



Application of soluble bio-organic substances (SBO) as photocatalysts for wastewater treatment: Sensitizing effect and photo-Fenton-like process

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ABSTRACT

Soluble bio-organic substances (SBO) isolated from urban biorefuses have been investigated in photocatalytic processes for wastewater treatment using a cationic dye, namely crystal violet (CV) as target compound. The SBO have been found to enhance the photobleaching of CV solutions with an optimal SBO concentration of ca. 20 mg L⁻¹. 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. SBO have also been tested for the implementation of photo-Fenton processes at circumneutral media: the observed pseudo first order rate constants for CV decoloration was higher for UV/SBO/Fe(II)/H₂O₂ (5.5 × 10⁻³ min⁻¹) than for UV/Fe(II)/H₂O₂ (1.5 × 10⁻³ min⁻¹). A modified mechanism, in which HO• are less relevant than at the acidic medium, is in agreement with results of experiments carried out with chemical probes.

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1. Introduction

Dissolved organic matter (DOM) has received much attention from researchers in recent years because of its photochemical properties. In particular, humic and fulvic acids have been shown to generate, upon solar irradiation, oxidizing species such as hydroxyl radical [1,2], singlet oxygen [3], superoxide radical ion [4] or reactive triplet excited states [5,6]. These species can react with chemicals present in surface waters and participate in the most important abiotic processes for xenobiotics removal [7]. A review on the use of organic compounds with photochemical activity (namely dyes) for water treatment has been very recently published [8]. Unfortunately, DOM cannot be considered at commercial level as viable agent for the detoxification of wastewater due to the low concentration in water and soil.

Recent work reports how urban bio-wastes (UBW) have become a sustainable source of soluble bio-organic substances (SBO) having similar origin, chemical nature and photosensitizing properties as DOM [9]. It is interesting to note, that bio-wastes may have a potential beneficial fall out for environment. The potential use of SBO as photocatalyst for water detoxification of aqueous effluents

may be considered a green process since it valorizes solid waste as a material of technological application.

The SBO are described as mixtures of macromolecules with weighted average molecular weight (M_w) ranging from 67 to 463 kg mol⁻¹ and polydispersity indexes (M_w/M_n) in the 6–53 range. When analyzing chemical composition data these macromolecules appear to be formed by long aliphatic C chains substituted by aromatic rings and several functional groups as COOH, CON, C=O, PhOH, O-alkyl, OAr, OCO, OMe, and NRR', with R and R' being alkyl substituents. These organic moieties are the likely memory of the main constituents of the sourcing bio-organic waste which are not completely mineralized during aging under aerobic fermentation conditions. For this reason, SBO may be considered to be the pristine material of DOM formed under longer aging conditions. The former, together with easier and continuous availability, seem to have some other interesting features. They can be obtained over a wide range of chemical composition depending on the type, location and treatment of the sourcing UBW [10]. Due to the presence of functional groups with strong metals' chelating power, the SBO contain a considerable fraction of minerals which are hard to separate from the organic matter. In principle some of these minerals, such as iron, could contribute to determine the SBO photochemical activity. Therefore, for their capacity to hold iron ions in solution at neutral–alkaline pH, SBO offer intriguing scope to investigate possible photo-Fenton-like processes occurring under pH conditions where iron ions are normally not soluble.

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To fully understand the rationale motivating the present work, it should be considered that the Fenton reagent consists of a mixture of iron salts and hydrogen peroxide which is able to generate highly oxidizing species, such as hydroxyl radical [11]. The process is highly enhanced by irradiation and sunlight can be employed for this purpose with ecological and economical advantages [12]. Although this method has proven to be efficient, it is limited by the acidic pH that is required, partly due to the low solubility of iron at neutral media. In order to overcome this inconvenience, complexing agents such as humic acids have been employed [13–16]. Although previous papers have reported interesting photosensitizing behavior [17,18], the applicability of SBO for photo-Fenton remains unexplored. The present paper is meant to contribute further insight into the applicability of SBO in photochemical processes for wastewater treatment. For this purpose, crystal violet (CV), a cationic dye, was used as model compound. The role of SBO in the photobleaching of CV solutions was then studied in two different directions, namely as photosensitizer and as complexing agent to drive photo-Fenton processes under non acidic conditions.

