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Sensitizing effect of bio-based chemicals from urban wastes on the photodegradation of azo-dyes

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ABSTRACT

To promote bio-based products for the industry, six bio-organic substances (cHALi) isolated from yard trimmings (green) and food (humid) urban residues aged under aerobic digestion for 0–60 days were investigated for their potential to perform as sensitizers for azo-dyes photodegradation. Ethylorange (EO) was used as probe molecule at 5 mg L^{-1} starting concentration and irradiated in a closed Pyrex® cell with a Xenon (1500 W) lamp and a cut-off filter for wavelengths below 340 nm or in a cylindrical photochemical reactor equipped with a 125 W medium pressure Hg lamp. The cHALi/EO ratio in the starting EO solution varied in the 0–200 (w/w) range. The % dye abatement was found a function of the irradiation time, of the type of cHALi substance and of the cHALi/EO ratio. The best results were achieved with cHALi isolated after 7 days biomass aerobic digestion. Total dye abatement was achieved within relatively short few hours. A progressive dye mineralization was observed under the same experimental conditions. On the contrary no significant degradation was evident for the cHALi substances within the same irradiation time. Several hydroxylated azo compounds were identified as likely responsible of residual color after total EO abatement. The results, coupled to the previously reported good performance of the same cHALi substances as auxiliaries for textile dyeing, augur well for the development of both efficient and environmentally friendly textile dyeing processes.

1. Introduction

In the global frame of waste management and sustainable development, urban wastes have been proposed as possible source of chemicals to recycle for industrial uses at commercial level [1–4]. They look nowadays rather attractive for several reasons. As a result of the increased production due to population urbanization, urban wastes are concentrated in confined areas by municipal collection. In addition, depending on the type of treatment and on composition, they may provide high yields of a large variety of bio-organic substances (BOS) fitting a wide range of uses. One very promising application has been shown in textile dyeing. Several BOS isolated from green and/or food urban wastes have been demonstrated to be efficient auxiliaries for dyeing cellulose acetate fabric [4]. For one BOS, isolated from urban yard trimming wastes, an additional property has also been reported [3], i.e., the capacity to accelerate the photodegradation of the azo-dye ethylorange (EO). These results allow predicting a rather unique opportunity for the whole textile dyeing process, i.e., to use one same substance to optimize both the dye adsorption by the fiber and the excess dye removal from the exhaust dyeing bath, thus improving both the production and waste management processes.

Actually the textile industry uses more than three thousand dyes, and it is estimated that about 15% of the world dyes production is lost in the environment during the dyeing process [5,6]. Azo-dyes constitute about 50% of the total dye consumption; their environmental impact is not only related to color, but also to reduction producing carcinogenic aromatic amines [7]. This poses the problem of their removal from industrial wastes or polluted natural water streams.

Photosensitizing properties have already been reported for BOS present in natural waters and soil [8–14] or isolated from mixtures of yard trimmings and/or sewage sludge undergoing aerobic biodegradation [15,16]. The photosensitizing properties of these substances have been studied using mostly phenol molecules or pesticide substances as probe substrates.

The present work concerns the EO photosensitized degradation in the presence of six BOS isolated from urban refuses which hereinafter will be referred to by the abbreviation cHALi, i = 2–7: cHAL2, cHAL3 and cHAL4 isolated from urban yard trimmings (green wastes) and cHAL5, cHAL6 and cHAL7 isolated from a 1:1 (w/w) mix of food (humid) and green residues at the start of the aer-

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obic digestion process (cHAL2 and cHAL5), and after 7 days (cHAL3 and cHAL6) and 60 days (cHAL4 and cHAL7) aging. Relatively to previous work performed with cHAL2 only [3], the investigation of the above six BOS addresses several issues: i.e., assessing chemical structure and photosensitizing properties as a function of the nature and treatment type of the product source, and the fate of photodegraded EO. These issues were rather challenging for several reasons. First, it should be considered that the investigated cHALi substances are new materials of biological origin with quite complex chemical composition for which several molecular models have been reported [1,23]. Secondly, the chemical variability of the urban refuses may prospect a desirable availability of multiple bioproducts, but also poses a major concern, regarding the capacity to yield bio-based products with constant performance specifications. Thirdly, it should be considered that the real cHALi performance to assist EO photodegradation should be rated on the basis of fate of both the dye and the photosensitizer. This requirement, considering the chemical structure complexity of the latter and the multiplicity of degradation products which might be expected to arise from both the dye and the photosensitizer, poses rather demanding analytical problems to face. In particular we focused our attention on the kinetics of EO degradation and on the identification of the intermediates formed in the initial degradation steps. High performance liquid chromatography coupled to high resolution mass spectrometry (HPLC–HRMS) was applied as a powerful tool.

Finally, the capacity of the cHALi to yield micellar aggregates [1] in water was also a matter of concern in this work. Indeed, the presence of aggregates could give rise to EO partitioning between the bulk water and the more hydrophobic micellar region, and this could influence the EO photodegradation kinetics and yield [17]. Thus, a study of the molecular aggregation of the cHALi was necessary to define the most suitable experimental concentration range to be investigated for preliminary evaluation of their photosensitizing properties.

For the above reasons, the issues of this work cannot be exhaustively dealt with in just one paper. The present manuscript therefore does not claim to provide specific problem solutions, but is rather meant as ground for prospecting the potential of urban refuses to become exploitable source of photosensitizing bio-substances.

2. Materials and methods

2.1. Bioproducts and reagents

Ethylorange, i.e., 4-(4-diethylaminophenylazo)benzene sodium sulfonate, 69% HNO_3 and 98% CH_3COONH_4 by Fluka, 99% NaOH and 99% KNO_3 by Merck, 99% Na_2SO_4 and 99.7% $NaHCO_3$ by Aldrich, analytical grade CH_3CN by Scharlau and MilliQ® reagent grade ultrapure water were used throughout this work as received, unless otherwise indicated. The cHALi (i = 2–7) substances investigated in this work were obtained from ground green wastes or from 1:1 (w/w) food and green residues mix collected in the province of Torino, Italy. Once collected and transported in a municipal waste treatment plant, the chopped green residues, eventually mixed with the mechanically selected (Ø < 12 mm) humid wastes, were aged under aerobic conditions for 0–60 days, sieved through a mechanic grid (Ø < 10 mm) and used for cHALi extraction. The cHALi isolation was performed as previously reported [2].

