{SBO}/k_0$ was slightly below 1 at pH 2.8 (Fig. 4), which indicates that the presence of SBO was detrimental for the photo-Fenton process under these conditions. Thus, the scavenging role of SBO (especially for HO·) predominates over its photosensitizing effect. In contrast, at pH 5.2, the $k_{SBO}/k_0$ values were in the range 6–9, which implies that photo-Fenton is significantly enhanced by the presence of SBO. A possible explanation to this behavior is that, similarly to HS [38], SBO act as complexing agents for iron, avoiding the formation of non-active iron oxides or hydroxides. Thus the presence of SBO increased the iron availability for the Fenton reaction. It is important to note that the degradation rates at pH 5.2 in the presence of SBO were comparable to those obtained at pH 2.8 without SBO ($k_0$ at pH = 2.8 was not higher than twice $k_{SBO}$ at pH = 5.2 for most EP) (Table S2, Supplementary data). These results are in agreement with Fenton studies performed in the presence of HS [38].
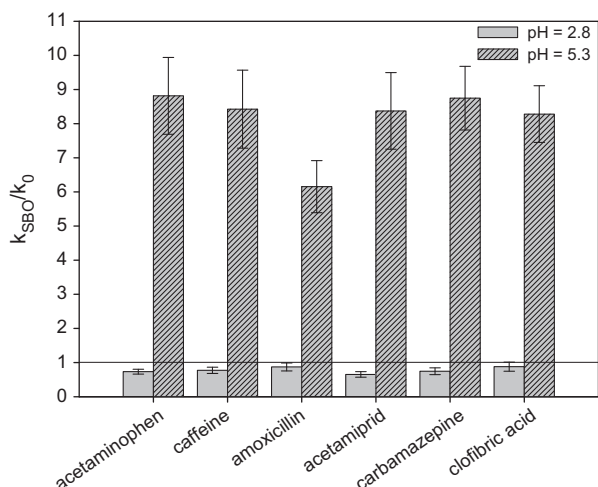
**Fig. 4.** Ratio of the rate constants obtained for the photodegradation of six EPs (5 mg L$^{-1}$ of each EP) in the presence of H$_2$O$_2$ (75 mg L$^{-1}$) and iron(II) (5 mg L$^{-1}$) with SBO (10 mg L$^{-1}$) and without SBO at pH = 2.8 and 5.2. Error bars represent standard deviations.

Hydroxyl radical has been reported to be a key reactive species in the photo-Fenton system at acidic pH. However, some recent papers have indicated that other mechanisms might be of importance at circumneutral pH [39,40]. In order to gain further insight into the reaction mechanism, pseudo-first order rate constants were determined with ($k_{tB}$) and without ($k$) *tert*-butyl alcohol, a well-known hydroxyl radical scavenger, at the pH values of 2.8 and 5.2 (see Table S2), and the $k_{tB}/k$ ratios were calculated (Fig. 5). A decrease in the rate constant was observed in all cases and the magnitude of this decrease could be associated to the role of HO$^{\cdot}$ in the process. For acetaminophen, relatively high ratios were calculated, which suggests a different behavior from the other EPs. In most of the other cases, decreases of ca. 90% were found, which might indicate that HO$^{\cdot}$ plays a major role in the process. Only for experiments performed at pH = 5.2 without SBO, higher $k_{tB}/k$ ratios were calculated, which means that an alternative mechanism might become more relevant. These results are in agreement with an enhanced role of the hydroxyl radical-mediated processes upon addition of SBO at pH = 5.2. Studies with HS concluded that Fe(II)–HS complexes formed at pH 5 are able to react more rapidly with
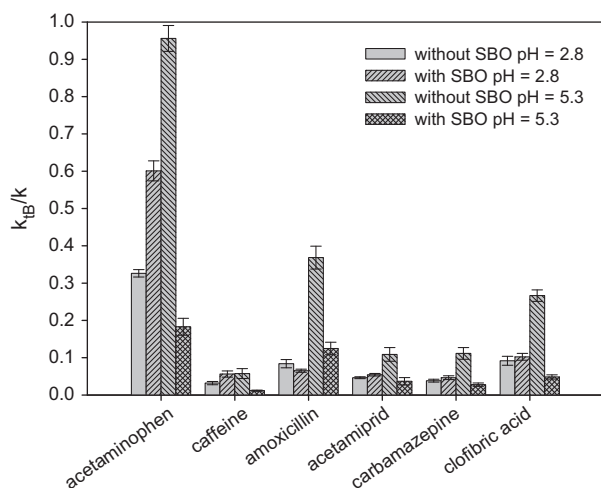


**Fig. 5.** Ratio of the rate constants obtained without and with *tert*-butyl alcohol ($k_{tB}/k$) for the photodegradation of six EPs (5 mg L$^{-1}$ of each EP) in the presence of H$_2$O$_2$ (75 mg L$^{-1}$) and iron(II) (5 mg L$^{-1}$) under different experimental conditions. *Tert*-butyl alcohol (10 mM) and SBO (10 mg L$^{-1}$).

