Photodegradation of monochlorophenols in the presence of bio-waste derived sensitizers

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Keywords

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Abstract

Soluble bio-based substances (SBO) isolated from urban waste promote the photodegradation of chlorophenols and the system detoxification. 2-chlorophenol, 3-chlorophenol and 4-chlorophenol were used as probe substrates. Experiments performed with 1.0×10^{-4} M substrate solutions irradiated for 24 h with UVa-vis light ($\lambda > 340$ nm) in the presence 500 mg L^{-1} SBO showed the progressive degradation of all the probe substrates. The experimental data were fitted to a pseudo-first order kinetics and the rate constant was found to decrease following the order: 2-chlorophenol > 3-chlorophenol > 4-chlorophenol. Experiments performed at different pH showed that the reaction rate was higher at pH value where the substrates are mainly present in ionized form. Additional experiments performed in the presence of singlet oxygen and hydroxyl radical scavengers, and EPR measurements further supported the main role of singlet oxygen in the substrate photodegradation mechanism. Data collected at variable SBO concentration showed that the substrate photodegradation rate increased upon increasing SBO concentration, up to a plateau value occurring in the presence of 1 g L^{-1} SBO. Possible explanations for this behaviour are discussed.

1. Introduction

In the last decades great attention has been devoted to the study of the so-called photochemical advanced oxidation processes (AOPs) for remediation of contaminated water [1-3]. These

techniques (e.g.: UV photolysis, heterogeneous photocatalysis, UV/hydrogen peroxide or UV/ozone) are based on the generation of highly reactive species, including reactive oxygen species (ROS), which are able to promote the degradation of organic substrates. Particularly interesting at this regard is the fact that this property is also exhibited by dissolved organic matter (DOM) present in terrestrial waters and soil. This material contains light-absorbing species capable of promoting photochemical reactions and it is considered as the major abiotic pathway for the removal of xenobiotics [4-6] from natural waters. In view that some organics have been demonstrated to act as photocatalysts for wastewater treatment, as recently reviewed, [6bis], studying the use of DOM for this purpose seems meaningful. A major drawback for this approach is that natural organic matter (NOM) is found at low concentration (< 3 %) in soil and water and hence NOM cannot be considered as a commercially viable source for those photochemically active DOM . Recently it has been shown that soluble bio-based substances (SBO) isolated from urban biowastes (UBW) have similar chemical composition [7] and photosensitizing properties [8-12] as DOM. What makes SBO more appealing is the fact that they may be obtained from easily available cost-effective sources, in sharp contrast with DOM; indeed, as result of increased production due to population urbanization, UBW are concentrated in confined areas by municipal collection. In addition, depending on the type of treatment and on composition, they have been shown to provide high yields of a large variety of bio-based products fitting a wide range of uses [13]. The performance of UBW sourced SBO as auxiliaries for the photochemical degradation of chlorophenols is now reported hereinafter.

Chlorophenols are toxic and hardly biodegradable. Due to their widespread use and origin, they are found in wastewaters, ground water, soils and also in the trophic chain. For this reason they have been often chosen as model compounds to study and optimize polluted water treatments [14]. With these probe substrates, the aim of the present study is to gain further insight into the main reactive species involved in the process and to evaluate the potential of the SBO-based photochemical process to be feasibly scaled up in future work. Mechanistic details of the photodegradation of the three monochlorophenol isomers under simulated solar light in the presence of SBO have been investigated as well as the effect of different operational parameters on the photocatalytic process

2. Experimental

2.1 Materials

Acetonitrile (gradient grade), 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), 2,2,6,6-tetramethyl-4-piperidone hydrochloride (4-oxo-TMP), 2-propanol, sodium azide, 2-chlorophenol (2-CP), 3-chlorophenol (3-CP) and 4-chlorophenol (4-CP) were purchased from Aldrich and used as received. All aqueous solutions were prepared with ultrapure water Millipore Milli-Q^{TM}.

The investigated SBO was isolated from UBW sampled from the process lines of ACEA Pinerolese waste treatment plant in Pinerolo (Italy). The UBW was obtained in the compost production section from urban public park trimming and home gardening residues aged for 230 days, and was further processed in a pilot plant [15] from Studio Chiono & Associati in Rivarolo Canavese, Italy. This comprised an electrically heated mechanically stirred 500 L reactor, a 102 cm long x 10.1 cm diameter polysulfone ultrafiltration (UF) membrane with 5 kD molecular weight cut-off supplied by Idea Engineering s.r.l., and a forced ventilation drying oven. According to the operating experimental conditions, UBW were digested 4 h at 60 °C, pH 13 and 4 V/w water/solid ratio. The liquid/solid mix was allowed to settle to yield the upper liquid phase containing the hydrolyzed soluble UBW. 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, which was finally dried at 60 °C. The solid SBO (namely CVT230) product obtained in 15-30 % w/w yield, relatively to the starting UBW dry matter, was characterized according to a previously reported procedure [13] by the chemical composition data reported in Table 1. Average values of triplicates are shown in Table 1; relative standard deviations as % of mean values were found about 10 %.

Table 1. Analytical data for CVT230.