2.2. Chemical and physical characterization of cHALi substances

C,H,N microanalytical data were obtained with a C. Erba (Rodano, Milan, Italy) NA-2100 elemental analyzer. The determination of the functional groups was accomplished by potentiometric titration and by solid-state ^{13}C NMR spectroscopy as previously reported [1]. The functional groups composition reported as C ratios relative to total unsaturated and aromatic C (Ct) in Table 1 was calculated from the above NMR signals area ratios, and from the total C and N microanalytical and acid groups concentration reported as supporting data in Appendix A under the assumption that the total N was present as amine or amide N and that all organic C in the sample was accounted for by the above NMR signals. Surface tension (γ) measurements of aqueous solutions containing the sample of the investigate substances at variable concentrations (Cs = 0.005–3 g L^{-1}) were carried out at 25 °C and pH 7 with a Kruss K100 automatic tensiometer and the critical micellar concentration (cmc) was calculated from γ–Cs plots as previously reported [2].

2.3. Ethylorange irradiation experiments

A stock 1 g L^{-1} cHALi aqueous solutions was prepared by taking up solid cHALi with MilliQ® water at 250–200 (v/w) ratio, stirring 1 h, then adding aliquots 0.2 M NaOH to keep pH in the 8–9 range until the complete solid dissolution occurred. The solution was finally filtered through a 0.45 μm Millex–HA membrane (Millipore) and brought to the required volume with MilliQ® water. The stock solution was kept frozen before use. Aliquots of the stock solution were used to obtain 5 g L^{-1} EO solutions containing variable amounts of cHALi. The degradation trials were performed by irradiating 5 mL cHALi–EO aqueous solution in a closed Pyrex® cell with a Xenon (1500 W) lamp (Solarbox) and a cut-off filter for wavelengths below 340 nm. Experiments were also performed on 500 mL cHALi–EO aqueous solutions in a cylindrical photochemical reactor (Helios-Italquartz, Milan), equipped with a 125 W medium pressure Hg lamp. The system was kept under continuous stirring in order to avoid the formation of concentration gradient and air or nitrogen was bubbled to saturate the solutions with the gases. Cold water circulating in the jacket surrounding the lamp kept the temperature within the reactor at 20 °C; a Pyrex® glass jacket acting as a cut-off filter for wavelengths below 300 nm was employed, in order to avoid any possible contribution coming from direct dye photolysis.

2.4. Analyses of the irradiated solutions

The dye abatement was calculated from the starting EO concentration (Co) and the found EO concentration (Cir) after irradiation. The Cir value was determined by HPLC–DAD–UV–vis (Surveyor, Thermo Scientific) analysis under the experimental conditions reported in Appendix A. The analysis of the EO photodegradation products was performed by HPLC–MS. A Dionex Ultimate 3000 HPLC coupled with a Surveyor PDA UV detector and a LTQ Orbitrap mass spectrometer (Thermo Scientific) equipped with an atmospheric pressure interface and an ESI ion source was used; N_2 was used as sheath and auxiliary gas. The source voltage was set to 3.1 kV. The heated capillary temperature was maintained at 275 °C. The main tuning parameters adopted for ESI source were: capillary voltage −34.00 V, tube lens offset −68.57 V. Mass accuracy of recorded ions (versus calculated) was ±15 ppm (without internal calibration). The chromatographic separations were performed on a Phenomenex Synergi C18 column, 150 mm × 2.0 mm, 3 μm particle size. Injection volume was 20 μL and flow rate 200 μL/min. Gradient mobile phase composition was adopted: acetonitrile/ammonium acetate 0.1 mM 5/95 to 100/0 in 30 min. Total organic carbon (TOC) in the irradiated solutions was also measured, by means of Shimadzu TOC-5000 analyzer (catalytic oxidation on Pt at 680 °C), which was previously calibrated using potassium phthalate standard solutions. Color bleaching in the irradiated solutions was quantified by means of a double beam CARY 100 SCAN-VARIAN,

Table 1
Ratios for aliphatic C (Cal), methoxy C (OMe), amine C (NC), O-alkyl C (OR), diO-alkyl C (ROCOR), aromatic and/or olefinic C (C=C) excluding PhO, phenol (PhOH), phenyl ether (PhOX, X = R, Ar), carboxylic acid C (COOH) amide C (CON) and keto C, relative to the sum (Ct) of C=C, PhOH and PhOX C.

	Cal	OMe	NC	OR	ROCOR	C=C	PhOH	PhOX	COOH	CON	C=O
cHAL2	3.05	0.13	0.33	0.84	0.26	0.64	0.12	0.24	0.37	0.07	0.18
cHAL3	2.54	0.20	0.22	0.78	0.27	0.70	0.19	0.11	0.34	0.14	0.20
cHAL4	2.25	0.15	0.26	0.71	0.26	0.69	0.22	0.09	0.35	0.07	0.12
cHAL5	4.90	0.23	0.50	1.12	0.21	0.68	0.29	0.03	0.55	0.07	0.30
cHAL6	4.50	0.00	0.56	0.90	0.66	0.61	0.39	0.00	0.49	0.05	0.19
cHAL7	2.96	0.08	0.43	0.68	0.16	0.72	0.17	0.11	0.43	0.09	0.24

UV–vis spectrophotometer by measuring the absorbance at 467 nm where the EO irradiated solution exhibits the maximum absorptivity. The absorbance was then corrected for the cHALi contribution.

