

## Chapter 2

# Photogeneration of Reactive Oxygen Species by SBO and Application in Waste-Water Treatment

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**Abstract** Soluble bio-based substances (SBO) extracted from urban bio-wastes have similar chemical properties to humic substances (HS) present in natural waters and soils. Therefore, SBO are also expected to have photochemical properties similar to HS. In this chapter, a summary of the photochemistry of HS is presented along with the recent advances related to the photogeneration of reactive species upon irradiation of aqueous solutions of SBO and some examples of pollutant degradation photo-induced by SBO.

**Keywords** Soluble bio-based substances (SBO) • Humic substances • Reactive oxygen species (ROS) • Wastewater • Emerging pollutants • Solar processes • Photo-Fenton

## 2.1 Introduction

Recently, urban bio-wastes have been shown as a potential cost-effective renewable source of soluble bio-based substances (SBO) [1]. The organic fraction of these materials has similar chemical nature and properties to humic substances (HS) present in natural waters and soils [2–4]. Therefore, SBO is expected to have photochemical properties similar to HS, which represent the main fraction of chromophoric dissolved organic matter (CDOM) that absorbs solar radiation. For this reason, a summary of the photochemically mediated processes induced by HS is outlined below.

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## 2.2 Photochemistry of HS

The UV-vis absorption spectra of Pahokee Peak humic acid (Fig. 2.1) decreases exponentially with increasing wavelength [5, 6], providing to aquatic organisms protection from damaging UV radiation, and giving color to surface waters. Spectra are often fit to Eq. 2.1, where  $a(\lambda)$  is the absorption coefficient at wavelength  $\lambda$ ,  $a(\lambda_0)$  is the absorption coefficient at a reference wavelength, and  $S$  is the spectral slope parameter [7].

$$a(\lambda) = a(\lambda_0) \times e^{-S(\lambda-\lambda_0)} \quad (2.1)$$

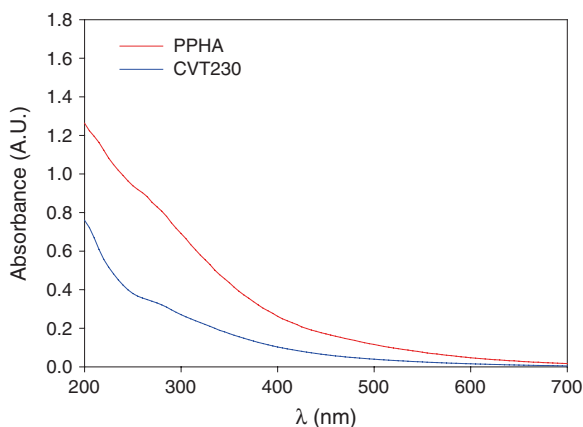
Higher values of  $S$  indicate a more rapid decline and a lower absorption contribution in the visible wavelengths. The ratio at two different wavelengths, e.g. 465 and 665 nm (namely E4/E6 ratio) was also employed to characterize the spectra [8]. The increase of molecular complexity of HS by formation of more extended and oxidized aromatic systems is expected to decrease the E4/E6 due to the relative increment of the absorption coefficient in the red region of the visible spectrum [9].

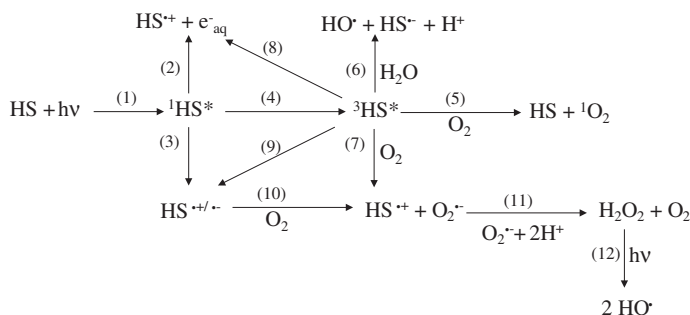
Recently, a model of the optical properties of HS was proposed [10]. In this model the absorption and emission spectra of HS arise from a very large number of absorbing and emitting states, where intramolecular electronic interactions between donor–acceptor chromophores play an important role. These electronic interactions between chromophores produce an array of photophysical and photochemical reaction channels. The relative importance of each channel varies with the HS source and environmental conditions due to varying abundance of electron donating and accepting groups and the effects of solution chemistry on excited-state energies [11].