Volatile Solids, w/w % [a]	C, w/w % [a]	N, w/w % [a]	C/N
72.1	38.25 ± 0.09	4.01 ± 0.03	9.54

Mineral elements, % w/w [a]						
Si	Fe	Al	Mg	Ca	K	Na
2.55 ± 0.01	0.77 ± 0.04	0.49 ± 0.04	1.13 ± 0.06	6.07 ± 0.38	3.59 ± 0.21	0.16 ± 0.01

C types and functional groups [b] concentration as mole fraction of total organic C												
Af	NR	OMe	OR	OCO	Ph	PhOH	PhOY	COOH	CON	C=O	Af/Ar	LH
0.37	0.07	0.01	0.14	0.04	0.13	0.05	0.02	0.12	0.01	0.05	1.80	3.60

[a] Concentration values referred to dry matter: averages and standard deviation calculated over triplicates.
[b] LH = liphophilic to hydrophilic C ratio; liphophilic C = sum of aliphatic (Af), aromatic (Ph), methoxy (OMe), amide (CON), ammine (NR), alkoxy (OR), phenoxy (PhOY) and anomeric (OCO) C atoms; hydrophilic C = sum of carboxylic acid (COOH), phenol (PhOH) and ketone (C=O) C.

Before use, CVT230 was taken up with Milli-Q™ water under sonication, centrifuged and filtered through a cellulose acetate 0.45 μm pore diameters filter (Millipore) to remove any residual

insoluble matter. A typical UV-vis spectrum of an aqueous solution of CVT230 is reported in Figure 1S in Supplementary Information (S.I.).

2.2 Photodegradation and analytical procedures

Lab scale experiments were carried out by irradiating, under continuous stirring, 5 mL of aqueous samples containing CVT230 and each substrate in a closed Pyrex® cell with a Xenon (1500W) lamp (Solarbox) equipped with a 340 nm cut-off filter. The irradiance of the lamp, measured with a UV-Multimeter system, was 26.7 W m^{-2}. The use of a cut-off filter was motivated by the aim of discarding the contribution of substrate photolysis through direct excitation, even at pH values at which 4-CP is mainly present in the phenate form.

Photodegradation experiments under natural solar light were performed circulating the sample solution through a SOLARDETOX® ACADUS-2005/0.25 (Ecosystem) system (Figure 2S in Supplementary Information, S.I.) placed on the roof of the Escuela Politécnica Superior de Alcoy (Spain). The system, based on Compound Parabolic Collector (CPC) technology, consists of an array of four parallel borosilicate tubes. Each tube, having 75 cm length and 29.2 mm internal diameter, is equipped with two aluminium parabolic mirrors to concentrate the solar radiation along the tube axis. The whole set up has 0.26 m^2 total surface and contains 5 L total sample, with 1.83 L exposed to solar irradiation. A radiometer (Acadus 85) measures the incident light in the 300-400 nm wavelength range peaking at 370 nm and accounting for ca. 7 % of the total solar energy. The accumulated energy values were obtained for any irradiation period by means of a programmable logic controller.

Experiments in modified atmosphere were performed in a cylindrical photochemical stirred batch reactor from Helios-Italquartz (Milan), equipped with a 125 W medium pressure Hg lamp (125 W), surrounded by a Pyrex glass jacket acting as a cut-off filter for wavelengths shorter than 300 nm.

The substrate degradation was monitored by HPLC, employing a Merck-Hitachi instrument, equipped with Lichrospher RP-C18 (125 mm x 4 mm i.d., particle diameter = 5 μm, from Merck), L-6200 pumps and UV/Vis L-4200 detector. Elution was carried out with 60:40 v/v water/acetonitrile at 1 mL min^{-1} flow rate. The analytical detection wavelength was 220 nm. Chloride evolution was followed by a suppressed ion chromatography, employing a Dionex DX 500 instrument equipped with a Dionex IonPac® AS9-HC column (200 mm x 4 mm i.d.), GP40 pump (Dionex), an electrochemical detector ED40 (Dionex) and an Anion Self-Regenerating Suppressor-Ultra (ARSR®-ULTRA, 4-mm, Dionex). Elution was performed in isocratic conditions with 90 % of aqueous solution of K_2CO_3 $12x10^{-3}$ M and $NaHCO_3$ $5x10^{-3}$ M, and 10 % of water, at 1.0 mL min^{-1} flow rate.

A Cary 100 Scan - Varian spectrophotometer was used to follow the evolution of UV-Vis absorbance of the system during the irradiation process.

2.3 Toxicity measurements

The Microtox® system was used to determine short-term biotoxicity of the CVT230-substrate solution. This test employs the *Vibrio fischeri* bacterium as a probe organism; this bioluminescent bacterium is characterized by peak light emission at 490 nm. In the presence of toxic substances a light emission decrease proportional to the toxic effect (inhibition effect, E %) occurs [16]. All tests were conducted following the standard Microtox® protocol, and data analysis was performed using the Microtox® Omni Software. For colored or turbid samples, the toxicity was corrected by subtracting the sample absorbance at 490 nm according to the method described elsewhere [17].

2.4 Surface tension measurement

Surface tension was measured in order to calculate the critical micellar concentration (CMC) of CVT230. A digital tensiometer (K10, Krüss) equipped with a platinum Wilhelmy plate was employed. Surface tension measurements were performed on CVT230 solutions in a concentration range from 0.1 to 5.0 g L^{-1}; the concentration range was selected on the basis of CMC values of other previously studied SBO [18, 19].