3. Results and discussion

3.1. Chemical nature of cHALi and molecular association in solution

The chemical composition of the investigated cHALi substances is reported in Table 1. It appears that on basis of the Cal, OR, NC and COOH parameters the chemical nature of the cHALi substances is significantly affected by both the type and aging of the sourcing biomass waste. Specifically, the substances isolated from food and green residues mix (cHAL5–7) seem to have higher Cal, NC and COOH content relatively to aromatic C than those isolated from sole green residues (cHAL2–4). This result suggest that the cHAL5–7 substances have a higher content of residual fatty acid and protein moieties formed by the microbial degradation of the starting bio-organic matter. Also, for each group of substances, it seems that increasing the aging time of the sourcing waste causes a decrease of the Cal, OR and COOH relative C ratio. These changes may be consistent with the relatively higher sensitivity of aliphatic C to microbial degradation which has been already reported for other cases [1]. The data confirm the variability of chemical composition on the substances source which has already been observed also for other similar BOS [1,18,19] present in soil, water and city refuses from other locations.

The apparent critical micellar concentration (cmc) values for the investigated substances (see Appendix A) were 0.73–0.77 g L^{-1} for cHAL2–4 and 0.98–1.01 g L^{-1} for cHAL5–7. These appeared therefore relatively constant within each group of substances obtained from the same source material, but changing significantly from one group to the other (i.e., from cHAL2–4 to cHAL5–7).

3.2. Irradiation experiments and % dye abatement

Based on the cmc data, the upper limit of 1 g L^{-1} cHALi concentration was established in order to avoid or limit the presence of cHALi aggregates and their potential effect on EO photodegradation kinetics and yield [17]. A preliminary ranking of the isolated cHALi substances has been considered on the basis of their sensitizing effect on the photodegradation of EO. The experiments were performed irradiating the samples in closed cells for 5 h. Sample solutions were prepared by dissolving EO at 5 mg L^{-1}, either alone or in the presence of 100 mg L^{-1} cHALi (i = 2–7). Under these conditions, the neat EO solution exhibited a negligible 1.8% dye abatement, whereas rather high dye abatement rates were observed in the presence of cHALi (Fig. 1), with the cHAL5–7 substances isolated from the mix of green and food residues performing better than the cHAL2–4 substances isolated from sole green residues. This fact seems to point out a significant material source effect on the catalytic performance of the above cHALi substances for EO photodegradation. Moreover for each group of substances isolated from the same type of source waste a peak effect seems to be reached with the substances isolated from 7 days aged source materials, i.e., cHAL3 and cHAL6. The effect of the source material aging is not as straightforward. Analogously to our findings, two recent papers have reported on the photosensitizing properties of BOS isolated from mixtures of yard trimmings, sewage sludge, and/or animal manure and grapes residues, which were collected after composting for 0–130 days [15,20]. The photodegrading activity of such substances appeared to increase between 0 and 70 days composting and to remain quite constant for the next further 60 days. Searching for possible structure–property relationships, our data show a trend for % dye abatement to increase with the relative phenol content in Table 1. The linear regression analysis performed over all data points, excluding the one for cHAL7 that was clearly deviating from the general trend, yields a regres-

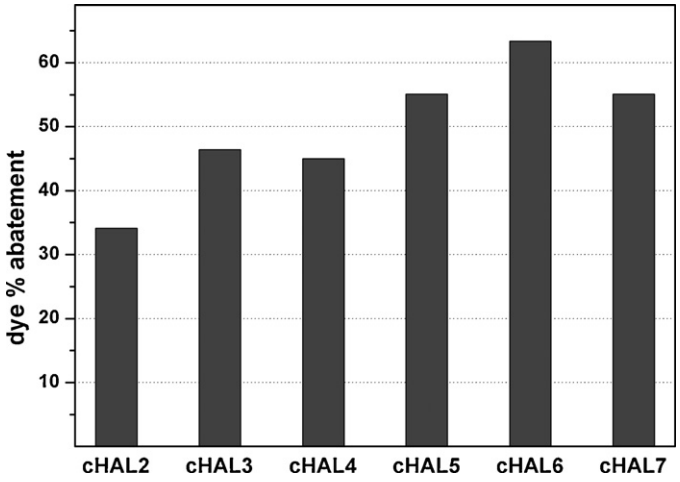


Fig. 1. Dye abatement (%) of 5 mg L^{-1} EO solution in the presence of 100 mg L^{-1} cHALi after 5 h irradiation in Solarbox.

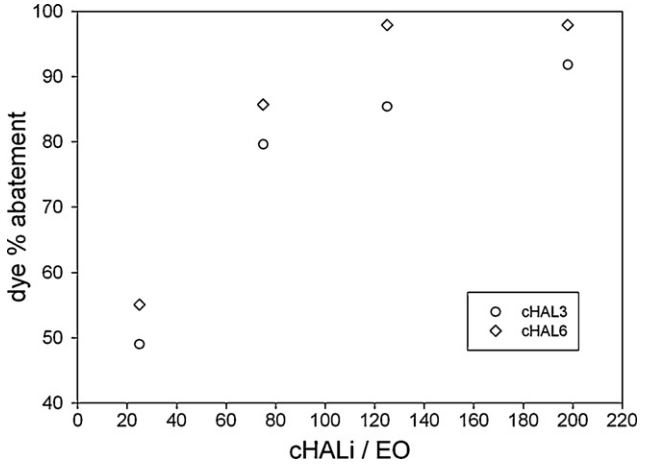


Fig. 2. Dye % abatement versus cHALi (i = 3 or 6)/EO (w/w) ratio after 3 h irradiation of 5 mg L^{-1} EO solutions in Solarbox.

