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Abstract

Soluble bio-based substances (SBO) isolated from urban waste are efficient auxiliaries for remediating the environmental impact caused by industrial activities. In this work they are shown to promote the photodegradation of monochlorophenols. Experiments performed with 1.0×10^{-4} M substrate solutions irradiated for 24 h by simulated solar

light in the presence of 500 mg L^{-1} 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 following the 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 in the presence of SBO complete detoxification of the system can be achieved at longer irradiation time; no significant contribution of SBO to the whole system toxicity was observed. The overall results prospect the appealing scenario for organic wastes to be exploited as cost-effective source of chemicals for sustainable environmental.

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 from natural waters.[4-7] The use of organic photocatalysts for water treatment has been very recently reviewed.[8] Unfortunately, DOM cannot be

considered a commercially viable photocatalyst due to its low concentration (< 3 %) in soil and water.

Recently, it has been shown that urban bio-wastes (UBW) are a potential cost-effective renewable source of soluble bio-based substances (SBO) having similar chemical nature and properties as DOM.[9] 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.[9] The above SBO have been produced in relatively large scale by alkaline hydrolysis of UBW sampled from various process streams of the Acea Pinerolese waste treatment plant located in Piemonte, Italy. Although these substances are not commercial yet, research samples are available in quantities adequate for carrying out on field trials. In this fashion, it has been possible to demonstrate that they are rather effective in a wide number of applications, such as polluted soil washing,[10] agriculture,[11] animal husbandry,[12] and material chemistry.[13] At laboratory scale, successful trials have also been carried out for the photodegradation under simulated solar light of some chemicals found in industrial effluents such as azo and cationic dyes,[14,15] phenols,[16] and aromatic sulphonic acids.[17] The potential use of SBO as photocatalyst for water detoxification may be considered a green process since it valorizes solid waste as a material of technological application.

In the present work we studied the performance of SBO isolated from the alkaline hydrolyzate of urban private gardening and public park trimming residues 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 optimize the photodegradation process at laboratory scale under simulated solar light; iii) to verify the system detoxification in view of an environmental and industrial relevant process scale up. Monochlorophenols were good probe substrates since they are toxic and hardly biodegradable compounds that have been found in wastewaters, ground water, soils and also in the trophic chain; moreover they have been often chosen as model compounds for water treatments studies by other authors.[18]

EXPERIMENTAL

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 (hereinafter referred to by the CVT230 acronym) 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,[19] (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 by the chemical composition data reported in Table S1, Supporting Information (S.I.).[20] Average values of triplicates are shown in Table 1; relative standard deviations as % of mean values were found about 10 %.

Before use, CVT230 was taken up with Milli-Q^{TM} 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 in S.I.

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}. The use of a cut-off filter was motivated by the aim of discarding the contribution of substrate photolysis through direct excitation, since neither the phenol nor phenate form of chlorophenols absorbs above 340 nm (Figure S2 in S.I.). 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).

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

RESULTS AND DISCUSSION

Degradation of chlorophenols. Preliminary control experiments were run with 1.0×10^{-4} M aqueous solutions of each chlorophenol. Irradiation in Solarbox in the absence of CVT230, performed both at pH 7.0 and 9.8, 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 (1.0×10^{-4} M) were then irradiated in the presence of CVT230 (500 mg L^{-1}) at the initial pH of 9.4 given by the dissolved neat CVT230 sample without addition of any acid or base. Figure 1 reports the decrease of the probe substrate concentration (C) relatively to the starting value (C_0) versus the solution irradiation time. The results show that the progressive degradation of all the probe substrates follows a pseudo-first order kinetic (see the linear ln C/C_0 vs. irradiation time plots in Figure 1 inset). Table 1 reports the calculated rate constants (k_{obs}). These indicate that the probe substrate reactivity decreases in the order 2-CP > 3-CP > 4-CP.

Figure 1

Table 1

Table 1 reports also literature data for the second-order rate constants of the reactions of chlorophenols with $^{\bullet}OH$ and $^1O_2$. These data are relevant to understand the SBO assisted photodegradation process. Indeed the formation of such species upon irradiation of aqueous solutions of the AC8 SBO has been previously demonstrated.[16] From the literature data, one may observe 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 second-order rate constant for 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.[24] The plot of k_r versus pH for each probe substrates is shown in Figure S3 of the S.I.. It may be observed that the k_r values at pH 9.4 follow the same order as that observed for the k_{obs} values in Table 2. This suggests that singlet oxygen might play a major role in the photooxidation of chlorophenols under the studied experimental conditions.