2.5 Electron paramagnetic resonance (EPR) measurements

EPR spectra were registered at room temperature with a Bruker ESR 300E spectrometer operating at X-band and equipped with a flat quartz EPR cell. The acquisition parameters were as follows: frequency = 9.69 GHz, microwave power = 5.024 mW, center field = 3450 G ($^1O_2$) / 3440 G ($^\bullet$OH), sweep width = 80 G ($^1O_2$) / 20 G ($^\bullet$OH), number of scans = 62 ($^1O_2$) / 120 ($^\bullet$OH), receiver gain = 1 x 105, modulation amplitude = 0.52 G, conversion time = 40.96 ms ($^1O_2$) / 10.24 ms ($^\bullet$OH). 2,2,6,6-tetramethyl-4-piperidone hydrochloride (4-oxo-TMP, 45 mM) and 5,5–dimethyl-1-pyrroline-N-oxide (DMPO, 17.4 mM) were employed as trapping agent for $^1O_2$ and $^\bullet$OH respectively, according to the literature [20]. All experiments were carried out by adding the spin trap in the cell before irradiating CVT230 and the EPR spectra were acquired immediately after the irradiation.

3 Results and discussion

3.1 Degradation of chlorophenols

Preliminary control experiments were run with $1.0x10^{-4}$ M aqueous solutions of each chlorophenol. Irradiation in Solarbox in the absence of CVT230, performed both at pH 7.0 and 9.4, showed that direct photolysis of substrates was not higher than 5-7 % after 24 h. Dark controls in the presence of CVT230 (500 mg L^{-1}) resulted in no variation in the substrate concentration. Aqueous solutions of each chlorophenol ($1.0x10^{-4}$ M) were then irradiated in the presence of CVT230 (500 mg L^{-1}) at an initial pH of 9.4. This pH value corresponds to the naturally occurring pH of 500 mg L^{-1} CVT230 aqueous solution; in Figure 3S in S.I. the effect of pH variation on the 4-CP UV absorption has been reported as an example. The kinetic profile reported in Figure 1 shows a progressive degradation of all the probe substrates, following a pseudo-first order kinetic low; the linear form of pseudo-first-order kinetics is shown in the inset of Figure 1 and the corresponding rate constants (k_{obs}) were calculated and reported in Table 2. The results show that the probe substrate reactivity decreases in the order 2-CP > 3-CP > 4-CP.

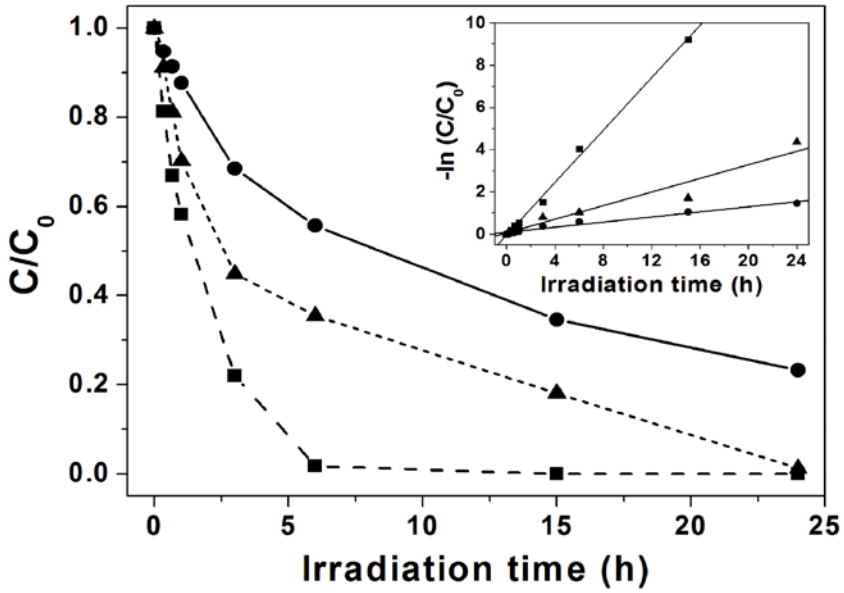

Figure 1. Degradation of chlorophenols ($1.0x10^{-4}$ M) in the presence of CVT230 (500 mg L^{-1}): 2-CP (■), 3-CP (▲) and 4-CP (●). Irradiation performed in Solarbox (cut-off filter 340 nm). Inset: plots of -ln (C/C_0) vs. irradiation time.

Table 2. Acidic dissociation (pK_a) and kinetic constants of the investigated probe substrates.

	k_{obs}[a]	pK_a	k_P $^1O_2$[b]	k_{P^-} $^1O_2$[b]	k_P $^{\bullet}OH$[c]	$k_{P,\ P^-}$ $^{\bullet}OH$[d]
2-CP	0.621	8.55	9.2×10^6	1.92×10^8	1.65×10^{10}	1.20×10^{10}
3-CP	0.110	9.12	5.4×10^6	1.60×10^8	0.86×10^{10}	0.72×10^{10}
4-CP	0.070	9.41	6.0×10^6	1.93×10^8	2.82×10^{10}	0.76×10^{10}

[a] rate constants calculated from Figure 1 data;
[b] rate constants for reaction of the phenol (k_P) and phenate (k_{P-}) species with $^1O_2$ [21];
[c] rate constants for reaction of the phenol (k_P) species with $^{\bullet}OH$ determined at pH=7.0 [21];
[d] rate constant for reaction of the phenol and phenate ($k_{P,\ P-}$) species with $^{\bullet}OH$ determined at pH=9.0 [22, 23].