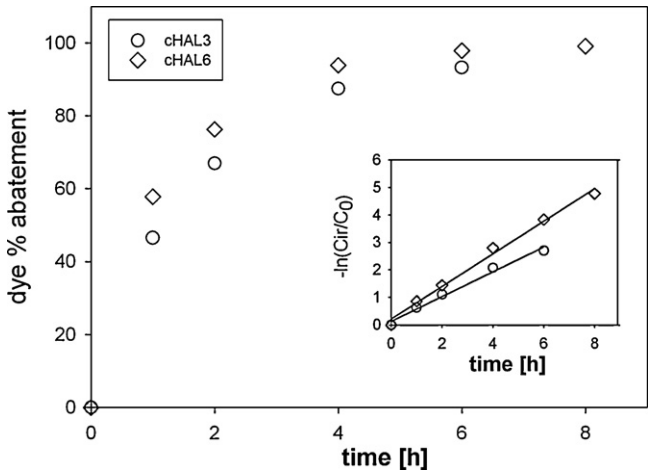


Fig. 3. Dye % abatement and ln(Cir/Co) (Cir and Co = concentrations at time $t > 0$ and $t = 0$ respectively) versus irradiation time in Solarbox for 5 mg L^{-1} starting EO solutions at 75 (w/w) cHALi ($i = 3$ or 6)/EO ratio.

sion coefficient of 0.95 and the empirical equation DA = 23.2 + 106 PhOH/Ct, with DA = % dye abatement. Consistently with previous work [20] phenol functional groups are likely to have an active role in the photosensitizing process, although other chemical structural factors may also contribute to the cHALi performance. Regardless of this empirical relationship, to verify the effect of the source composition on the photosensitizing power of BOS, successive experiments were performed with two cHALi selected from each group based on their % dye abatement rather than on the phenol content: i.e., cHAL3 and cHAL6, which showed the highest % dye abatement within the products isolated from sole green wastes and from the mix of green and humid refuses respectively.

Fig. 2 reports the results of experiments performed by irradiating for 3 h solutions containing 5 g L^{-1} EO in the presence of 125–1000 mg L^{-1} cHAL3 or cHAL6. The results indicate that cHAL6 performs significantly better than cHAL3 and that, for both substances, the measured degradation yield increases with the cHALi/EO (w/w) ratio, reaching nearly 100% at about 130 cHAL6/EO (w/w) ratio.

Fig. 3 reports the results of EO photodegradation experiments at 75 (w/w) cHALi ($i = 3$ or 6)/EO ratio as a function of irradiation time. It may be observed that even at this low cHALi/EO ratio, nearly total dye abatement is still reached within reasonably short 4 h time. The data well fit in a first-order kinetic law as clearly shown by the ln(Cir/Co)–time plot. The higher performance of cHAL6 relatively to cHAL3 is confirmed throughout the investigated time range. Analogous kinetics profiles were obtained using the photochemical reactor; in comparison with the results obtained in Solarbox, a slower abatement rate was observed. This difference is most likely due to the different geometries and light source intensities present in the two systems.

Other experiments were performed with solutions containing 5 mg L^{-1} EO and 75 (w/w) cHALi ($i = 3$ or 6)/EO ratio which were irradiated in the photochemical reactor under continuous air or

Table 2
First-order kinetic constant (k_{obs}) values for the photodegradation of EO in the presence of cHAL3 and cHAL6 calculated from the data reported in Fig. 3 and in Fig. 1S of the Appendix A.

Experimental conditions	k_{obs}, min^{-1}	
	cHAL3	cHAL6
Solarbox	0.45	0.59
Photochemical reactor in air	0.09	0.13
Photochemical reactor in N_2	0.03	0.08