**Table 2**
Second-order rate constant between the EPs and HO$^{\cdot}$ ($k_{HO^{\cdot},EP}$). Errors are calculated from the standard deviation of the data obtained in two independent experiments. For comparison available literature data are also included.

| EPs | $k_{HO^{\cdot},EP}$ (M$^{-1}$ s$^{-1}$) (this work) | $k_{HO^{\cdot},EP}$ (M$^{-1}$ s$^{-1}$) (literature data) |
|---|---|---|
| Acetaminophen | $(2.8 \pm 0.2) \times 10^9$ | $2.2 \times 10^9$ [42] |
| Caffeine | $(4.6 \pm 0.1) \times 10^9$ | $5.9 \times 10^9$ [43] |
| Amoxicillin | $(9.8 \pm 1.0) \times 10^9$ | $6.9 \times 10^9$ [44] |
| Acetamiprid | $(2.3 \pm 0.1) \times 10^9$ | $5.5 \times 10^{10}$ [45] |
| Carbamazepine | $(10.8 \pm 0.4) \times 10^9$ | $8.8 \times 10^9$ [46] |
| Clofibric acid | $(7.6 \pm 0.9) \times 10^9$ | $8.0 \times 10^9$ [47] |

H$_2$O$_2$ than Fe(II)–aquo complexes, leading to a higher rate of HO$^{\cdot}$ production [41]. These results are in line with those obtained with SBO at pH = 5.2.

Within the experimental error, at pH = 2.8 the presence of SBO did not seem to affect the reaction mechanism, except for acetaminophen. On the other hand, preliminary results recently published with SBO-mediated photo-Fenton at pH = 7 under UV irradiation (low pressure mercury lamp) with crystal violet indicated that ferryl ion might be a key species [25]. Hence, the mechanism might be strongly influenced by the experimental conditions, as already shown for the degradation of EPs by photo-Fenton at different pH and in the presence of HS [29].

In order to gain further insight into the involvement of HO$^{\cdot}$ under the studied conditions, the bimolecular rate constant for the reaction between each EP and the HO$^{\cdot}$ radical ($k_{HO^{\cdot},EP}$) was determined by means of competitive kinetics, as described in the experimental section. The experimental rate constants obtained in this study (Table 2), agree well with reported values obtained with other methodologies, such as pulse radiolysis or UV/H$_2$O$_2$ method, except for acetamiprid, for which a lower value is obtained compared to that previously reported using SCN$^-$ as a probe.

Interestingly, the quantitative order of $k_{HO^{\cdot},EP}$ (carbamazepine > amoxicillin > clofibric acid > caffeine > acetaminophen > acetamiprid) show a similar trend as the reactivity of the EPs in the photo-Fenton process at both pH values and in the presence and absence of SBO. However, some slight differences can be observed between the reactivity of HO$^{\cdot}$ and photo-Fenton, which might indicate that despite the predominating role of this radical, other species might also be partly responsible of the EPs degradation. On the contrary, in the experiments conducted with *tert*-butyl alcohol, where HO$^{\cdot}$ have been suppressed from the reaction medium, a significantly different trend was obtained (amoxicillin > acetaminophen > clofibric acid > carbamazepine $\geqslant$ caffeine > acetamiprid; see Table S2, Supplementary data).

### 3.4. Photo-Fenton processes in a solar pilot plant

Based on the results reported above, where a favorable effect of SBO was observed under simulated solar light, a series of experiments was carried out to assess if the photo-Fenton process operated also under direct sunlight at pH 5.2. First, controls showed that direct photolysis of the pollutants was negligible under these conditions and irradiation in the presence of H$_2$O$_2$ only resulted in a moderate degradation of amoxicillin (ca. 25% for amoxicillin and lower than 10% for the other EPs after $t_{30W}$ = 150 min). In sharp contrast, experiments carried out with SBO, hydrogen peroxide and iron at pH = 5.2 resulted in a fast removal of the pollutants, as shown in Fig. 6A. In fact, most of the EPs were completely removed at $t_{30W}$ of approximately 30 min; only acetamiprid was more persistent, as also observed in solar simulated experiments. When the experiment was performed in the absence of SBO, most of the EPs were also removed but longer irradiation time was
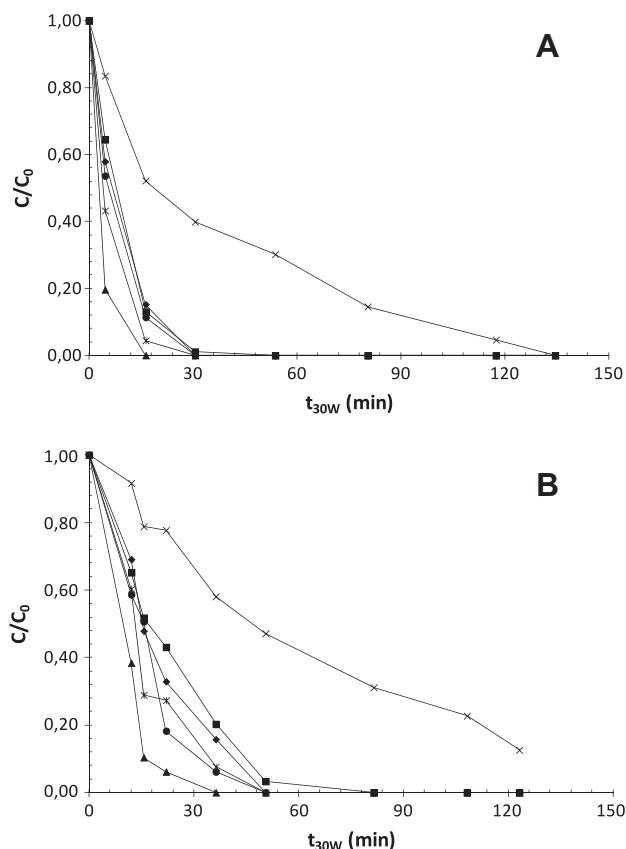
Fig. 6. Photodegradation of a mixture of 6 EPs by means of a solar photo-Fenton process at pH = 2.8 with (A) and without SBO (B). Plot of the relative concentration vs time: amoxycillin (▲), acetaminophen (♦), acetemiprid (×), caffeine (■), clofibric acid (●) and carbamazepine (∗). $[EP]_0$ = 5 mg $L^{-1}$; $[Fe(II)]_0$ = 5 mg $L^{-1}$; $[H_2O_2]_0$ = 5 - mg $L^{-1}$; $[SBO]_0$ = 10 mg $L^{-1}$.

