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Waste Cleaning Waste: Photodegradation of Monochlorophenols in the Presence of Waste-Derived Photosensitizer

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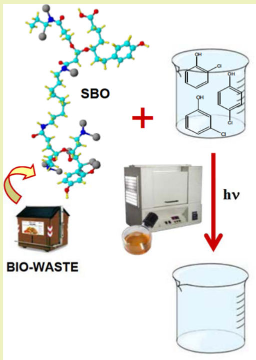
Supporting Information



ABSTRACT: Soluble bio-based substances (SBO) have been isolated from urban waste. Their structural similarity with natural organic matter suggested exploring their activity in the photodegradation of organic substrates. In this work, they are shown to promote the photodegradation of monochlorophenols. Experiments performed with 1.0×10^{-4} M substrate solutions irradiated by simulated solar light in the presence of 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 in the following order: 2-chlorophenol > 3-chlorophenol > 4-chlorophenol. The effect of pH and SBO concentration on chlorophenols degradation was assessed. Experiments performed in the presence of selective scavengers along with EPR measurements supported the main role of singlet oxygen in the substrate photodegradation mechanism. Toxicity assays showed that the photodegradation of chlorophenols in the presence of SBO is accompanied with a progressive up to complete detoxification of the system. Moreover, no significant contribution of SBO to the whole system toxicity was observed. The results show how urban wastes can be a resource of photosensitizing bio-based substances to be explored in wastewater treatments.

KEYWORDS: *Biowaste, Photolysis, Chlorophenols, Wastewater, Singlet oxygen, Renewable feedstock*

INTRODUCTION

The environmental impact of urban wastes has dramatically increased as a result of increasing population, urbanization, and consumption habits. Although nowadays this fact contributes to society's significant economic burden for management and/or disposal, in turn, the concentration of wastes in urban areas has allowed the collection of natural bio-organic matter in well-confined spaces. This aspect favors the possible exploitation of urban biowastes (UBW) as source of energy and/or materials. Recent research[1] has shown that the recalcitrant lignin-like fraction of urban biowastes is a cost-effective source of soluble bio-based product (SBO) that can find application in the formulation of detergents, textile dyeing baths, emulsifiers, auxiliaries for soil/water remediation, flocculants, and dispersants, as binding agents for ceramics manufacture, and as nanostructured materials for chemical and biochemical catalysis, as well as for application in agriculture and animal husbandry.[2]

SBO have been found to be mixtures of molecules differing in molecular weight (from 67 to 463 kg mol^{-1}) and in C-type, content, and functional groups. They are described as likely mixtures of substances formed by long aliphatic carbon chains substituted by aromatic rings and functional groups such as COOH, CON, C=O, PhOH, O alkyl, O aryl, OCO, OMe, and NRR′, (R and R′ = alkyl or H).[2] Hence, SBO bear chemical similarities with dissolved organic matter (DOM) present in terrestrial waters and soil. These structural similarities between DOM and SBO are not surprising as while the first is generated by partial biodegradation of vegetal and animal debris, the last is obtained by a mimetic process from organic wastes. Particularly interesting in this regard is the fact that DOM contains light-absorbing species capable of promoting photochemical transformation of organics of anthropogenic origin, and for this reason, DOM is considered to play a relevant role in the autoremediation of surface waters by solar light.[3−6] Unfortunately, DOM cannot be considered a commercially viable photosensitizer to be studied for wastewater treatments due to its low concentration (<3%) in soil and water, whereas composted UBW are cost-effective sources that may contain up to 40% SBO. The development of SBO for water detoxification was therefore attempted as a green process, taking organic urban wastes as a source of material for environmental application.

At the laboratory scale, successful trials have been carried out testing SBO from composted UBW as well as crude compost

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itself for the photodegradation under simulated solar light of chemicals that can be found in agricultural and industrial effluents such as azo and cationic dyes,[7,8] phenols,[9] aromatic sulfonic acids,[10] herbicides,[11,12] and other micropollutants.[13]

In the present work, we have studied the performance of SBO isolated from the alkaline hydrolyzate of urban private gardening and public park trimming residue compost as auxiliaries for the photochemical degradation of monochlorophenols with three main objectives: (i) to gain further insight into the main reactive species involved in the SBO-assisted photodegradation process, (ii) to test the effect of operational conditions in the photodegradation process at laboratory scale under simulated solar light, and (iii) to verify the system detoxification in view of future studies concerning the development of SBO for the treatment of real effluents. Monochlorophenols were good probe substrates because they are toxic and not biodegradable compounds that have been found in wastewaters, groundwater, soils, and also in the trophic chain; moreover they have been often chosen as model compounds for water treatments studies by other authors.[14]

EXPERIMENTAL SECTION

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).