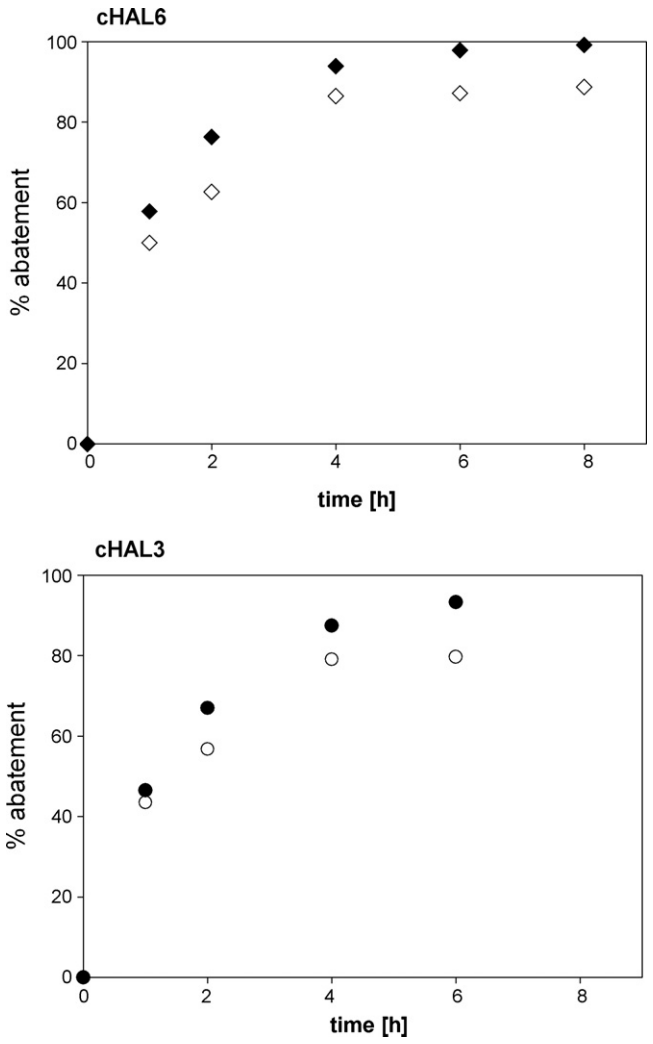


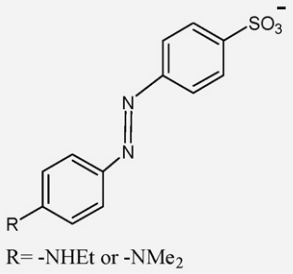
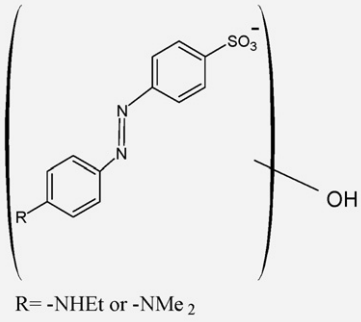
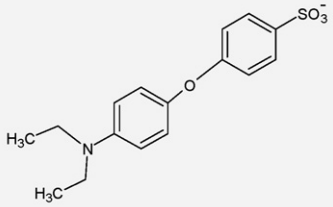
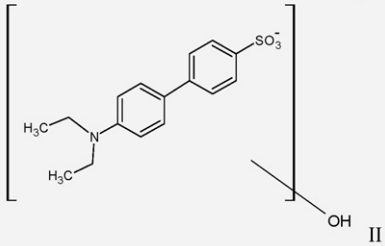
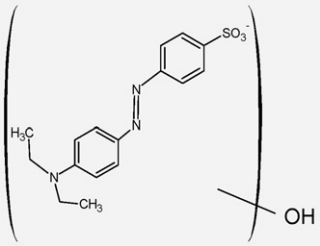
Fig. 4. Color (open symbols) and dye (solid symbols) % abatement versus irradiation time in closed cells operating with 5 mg L^{-1} starting EO solutions at 75 (w/w) cHAL3/EO (lower plots) or cHAL6/EO (upper plots).

nitrogen bubbling in order to evaluate the effect of the atmosphere on the degradation process. The results (reported in the Appendix A) show a relevantly lower dye abatement rate in the presence of pure N_2 compared to air, as demonstrated by the calculated first-order kinetic constants in Table 2. This fact suggests a possible reaction mechanism involving reactive oxygenated species (ROS) as already proposed for BOS present in soil and terrestrial waters [13,21]. Analogously to the mechanism proposed for humic substances, the light absorption by cHALi may produce excited triplet states that can in turn react with organic substrate by two main mechanism: hydrogen-transfer and energy-transfer. The former one could be proposed in our case; the presence of dissolved oxygen should favor indeed the dye degradation since the generated hydrogen atom can be transferred to the dissolved oxygen with the formation of various ROS such as $^{\bullet}OH$, $^1O_2$, $^{\bullet}O_2^-$ and H_2O_2 which also contribute to the dye degradation. Experiments in the presence of scavengers for $^1O_2$, $^{\bullet}OH$ would add useful information. These offered scope for future research and were not included herewith, since the specific investigation of the photodegradation mechanism was beyond the scope of the present work.

3.3. Analyses of irradiated solutions

In addition to the analysis of residual EO to determine the % dye abatement reported above, other analyses for TOC, color

Table 3
Products from EO photodegradation identified in cHALi (*i* = 3 or 6)/EO 7.5 (w/w) ratio solutions after 1–2 h irradiation in Solarbox.

EA	
m/z	t_R (min)[a]
304.0747  R= -NHEt or -NMe_2	17.5
320.0694  R= -NHEt or -NMe_2	16.5
320.0945  I  II	12.0[b] 12.9[c]
348.1006 	13.3 16.0 17.9 20.3

[a] Multiple retention time values for the same *m/z* ratio assigned to the presence of isomers differing for the position of the OH functional group in the aromatic ring.
[b] Assigned to compound I.
[c] Assigned to compound II.

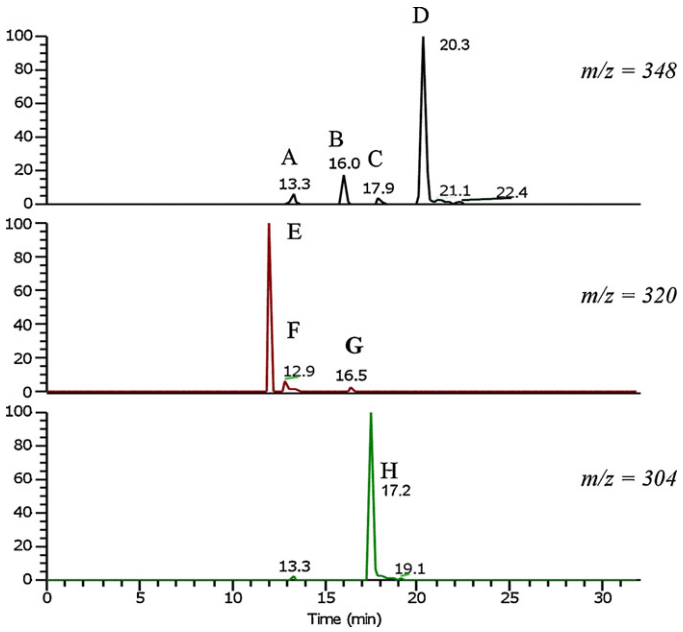


Fig. 5. Products relative abundance versus retention time (min) and associated *m/z* values for HPLC-ESI–HRMS analysis of EO solution irradiated for 1 h in the presence of cHAL3 under the experimental conditions reported in Table 3.

abatement and EO intermediates identification were performed in the attempt to trace the fate of the photodegraded dye. The TOC measurements were designed in order to distinguish organic C contributed by EO and its degradation products from the cHALi contribution. Thus, parallel irradiation experiments were performed for the EO–cHALi solutions and also for solutions containing cHALi and no EO. The results showed no significant TOC depletion in the solutions containing cHALi only. On the contrary, in the EO–cHALi solutions, a progressive TOC depletion versus irradiation time was observed, which was therefore assigned to the dye disappearance. The TOC analyses in the EO–cHALi solutions where no dye was detected after irradiation were consistent with 60% dye mineralization.