The absorption of light by aqueous HS leads to the formation of several reactive species, as shown in Scheme 2.1.

The excited singlet states of HS ( $^1\text{HS}^*$ ) populated upon light absorption process (reaction 1) decay by: (i) fluorescence and internal conversion to ground state

**Fig. 2.1** UV-vis absorption spectra of Pahokee peat humic acid ( $20 \text{ mg L}^{-1}$ ) and SBO, namely CVT230 ( $20 \text{ mg L}^{-1}$ ) in water at pH 7.0





**Scheme 2.1** Photogeneration of reactive species

(pathways not shown in Scheme 2.1), (ii) to yield radical cations ( $\text{HS}^{++}$ ) and solvated electrons  $e^-_{\text{aq}}$  (photoionization process 2), (iii) to charge-separated species ( $\text{HS}^{+/-}$ ) formed by donor–acceptor electron transfer (reaction 3) or (iv) through intersystem crossing to the excited triplet states ( ${}^3\text{HS}^*$ ) (reaction 4).

Photoionization of aromatic groups of HS at excitation wavelengths from 250 to 400 nm leads to the formation of hydrated electrons  $e^-_{\text{aq}}$  [12, 13]. The quantum yields of  $e^-_{\text{aq}}$  generation is about  $10^{-5}$  to  $10^{-4}$  over the wavelength range from 300 to 400 nm [12, 14].

Triplet quantum yields are estimated to lie between 0.01 and 0.1 [15]. Reported values of the energy of the excited triplet states of HS ( ${}^3\text{HS}^*$ ) are over the range 180–250  $\text{kJ mol}^{-1}$  [16, 17]. Production of  ${}^1\text{O}_2$  by HS occurs via energy transfer from  ${}^3\text{HS}^*$  to ground-state  $\text{O}_2$  (reaction 5). Other decay routes of  ${}^3\text{HS}^*$  involve electron transfer processes (reactions 6–9).

The quantum yield of  ${}^1\text{O}_2$  formation lies in the range of 0.01–0.1, increases with decreasing excitation wavelength in the visible and near-UV and depends on the HS source and solution pH [18, 19].

Photogeneration of  $\text{O}_2^-$  is mainly related to the population of charge-transfer states ( $\text{HS}^{+/-}$ ) from  ${}^1\text{HS}^*$  and  ${}^3\text{HS}^*$  (reactions 3 and 9) of HS and subsequent reduction of oxygen to  $\text{O}_2$  (reaction 10) [19]. Hydrogen peroxide is produced by dismutation of  $\text{O}_2^-$  (reaction 11) [20]. Quantum yields for  $\text{H}_2\text{O}_2$  production are also wavelength-dependent and at ca. 350 nm range from  $5 \times 10^{-5}$  to  $10^{-3}$  for different samples [11].

The photogeneration of hydroxyl radical ( $\text{HO}^\bullet$ ), a highly reactive oxidant that unselectively reacts at near diffusion-controlled rates with most organic substrates, was widely investigated [21–23]. Although there is evidence for the involvement of oxygen-dependent, oxygen-independent and hydrogen peroxide-dependent pathways, the mechanism still remains unclear [21, 22]. Possible generation pathways include the photolysis of hydrogen peroxide (reaction 12) and hydrogen abstraction from water by the excited triplet state of substituted benzoquinones, which are components of HS (reaction 6). In the presence of iron,  $\text{HO}^\bullet$  can also be formed through Fenton-like chemistry involving  $\text{H}_2\text{O}_2$  and a HS photo-reductant [21, 24].

