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

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1 ABSTRACT

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

17

18

19 **KEYWORDS** azo-dye, photodegradation, sensitizers, urban refuses, dyeing baths, effluents
20 remediation,

21

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 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 take up by the fiber and the excess dye removal from the exhaust dyeing bath, thus improving both the production and wastes 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 phenols molecules or pesticides substances as probe substrates.

1 The present work concerns the EO photosensitized degradation in the presence of six BOS isolated
2 from urban refuses which hereinafter will be referred to by the abbreviation cHAL_i, $i = 2-7$: cHAL₂,
3 cHAL₃ and cHAL₄ isolated from urban yard trimmings (green wastes) and cHAL₅, cHAL₆ and
4 cHAL₇ isolated from a 1:1 w/w mix of food (humid) and green residues at the start of the aerobic
5 digestion process (cHAL₂ and cHAL₅), and after 7 days (cHAL₃ and cHAL₆) and 60 days (cHAL₄ and
6 cHAL₇) aging. Relatively to previous work performed with cHAL₂ only [3], the investigation of the
7 above six BOS addresses several issues: i.e., assessing chemical structure and photosensitizing
8 properties as a function of the nature and treatment type of the product source, and the fate of
9 photodegraded EO. These issues were rather challenging for several reasons. First, it should be
10 considered that the investigated cHAL_i substances are new materials of biological origin with quite
11 complex chemical composition for which several molecular models have been reported [1,23].
12 Secondly, the chemical variability of the urban refuses may prospect a desirable availability of multiple
13 bioproducts, but also poses a major concern, regarding the capacity to yield bio-based products with
14 constant performance specifications. Thirdly, it should be considered that the real cHAL_i performance
15 to assist EO photodegradation should be rated on basis of the fate of both the dye and the
16 photosensitizer. This requirement, considering the chemical structure complexity of the latter and the
17 multiplicity of degradation products which might be expected to arise from both the dye and the
18 photosensitizer, poses rather demanding analytical problems to face. In particular we focused our
19 attention on the kinetics of EO degradation and on the identification of the intermediates formed in the
20 initial degradation steps. High performance liquid chromatography coupled to high resolution mass
21 spectrometry (HPLC-HRMS) was applied as a powerful tool.

22 Finally, the capacity of the cHAL_i to yield micellar aggregates [1] in water was also a matter of
23 concern in this work. Indeed, the presence of aggregates could give rise to EO partitioning between the
24 bulk water and the more hydrophobic micellar region, and this could influence the EO

1 photodegradation kinetics and yield [17]. Thus, a study of the solution behavior of the molecular
2 aggregation behavior of the cHALi was necessary to define the most suitable experimental
3 concentration range to be investigated for preliminary evaluation of their photosensitizing properties.

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

8

9

10 **2. Materials and methods**

11

12 **2.1 Bioproducts and reagents.**

13

14 Ethylorange, i.e., 4-(4-diethylaminophenylazo)benzene sodium sulfonate, 69 % HNO₃ and 98 %
15 CH₃COONH₄ by Fluka, 99 % NaOH and 99 % KNO₃ by Merck, 99 % Na₂SO₄ and 99.7 % NaHCO₃ by
16 Aldrich), analytical grade CH₃CN by Scharlau and MilliQ[®] reagent grade ultra pure water were used
17 throughout this work as received, unless otherwise indicated. The cHALi (i = 2-7) substances
18 investigated in this work were obtained from ground green wastes or from 1:1 w/w food and green
19 residues mix collected in the province of Torino, Italy. Once collected and transported in a municipal
20 waste treatment plant, the chopped green residues, eventually mixed with the mechanically selected (Ø
21 < 12 mm) humid wastes, were aged under aerobic conditions for 0-60 days, sieved through a mechanic
22 grid (Ø < 10 mm) and used for cHALi extraction. The cHALi isolation was performed as previously
23 reported [2].

24

1
2 **2.2 Chemical and Physical Characterization of cHALi substances.**

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

15
16 **2.3 Ethylorange irradiation experiments.**

17
18 A stock $1 \text{ g}\cdot\text{L}^{-1}$ cHALi aqueous solutions was prepared by taking up solid cHALi with MilliQ[®] water
19 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
20 the complete solid dissolution occurred. The solution was finally filtered through a 0.45 μm Millex-HA
21 membrane (Millipore) and brought to the required volume with MilliQ[®] water. The stock solution was
22 kept frozen before use. Aliquots of the stock solution were used to obtain $5 \text{ g}\cdot\text{L}^{-1}$ EO solutions
23 containing variable amounts of cHALi. The degradation trials were performed by irradiating 5 mL
24 cHALi-EO aqueous solution in a closed Pyrex[®] cell with a Xenon (1500W) lamp (Solarbox) and a cut-

1 off filter for wavelengths below 340 nm. Experiments were also performed on 500 mL cHALi-EO
2 aqueous solutions in a cylindrical photochemical reactor (Helios-Italquartz, Milan), equipped with a
3 125 W medium pressure Hg lamp. The system was kept under continuous stirring in order to avoid the
4 formation of concentration gradient and air or nitrogen was bubbled to saturate the solutions with the
5 gases. Cold water circulating in the jacket surrounding the lamp kept the temperature within the reactor
6 at 20°C; a Pyrex[®] glass jacket acting as a cut-off filter for wavelengths below 300 nm was employed, in
7 order to avoid any possible contribution coming from direct dye photolysis.

8

9

10 **2.4 Analyses of the irradiated solutions.**

11

12 The dye abatement was calculated from the starting EO concentration (C_0) and the found EO
13 concentration (C_{ir}) after irradiation. The C_{ir} value was determined by HPLC-DAD-UV-VIS (Surveyor,
14 Thermo Scientific) analysis under the experimental conditions reported in the Appendix A. The
15 analysis of the EO photodegradation products was performed by HPLC-MS. A Dionex Ultimate 3000
16 HPLC coupled with a Surveyor PDA UV detector and a LTQ Orbitrap mass spectrometer (Thermo
17 Scientific) equipped with an atmospheric pressure interface and an ESI ion source was used;. N_2 was
18 used as sheath and auxiliary gas. The source voltage was set to 3.1 kV. The heated capillary
19 temperature was maintained at 275 °C. The main tuning parameters adopted for ESI source were:
20 capillary voltage -34.00 V, tube lens offset -68.57 V. Mass accuracy of recorded ions (vs calculated)
21 was ± 15 ppm (without internal calibration). The chromatographic separations were performed on a
22 Phenomenex Synergi C18 column, 150 \times 2.0 mm, 3 μ m particle size. Injection volume was 20 μ L and
23 flow rate 200 μ L/min. Gradient mobile phase composition was adopted: acetonitrile/ammonium acetate
24 0.1 mM 5/95 to 100/0 in 30 min. Total organic carbon (TOC) in the irradiated solutions was also

1 measured, by means of Shimadzu TOC-5000 analyzer (catalytic oxidation on Pt at 680 °C), which was
2 previously calibrated using potassium phthalate standards solutions. Color bleaching in the irradiated
3 solutions was quantified by means of a double beam CARY 100 SCAN-VARIAN, UV-VIS
4 spectrophotometer by measuring the absorbance at 467 nm where the EO irradiated solution exhibits
5 the maximum absorptivity. The absorbance was then corrected for the cHALi contribution.