Fig. 4 reports the results of the analyses for color bleaching evaluated by monitoring the solution absorbance at the wavelength corresponding to the maximum of EO absorbance in the visible region (λ = 467 nm), next to the data for % dye abatement as a function of time for the solutions containing 5 mg L^{-1} starting EO at 75 (w/w) cHAL3/EO or cHAL6/EO irradiated in closed cells. It may be observed that the color abatement increases parallel to the dye abatement, but it is always less than expected on basis of the dye abatement. Consistently with the TOC analyses, at nearly 100% dye abatement residual color is still observed, suggesting the formation of dye degradation products retaining chromophore groups. These products were therefore the likely source of the organic C left over from the dye photodegradation. On the basis of these results we further investigated the composition of the irradiated solutions searching for possible dye degradation intermediates. Our primary attention was devoted to sulfonated degradation products. These compounds, being highly soluble and mobile in the aqueous environmental compartments, could extend the potential pollution risk to larger areas.

Due to the hydrophilic nature of the above sulfonated compounds the HPLC–MS^n technique was chosen as a suitable analytical approach. Liquid chromatography appears the best technique for direct analysis of polar compounds, requiring neither derivatization nor complex extraction procedures. This separation technique, coupled with the LTQ Orbitrap [22] high resolution mass spectrometry (HRMS), affords powerful diagnostic identification

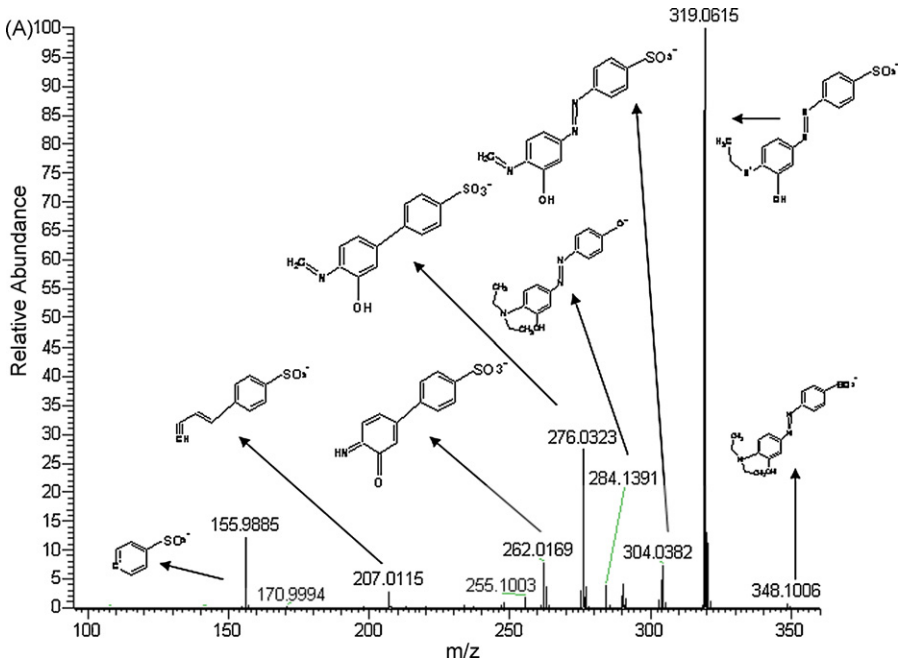


Fig. 6. ESI–HRMS spectra for product A in Fig. 5.

and characterization of degradation products as already proven in metabolomic approach for the identification of transformation products of small molecules [23].

In the present work several products were identified in the cHALi (i = 3 or 6)/EO 7.5 (w/w) ratio solutions after 1–2 h irradiation in Solarbox, as listed in Table 3 reporting HPLC retention times (t_R), mass to charge (m/z) ratios and chemical structures. Fig. 5 reports the digital reconstruction of a typical HPLC profile obtained after EO irradiation in the presence of cHAL3 by extracting from the total ionic current the m/z 348, 320 and 304 signals. It may be observed that several peaks corresponding to several chemically different products are found having the same 348 (peaks A–D) or 320 (peaks E–G) m/z, whereas only one product (peak H) having 304 m/z is obtained. Analogous results were collected for EO photodegradation in the presence of cHAL6. The electrospray ion source (ESI) and the high resolution (HRMS) allowed by the LTQ Orbitrap mass spectrometer used in this work (see Section 2) allow to distinguish well between isomers having exactly the same m/z value, i.e., products A–D with 348.1006 m/z, and products differing for rather small mass values, i.e., compound G with exactly 320.0694 m/z value and compounds E and F with exactly 320.0945 m/z values. Further structural assignments for products having exactly the same m/z value may be obtained from the analysis of the fragmentation pattern of the isolated neat compounds. Figs. 6–9 report the MS^2 spectra and the corresponding fragmentation pattern of the single A–D products isolated by HPLC. The structures, reported in each figure next to the parent peak with 348.1006 m/z, were assigned on the following basis. For compounds A–C the presence of the ion at

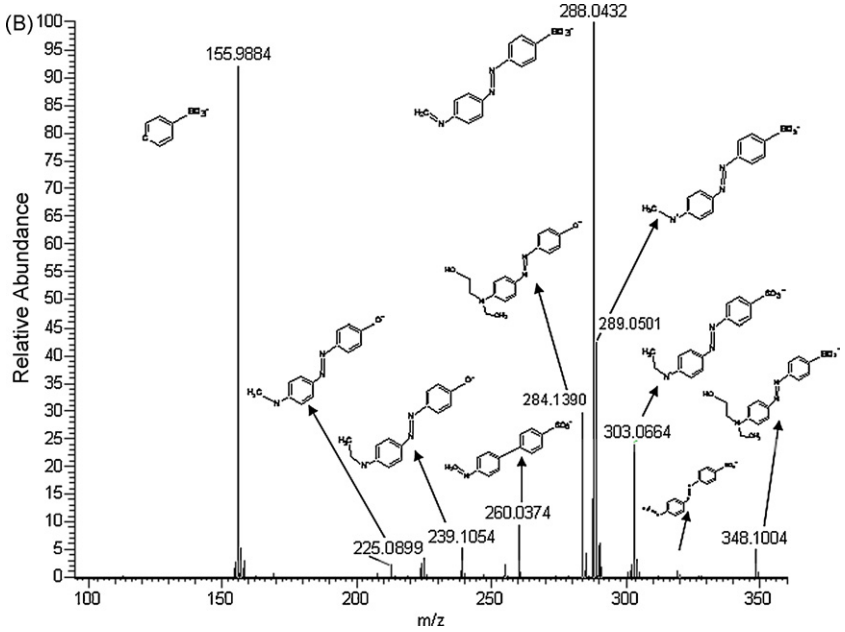


Fig. 7. ESI–HRMS spectra for product B in Fig. 5.