2. Experimental

2.1. Reagents

Crystal violet (Anedra), $\text{Fe}(\text{ClO}_4)_3 \cdot n\text{H}_2\text{O}$ (Aldrich), H_2O_2 (Perhydro 30%, Merck), furfuryl alcohol (99%, Aldrich) and 2-propanol (Anedra) were analytical grade and used as received. Water of Milli-Q quality was used in all the experiments.

2.2. SBO isolation and characterization

The investigated SBO, namely CVT230 was sourced from UBW sampled from the process lines of ACEA Pinerolese waste treatment plant in Pinerolo (Italy). The UBW was a material obtained in the compost production section from urban vegetable residues aged for 230 days. The UBW were processed further in a pilot plant made available from Studio Chiono e Associati in Rivarolo Canavese, Italy. This comprised an electrically heated mechanically stirred 500 L reactor, a 102 cm long \times 10.1 cm diameter polysulfone ultrafiltration (UF) membrane with 5 kDa molecular weight cut-off supplied by Idea Engineering s.r.l., and a forced ventilation drying oven. UBW were digested 4 h at 60 °C, pH 13 and 4V/w water/solid ratio. The liquid/solid mixture was allowed to settle to yield the supernatant liquid phase containing the soluble UBW hydrolyzate. The recovered liquid phase was circulated at 40 L h⁻¹ flow rate through the UF membrane operating with tangential flow at 7 bar inlet and 4.5 bar outlet pressure to yield a retentate with 5–10% dry matter content. The concentrated retentate was finally dried at 60 °C. The solid SBO product obtained in 15–30% (w/w) yield, relatively to the starting UBW dry matter, was found to contain 72.1% (w/w) of volatile solids. The carbon content was 38.3% which, in turn, could be classified according to the functional: aliphatic groups (37%), amines (7%), alkoxy (14%), anomeric (4%), aromatic (13%), phenolic (5%), phenoxy (2%), carboxylic (12%), amide (1%) and ketone (5%). It is remarkable that ca. 0.77% (w/w) of iron was found in the chemical composition of CVT230.

2.3. Experimental conditions

Photochemical experiments were carried out in a 500 mL glass reactor equipped with a medium-pressure mercury arc lamp (Philips HPK 125 W) with a glass jacket that cut-off the radiation with wavelengths shorter than 300 nm. The solution was continuously bubbled with analytical air and the temperature of the system was kept at 25 °C. The photon flux per unit volume sample (P_0), measured using potassium ferrioxalate as actinometer

[19], was 3.2×10^{-6} einstein s⁻¹ L⁻¹. In all the experiments, the pH of the medium was adjusted to 7.0. The initial concentration of CV was 10 mg L⁻¹ which corresponded to an absorbance of ca. 1.6 AU in order to allow an easy monitoring of the reaction. Similar concentration was employed by Bianco Prevot et al. [17] when studying the SBO-mediated photodegradation of ethylorange. The initial concentrations of SBO varied over the range from 1 to 200 mg L⁻¹. Samples were eventually taken from the reaction and their absorption spectra were recorded on a double-beam Shimadzu spectrophotometer using quartz cells of 1.0 cm optical path length.

In the case of photo-Fenton, the concentration of SBO was 100 mg L⁻¹, as under these conditions precipitation of iron could be avoided. The amount of hydrogen peroxide was 8.3 mg L⁻¹, this accounts for a 1:10 molar ratio CV:H₂O₂, which has been commonly employed for aromatics in photo-Fenton reaction. The pH was adjusted to 7 by adding either NaOH or H₂SO₄.