Table 2 reports also literature data for the rate constants of chlorophenols with $^{\bullet}OH$ and $^1O_2$; indeed, the formation of such species upon irradiation of aqueous solutions of SBO has been previously demonstrated [20]. It may be observed that the reactivity order of chlorophenols with $^{\bullet}OH$ is different from the reactivity with $^1O_2$. However none of these trends is consistent with that observed for the experimental k_{obs} values and it might be attributed to the phenol/phenate ratio in the investigated solutions. Since the working pH for Figure 1 data was close to the pK_a values of the chlorophenols, an appreciable amount of phenate ions is expected in solution. The literature data reported in Table 2 indicate that, for singlet oxygen, rate constants strongly depend on the acid/base properties, as those of phenate ions are two orders of magnitude higher than those for the undissociated phenol. By comparison, for $^{\bullet}OH$ the change of reactivity observed for phenol and phenate ions was small. The dependence of the effective rate constant for the reaction of singlet oxygen with chlorophenols, $k_{eff}(^1O_2)$, on the phenol/phenate species composition fits the equation $k_{eff}(^1O_2) = \alpha_p k_p(^1O_2) + \alpha_{p-} k_{p-}(^1O_2)$ where α_p and α_{p-} are the initial molar fractions of the phenol and phenate species respectively [24]. Figure 2 shows the plot of $k_{eff}(^1O_2)$ versus pH for each probe substrates. It may be observed that the $k_{eff}(^1O_2)$ values at pH 9.4 follow the same order as that observed for the k_{obs} values in Table 2.Lucho si quieres cambia esta parte y dime si hay que cambiar tambien la Figura 2. This suggests that singlet oxygen might play a major role in the photooxidation of chlorophenols under the studied experimental conditions.

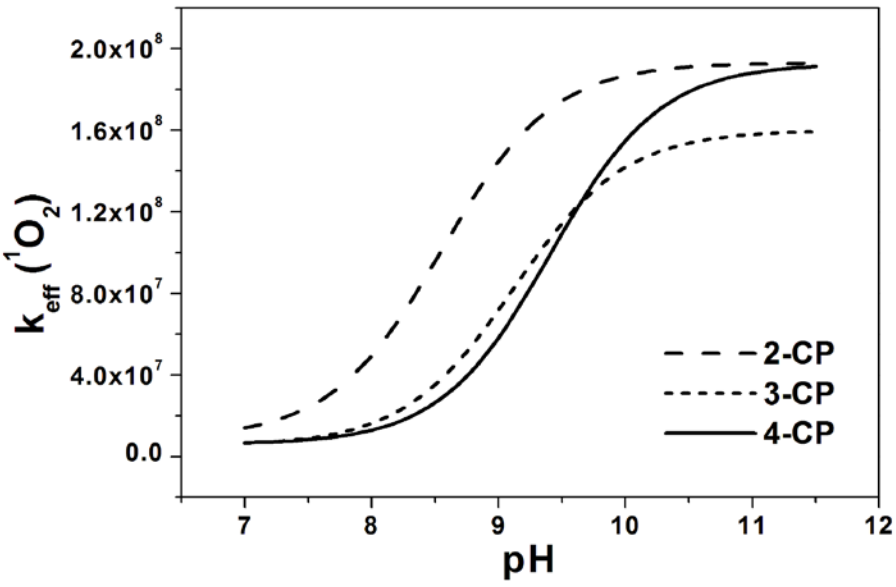

Figure 2. "Effective" rate constant for chlorophenols with singlet oxygen.

3.2 Chloride release in solution

In previous studies concerning chlorophenols degradation [14] the cleavage of C-Cl bond was indicated as one of the possible degradation paths. Under the applicative point of view, this degradation step is highly relevant since the toxicity of chlorinated species is particularly high; formation of chloride ions might be the preliminary hint of remediation taking place. In Figure 3, the release of chloride ions in solution is plotted versus the irradiation time. The data show that more than 50 % of the stoichiometric amount of chlorine is detected as chloride after 15 h of irradiation. After 24 h the mineralization of organic Cl is 70 % for 4-CP and nearly quantitative for 2-CP and 3-CP. Interestingly, a close relationship between the degradation of each chlorophenol (C/C_0 in Figure 1) and the chloride ion increase was found. This suggests that dechlorination occurs at the early stages of the reaction and formation of important amounts of chlorinated organic by-products should not be expected.