6

7

8 **3. Results and Discussion**

9

10 **3.1 Chemical Nature of cHALi and Molecular Association in Solution**

11

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

1 The apparent critical micellar concentration (cmc) values for the investigated substances (see
2 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
3 therefore relatively constant within each group of substances obtained from the same source material,
4 but changing significantly from one group to the other (i.e. from cHAL2-4 to cHAL5-7).

5
6

7 **3.2 Irradiation experiments and % dye abatement.**

8

9 Based on the cmc data, the upper limit of 1 g·L⁻¹ cHALi concentration was established in order to
10 avoid or limit the presence of cHALi aggregates and their potential effect on EO photodegradation
11 kinetics and yield [17]. A preliminary ranking of the isolated cHALi substances has been considered on
12 basis of their sensitizing effect on the photodegradation of EO. The experiments were performed
13 irradiating the samples in closed cells for 5 hours. Sample solutions were prepared by dissolving EO at
14 5 mg·L⁻¹, either alone or in the presence of 100 mg·L⁻¹ cHALi (i = 2-7). Under these conditions, the
15 neat EO solution exhibited a negligible 1.8 % dye abatement, whereas rather high dye abatement rates
16 were observed in the presence of cHALi (Fig. 1), with the cHAL5-7 substances isolated from the mix
17 of green and food residues performing better than the cHAL2-4 substances isolated from sole green
18 residues. This fact seems to point out a significant material source effect on the catalytic performance
19 of the above cHALi substances for EO photodegradation. Moreover for each group of substances
20 isolated from the same type of source waste a peak effect seems to be reached with the substances
21 isolated from 7 days aged source materials, i.e., cHAL3 and cHAL6. The effect of the source material
22 ageing is not as straightforward. Analogously to our findings, two recent papers have reported on the
23 photosensitizing properties of BOS isolated from mixtures of yard trimmings, sewage sludge, and/or
24 animal manure and grapes residues, which were collected after composting for 0-130 days [15, 20]. The

1 photo-degrading activity of such substances appeared to increase between 0 and 70 days composting
2 and to remain quite constant for the next further 60 days. Searching for possible structure-property
3 relationships, our data show a trend for % dye abatement to increase with the relative phenol content in
4 Table 1. The linear regression analysis performed over all data points, excluding the one for cHAL7
5 that was clearly deviating from the general trend, yields a regression coefficient of 0.95 and the
6 empirical equation $DA = 23.2 + 106 \text{ PhOH/Ct}$, with $DA = \% \text{ dye abatement}$. Consistently with
7 previous work [20] phenol functional groups are likely to have an active role in the photosensitizing
8 process, although other chemical structural factors may also contribute to the cHALi performance.
9 Regardless of this empirical relationship, to verify the effect of the source composition on the
10 photosensitizing power of BOS, successive experiments were performed with two cHALi selected
11 from each group based on their % dye abatement rather than on the phenol content: i.e., cHAL3 and
12 cHAL6, which showed the highest % dye abatement within the products isolated from sole green
13 wastes and from the mix of green and humid refuses respectively.

14 Fig. 2 reports the results of experiments performed by irradiating for 3 h solutions containing 5 gL^{-1}
15 EO in the presence of $125\text{-}1000 \text{ mgL}^{-1}$ cHAL3 or cHAL6. The results indicate that cHAL6 performs
16 significantly better than cHAL3 and that, for both substances, the measured degradation yield increases
17 with the cHALi/EO w/w ratio, reaching nearly 100 % at about 130 cHAL6/EO w/w ratio.

18 Fig. 3 reports the results of EO photodegradation experiments at 75 w/w cHALi (i = 3 or 6)/EO ratio
19 as a function of irradiation time. It may be observed that even at this low cHALi /EO ratio, nearly total
20 dye abatement is still reached within reasonably short 4 h time. The data well fit in a first-order kinetic
21 law as clearly shown by the $\ln(C_{ir}/C_0)$ -time plot. The higher performance of cHAL6 relatively to
22 cHAL3 is confirmed throughout the investigated time range. Analogous kinetics profiles were obtained
23 using the photochemical reactor; in comparison with the results obtained in Solarbox, a slower

1 abatement rate was observed. This difference is most likely due to the different geometries and light
2 source intensities present in the two systems.

3 Other experiments were performed with solutions containing $5 \text{ mg}\cdot\text{L}^{-1}$ EO and 75 w/w cHALi (i = 3
4 or 6) / EO ratio which were irradiated in the photochemical reactor under continuous air or nitrogen
5 bubbling in order to evaluate the effect of the atmosphere on the degradation process. The results
6 (reported in the Appendix A) show a relevantly lower dye abatement rate in the presence of pure N_2
7 compared to air, as demonstrated by the calculated first order kinetic constants in Table 2. This fact
8 suggests a possible reaction mechanism involving reactive oxygenated species (ROS) as already
9 proposed for BOS present in soil and terrestrial waters [13, 21]. Analogously to the mechanism
10 proposed for humic substances, the light absorption by cHALi may produce excited triplet states that
11 can in turn react with organic substrate by two main mechanism: hydrogen-transfer and energy-transfer.
12 The former one could be proposed in our case; the presence of dissolved oxygen should favor indeed
13 the dye degradation since the generated hydrogen atom can be transferred to the dissolved oxygen with
14 the formation of various ROS such as $\bullet\text{OH}$, $^1\text{O}_2$, $\bullet\text{O}_2^-$ and H_2O_2 which also contribute to the dye
15 degradation. Experiments in the presence of scavengers for $^1\text{O}_2$, $\bullet\text{OH}$ would add useful information.
16 These offered scope for future research and were not included herewith, since the specific investigation
17 of the photodegradation mechanism was beyond the scope of the present work.