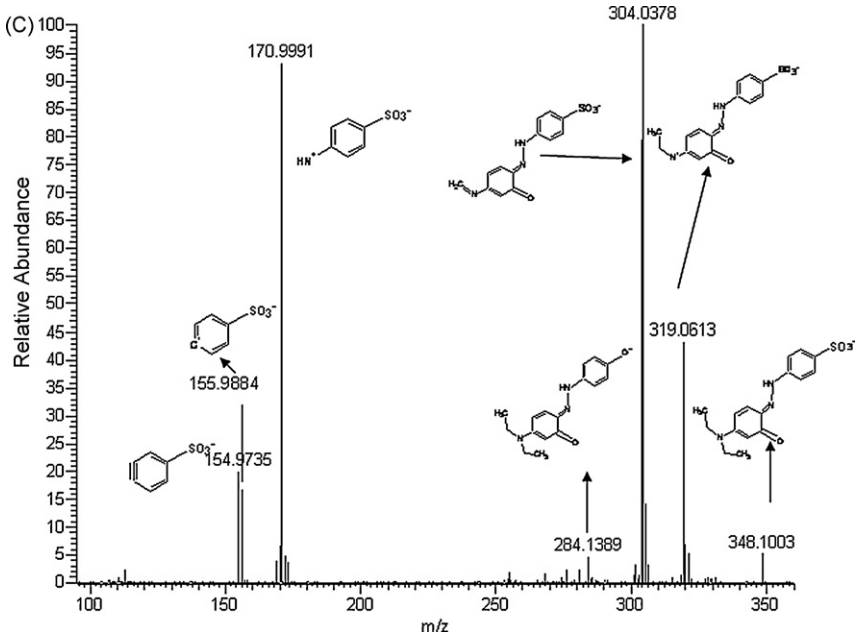


Fig. 8. ESI–HRMS spectra for product C in Fig. 5.

m/z = 156 (Figs. 6–8) is compatible with the OH attack on the ring not bearing the SO_3^- group. For compound A (Fig. 6), the structure attributed to the fragment at m/z = 262 is possible only if the ring hydroxylation took place in meta position with respect to the azo group. For compound B (Fig. 7) the species having m/z = 239, 260, 288 and 303 can arise only from the isomer bearing the OH group in the ethyl chain. The structure of compound C with the OH in ortho to the azo group is suggested by the presence of the ion at m/z = 171 (Fig. 8), presumably formed from the hydrazo form present in an azo-hydrazo tautomery. For compound D (Fig. 8) the absence of the phenylsulfonic radical (m/z 156) and the presence of the fragment at m/z 172, corresponding to the hydroxyphenylsulfonic radical, allow one to suppose the introduction of the OH group in the sulfonated ring.

The formation of different isomers differing for the position of the OH groups can be easily explained taking into account that radical reactions are usually not selective.

The key role of HRMS appeared for the structure assessment in the case of intermediates having m/z = 320 (Fig. 5). For the compound with 16.5 min t_R, an exact m/z value of 320.0694 was found, whereas for the compounds with 12.0 and 12.9 min t_R the exact m/z value was 320.0945. Based on these data two degradation paths could be hypothesized: the attack on the alkyl chain and the contemporary ring hydroxylation or the cleavage of the azo group. In the latter case no further data are available in order to propose formula I rather than II (Table 3). The presence of intermediates containing not N, such as I and/or II, indirectly confirms the formation of molecular nitrogen proposed in the literature as a possible expla-

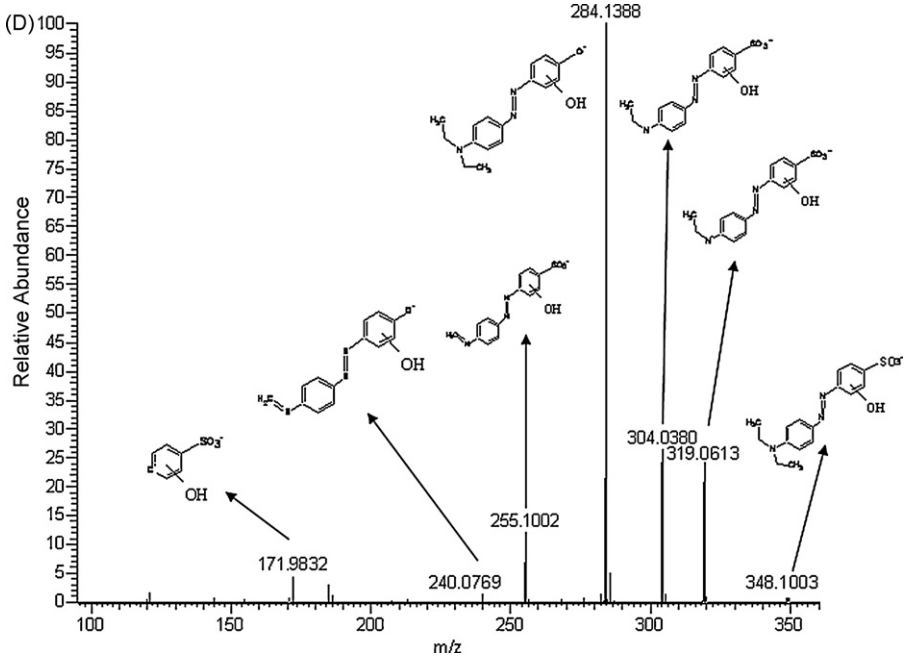


Fig. 9. ESI–HRMS spectra for product D in Fig. 5.

nation for the lack in the nitrogen mass balance, often evidenced in oxidative processes [24].