Chloride release in solution. In previous studies concerning chlorophenols degradation the cleavage of C-Cl bond was indicated as one of the possible degradation paths.[18] 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 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 (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 2

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. For humic acids having similar chemical nature as SBO, it has been reported that the formation of molecular aggregates can influence the kinetic of the reaction with singlet oxygen.[25] Figure S4 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 (1.0×10^{-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. The results reported in Figure 3 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 in the presence of a different SBO.[17] 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 known behavior 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 S5 in the S.I.). A similar dose-effect pattern has been reported also for processes occurring in the presence of DOM.[27]

Figure 3

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 S6, 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.

Role of singlet oxygen and hydroxyl radicals. Before gaining further insight into the role of $^1O_2$ and $^•OH$ on the 4-CP degradation, the possible role of CVT230 excited triplet 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 S7, S.I. It clearly appears the detrimental effect of nitrogen; since oxygen is a well known triplet state quencher, the results allow to exclude that excited triplet state is actively involved in 4-CP photodegradation.

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 $^•OH$ and $^1O_2$ scavengers, namely 2-propanol,[28] and sodium azide,[29] respectively. Figures 4a and 4b 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) no kinetic modification is evident. 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 4a and 4b

These results seem to indicate that at high CVT230 concentration the degradation process is mainly driven by $^1O_2$ whereas at low CVT230 concentration also $^•OH$ is actively involved. This behavior could be explained by taking into account that the experiments were performed without modifying the pH of the solution as given by dissolving the neat CVT230: i.e. pH 8.5 at 100 mg L^{-1} and 9.8 at 5000 mgL^{-1} CVT230

concentrations. 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 $^{\bullet}OH$. In order to asses if also the production of $^1O_2$ and $^{\bullet}OH$ was related to 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 (see Inset in Figure 5) and the signals intensity allows to estimate the relative amount of each trapped species.[16] Figure 5 reports the signal intensities, respectively measured for $^1O_2$ trapped by 4-oxo-TMP (a) and for $^{\bullet}OH$ trapped by DMPO (b).

Figure 5a and 5b

The trend of the EPR signal intensity reported in Figure 5a 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 favored 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 SBO isolated from a different bio-waste.[16]

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 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 minutes of contact between samples and bacteria.