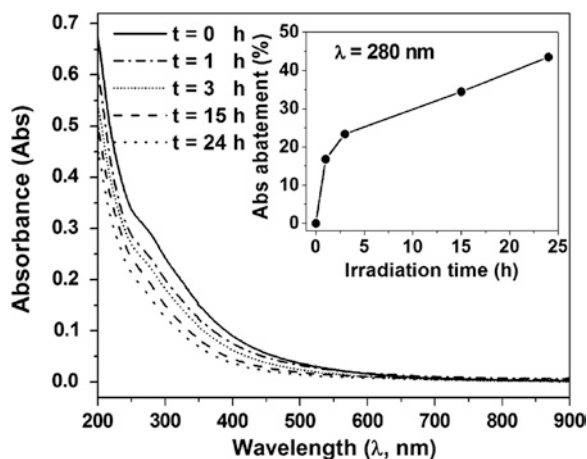
The UV-visible absorption of HS is very sensitive to changes produced by photolysis [25]. Bosio et al. [26] investigated the changes in the absorption spectra of 0.1 g L<sup>-1</sup> solution of Aldrich Humic Acid upon irradiation with excitation wavelengths  $\lambda > 320$  nm. From changes in the UV-visible spectra taken at different irradiation times and under various conditions it was possible to elucidate the involvement of the photogenerated reactive oxygen species (ROS) in the photodegradation of the humic acid. The observed changes increase with increasing oxygen concentration in the solutions, in line with ROS involvement in the photodegradation process. Experiments carried out with specific chemical probes showed that the participation of <sup>1</sup>O<sub>2</sub> and HO<sup>•</sup> in the photodegradation of HS seems to be more relevant than that of O<sub>2</sub><sup>-</sup>. The effect of H<sub>2</sub>O<sub>2</sub> was found to be negligible.

### 2.3 Photochemical Generation of ROS by SBO

Generation of ROS upon irradiation of HS solutions was discussed in the previous section. Because of the similar estimated molecular weights and the pH-dependence of their solubility, SBO should be compared to humic rather than to fulvic acids. The generation of ROS upon irradiation of two types of SBO, namely AC8 and CVT230, has been investigated with the purpose of employing these substances as photosensitizers in the degradation of organic contaminants present in waste waters. To this aim in situ electronic paramagnetic resonance (EPR) experiments using the spin trapping approach were performed [27, 28]. This method involves the addition of transient radical species to a diamagnetic compound (spin trap), with the formation of a paramagnetic persistent radical (spin-adduct). In general, the spin-adduct is more stable than the original free radical and can be analyzed afterwards with EPR spectroscopy. The spin trap, generally a nitron or nitroso compound, must be stable under the reaction conditions, undergo radical addition quickly in order to avoid further reactions of the radicals before the trapping, and not suffer secondary. The compounds 4-oxo-TMP (45 mM) and DMPO (17.4 mM) were employed as trapping agents for <sup>1</sup>O<sub>2</sub> and HO<sup>•</sup>, respectively [29].

Irradiation experiments in the presence of various amount of SBO (concentration  $\leq 2$  g L<sup>-1</sup>) showed that the intensity of 4-oxo-TEMPO is proportional to AC8 concentration. Similar experiments performed with CVT230 in the concentration range up to 5 g L<sup>-1</sup> showed the same trend. However, the concentration of the DMPO-OH adduct increases as SBO (either AC8 or CVT230) concentration increases until a maximum value of about 20–50 mg L<sup>-1</sup>, and then decreases at higher concentration of SBO. This behavior can be explained considering the competition between production and scavenging of HO<sup>•</sup> radicals. This result is in line with reported changes in the UV-visible spectrum of SBO upon irradiation (see next section).

**Fig. 2.2** UV-vis spectra of 150 mg L<sup>-1</sup> AC8 aqueous solution at variable irradiation times, recorded after 10× sample dilution. Inset: absorbance (Abs) abatement % at 280 nm versus irradiation time. From Ref. [30]. Reproduced with permission of Elsevier



## 2.4 Photostability of SBO

The photostability of SBO in aqueous solution under steady-state irradiation was followed by measuring its UV-visible spectrum concentration at different irradiation times. Figure 2.2 shows the decrease in the UV-VIS absorbance of a 150 mg L<sup>-1</sup> AC8 solution upon irradiation ( $\lambda > 340$  nm). The inset of Fig. 2.2 shows the evolution of the absorbance at 280 nm. Several functional groups could be responsible for the absorption around 280–300 nm, which arises from  $\pi$  to  $\pi^*$  electron transitions occurring in phenolic arenes, benzoic acids, aniline derivatives, polyenes and polycyclic aromatic hydrocarbons with two or more rings [30]. Moreover, the presence of aromatic moieties as major molecular components of AC8 was confirmed by <sup>13</sup>C NMR spectroscopy [29]. Since irradiation was performed with  $\lambda > 340$  nm, direct photolysis of chromophores absorbing at 280 nm should be neglected. Thus, the AC8 photodegradation should arise from population of excited states of other chromophores, which promote the formation of reactive species able to react with aromatic moieties. As a result, the absorbance of SBO at 280 nm decreases.