Dissolved organic carbon (DOC) was analyzed with a Shimadzu model TOC-V CSH apparatus. COD was determined photometrically according to the dichromate method; digestions were carried out at 148 °C in a Thermoreaktor TR300 (Merck) and a Spectroquant NOVA 60 (Merck) was used for the photometric determination.

2.4. Mathematical analysis

Multivariate curve resolution-alternating least squares (MCR-ALS) was applied for investigating CV–SBO interactions. This procedure has already been successfully applied to the study of equilibria, when neither models nor prior information about the number and identity of the species involved were available [20,21]. This method is based on the resolution of the experimental data matrix, $\mathbf{A}(m \times w)$, into matrices $\mathbf{C}(m \times n)$ and $\mathbf{S}^T(n \times w)$, by the iterative application of the following matrix product: $\mathbf{A} = \mathbf{C}\mathbf{S}^T + \mathbf{E}$, where $\mathbf{C}(t \times n)$ is the concentration profile matrix; $\mathbf{S}^T(n \times w)$ is that containing the pure spectra of the chemical species involved, and $\mathbf{E}(m \times w)$ represents the error matrix. Symbols m , n , and w denote the SBO concentration for each spectrum, the number of absorbing species, and the recorded wavelengths, respectively. The value of n is usually unknown and, thus, singular value decomposition (SVD) was applied for the estimation of n [21].

3. Results and discussion

3.1. Photolysis of CV in the presence of SBO

The role of SBO on the decoloration of CV in aqueous solution was investigated by recording the absorption spectra of CV at different irradiation times under the following experimental conditions: $[\text{CV}] = 10 \text{ mg L}^{-1}$ and $[\text{SBO}] = 25 \text{ mg L}^{-1}$ at pH = 7.0. Fig. 1 shows a noticeable decrease in the band with a maximum at 532 nm, which can be associated to the removal of CV. The discoloration kinetics, based on the absorbance recorded at 532 nm, can be fitted to a pseudo-first order law (Fig. 1, inset). Although this simple model cannot be considered to account in detail for the complexity involved in this kind of photoreactions, it can represent a useful tool for comparison purposes, allowing calculating an apparent bleaching constant (k_{app}) for each experimental condition. In order to ascertain the possible role of direct photolytic degradation, the irradiation of CV solution was also performed in the absence of SBO. The trends reported in the inset in Fig. 1, together with the calculated k_{app} of $3.5 \times 10^{-3} \text{ min}^{-1}$ and $5.8 \times 10^{-4} \text{ min}^{-1}$ in the presence and in the absence of SBO, respectively, clearly show that SBO promote the indirect photochemical degradation of CV.

The effect of the concentration of SBO on the decoloration rate was investigated. Fig. 2 shows the plot of k_{app} as a function of the

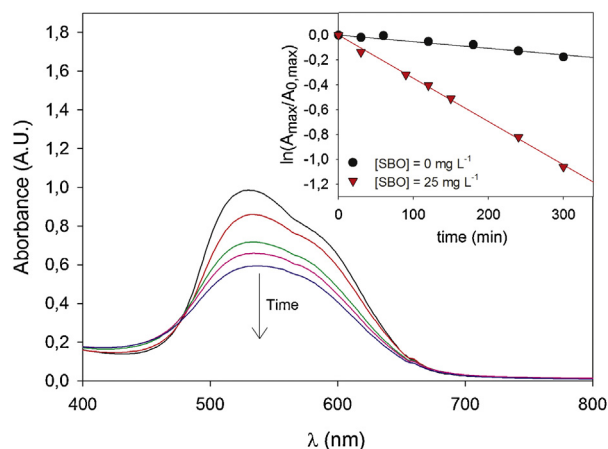


Fig. 1. Absorption spectra of aqueous solutions of CV in the presence of SBO obtained at different irradiation times. [CV] = 10 mg L⁻¹; [SBO] = 25 mg L⁻¹; pH = 7. Inset: plot of $\ln(A_{\max}/A_{0,\max})$ vs. time obtained for photolysis of CV (10 mg L⁻¹) in the absence and in the presence of SBO (25 mg L⁻¹).