18

19 **3.3 Analyses of irradiated solutions.**

20

21 In addition to the analysis of residual EO to determine the % dye abatement reported above, other
22 analyses for TOC, color abatement and EO intermediates identification were performed in the attempt
23 to trace the fate of the photodegraded dye. The TOC measurements were designed in order to
24 distinguish organic C contributed by EO and its degradation products from the cHALi contribution.

1 Thus, parallel irradiation experiments were performed for the EO-cHALi solutions and also for
2 solutions containing cHALi and no EO. The results showed no significant TOC depletion in the
3 solutions containing cHALi only. On the contrary, in the EO-CHALi solutions, a progressive TOC
4 depletion versus irradiation time was observed, which was therefore assigned to the dye disappearance.
5 The TOC analyses in the EO-CHALi solutions where no dye was detected after irradiation were
6 consistent with 60 % dye mineralization.

7 Fig. 4 reports the results of the analyses for color bleaching evaluated by monitoring the solution
8 absorbance at the wavelength corresponding to the maximum of EO absorbance in the visible region
9 ($\lambda = 467$ nm), next to the data for % dye abatement as a function of time for the solutions containing
10 5 mgL^{-1} starting EO at 75 w/w cHAL3/EO or cHAL6/EO irradiated in closed cells. It may be observed
11 that the color abatement increases parallel to the dye abatement, but it is always less than expected on
12 basis of the dye abatement. Consistently with the TOC analyses, at nearly 100 % dye abatement results
13 residual color is still observed, suggesting the formation of dye degradation products retaining
14 chromophore groups. These products were therefore the likely source of the organic C left over from
15 the dye photodegradation. On the basis of these results we further investigated the composition of the
16 irradiated solutions searching for possible dye degradation intermediates. Our primary attention was
17 devoted to sulfonated degradation products. These compounds, being highly soluble and mobile in the
18 aqueous environmental compartments, could extend the potential pollution risk to larger areas.

19 Due to the hydrophilic nature of the above sulfonated compounds the HPLC-MSⁿ technique was
20 chosen as a suitable analytical approach. Liquid chromatography appears the best technique for direct
21 analysis of polar compounds, requiring neither derivatization nor complex extraction procedures. This
22 separation technique, coupled with the LTQ-Orbitrap [22] high resolution mass spectrometry (HRMS),
23 affords powerful diagnostic identification and characterization of degradation products as already

1 proven in metabolomic approach to the identification of transformation products of small molecules
2 [23].

3 In the present work several products were identified in the cHALi ($i = 3$ or 6)/EO 7.5 w/w ratio
4 solutions after 1-2 h irradiation in solar box, as listed in Table 3 reporting HPLC retention times (t_R),
5 mass to charge (m/z) ratios and chemical structures. Figure 5 reports the digital reconstruction of a
6 typical HPLC profile obtained after EO irradiation in the presence of cHAL3 by extracting from the
7 total ionic current the m/z 348, 320 and 304 signals. It may be observed that several peaks
8 corresponding to several chemically different products are found having the same 348 (peaks A-D) or
9 320 (peaks E-G) m/z , whereas only one product (peak H) having 304 m/z is obtained. Analogous
10 results were collected for EO photodegradation in the presence of cHAL6. The electrospray ion source
11 (ESI) and the high resolution (HRMS) allowed by the LTQ Orbitrap mass spectrometer used in this
12 work (see experimental) allows to distinguish well between isomers having exactly the same m/z value,
13 i.e., products A-D with 348.1006 m/z , and products differing for rather small mass values, i.e.,
14 compound G with exactly 320.0694 m/z value and compounds E and F with exactly 320.0945 m/z
15 values. Further structural assignments for products having exactly the same m/z value may be obtained
16 from the analysis of the fragmentation pattern of the isolated neat compounds. Figure 6-9 report the
17 MS^2 spectra and the corresponding fragmentation pattern of the single A-D products isolated by HPLC.
18 The structures, reported in each figure next to the parent peak with 348.1006 m/z , were assigned on the
19 following basis. For compounds A-C the presence of the ion at $m/z = 156$ (Fig. 6-8) is compatible with
20 the OH attack on the ring not bearing the SO_3^- group. For compound A (Fig 6), the structure attributed
21 to the fragment at $m/z = 262$ is possible only if the ring hydroxylation took place in meta position with
22 respect to the azo group. For compound B (Fig. 7 the species having $m/z = 239, 260, 288$ and 303 can
23 arise only from the isomer bearing the OH group in the ethyl chain. The structure of compound C with
24 the OH in ortho to the azo group is suggested by the presence of the ion at $m/z = 171$ (Fig. 8),

1 presumably formed from the hydrazo form present in an azo-hydrazo tautomery. For compound D (Fig.
2 8) the absence of the phenylsulfonic radical (m/z 156) and the presence of the fragment at m/z 172,
3 corresponding to the hydroxyphenylsulfonic radical, allows one to suppose the introduction of the OH
4 group in the sulfonated ring.

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

7 The key role of HRMS appeared for the structure assessment in the case of intermediates having
8 $m/z = 320$ (Fig. 5). For the compound with 16.5 min t_R , an exact m/z value of 320.0694 was found,
9 whereas for the compounds with 12.0 and 12.9 min t_R the exact m/z value was 320.0945. Based on
10 these data two degradation paths could be hypothesized: the attack on the alkyl chain and the
11 contemporary ring hydroxylation or the cleavage of the azo group. In the latter case no further data are
12 available in order to propose formula I rather than II (Table 3). The presence of intermediates
13 containing not N, such as I and/or II, indirectly confirms the formation of molecular nitrogen proposed
14 in the literature as a possible explanation for the lack in the nitrogen mass balance, often evidenced in
15 oxidative processes [24].

16 The chemical structures in Table 3 may suggest that the main reactions taking place at the
17 photolysis onset were the hydroxylation of both aliphatic and aromatic C combined with cleavage of
18 alkyl chains and azo groups, followed by some fragments rearrangement. Similar findings are reported
19 [25] for the photodegradation of EO in the presence of TiO_2 where the $\bullet OH$ radical attack is considered
20 the main process step.