Figure 6

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 behavior 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. 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 S2 in S.I.).
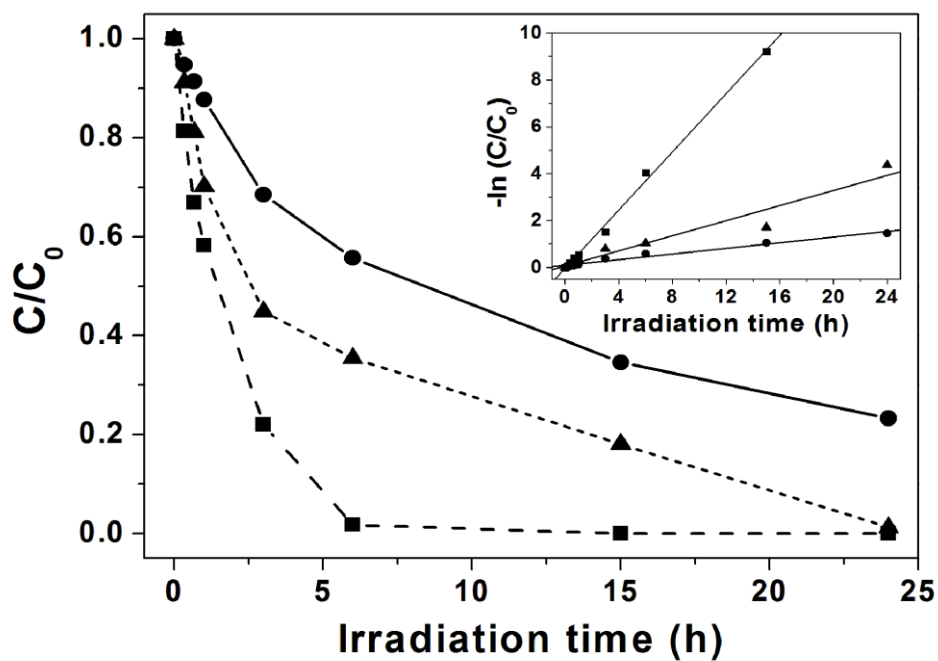
Figure 1. Degradation of chlorophenols (1.0×10^{-4} M) in the presence of CVT230 (500 mg L^{-1}): 2-CP (■), 3-CP (▲) and 4-CP (●). Irradiation performed in Solarbox (cut-off filter 340 nm). Inset: plots of -ln (C/C_0) vs. irradiation time.
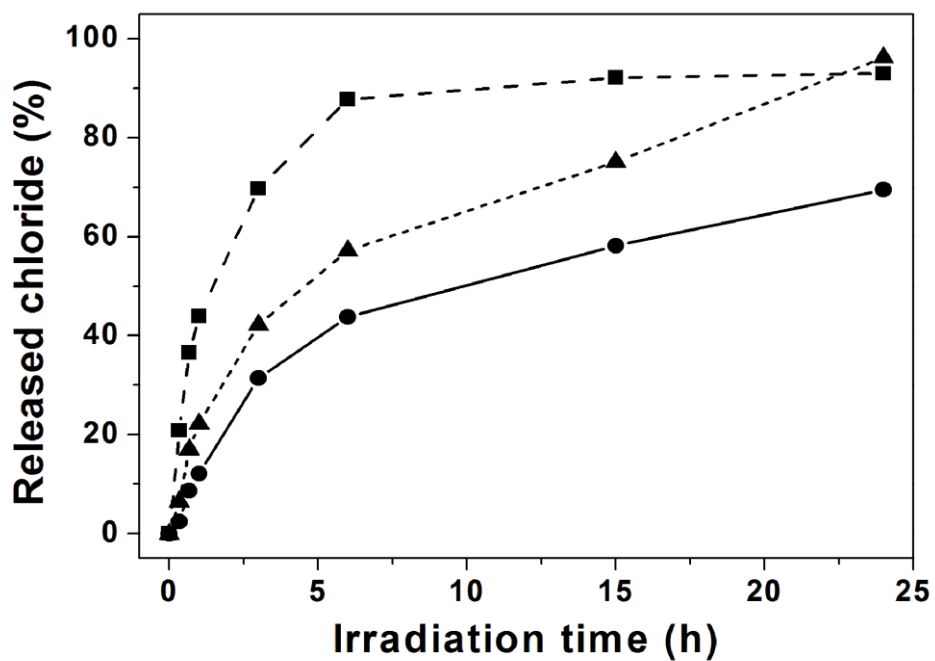