concentration of added SBO. The bleaching rate of CV was observed to increase upon increasing the concentration of SBO, reaching a maximum value at [SBO] = 15–25 mg L⁻¹. Beyond this point, further SBO additions lead to lower k_{app} values. Analogous behaviors have also been reported for heterogeneous photochemical systems, such as TiO₂ [12] and for heterogenized organic photocatalysts [22]. In those cases, the existence of a maximum was attributed to a light screening effect at higher concentrations of the photocatalyst. However, in the system examined in this work other concentration-dependent processes cannot be ruled out, among them scavenging by SBO of the generated reactive species, or the formation of photoactive complexes between SBO and CV.

3.2. Mechanistic studies

A series of experiments was therefore devoted to gain further insight into the mechanistic aspects of the bleaching of CV in the presence of SBO. First, the role of different reactive species was investigated using chemical quenchers. For this purpose, solutions containing CV and SBO were irradiated in the presence of either 2-propanol, an HO[•] scavenger [23] or furfuryl alcohol, a singlet oxygen trapping agent [24]. None of these probes had any effect on the degradation rate (Fig. 3). This implies that none of these reactive species plays a major role in the CV photobleaching process. On the other hand, when nitrogen purged (deoxygenated) solutions were

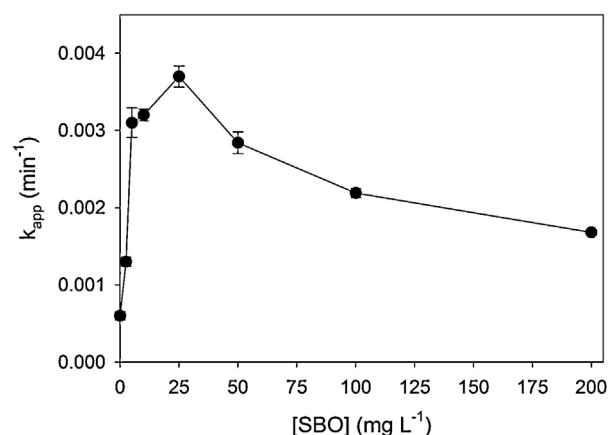


Fig. 2. Apparent bleaching constant (k_{app}) as a function of SBO content. [CV] = 10 mg L⁻¹; pH = 7. The error bars represent standard deviations.

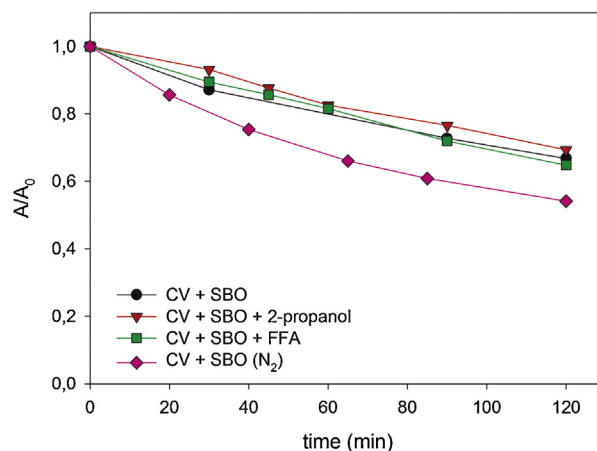


Fig. 3. Photodegradation of CV (10 mg L⁻¹) with SBO (25 mg L⁻¹) in the presence of 2-propanol (0.03 M) and furfuryl alcohol (FFA) (0.001 M). For comparison purpose an experiment without oxygen (purged with N₂) was added.

employed, a faster CV bleaching was observed (Fig. 3). As molecular oxygen is known to be a triplet quencher, the faster CV bleaching observed in the absence of oxygen suggests that a triplet state could be involved in the CV degradation process.