21

22

23 **4. Conclusions**

24

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

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

16

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18

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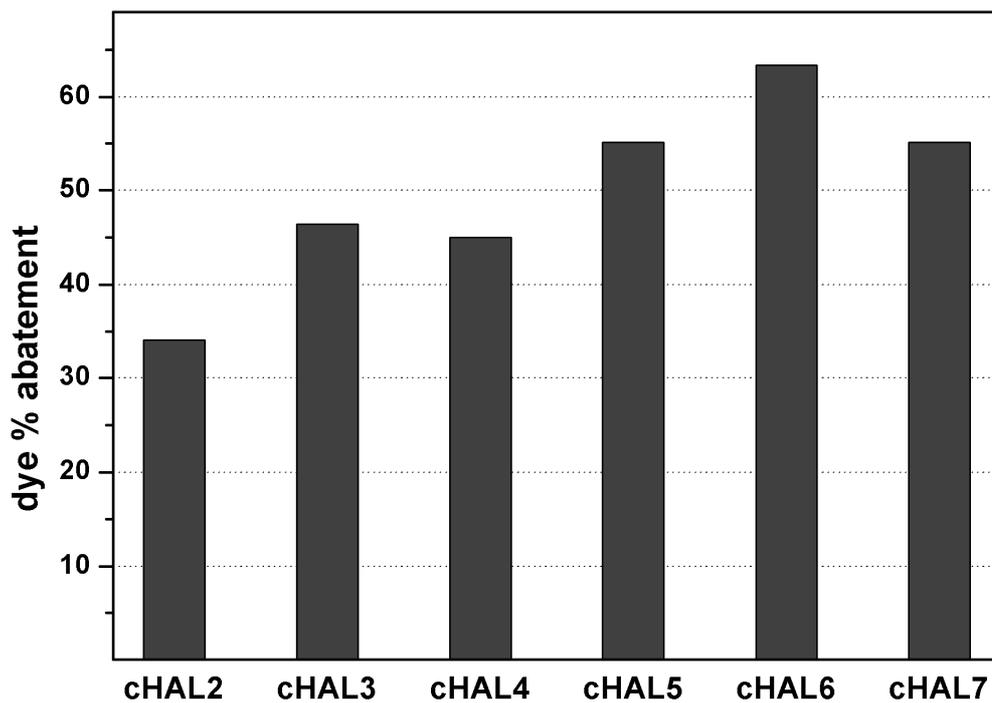
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23 **Appendix A. Supplementary data.**

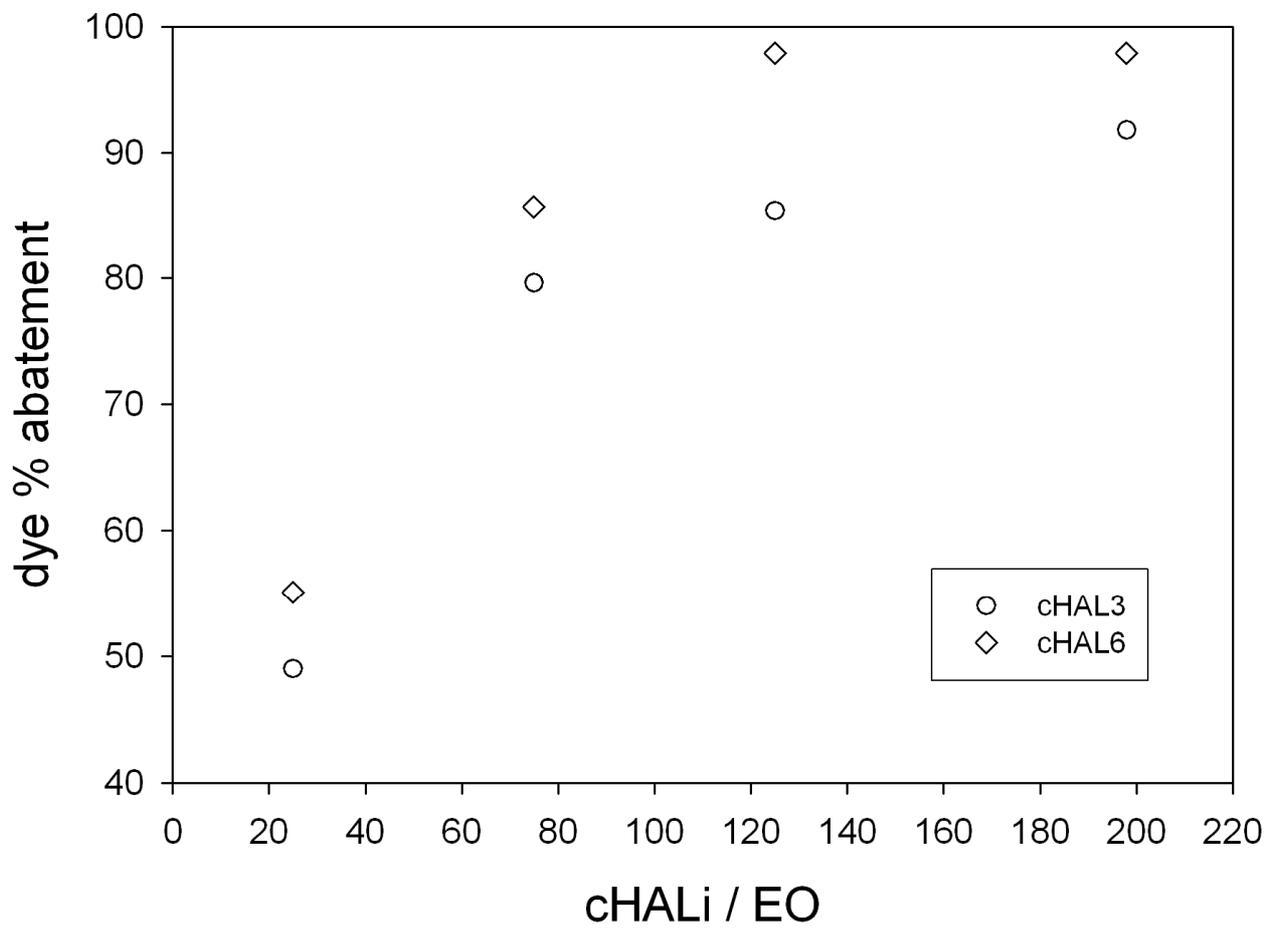
1 Supplementary data associated with this article can be found, in the online version, at
2 <http://www.sciencedirect.com/science/journal/10106030>