Figure 2. Percentage of chloride ions released in solution, calculated with respect to the theoretical value of organic chlorine in the probe substrate, as function of the irradiation time. Experimental conditions as in Figure 1; 2-CP (■), 3-CP (▲) and 4-CP (●).
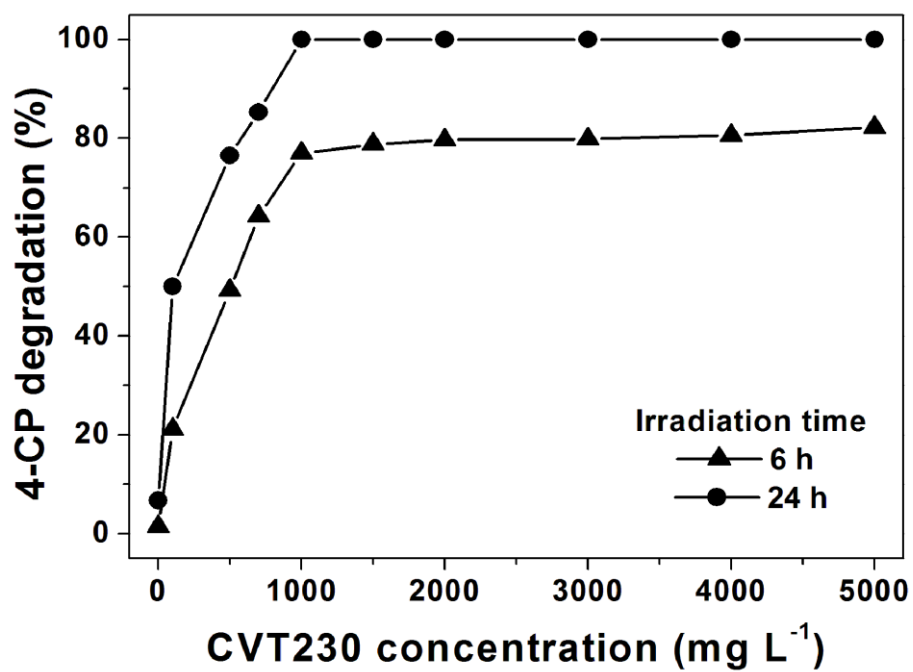
Figure 3. Effect of CVT230 concentration on the percentage of 4-CP $(1.0 \times 10^{-4}$ M) degradation after 6 and 24 h irradiation.
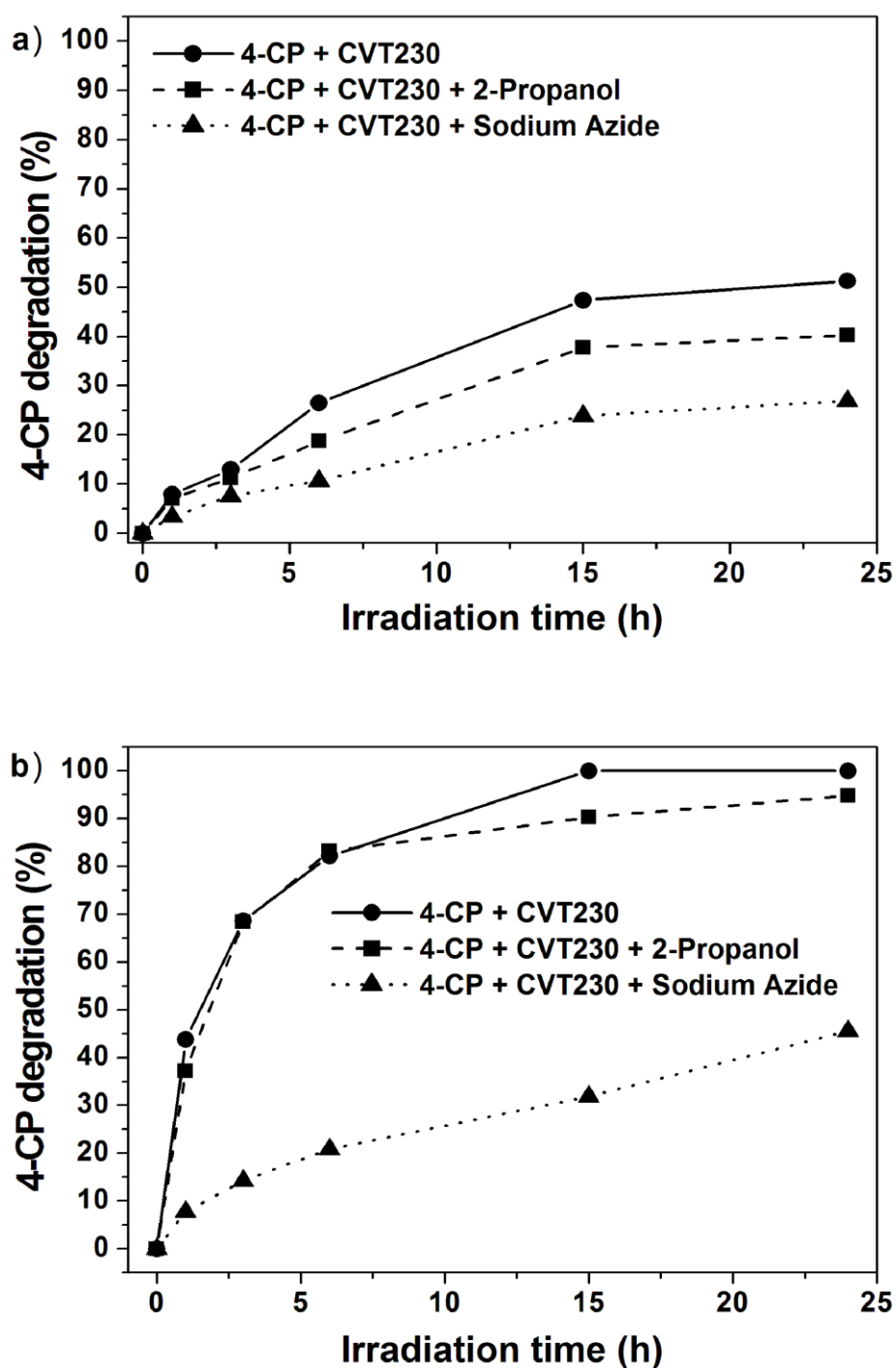