It is worth to be mentioned that CV has been reported to form complexes with humic substances [25]. Hence similar CV–SBO complexes might be formed and play a relevant role in the process which deserves to be investigated too. In fact, mechanisms involving photosensitizer–pollutant complexes have already been proposed for organic photocatalysts, such as for the photochemical elimination of pesticides in the presence of triphenylpyrylium [26]. In order to gain further insight into this possible mechanistic route, the absorption spectra of CV were recorded in the range 400–800 nm with different amounts of SBO in aqueous solutions at pH = 7. Fig. 4 shows that addition of SBO resulted in significant changes in the visible spectrum of CV. Neat CV exhibited an absorption band with a maximum at 583 nm and a shoulder at ca. 540 nm. The presence of increasing SBO concentrations resulted in a decrease of the intensity of the band at 583 nm and affected the maximum/shoulder absorbance ratio. Similar changes in the absorption spectra of CV in the presence of anionic surfactants were attributed to the formation of ion pairs and subsequent dye dimerization [27–29]. The latter phenomenon could be justified by assuming that association of anionic surfactants with the cationic dye results in a decrease of the electrostatic repulsions between the =N⁺(CH₃)₂ groups of the dye, thus favoring dimerization of

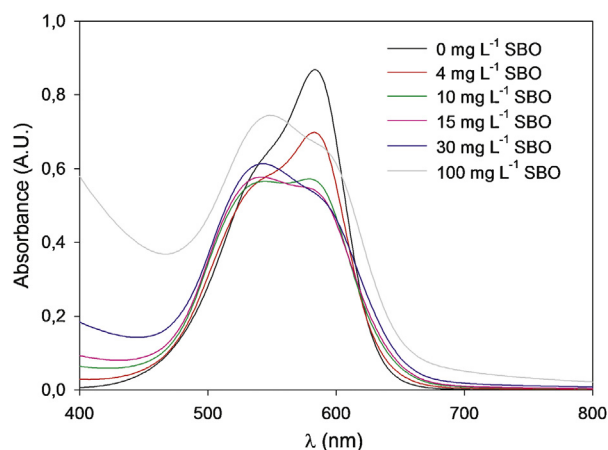


Fig. 4. UV-vis spectra of CV with different amounts of SBO. pH = 7.

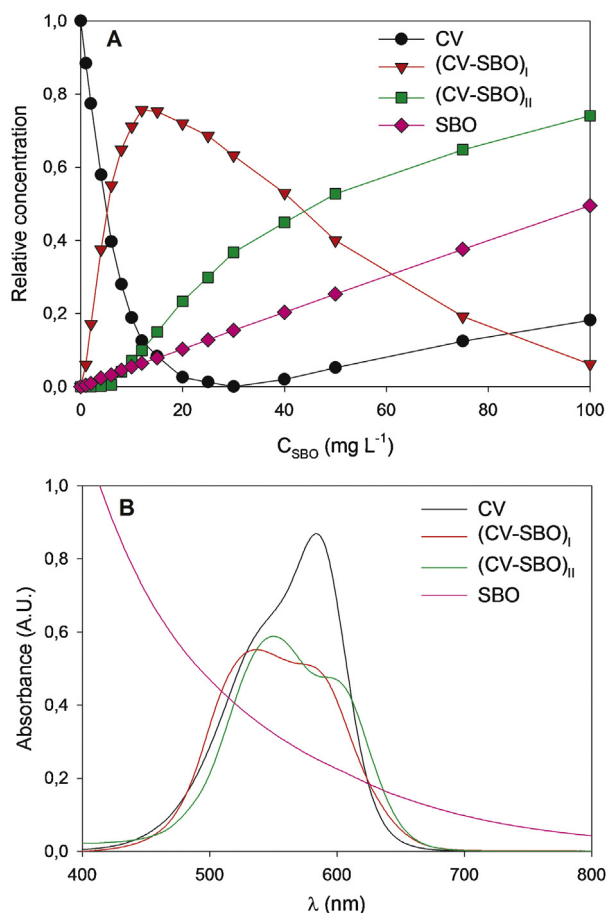


Fig. 5. (A) The concentration profiles at different SBO concentrations and (B) the pure spectra of the four components calculated using MCR-ALS.