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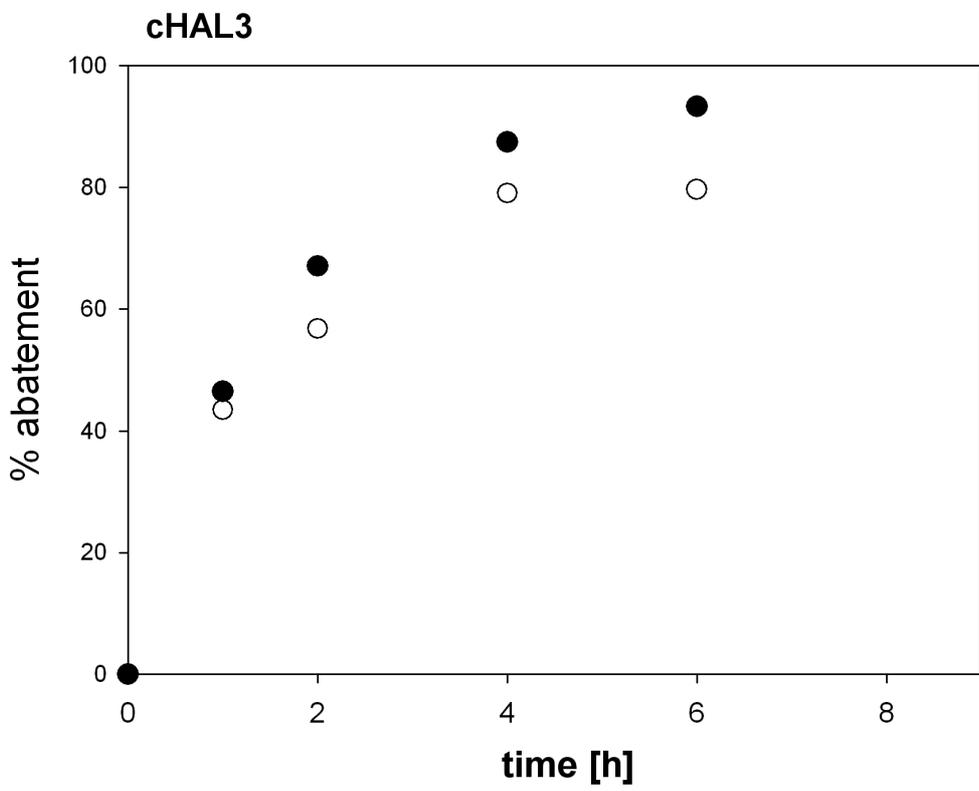
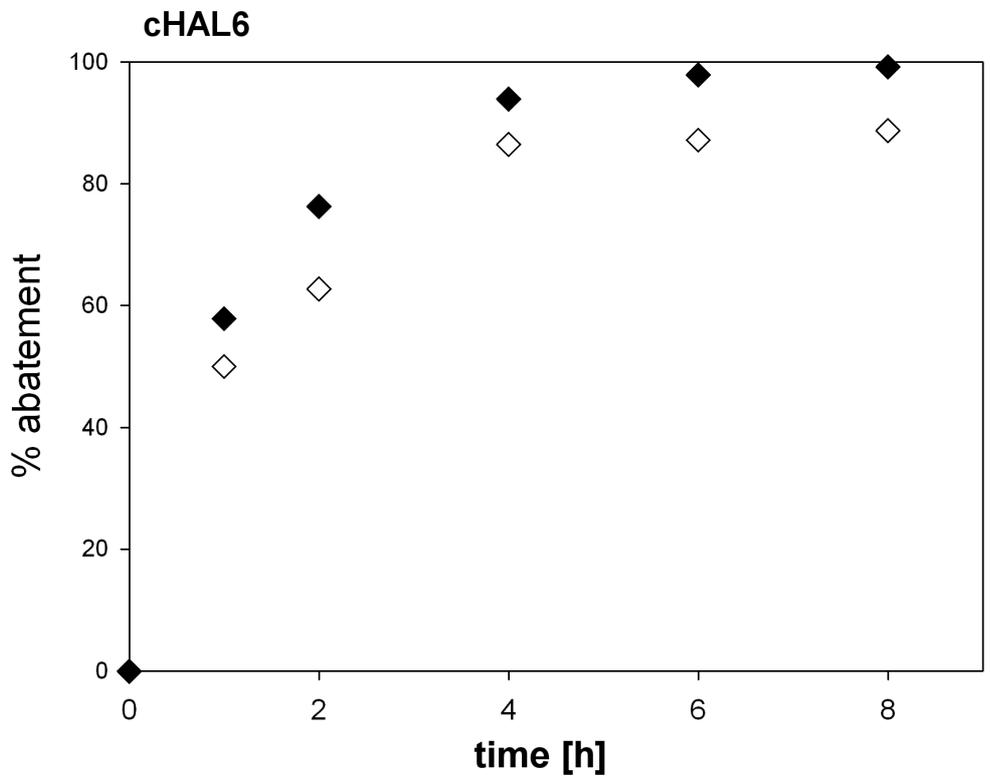
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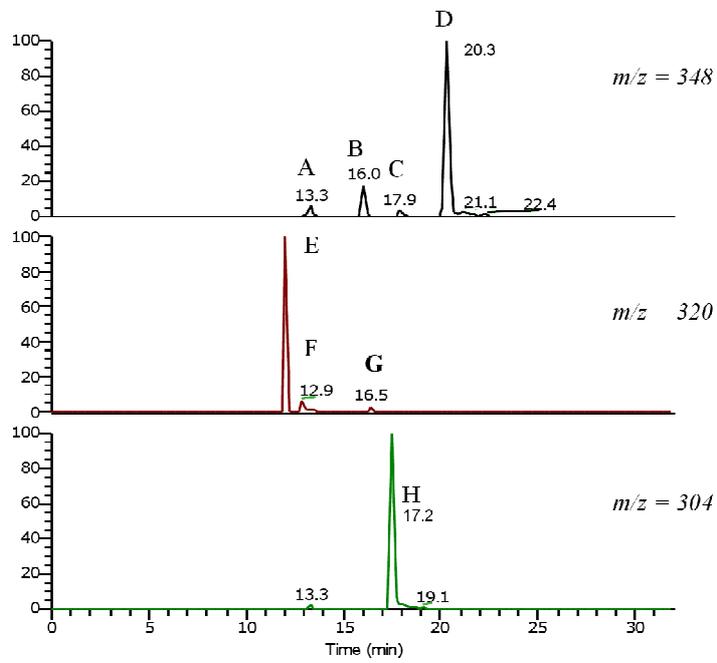