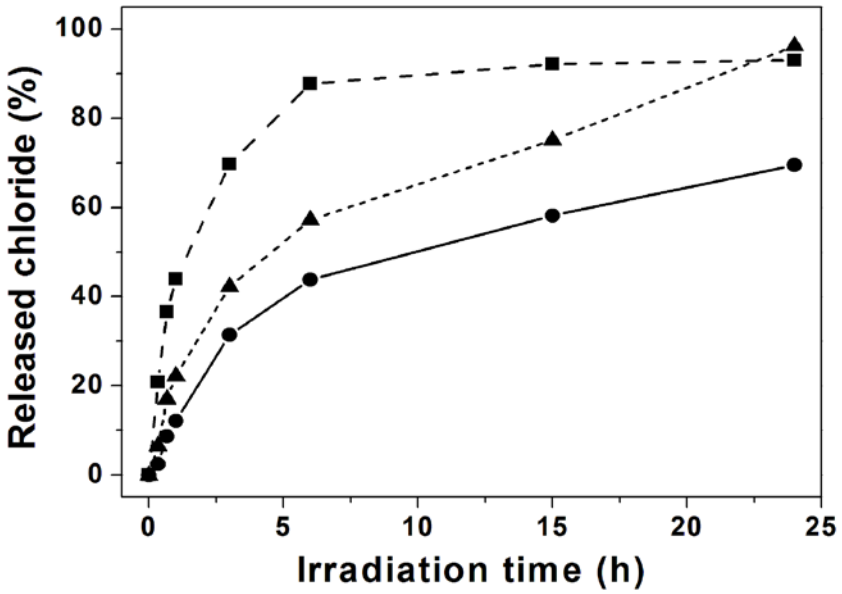

Figure 3. Percentage of chloride ions released in solution, calculated with respect to the theoretical value of organic chlorine in the probe substrate, as function of the irradiation time. Experimental conditions as in Figure 1; 2-CP (■), 3-CP (▲) and 4-CP (●).

3.3 Effect of CVT230 concentration

To better characterize the behavior of CVT230, experiments were performed at different CVT230 concentration, choosing 4-CP as probe substrate. To define the concentration range, the surfactant properties of CVT230 were taken into account and additional experiments were performed in order to evaluate the formation of micellar aggregates. Micelles could indeed influence the process

depending on the substrate partition between the bulk solution and the micellar phase. Moreover, it has been reported that the humic acid aggregate formation can influence the singlet oxygen kinetic behavior [25]. Figure 4S in S.I. reports surface tension values (γ, mN m^{-1}) versus CVT230 concentration (g L^{-1}); a critical micellar concentration (CMC) value of 2.60 g L^{-1} was calculated for CVT230, in correspondence of a surface tension value of 53.1 mN m^{-1}. An aqueous solution of 4-CP ($1.0x10^{-4}$ M) was therefore irradiated in the presence of CVT230, and the effect of its concentration was studied up to 5 g L^{-1} in order to evidence any possible influence of CVT230 molecular aggregates on the degradation process. The results reported in Figure 4 show that the degradation rate increases progressively, up to 1 g L^{-1} CVT230 concentration. In this condition, the 4-CP abatement was found 77 % after 6 hours irradiation and 100 % after 24 hours. A further increase of CVT230 concentration did not result in any degradation rate enhancement. Moreover, when CVT230 was added in concentration above its CMC value, no peculiar kinetic behavior was observed, suggesting that the CVT230 molecular solution conformation does not influence significantly the photosensitizing mechanism. The lack of sensitivity of the probe substrate degradation rate to CVT230 concentration, above a certain concentration value, has been observed in a previous study on the photodegradation of naphthalene sulfonic compounds [10] in the presence of a different SBO. This behavior might be attributed to two different effects. Light screening could be relevant at high CVT230 concentration, explaining that further addition of this material does not result in faster degradation of the probe substrate. This is a well know behaviour in photocatalysis [26]. In addition, CVT230 can compete with the probe substrate for oxidizing species and this effect is expected to increase with the CVT230/probe substrate ratio. Actually, photobleaching of CVT230 slowly occurs during the irradiation (Figure 5S in the S.I.). A similar dose-effect pattern has been reported also for processes occurring in the presence of NOM [27].

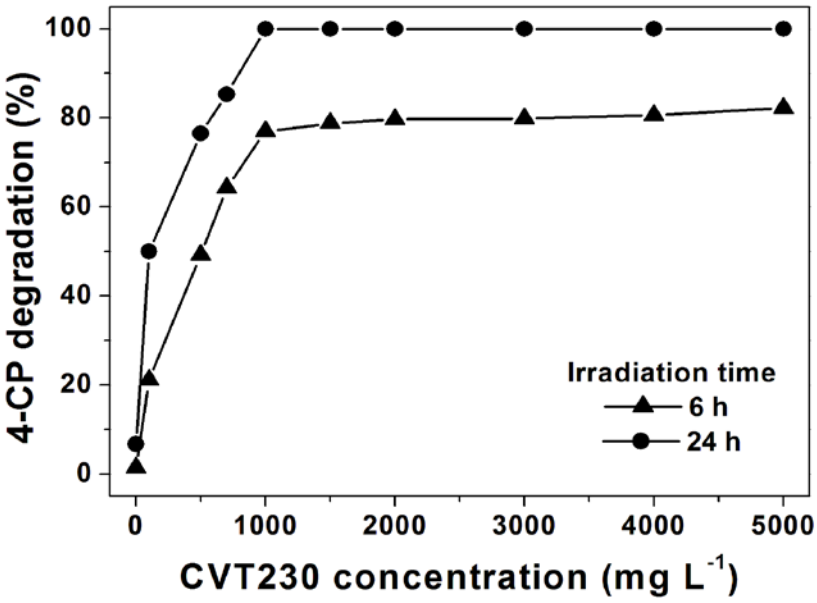

Figure 4. Effect of CVT230 concentration on the percentage of 4-CP ($1.0x10^{-4}$ M) degradation after 6 and 24 hours irradiation.