## 2.5 Application of SBO for the Photo-Degradation of Pollutants in Waters

Based on the photochemical properties of SBO and their capacity of generating reactive species, the application of these substances as photosensitizers in wastewater treatment could constitute a very convenient and sustainable alternative to the conventional treatments from both the economic and ecological point of view. Moreover, the use of SBO for water detoxification may be considered a green

process since it valorizes solid waste as a material of technological application. Taking this into account, many studies were encouraged to elucidate the potential applications of SBO employing UVB-UVA, simulated solar light and real solar light as irradiation sources to degrade different kind of pollutants, such as dyes, naphthalene sulfonates, chlorophenols, and emerging pollutants.

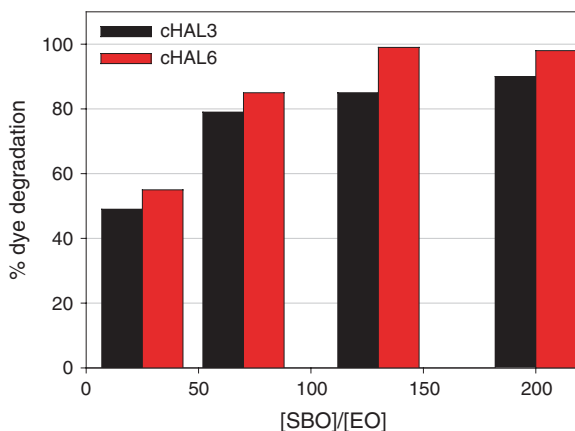
In this section, we have compiled different investigations of the degradation of the pollutants specified above photo-induced by SBO.

### 2.5.1 Dye Degradation

Three commercial sulfonated azo-dyes, ethylorange (EO), Orange I (OI) and Orange II (OII) were photo-degraded under simulated solar irradiation in the presence of SBO isolated from urban yard trimmings (cHAL3) and from a 1:1 (w/w) mix of food (humid) and green residues at the start of the aerobic digestion process (cHAL6) [31]. Aqueous solutions of these azo-dyes at  $5 \text{ mg L}^{-1}$  concentration have been irradiated in the presence of variable amounts of cHAL3 and cHAL6. Figure 2.3 shows that an increase in the SBO/EO ratio, yields higher dye % abatement. In particular a complete removal of EO can be achieved with cHAL6, indicating that SBO can be successfully used as photosensitizers. Also, the results demonstrate that in all cases nearly quantitative dyes abatement can be achieved with kinetics following a pseudo first-order law. On the other hand, the comparison of dye abatement rate, solution bleaching and sulfate evolution (as indicator of the dye mineralization) showed that the photobleaching is delayed compared to the dye disappearance and the amount of sulfate is lower than the stoichiometric value. These results can be associated with the formation and accumulation of colored intermediates containing the sulfonic group.

The photodegradation of aqueous solutions of the cationic xanthenic dye crystal violet (CV) was also studied. In this case, photochemical experiments were carried

**Fig. 2.3** Dye % degradation versus cHALi ( $i = 3$  or  $6$ )/EO (w/w) ratio after 3 h irradiation in Solarbox



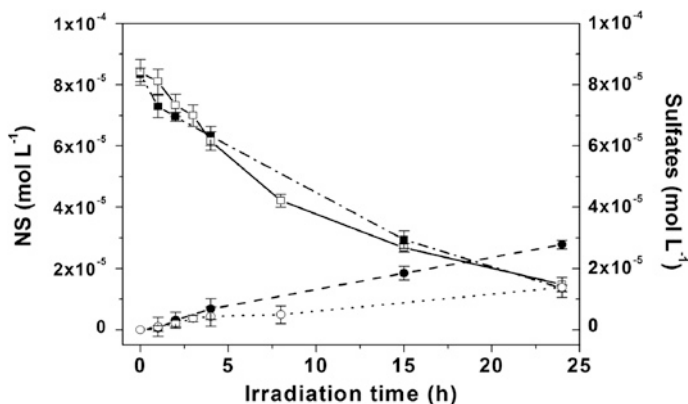
**Table 2.1** Apparent bleaching constant ( $k_{app}$ ) as a function of SBO content