The investigated SBO (hereinafter referred to by the CVT230 acronym) was isolated from UBW sampled from the process lines of the 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[2] (Rivarolo Canavese, Italy). This comprised an electrically heated mechanically stirred 500 L reactor, a 102 cm long × 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 CVT230 obtained in 15−30% w/w yield, relatively to the starting UBW dry matter, was characterized according to a previously reported procedure.[15] 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 S1 of the Supporting Information.

Photodegradation and Analytical Procedures. 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}. A cut off filter was used in order to eliminate any contribution of substrate photolysis through direct excitation because neither the phenol nor phenate form of chlorophenols absorbs above 340 nm (Figure S2, Supporting Information). Experiments in modified atmosphere were performed in a cylindrical photochemical stirred batch reactor from Helios-Italquartz (Milan, Italy), equipped with a medium pressure Hg lamp (125 W).

Details regarding the general instrumentation and measurements of residual chlorophenols, chloride, toxicity, surface tension, and electron paramagnetic resonance (EPR) are provided in the analytical procedures of the Supporting Information.

RESULTS AND DISCUSSION

Degradation of Chlorophenols. Aqueous solutions of each chlorophenol (1.0×10^{-4} M) were irradiated in the presence of CVT230 (500 mg L^{-1}) at the initial pH of 9.8 given by the dissolved neat CVT230 sample without addition of any acid or base. Figure 1 reports the normalized kinetic profiles for each probe substrate. The results show that the progressive degradation of all the probe substrates follows a pseudo-first-order kinetic (see inset of Figure 1). The observed pseudo-first-order rate constants (k_{obs}), reported in Table 1, show that the probe substrate reactivity decreases in the order of 2-CP > 3-CP > 4-CP.

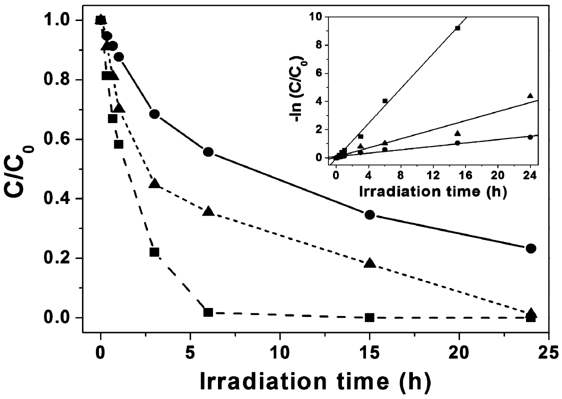

Figure 1. Degradation of chlorophenols (1.0×10^{-4} M) in the presence of CVT230 (500 mg L^{-1}): 2-CP (■), 3-CP (▲), and 4-CP (●). Irradiation performed in Solarbox (cut off filter 340 nm). Inset: plots of $-\ln (C/C_0)$ vs irradiation time.

Control experiments, performed by irradiating aqueous solutions of each chlorophenol (1.0×10^{-4} M) both at pH 7.0 and 9.8 in the absence of CVT230, showed that direct photolysis of substrates was not higher than 5−7% after 24 h. Also, dark controls in the presence of CVT230 (500 mg L^{-1}) resulted in no variation in the substrate concentration. These results show that the significant abatement of each substrate observed in Figure 1 is mainly due to the photosensitizing properties of CVT230.

Table 1 also reports literature data for the bimolecular rate constants of the reactions of chlorophenols with $^{\bullet}OH$ and $^1O_2$. These data are relevant to understanding the SBO-assisted photodegradation process. Indeed the formation of $^{\bullet}OH$ and $^1O_2$ upon irradiation of aqueous solutions of other SBO has been previously demonstrated.[9] The literature data reported in Table 1 indicate that for singlet oxygen the rate constants strongly depend on the acid/base properties, as those of phenate ions are 2 orders of magnitude higher than those for the undissociated phenol. By comparison, for $^{\bullet}OH$, the change in reactivity observed for phenol and phenate ions is small. The dependence of the bimolecular rate constant for the chemical reaction between singlet oxygen and chlorophenols, k_r, on the phenol/phenate species composition fits the equation $k_r = \alpha_P k_P(^1O_2) + \alpha_{P-} k_{P-}(^1O_2)$, where α_P and α_{P-} are the initial molar fractions of the phenol and phenate species respectively.[19] The plot of k_r versus pH for each probe substrates is