Based on the previously discussed effect of the acid/base properties on the degradation kinetics, the effect of CVT230 concentration was also studied at two different initial pH, i.e. 7.0 and 9.8. In all the investigated CVT230 concentration range, the process was significantly more efficient at pH 9.8 (Figure 6S, S.I.), where about 80 % of 4-CP is in the phenate form compared to pH 7.0 where this percentage decreases to less than 1 %. These outcomings can be taken as a further indication of the prevalent role of singlet oxygen in the photodegradation of 4-CP mediated by CVT230.

3.4 Role of singlet oxygen and hydroxyl radicals

Before gaining further insight into the role of $^1O_2$ and $^\bullet OH$ on the 4-CP degradation, the possible role of CVT320 excited triple state was considered. Irradiations were therefore performed in a closed reactor provided of lateral opening for gas inlet. Experiments were run under either air or nitrogen atmosphere. The results are shown in Figure 7S (S.I.) were it clearly appears the detrimental effect of nitrogen; since oxygen is a well known triple state quencher, according to these results excited triple state might not play a predominating role in 4-CP photodegradation under the studied conditions.

Afterwards. 4-CP was irradiated in the presence of CVT230 at two different concentrations (100 mg L^{-1} and 5000 mg L^{-1}), with and without the addition of $^\bullet OH$ and $^1O_2$ scavengers, namely 2-propanol [28] and sodium azide [28], respectively. Figures 5a and 5b show that the addition of 2-propanol leads to a reduction of 4-CP degradation from 50 % to 40 % after 24 h of irradiation in the

first case (100 mg L^{-1} CVT230), whereas in the second case (5000 mg L^{-1} CVT230) does not produce any kinetic modification. On the contrary, the addition of sodium azide leads in both cases to a decrease of 4-CP abatement, from 50 % to 27 % in the presence of 100 mg L^{-1} CVT230, and from 100 % to 46 % in the presence of 5000 mg L^{-1} CVT230

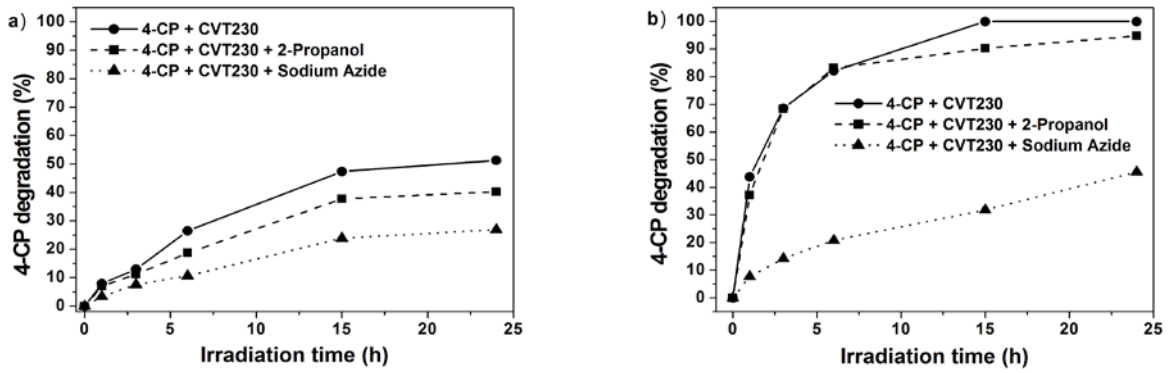

Figure 5. Degradation of 4-CP ($1.0x10^{-4}$ M) in the presence of 2-propanol (0.01 M) and sodium azide (0.03 M). Concentration of CVT230: a) 100 mg L^{-1}, b) 5000 mg L^{-1}.

These results seem to indicate that at high CVT320 concentration the degradation process is mainly driven by $^1O_2$ whereas at low CVT320 concentration also $^{\bullet}OH$ is actively involved. This behaviour could be explained by taking into account that the experiments were perfomed without modifying the natural occurring pH of the solution that was 8.5 at 100 mgL^{-1} of CVT320 and 9.8 at 5000 mgL^{-1}. In these conditions the substrate was present in the phenate form in a percentage equal to 10% and 80% respectively and phenate is more reactive with $^1O_2$ than phenol whereas the opposite is occurring towards •OH. In order to asses if also the production of $^1O_2$ and $^{\bullet}OH$ was related to CVT230 concentration EPR investigations were performed; with this approach the detection of $^1O_2$ and $^{\bullet}OH$ involves the formation of a persistent spin-adduct species from a compound acting as spin-trap and the target species. These adducts have a distinctive EPR spectrum and the signals intensity allows to estimate the relative amount of each trapped species [20]. Figure 6 reports the signal intensities, respectively measured for $^1O_2$ trapped by 4-oxo-TMP (a) and for $^{\bullet}OH$ trapped by DMPO (b).