SBO (mg L <sup>-1</sup> )	$k_{app}$ ( $\times 10^3$ min <sup>-1</sup> )
–	$0.60 \pm 0.05$
2.5	$1.30 \pm 0.06$
5	$3.10 \pm 0.19$
10	$3.20 \pm 0.08$
25	$3.70 \pm 0.13$
50	$2.84 \pm 0.14$
100	$2.19 \pm 0.06$
200	$1.68 \pm 0.04$

out in a reactor equipped with a medium-pressure mercury arc lamp with a glass jacket to cut-off the radiation with wavelengths shorter than 300 nm and with the specific SBO, referred to as CVT230, isolated from the alkaline hydrolyzate of urban private gardening and public park trimming residue compost. The role of CVT230 on the photobleaching of CV in aqueous solution was investigated by recording the absorption spectra of CV at different irradiation times. A noticeable decrease of the CV absorbance at 532 nm was observed. The discoloration kinetics was fitted to a pseudo-first order law and an apparent bleaching constant ( $k_{app}$ ) for each experimental condition was calculated. The irradiation of CV solutions performed in the absence and presence of different amounts of CVT230 clearly shows that SBO promote the indirect photochemical degradation of CV (Table 2.1). The results show that SBO enhance the photobleaching of CV solutions with an optimal SBO concentration of ca. 20 mg L<sup>-1</sup>. Mechanistic investigation based on chemical probes and changes in the absorption spectrum of CV in the presence of SBO seems to indicate that a complex formed between sensitizer and substrate plays a major role in the process [32].

### 2.5.2 Naphthalene Sulfonates Degradation

Naphthalene sulfonates are widely employed in many industrial processes as dispersants, stabilizers, suspending and wetting agents, and intermediates for dye synthesis. In this section, the removal efficiency of naphthalene sulfonates photo-induced by SBO is discussed. Four different naphthalene sulfonates, 1-naphthalenesulfonic sodium salt (1-NS), 2-naphthalenesulfonic sodium salt (2-NS), 1,5-naphthalenedisulfonic acid (1,5-NdS) and 2,6-naphthalenedisulfonic disodium salt (2,6-NdS), have been used as substrates. The SBO used in this study, referred to as AC8, was sourced from a UBW that was the product of the aerobic digestion of a 2:1 food/green residue mixture aged for 110 days. The results showed that 4 h irradiation of solutions containing 20 mg L<sup>-1</sup> of the probe substrates in the presence of 50–500 mg L<sup>-1</sup> AC8 increases the degradation yield to 15–30 %. Also, substrate and sulfate ion concentration were monitored at different irradiation times. The results obtained for experiments with 150 mg L<sup>-1</sup> AC8 are shown in



**Fig. 2.4** Concentrations of naphthalene sulfonates (NS) and sulfates ( $\text{mol L}^{-1}$ ) versus irradiation time (h) in the presence of  $150 \text{ mg L}^{-1}$  AC8: data for 1-NS (*filled square*) and 2-NS (*open square*) substrates and for the sulfates released from 1-NS (*filled circle*) or 2-NS (*open circle*) degradation. From Ref. [30]. Reproduced with permission of Elsevier

Fig. 2.4. The data, based on substrate depletion, indicate that after 24 h irradiation, 65–80 % of substrate removal is obtained. In the presence of AC8, photodegradation of the sulfonates seems to be slightly faster than that of the disulfonates. This lesser reactivity of the latter might result from the lower electron density of the aromatic nuclei and, thus, reduced electron availability for the electrophilic ROS.

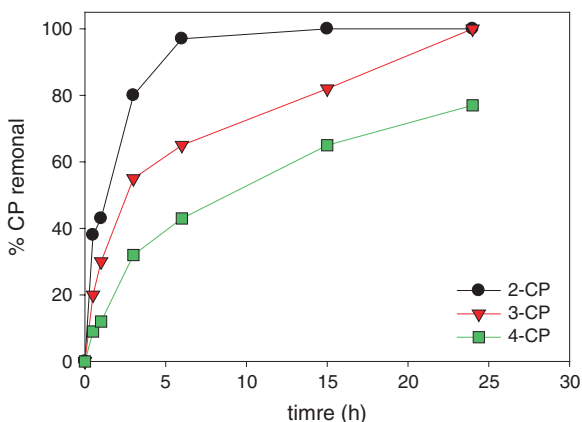
Among several possible ROS species formed upon AC8 irradiation, previous work has provided evidence for the formation of  $\text{HO}^\bullet$  radicals and singlet oxygen [29] (see Sect. 2.3). Irradiation experiments of 2-NS and 1,5-DNS in the presence of 2-propanol (0.01 M), an  $\text{HO}^\bullet$  radical scavenger [33], showed a significant decrease in the percentage degradation for both substrates. These results confirm the relevant role played by the  $\text{HO}^\bullet$  radicals in the photodegradation process [30].