Figure 4. Degradation of 4-CP (1.0×10^{-4} M) in the presence of 2-propanol (0.01 M) and sodium azide (0.03 M). Concentration of CVT230: a) 100 mg L^{-1}, b) 5000 mg L^{-1}.
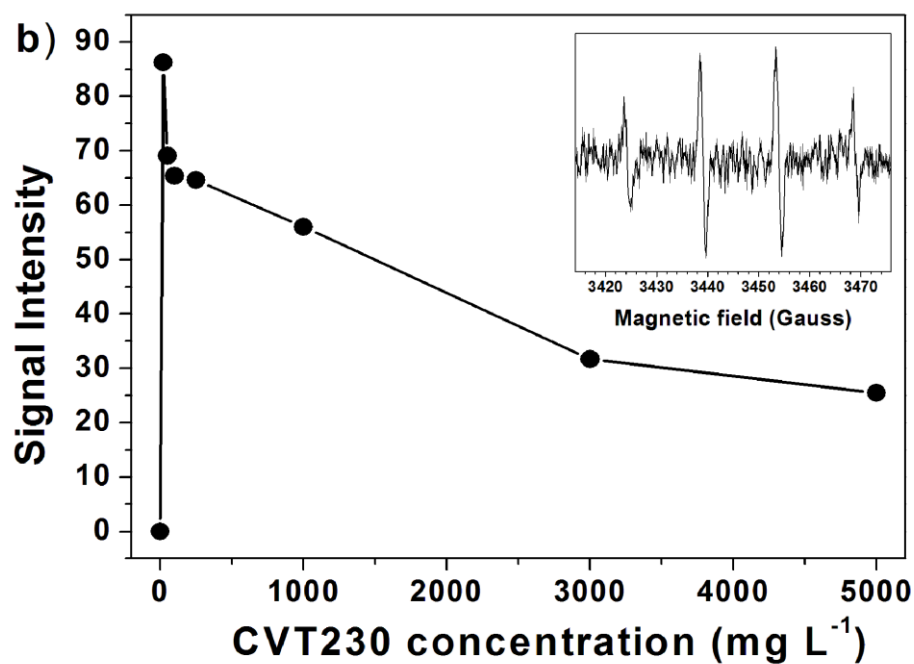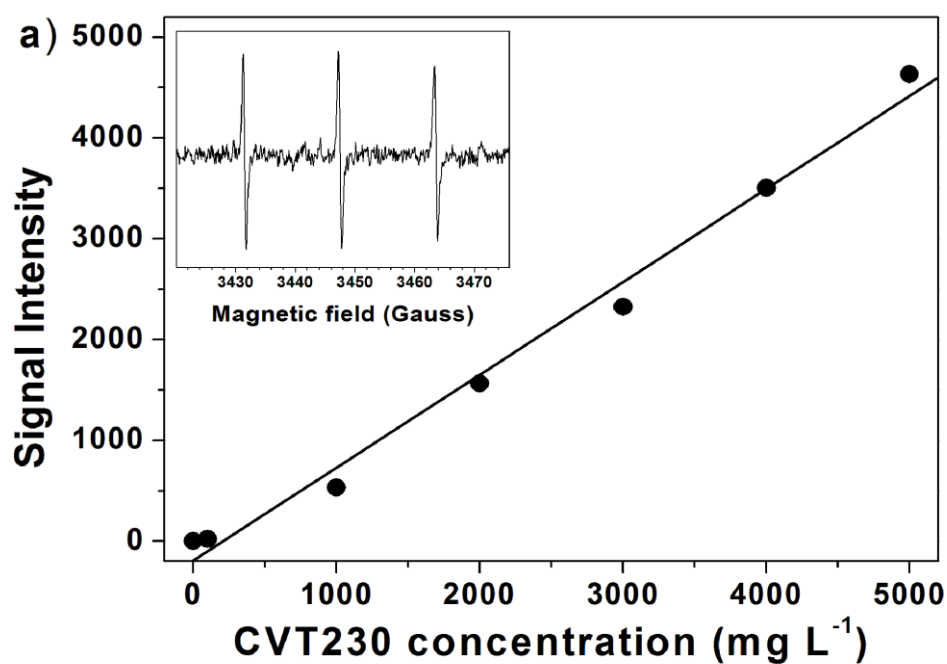
Figure 5. a) Intensity of 4-oxo-TEMPO EPR signal, after background subtraction, vs. CVT230 concentration. 4-oxo-TMP concentration = 45 mM; irradiation time = 15 minutes. Linear fit of data, slope = 0.9214, intercept = -190.7, r^2 = 0.9893. Inset: EPR spectrum of 4-oxo-TMP-$^1O_2$ adduct. b) Intensity of DMPO-OH EPR signal vs. CVT230