The chemical structures in Table 3 may suggest that the main reactions taking place at the photolysis onset were the hydroxylation of both aliphatic and aromatic C combined with cleavage of alkyl chains and azo groups, followed by some fragments rearrangement. Similar findings are reported [25] for the photodegradation of EO in the presence of TiO_2 where the $^{\bullet}OH$ radical attack is considered the main process step.

4. Conclusions

The results of this work evidence the good performance of bio-organic substances (cHALi) isolated from green and food urban residues aged under aerobic digestion for 0–60 days as sensitizers for ethylorange photodegradation. The chemical composition and photosensitizing effect of these substances have been shown to depend on the sourcing bio-waste material and its aging conditions. Although a statistically significant correlation has been found for the PhOH relative content of the cHALi substances and % dye abatement, the available data do not allow to assess a definite structure–properties relationship for the investigated substances.

For applied chemistry purposes, the 60% dye mineralization observed in relatively short irradiation time augurs rather well for the full potential of cHALi as photosensitizers to meet the requirements of reducing the environmental impact of dye effluents by the textile industry. The result encourage further work to investigate the photolysis of other dyes in the presence of cHALi, to optimize the conditions for achieving complete dye mineralization, to assess cHALi performance reproducibility as a function of the source nature and to demonstrate the development of both efficient and environmentally friendly textile dyeing processes by the use of cHALi either in the fibers dyeing and in the exhaust dyeing bath treatment stages.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2009.11.020.

References

[1] E. Montoneri, V. Boffa, S. Savarino, D.G. Perrone, G. Musso, R. Mendichi, M.R. Chierotti, R. Gobetto, ChemSusChem 2 (2009) 239.
[2] P. Quagliotto, E. Montoneri, F. Tambone, F. Adani, R. Gobetto, G. Viscardi, Environ. Sci. Technol. 40 (2006) 1686.
[3] E. Montoneri, P. Savarino, S. Bottigliengo, G. Musso, V. Boffa, A. Bianco Prevot, D. Fabbri, E. Pramauro, Bioresources 3 (2008) 217.
[4] P. Savarino, E. Montoneri, S. Bottigliengo, V. Boffa, T. Guizzetti, D.G. Perrone, R. Mendichi, Ind. Eng. Chem. Res. 48 (2009) 3738.
[5] H. Zollinger, Color Chemistry: Synthesis, Properties and Applications of Organic Dyes and Pigments, VHS Publishers, New York, 1991.
[6] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Bioresour. Technol. 77 (2001) 247.
[7] A. Gottlieb, C. Shaw, A. Smith, A. Wheatley, S. Forsythe, J. Biotechnol. 101 (2003) 49.
[8] S. Canonica, U. Jans, K. Stemmler, J. Hoigné, Environ. Sci. Technol. 29 (1995) 1822.
[9] V.A. Sakkas, D.A. Lambropoulou, T.A. Albanis, J. Photochem. Photobiol. A 147 (2002) 135.
[10] S. Halladja, A. Amine-Khodja, A. Ter Halle, A. Boulkamh, C. Richard, Chemosphere 69 (2007) 1647.
[11] J.R. Garbin, D.M.B.P. Milori, M. Simões, W.T.L. da Silva, L.M. Neto, Chemosphere 66 (2007) 1692.
[12] X. Ou, X. Quan, S. Chen, H. Zhao, Y. Zhang, J. Agric. Food Chem. 55 (2007) 8650.
[13] M. Zhan, X. Yang, Q. Xian, L. Kong, Chemosphere 63 (2006) 378.
[14] C. Richard, O.E. Trubetskaya, O.A. Trubetskoj, O.I. Reznikova, G.V. Afanas'eva, J.P. Aguer, G. Guyot, Environ. Sci. Technol. 38 (2004) 2052.
[15] A.A. Khodja, O. Trubetskaya, O. Trubetskoj, L. Cavani, C. Ciavatta, G. Guyot, C. Richard, Chemosphere 62 (2006) 1021.
[16] O. Trubetskoj, C. Richard, M. Grigatti, C. Ciavatta, O. Trubetskaya, Bioresour. Technol. 99 (2008) 5090.
[17] D. Fabbri, A. Bianco Prevot, E. Pramauro, Appl. Catal. B 62 (2006) 21.
[18] E. Montoneri, V. Boffa, P. Quagliotto, R. Mendichi, M.R. Chierotti, R. Gobetto, C. Medana, Bioresources 3 (2008) 123.
[19] P.L. Genevini, F. Tambone, F. Adani, H.M. Veeken, K.G.J. Nierop, E. Montoneri, Soil Sci. Plant Nutr. 49 (2003) 785.
[20] A. Amine-Khodja, C. Richard, B. Lavédrine, G. Guyot, O. Trubetskaya, O. Trubetskoj, Environ. Chem. Lett. 3 (2006) 173.
[21] C. Richard, D. Vialaton, J.P. Aguer, F. Andreux, J. Photochem. Photobiol. A 111 (1997) 265.
[22] Q.Z. Hu, R.J. Noll, H.Y. Li, A. Makarov, M. Hardman, R.G. Cooks, J. Mass Spectrom. 40 (2005) 430.
[23] W. Lu, B.D. Bennett, J.D. Rabinowitz, J. Chromatogr. B 871 (2008) 236.
[24] Puzenat, H. Lachheb, M. Karkmaz, A. Houas, C. Guillard, J.M. Herrmann, Int. J. Photoenergy 5 (2003) 51.
[25] A. Bianco Prevot, D. Fabbri, E. Pramauro, C. Baiocchi, C. Medana, J. Chromatogr. A 1202 (2008) 145.