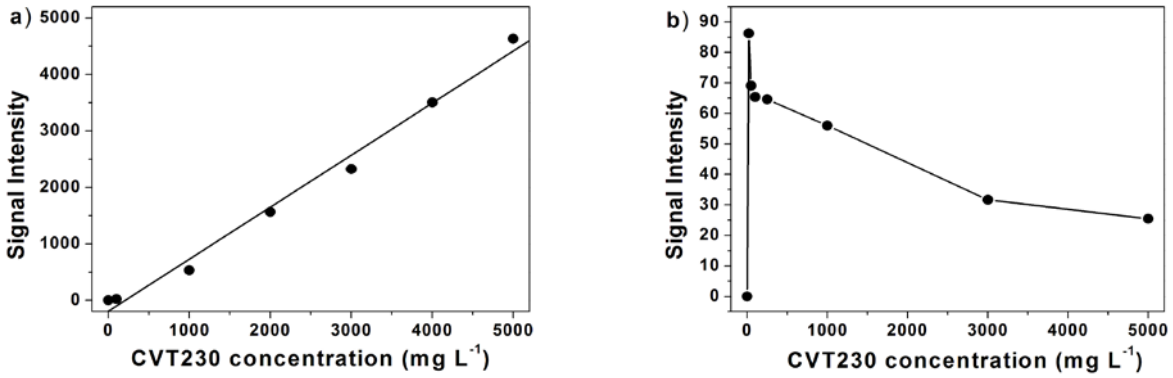

Figure 6. a) Intensity of 4-oxo-TEMPO EPR signal, after background subtraction, vs. CVT230 concentration. 4-oxo-TMP concentration = 45 mM; irradiation time = 15 minutes. Linear fit of data, slope = 0.9214, intercept = -190.7, r^2 = 0.9893. b) Intensity of DMPO-OH EPR signal vs. CVT230 concentration. DMPO concentration = 17.4 mM; irradiation time = 3 minutes. pH 9.4.

The trend of the EPR signal intensity reported in Figure 6a evidences that $^1O_2$ production is directly proportional to CVT230 concentration and that the presence of micellar aggregates has no influence. On the contrary, the intensity of the signal corresponding to the formation of the DMPO-OH adduct increases with the CVT230 concentration until a maximum value, recorded at about 50 mg L^{-1} CVT230, and then decreases at higher CVT230 concentrations. This profile can be explained by considering the simultaneous occurrence of two different processes: production and scavenging of $^{\bullet}OH$ by irradiated CVT230: at low CVT230 concentration, formation of $^{\bullet}OH$ is favoured by further addition of this photosensitizing material; however, beyond a given concentration the scavenging role of CVT230 becomes predominating, resulting in a decrease in the available amounts of $^{\bullet}OH$.

These results are consistent with those obtained in the presence of scavengers and are analogous to the ones previously obtained with another SBO [20].

3.5 Evaluation of the toxicity of the system

Although the above reported results demonstrate that CVT230 is able to promote the oxidation of chlorophenols, removal of the parent pollutant does not guarantee detoxification of the solution. Due to the complexity of the system investigated in the present study, dissolved organic carbon analysis and identification of the intermediate products are not useful tools to gain further insight into the process. As alternative approach to exclude the formation of intermediate by-products more toxic than the starting substrates, the global toxicity of the system was evaluated by means of Microtox® test. This test yields the percentage of bioluminescence inhibition value for the *Vibrio fischeri* bacterium produced by the investigated solutions (see the experimental section). The

significance of the experimental data is that, the higher the inhibition effect (E %), the higher the toxicity level. Specifically, E % < 20 corresponds to the absence of toxicity, whereas a higher E % value, between 20 and 50, indicates weak toxicity. Experiments were performed on aqueous solutions containing CVT230 alone or CVT230 and 4-CP. In order to better evidence the 4-CP toxicity, its concentration was raised up to 4.0×10^{-4} M while the concentration of CVT230 was decreased down to 100 mg L^{-1}. The Microtox® test is in fact optimized for slightly colored solutions, showing an absorbance lower than 0.5, and this condition was not respected with the high CVT230 concentration used throughout the study.

Figure 7 shows the plot of the E % values versus the irradiation time, along with the photodegradation kinetic profile. The bioluminescence measurement was performed after 30 minutes of contact between samples and bacteria.

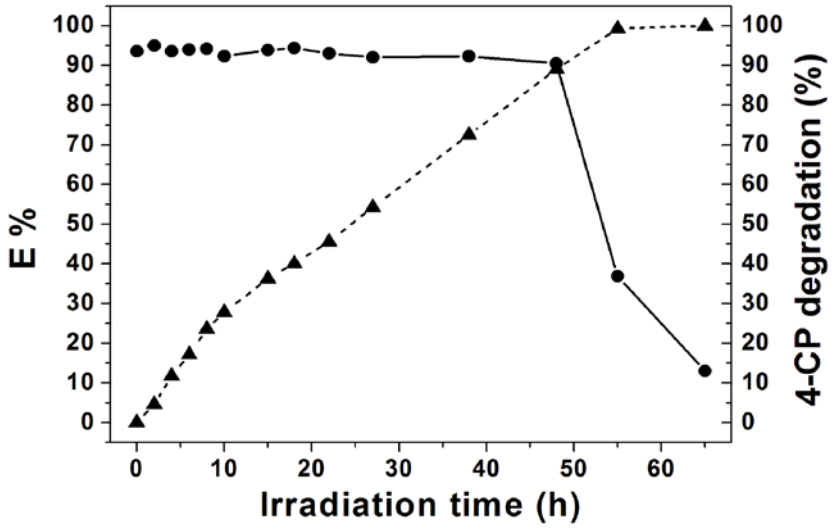

Figure 7. Photodegradation of 4-CP (4.0×10^{-4} M) in Solarbox (cut off filter 340 nm) in the presence of CVT230 (100 mg L^{-1}). Solid line (●): E % vs. irradiation time. Dotted line (▲): percentage of substrate degradation vs. irradiation time.