the dye molecules [30]. Also with SBO several species could in principle be formed, and such an occurrence would explain the changes observed in the CV spectrum upon increasing SBO concentration. To better understand the system, the multivariate curve resolution-alternative least square (MCR-ALS) method was chosen as a powerful tool for resolving spectra and concentration profiles of the mixture. This method allows the estimation of changes in concentration and spectra without any previous assumptions. The SVD analysis of the absorption matrix shows that all traces can be reproduced by considering at least four independent components whose concentration profiles and absorption spectra are shown in Fig. 5A and B, respectively.

Fig. 5A shows that for SBO concentration below 15 mg L⁻¹, addition of this material resulted in a decrease of free CV and in the formation of a new species, probably a complex between CV and SBO (CV-SBO)_I, which shows a blue shift in the UV-vis spectrum. The amount of this intermediate component decreased as the SBO concentration increased above 15 mg L⁻¹. Another species, (CV-SBO)_{II}, was formed and it became predominant above 40 mg L⁻¹ of SBO. As the concentration of SBO increases, molecular conformation changes and formation of pre-micellar aggregates are expected [31]. Hence, (CV-SBO)_{II} might result from the electrostatic interaction between CV and the SBO molecules in the changed solution conformation at this concentration. Fig. 5A also shows that at SBO concentrations higher than 30 mg L⁻¹, the amount of free CV starts to grow again. The same trend has also been reported for CV in the presence of sodium dodecylsulfate (an anionic surfactant) [32] and it has been attributed by the authors to the solubilization of CV in the surfactant aggregates.

Table 1

Apparent pseudo-first order rate constant for the photodecoloration of CV solutions under different conditions.

No. exp.	Conditions	$k_{app} (\times 10^3) (\text{min}^{-1})$
1	CV	0.58 ± 0.06
2	CV + H ₂ O ₂	1.57 ± 0.06
3	CV + H ₂ O ₂ + Fe(II)	1.49 ± 0.09
4	CV + SBO	1.79 ± 0.07
5	CV + SBO + H ₂ O ₂	2.79 ± 0.11
6	CV + SBO + H ₂ O ₂ + Fe(II)	5.54 ± 0.30
7	CV + SBO + H ₂ O ₂ + Fe(II) + 2-propanol	5.40 ± 0.20
8	CV + SBO + H ₂ O ₂ + Fe(II) + phenol	4.09 ± 0.30

[CV] = 10 mg L⁻¹; [H₂O₂] = 8.3 mg L⁻¹; [Fe(II)] = 5 mg L⁻¹; [SBO] = 100 mg L⁻¹; [2-propanol] = 1.8 g L⁻¹; [phenol] = 2.8 g L⁻¹. Initial pH = 7.0. The error bars represent standard deviations.

Interestingly, the maximum value of k_{app} is reached at SBO contents for which the MCR-ALS model yields the maximum concentration of the species associated with the complex (CV-SBO)_I. This results together with those obtained with chemical quenchers, in particular the observed enhancement of the degradation rate of CV in the absence of molecular oxygen (see Fig. 3), are in agreement with a triplet state of the complex playing a major role in the photochemical process. However, SBO are too complex to rule out other mechanistic routes.