Table 1. Acidic Dissociation (pK_a) and Kinetic Constants of the Investigated Probe Substrates

	k_{obs}[a] (h^{-1})	pK_a	k_P($^1O_2$[b]) (M^{-1} s^{-1})	k_{P-} ($^1O_2$[b]) (M^{-1} s^{-1})	k_P (•OH[c]) (M^{-1} s^{-1})	$k_{P,\,P-}$ (•OH[d]) (M^{-1} s^{-1})
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. [b] Rate constants for chemical reaction of the phenol (k_P) and phenate (k_{P-}) species with $^1O_2$.[16] [c] Rate constants for reaction of the phenol (k_P) species with •OH determined at pH 7.0.[16] [d] Rate constant for reaction of the phenol and phenate ($k_{P,\,P-}$) species with •OH determined at pH 9.0.[17,18]

shown in Figure S3 of the Supporting Information. The reactivity order observed for the chlorophenols in our conditions (k_{obs}) follows the same trend as that observed for k_r values at pH 9.8, while is not consistent with that reported for OH ($k_{P,\,P-}$ (•OH) values in Table 1). This suggests that singlet oxygen might play a major role in the photooxidation of chlorophenols under the studied experimental conditions.

In Figure 2, 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 (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 byproducts should not be expected.

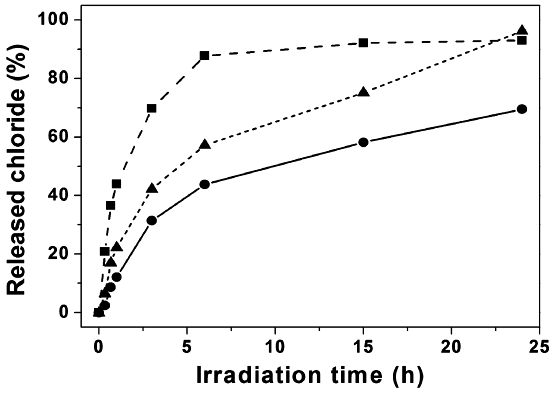

Figure 2. Percentage of chloride ions released in solution, calculated with respect to the theoretical value of organic chlorine in the probe substrate, as a function of irradiation time. Experimental conditions as in Figure 1; 2-CP (■), 3-CP (▲), and 4-CP (●).

Effect of CVT230 Concentration and pH. On the basis of the previously discussed effect of the acid/base properties on the degradation kinetics, to better characterize the behavior of CVT230, the effect of CVT230 concentration was studied at two different initial pH values, i.e., 7.0 and 9.8, choosing 4-CP as the probe substrate. To define the CVT230 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. For humic acids having similar chemical natures as SBO, it has been reported that the formation of molecular aggregates can influence the kinetics of the reaction with singlet oxygen.[20] Figure S4 of the Supporting Information 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 (1.0×10^{-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. Figure 3 reports the results obtained at pH 9.8; as observed, the degradation rate increases progressively up to 1 g L^{-1} CVT230 concentration. In this condition, the 4-CP abatement was found to be 77% after 6 h irradiation and 100% after 24 h. A further increase in 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 in the presence of a different SBO.[10] 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. 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 S5, Supporting Information). A similar dose−effect pattern has been reported also for processes occurring in the presence of DOM.[21]

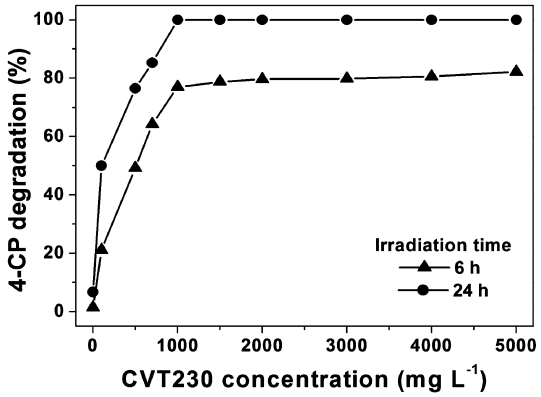

Figure 3. Effect of CVT230 concentration on the percentage of 4-CP (1.0×10^{-4} M) degradation after 6 and 24 h irradiation.

In all the investigated CVT230 concentration ranges, the process was significantly more efficient at pH 9.8 (Figure S6, Supporting Information), 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 further indication of the prevalent role of singlet oxygen in the photodegradation of 4-CP mediated by CVT230.

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 the CVT230 excited triplet state was considered. Irradiations were therefore performed in a closed reactor provided for a lateral opening for the gas inlet. Experiments were run under either air or nitrogen atmosphere. The results are shown in Figure S7 of the Supporting Information. It clearly shows the detrimental effect of nitrogen. Because oxygen is a well-known triplet state quencher, the results allow for exclusion that the excited triplet state is actively involved in 4-CP photodegradation.