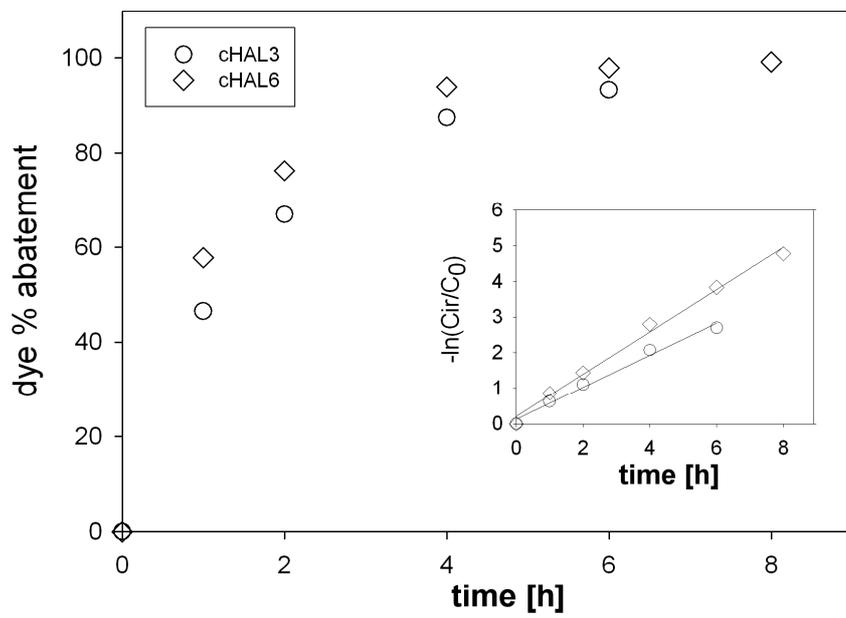
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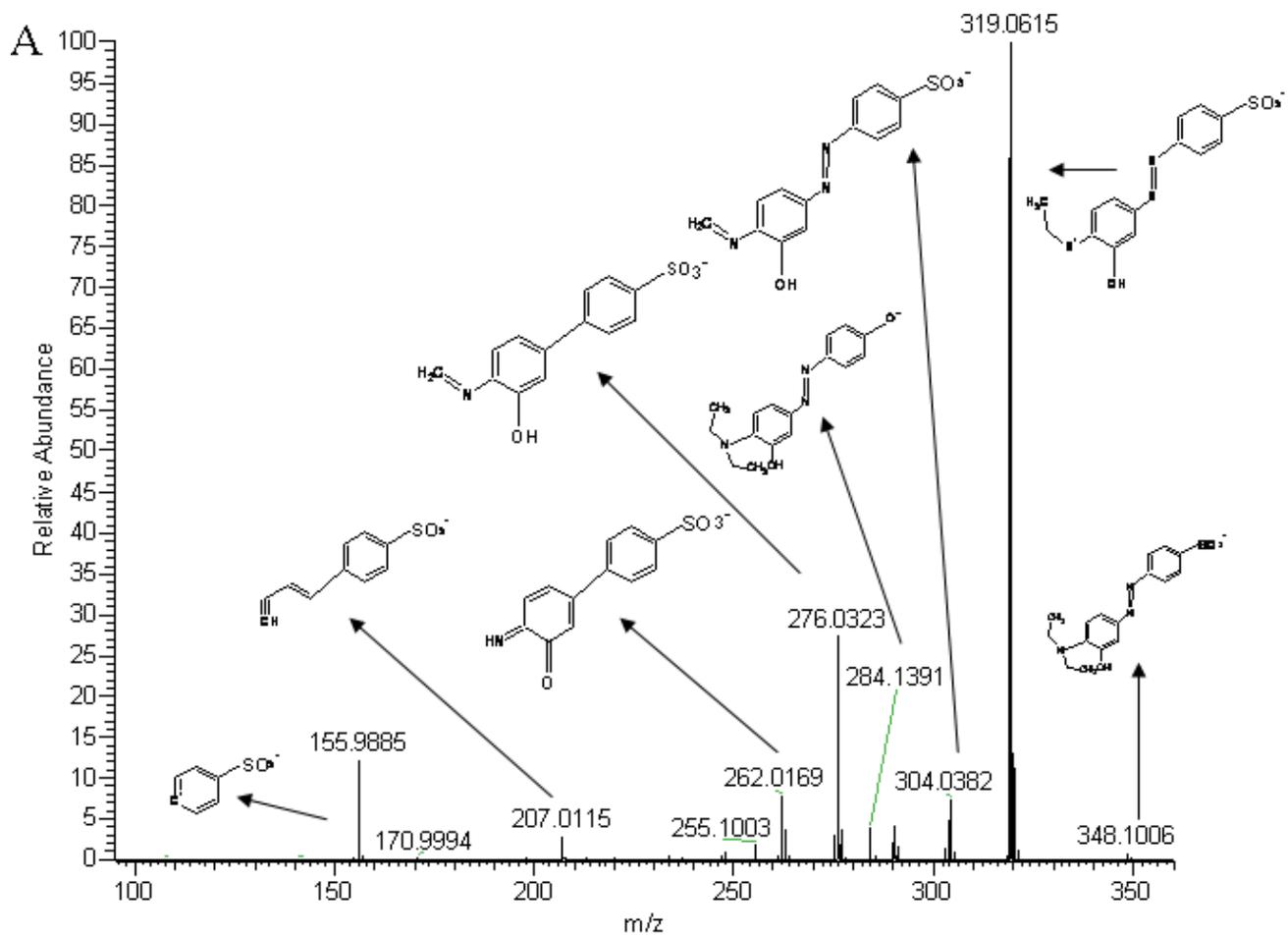
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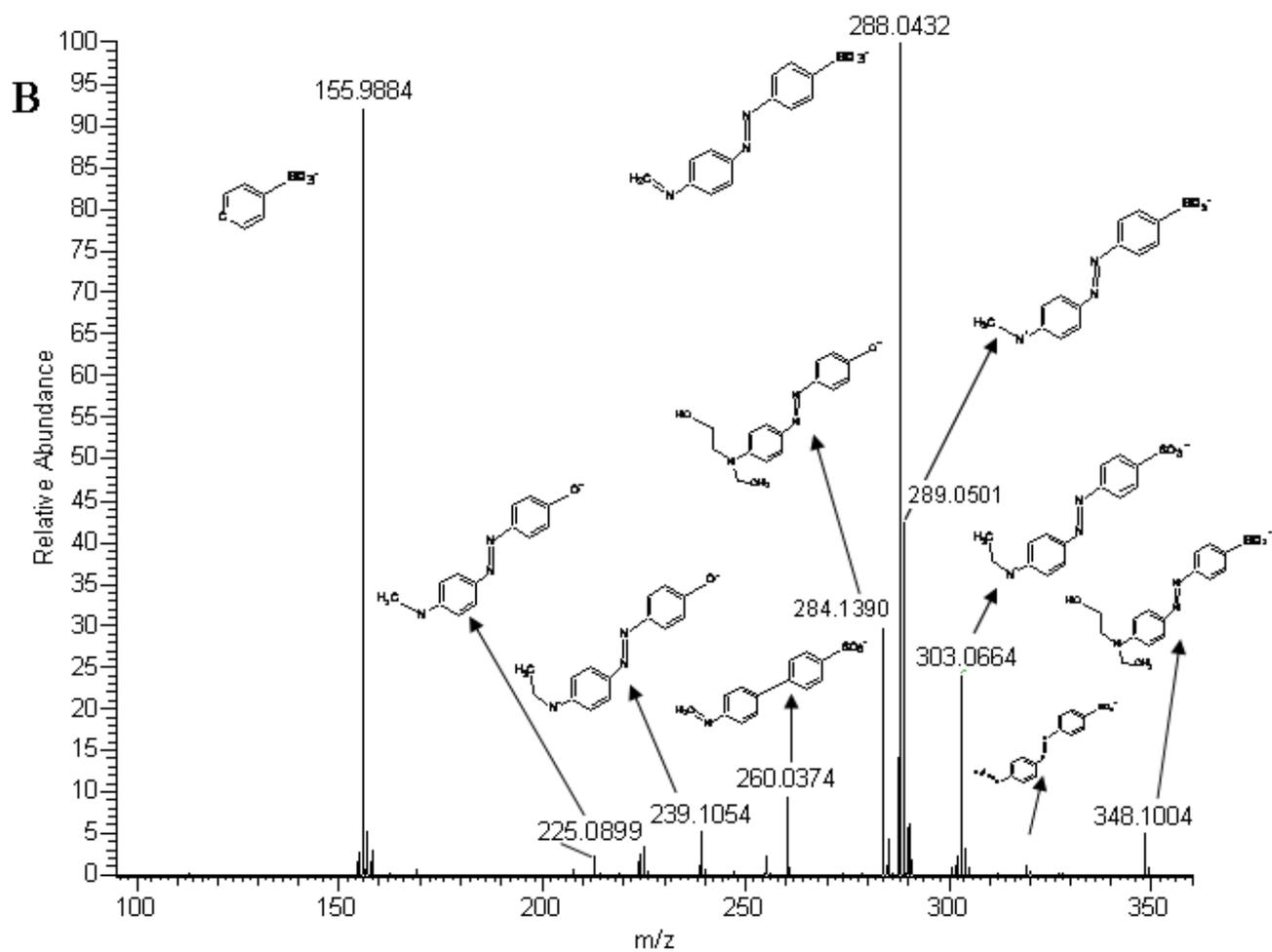