3.3. Neutral photo-Fenton in the presence of SBO

The SBO used in this work (CVT230), contain a significant mineral portion, in particular iron at 0.77% (w/w) level. This might be of interest as the possibility of driving a (photo)-Fenton process at circumneutral conditions in the presence of organics able to complex iron, as recently reported for humic acids [15,16,32,33]. To check the possible use of SBO as Fenton additives, solutions containing CV were irradiated under the following experimental conditions: (a) in the presence of SBO (100 mg L⁻¹), (b) with H₂O₂ (8.3 mg L⁻¹), (c) in the presence of both SBO and H₂O₂. The bleaching rate was fitted to a pseudo-first order kinetics and the apparent rate constant (k_{app}) was determined in all cases (see Table 1). A comparison among the k_{app} values shows that although some bleaching was observed with SBO or H₂O₂, the fastest reaction was reached when both species were combined. Experiments with extra amounts of iron(II) (5 mg L⁻¹) were also performed. Table 1 shows that the combination of iron salts and hydrogen peroxide without SBO has scarce effect on the CV decoloration. Similar results are obtained in experiments with H₂O₂ in the absence of iron. On the other hand, when SBO were present in the reaction media, the reaction rate was greatly enhanced. A possible explanation of this behavior is that when iron is complexed by the SBO, it is able to participate in a photo-Fenton like process, while in the absence of this substance iron precipitates to form non-active oxides or hydroxides that inhibit the reaction.

Several recent studies support the existence of a modified mechanism for the (photo)-Fenton reaction at circumneutral pH values [32,34,35]. Although the nature of the oxidants is still a controversial issue, strong evidence suggests that an oxidant other than HO•, such as the ferryl ion (FeO²⁺), is formed when the pH is close to neutral values [36]. Moreover, the presence of organic ligands (e.g., EDTA) plays an important role in determining the nature of the oxidant species formed [37]. Since in the present work the experiments have been conducted at neutral pH and probably in the presence of complexed iron, the conditions seem appropriate to gain further insight into the nature of the reactive species. For this purpose, the photodegradation of CV in solutions

containing SBO, H₂O₂ and extra amounts of iron was performed in the presence of: (i) 2-propanol, a selective scavenger of hydroxyl radical, which exhibits low reactivity against ferryl ion [34] and (ii) phenol, which has been reported to react with both HO• and ferryl ion [38]. Table 1 shows that while 2-propanol had a scarce effect on the decoloration rate of CV, in the case of phenol a noticeable inhibition of the reaction was observed. This is compatible with ferryl ion playing a more important role in the process than HO•. This hypothesis is in agreement with the above cited observation for neutral photo-Fenton.

Dark experiments were also carried out with SBO, CV and 5 mg L⁻¹ of iron (Fenton process) at pH = 7. Under those conditions, bleaching of CV was negligible (less than 6% after 3 h, data not given) indicating that the photo-Fenton process was much efficient than Fenton performed in the dark.

It has been previously reported that SBO analogous to the one employed in the present work undergo slight degradation when submitted to irradiation [39]. To confirm this behavior an extra experiment consisting in irradiation of SBO was performed and a decrease in TOC and COD of 10% and 15%, respectively, was observed after 3 h of irradiation. However, being photo-Fenton a stronger process higher oxidation of SBO could be expectable. In order to clarify this point, photo-Fenton (5 mg L⁻¹ of iron, 8.3 mg L⁻¹ of H₂O₂, neutral medium) was performed on this material (100 mg L⁻¹) in the absence of CV. Chemical oxygen demand (COD) and total organic carbon (TOC) were determined before and after 3 h of irradiation. There was a noticeable decrease in COD of ca. 35%; similar behavior was found for TOC (also 25% decrease). However, this is not necessarily a drawback, but it could be an advantage if the pollutant has been removed and the biodegradability of SBO increases, improving the biocompatibility of the sample. In fact, it has been recently published that the toxicity of SBO is low and no significant increase is found along the reaction [39]. However, this is an important issue that deserves future research.

4. Conclusions

Soluble bio-organic substances (SBO) have been demonstrated to be materials of interest for photochemical wastewater treatment processes, as photosensitizers and/or for the implementation of circumneutral photo-Fenton processes. Hence, further research is needed, in particular: (a) to evaluate the potential applicability of SBO for the photoremediation of major occurring environment pollutants, such as pesticides and pharmaceuticals, (b) to gain further insight into the reaction mechanism and the species involved in the process, (c) to optimize new promising photoremediation processes and (d) to study in detail the photostability of SBO and changes in their biocompatibility along the treatment.

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