In order to verify the production of $^1O_2$ and $^\bullet OH$ and to assess any possible relationship with CVT230 concentration, EPR investigations were performed. By this instrumental analysis, 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 (inset in Figure 4), and the signal intensity allows for estimation of the relative amount of each trapped species.[16] Figure 4 reports the signal intensities, respectively, measured for $^1O_2$ trapped by 4-oxo-TMP and for $^\bullet OH$ trapped by DMPO.

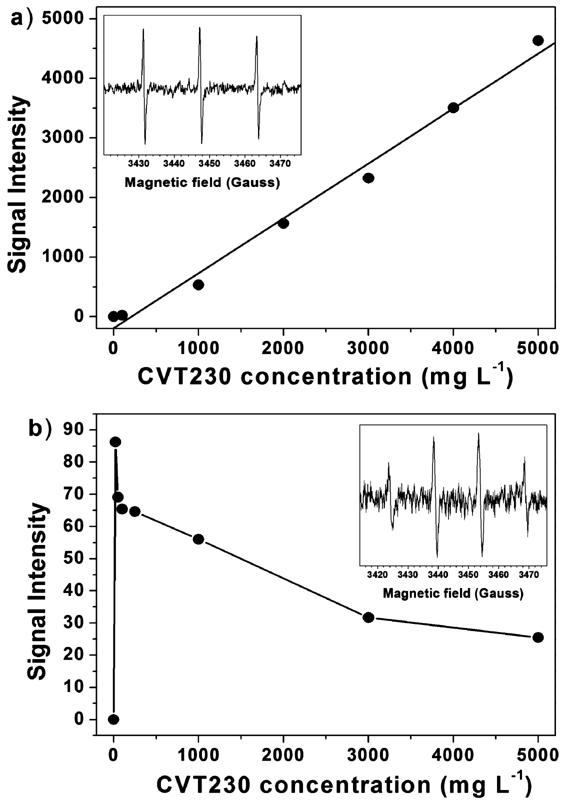

Figure 4. (a) Intensity of 4-oxo-TEMPO EPR signal, after background subtraction, vs CVT230 concentration; 4-oxo-TMP concentration = 45 mM; irradiation time = 15 min. Linear fit of data, slope = 0.9214, intercept = −190.7, r^2 = 0.9893. Inset: EPR spectrum of 4-oxo-TMP−$^1O_2$ adduct. (b) Intensity of DMPO−OH EPR signal vs CVT230 concentration. DMPO concentration = 17.4 mM; irradiation time = 3 min. Inset: EPR spectrum of DMPO−OH adduct.

The trend of the EPR signal intensity reported in Figure 4a is evidence that $^1O_2$ production is directly proportional to CVT230 in the concentration range studied. 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 favored by further addition of this photosensitizing material. However, beyond a given concentration, the scavenging role of CVT230 becomes predominant, resulting in a decrease in the available amounts of $^\bullet OH$. These results are analogous to the ones previously obtained with SBO isolated from a different biowaste.[9]

Afterward, 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[22] and sodium azide,[23] respectively. Figure 5a and 5b show the obtained degradation profiles.

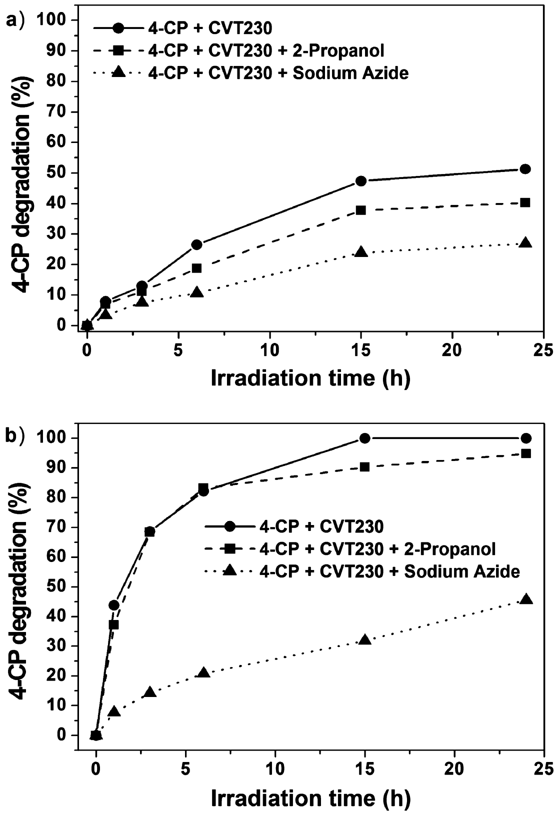

Figure 5. Degradation of 4-CP (1.0 × 10^{-4} M) in the presence of 2-propanol (0.01 M) and sodium azide (0.03 M). Concentration of CVT230: (a) 100 mg L^{-1}, (b) 5000 mg L^{-1}.