It may be observed that the 4-CP-CVT230 solution shows a high initial toxicity level (> 90 %), maintained up to 48 hours of irradiation. Above this irradiation time a sharp decrease of the E % is observed, proving substantial detoxifications of the solution. This behaviour allows to hypothesize that up to 48 hours of irradiation the toxicity observed can be ascribed to the presence of residual 4-CP together with other intermediate compounds (decimos algo mas?). Finally, controls performed with CVT230 (100 mg L^{-1}) demonstrated that this material showed a negligible toxicity, when compared with 4-CP, and irradiation of CVT230 did not result in significant variation of this parameter (Table 1S in S.I.).

3.6 Scaling up of the process in a pilot solar plant (esperamos los datos de Antonio y vemos como cambiar esta parte) (yo eliminaría toda esta parte y la información correspondiente de)

Experiments at pilot plant scale with real sunlight are a logical step forward to check the real applicability of SBO in remediation photochemical processes. Experiments were performed degrading 5 L of aqueous solutions of 4-CP ($1.0x10^{-4}$ M), in the presence of CVT230 at different concentrations ranging from 0 to 1600 mg L^{-1}, working in the pilot plant described in the experimental section. Figure 8 shows the substrate concentration values normalised with respect to the initial concentration value, versus the accumulated radiation. As can be observed, CVT230 is able to promote the degradation of 4-CP also under irradiation with real solar light, and the direct photolysis is negligible compared to the degradation attained in the presence of CVT230. Substrate degradation curves were fitted to a pseudo-first order kinetics (inset in Figure 8) and the rate constants (k_{obs}) were calculated. As can be seen in Figure 8 and in Figure 8S in S.I., the abatement rate increased when increasing CVT230 concentration; moreover the plot of k_{obs} versus CVT230 shows that k_{obs} tends toward a plateau limit for concentration of CVT230 higher than 1000-1200 mg L^{-1}. This finding is relevant due to its analogy with the trend observed for degradations carried out in Solarbox, showing a similar upper limit for CVT230 concentration. It can therefore be hypothesized that, in the presence of CVT230, the change from simulated to real solar light as radiation source, does not implies any significant variation of the degradation mechanism.

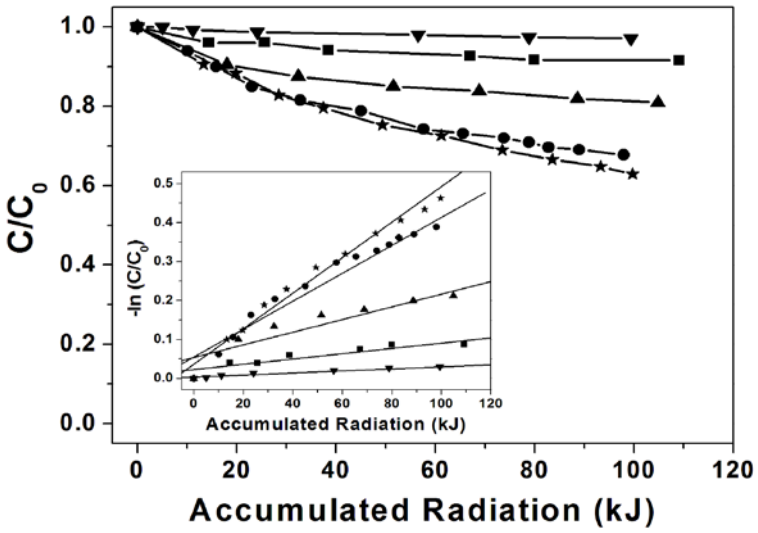

Figure 8. 4-CP concentration values normalised with respect to the initial concentration value ($1.0x10^{-4}$ M) vs. the accumulated radiation. Experiments performed in the solar pilot plant in the presence of different CVT230 concentrations: 1600 mg L^{-1} (⋆), 800 mg L^{-1} (●), 500 mg L^{-1} (▲), 100 mg L^{-1} (■), no CVT230 (▼). Inset: plots of -ln (C/C_0) vs. accumulated radiation.

4. Conclusions

The results obtained in the present work confirm the capability of SBO to promote the degradation of pollutants in aqueous solution and improve the knowledge on the operating mechanism, thus allowing to better clarify the role of experimental parameters, in particular the initial pH, and to optimize the degradation process. Similarly to NOM, anthropogenic bio-wastes might be proven an environmental benefit, rather than merely a cost for society. However, before the real applicability of this methodology can be evaluated further research is still required in order to gain further insight into the biocompatibility and stability of the employed SBOs. Furthermore, as promising results have been achieved with artificial UVA-vis light, the possibility of using real solar irradiation also deserves to be investigated in future workt

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