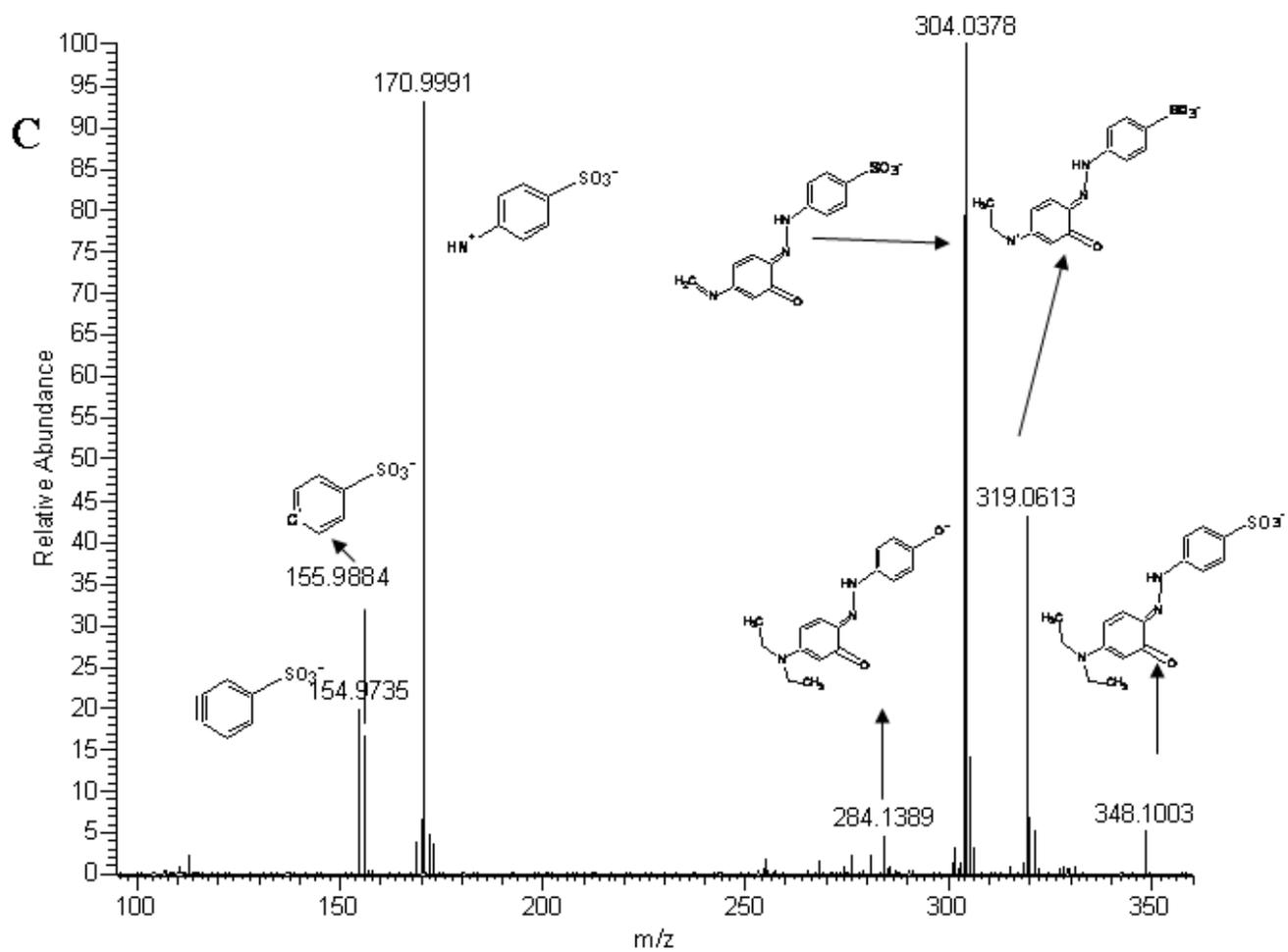
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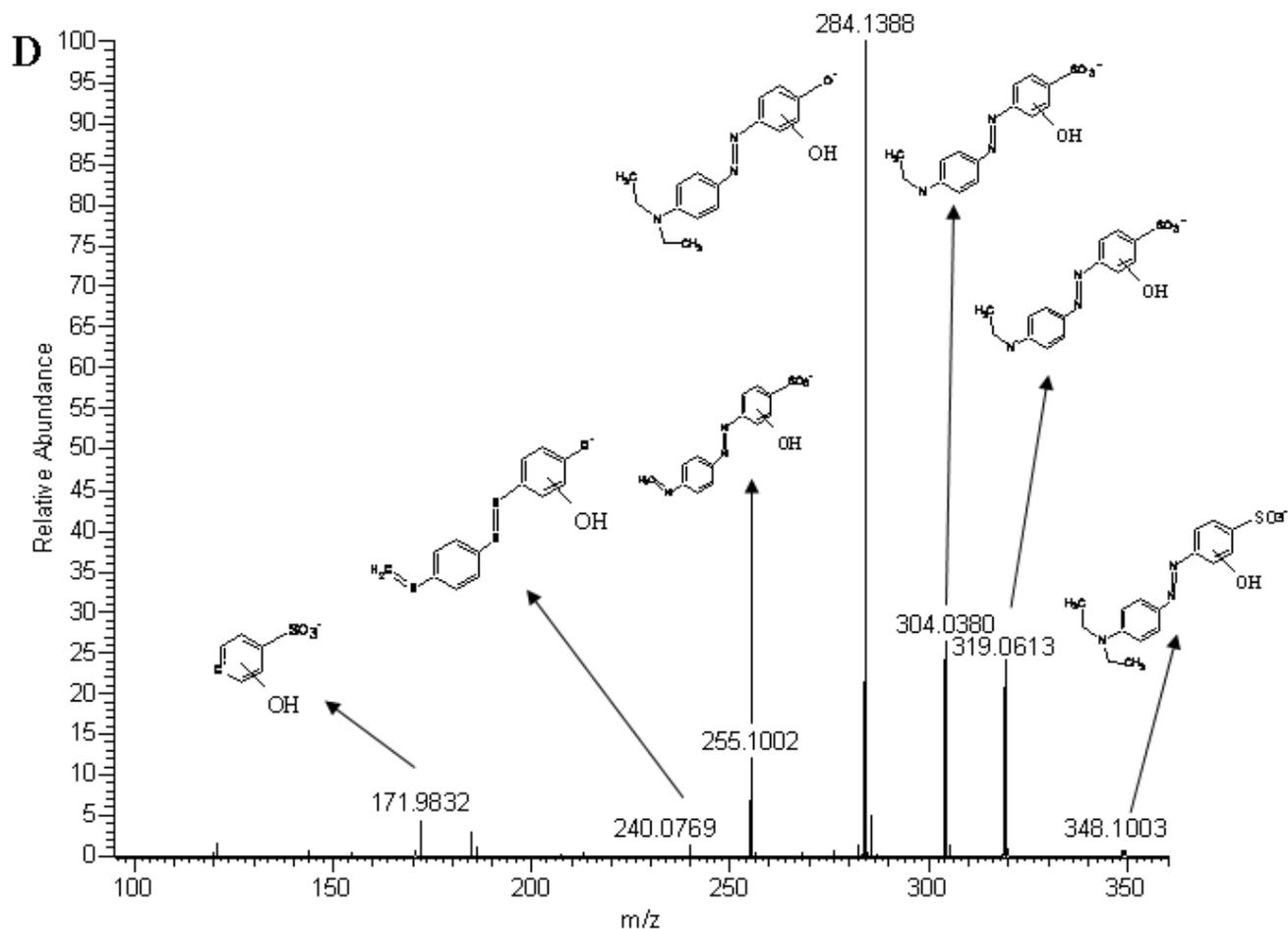
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2 **Table 1.** Ratios for aliphatic C (Cal), O-Me, ammine C (NC), O-alkyl C (OR), di-O-alkyl C (ROCOR),
 3 aromatic and/or olefinic C (C=C) excluding PhO , phenol (PhOH), phenyl ether (PhOX, X = R, Ar),
 4 carboxylic acid C (COOH) amide C (CON) and keto C, relative to the sum (Ct) of C=C, PhOH and
 5 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