concentration. DMPO concentration = 17.4 mM; irradiation time = 3 minutes. pH 9.4.
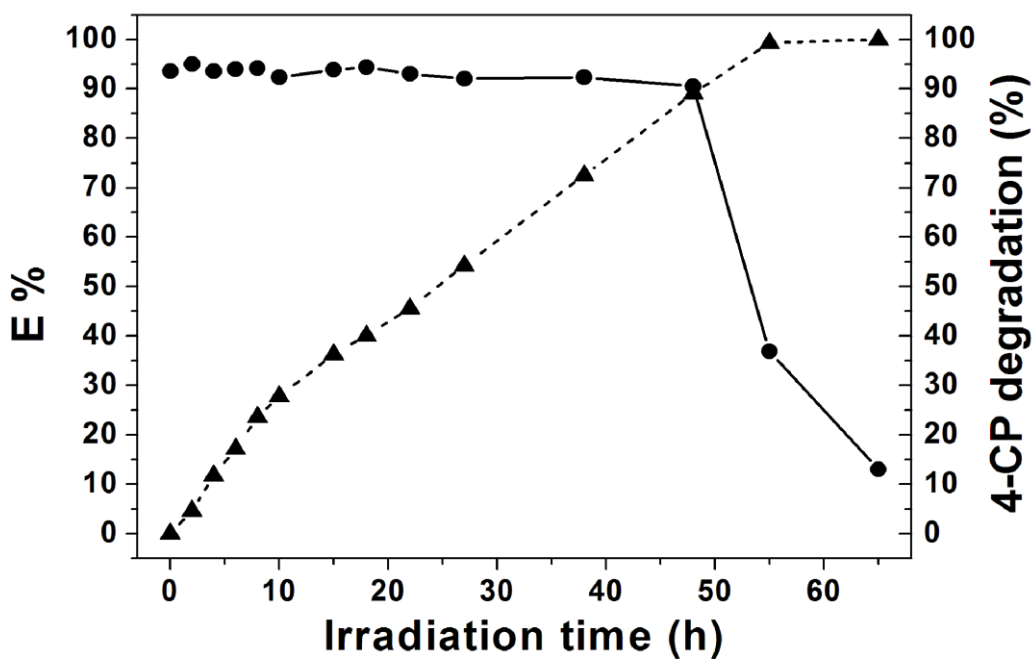
Inset: EPR spectrum of DMPO-OH adduct.

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.

Table 1. Acidic dissociation (pK_a) and kinetic constants of the investigated probe substrates.

	k_{obs}[a]	pK_a	$k_P(^1O_2$[b]$)$	$k_{P\text{-}}$ $(^1O_2$[b]$)$	k_P ($^•OH$[c])	$k_{P,\,P\text{-}}$ ($^•OH$[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 ($k_{P\text{-}}$) species with $^1O_2$ [21];

[c] rate constants for reaction of the phenol (k_P) species with $^•OH$ determined at pH=7.0 [21];

[d] rate constant for reaction of the phenol and phenate ($k_{P,\,P\text{-}}$) species with $^•OH$ determined at pH=9.0 [22,23].

SUPPORTING INFORMATION

Experimental details concerning instrumentation, toxicity test, surface tension measurements and electron paramagnetic resonance (EPR) technique. Tables S1-S2 and Figures S1-S7.

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