required. At $t_{30W}$ = 30 min only amoxicillin was removed from the reaction medium, clofibric acid, carbamazepine, acetaminophen and caffeine (in a 20–30% range) and acetamiprid (ca. 60%) still remained in the reaction mixture (Fig. 6B). The pH variation was followed throughout the experiment: a slight acidification of the sample was detected to reach a final value of 4.7. This could be due to the formation of carboxylic acids during the oxidation of organics; this slight acidification might contribute to some enhancement of the photo-Fenton and hence, it is a desirable effect from the technical point of view.

Preliminary experiments were performed in order to check changes in the toxicity of the photo-treated sample according to the *V. fischeri* assay. Initial toxicity of the mixture of the 6 EPs and SBO was ca. 20%. In the early stages of the process some increase in the inhibition was observed to reach values in the range 30–40% after 30–60 min of irradiation. Beyond this point, toxicity decreased slowly to be systematically below 30%. This indicates that although some intermediates which are more toxic that the parent products might be released, as reported by other authors for advanced oxidation processes at mild conditions, they do not constitute a significant concern as toxicity was always below 50% even for this highly sensitive assay. Furthermore, SBO do not seem to be toxic at the concentrations employed in this work according to this procedure; however, further research to determine its real biocompatibility is needed, as well as to completely rule out the release of toxic by-products.

Finally, in order to test the pH effect, experiments were conducted a pH = 2.8 and 7. At pH = 7 only amoxicillin and acetaminophen were removed after 150 min of normalized irradiation (90%

and 60%, respectively; see Fig. S5, Supplementary data). Although SBO was able to improve the performance of photo-Fenton at this pH, the process is not applicable under these conditions because of its low efficiency; the pH remained stable during the process (final pH was 7.1), in agreement with the poor oxidation that was achieved. Interestingly, the two EPs that show some degradation under these conditions (amoxicillin and acetaminophen) are also the EP showing faster photo-oxidation in the presence of *tert*-butyl alcohol, i.e. when HO· radicals were scavenged from the reaction medium. This is in agreement with a modified mechanism for photo-Fenton at neutral medium where HO· are not efficiently formed and alternative species (e.g. ferryl ions) predominate. At pH = 2.8, although higher degradation rates compared to pH 5.2 and 7 were observed (a complete degradation was achieved for 5 of the EPs and only less than 20% of acetamiprid remained after 25 min of normalized time; see Fig. S6, Supplementary data), the effect of SBO was slightly detrimental, in agreement with laboratory scale experiments.

## 4. Conclusions

Results reported in this paper show the potential applicability of SBO in photochemical methods for wastewater treatment. Irradiation experiments carried out in the presence of SBO show that the EPs can undergo significant indirect photoprocesses, whose contribution is similar to that obtained for humic substances. The addition of SBO to solutions containing the EPs and $H_2O_2$ at pH = 2.8 resulted in a significant increase of the degradation rate of each EP due to the participation of the iron contained in SBO in a photo-Fenton process.

The most promising results were obtained from experiments with extra amounts of iron either at laboratory scale or in pilot plant, which show that SBO are useful to enhance a photo-Fenton process at slightly acidic conditions. As a remarkable result, the degradation rates at pH 5.2 in the presence of SBO rank in the same order as those obtained at pH 2.8 in the absence of SBO.

Further research on the SBO effect for the photo-Fenton processes is still needed in order optimize the operational parameters that influence the process (e.g. hydrogen peroxide, SBO and iron concentration, pH), the possibility of using SBO with other composition as well as their biocompatibility and photostability. In addition elucidation of the photo-Fenton mechanism in the presence of SBO to identify additional reactive species is another important issue to be addressed in future work.

## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2013.09.009.

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