It is worth noting that a relevant decrease in 4-CP abatement can be observed when adding sodium azide to the solution containing 5000 mg L^{-1} of CVT230, suggesting that in this condition the degradation process is mainly driven by $^1O_2$. On the contrary, the addition of 2-propanol does not modify the kinetics of the process when working in the presence of the same amount of CVT230, thus allowing for hypothesizing that, in this case, $^\bullet OH$ does not play a significant role in 4-CP degradation. At lower CVT230 concentration, a decrease in the reaction rate can be observed in the presence of each scavenger, thus both $^{\bullet}$OH and $^1O_2$ should have a role in the degradation process. Because the experiments were performed without modifying the pH of the solution as given by dissolving the neat CVT230, it has to be taken into account that at 100 mg L^{-1} of CVT230 the pH was 8.5, whereas it was raised to 9.8 at a 5000 mg L^{-1} CVT230 concentration. On the basis of its k_a value (Table 1), 4-CP was present in the phenate form in a percentage equal to 10% and 80%, respectively. On the basis of the kinetic constants reported in Table 1, it can be observed that the reactivity with $^1O_2$ is strongly influenced by pH variation, whereas the opposite is occurring toward $^{\bullet}$OH. Moreover, phenate reactivity with $^1O_2$ and with $^{\bullet}$OH is very similar, whereas a difference of 4 orders of magnitude exists when considering the associated 4-CP. These results, in agreement with EPR findings, allow for hypothesizing that the degradation mechanism is significantly influenced by pH and CVT230 concentration that in turn affect phenol dissociation and $^1O_2$ and $^{\bullet}$OH production, respectively.

Evaluation of 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. Because of the relevant contribution of CVT230 to the organic content, both in terms of TOC and of possible low mass intermediates degradation products, it would be difficult to discriminate the mineralization extent of chlorophenols upon irradiation. Moreover, also the contribution of CVT230 to the overall system toxicity must be taken into account. In order to exclude the formation of intermediate byproducts more toxic than the starting substrates, the global toxicity of the system was therefore 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 (Supporting Information). The significance of the experimental data is that the higher the inhibition effect (E %), the higher the toxicity level. Specifically, an 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 to 4.0×10^{-4} M, while the concentration of CVT230 was decreased 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 6 shows the plot of the E % values versus the irradiation time, along with the photodegradation kinetic profile. The bioluminescence measurement was performed after 30 min of contact between samples and bacteria.

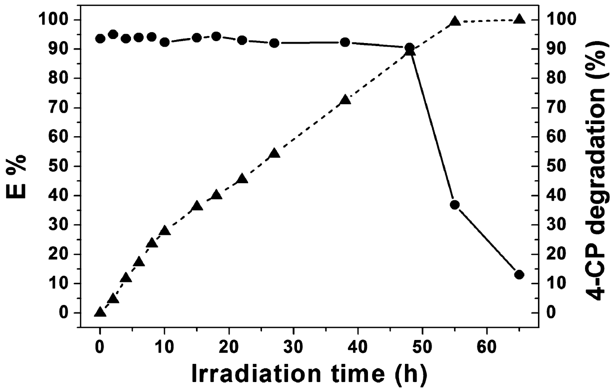

Figure 6. Photodegradation of 4-CP (4.0×10^{-4} M) in Solarbox (cut off filter 340 nm) in the presence of CVT230 (100 mg L^{-1}). Solid line (●): E % vs irradiation time. Dotted line (▲): percentage of substrate degradation vs irradiation time.

It may be observed that the 4-CP-CVT230 solution shows a high initial toxicity level (>90%), maintained up to 48 h of irradiation. Above this irradiation time, a sharp decrease of the E % is observed, proving substantial detoxifications of the solution. This behavior allows for hypothesizing that for up to 48 h of irradiation the toxicity observed can be ascribed to the presence of residual 4-CP together with other intermediate compounds. 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 S1, Supporting Information).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table S1 and Figures S1−S7: Experimental details concerning analytical procedures, instrumentation, toxicity test, surface tension measurements, and electron paramagnetic resonance (EPR) technique. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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