### 2.5.3 Chlorophenols Degradation

2-chlorophenol (2-CP), 3-chlorophenol (3-CP) and 4-chlorophenol (4-CP) were chosen as target substrates because of their environmental relevance. They belong to a class of priority toxic pollutants listed by the US EPA; they are toxic, hardly biodegradable and their removal from the environment is complex.

Photochemical experiments using a solarbox as irradiation source and in the presence of CVT230 as SBO source were conducted. Aqueous solutions of each chlorophenol ( $1 \times 10^{-4} \text{ M}$ ) were irradiated in the presence of CVT230 ( $500 \text{ mg L}^{-1}$ ), at an initial  $\text{pH} = 9.4$ , value obtained by simply dissolving SBO in water at the indicated concentration. A progressive degradation for all the substrates up to their complete disappearance within 24 h of irradiation is obtained





**Fig. 2.5** Percentage of substrate degradation in the function of the irradiation time.  $[\text{chlorophenols}]_0 = 1.0 \times 10^{-4} \text{ M}$ ;  $[\text{CVT230}]_0 = 500 \text{ mg L}^{-1}$

(Fig. 2.5). Substrate degradation curves can be fitted to a pseudo-first order degradation law. The reactivity order observed for the three substrates was  $2\text{-CP} > 3\text{-CP} > 4\text{-CP}$ . On the other hand, the monitoring of chloride ion in this experiment, revealed that a close relationship between the degradation of each chlorophenol and the chloride ion formation [34]. After 24 h, the mineralization of organic Cl is 70 % for 4-CP and nearly quantitative for 2-CP and 3-CP. These results suggest that dechlorination occurs at the early stages of the reaction, and formation of major amounts of chlorinated organic byproducts should not be expected.

The pH showed to play a significant role in the degradation of chlorophenols. Lower degradation rates were obtained in experiments performed at neutral pH. This result can be discussed taking into account the acid/base properties of chlorophenols ( $\text{pK}_a$  values around 9–10). The bimolecular rate constants for the reactions of singlet oxygen with the basic forms of chlorophenols are two orders of magnitude higher than those corresponding to the acidic forms [35]. Instead, the reactions of HO radical with chlorophenols are not significantly affected by the dissociation of the substrates. This suggests that singlet oxygen might play a major role in the photooxidation of chlorophenols under the studied experimental conditions.

### 2.5.4 Emerging Pollutants Degradation

A solution containing a mixture of the six emerging pollutants (EP), namely acetaminophen, caffeine, amoxicillin, carbamazepine, acetamiprid and clofibric acid ( $5 \text{ mg L}^{-1}$  of each EP) was used as probe in the photochemical experiment.

A solar simulator as irradiation source and different amounts of CVT230 (20 and 200 mg L<sup>-1</sup>) were used. It is important to mention that almost all the EPs were significantly degraded in the absence of CVT230 by direct photolysis (except for carbamazepine and caffeine which present low quantum efficiencies of consume) [36]. The presence of the CVT230 in the experiments resulted in a significant decrease in the photolysis rate of the pollutants, as shown by the calculated pseudo-first order rate constants of each EP which were reduced up to 50 % in the presence of 20 mg L<sup>-1</sup> of CVT230 and even 80 % with 200 mg L<sup>-1</sup>. This behavior can be attributed to a light screening effect of the highly colored organics CVT230 over the direct photolysis of each EP. Despite these results, CVT230-mediated photogeneration of reactive species that contribute to the indirect photolysis of the EP should not be ruled out [37].

The addition of H<sub>2</sub>O<sub>2</sub> to the reaction medium at pH 7 resulted in a faster photodegradation of the EPs in the absence of CVT230 for almost all the EPs (except for clofibric acid and acetamiprid). Moreover, the effect of H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub>. Since a low rate of production of HO radicals is expected from the absorption coefficients of H<sub>2</sub>O<sub>2</sub> above 280 nm [38], 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<sup>-1</sup> of CVT230, although lower rates were obtained for each EP, most probably due to the light screening effect and scavenging of HO radicals by SBO. These results (in absence and presence of H<sub>2</sub>O<sub>2</sub>) indicate that SBO are not effective as photosensitizers when pollutants have significant direct photolysis.

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