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

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Experimental conditions	$k_{\text{obs}}, \text{min}^{-1}$	
	cHAL3	cHAL6
Solar box	0.45	0.59
Photochemical reactor in air	0.09	0.13
Photochemical reactor in N ₂	0.03	0.08

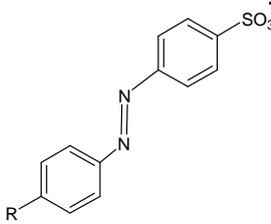
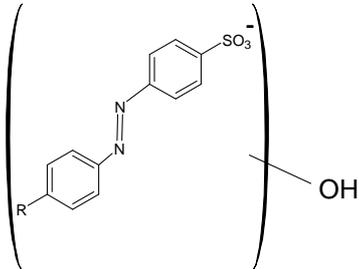
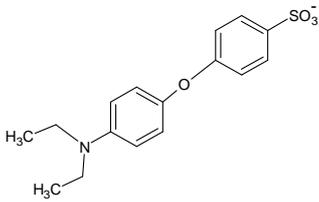
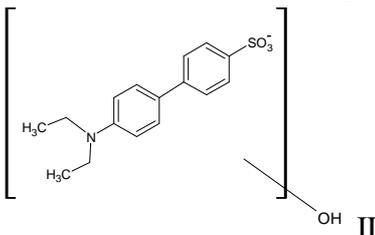
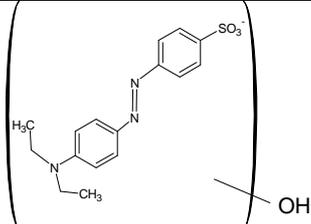
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9 **Table 3.** Products from EO photodegradation identified in cHALi (i = 3 or 6)/EO 7.5 w/w ratio

1 solutions after 1-2 h irradiation in solar box .

EA

m/z		$t_R(\text{min})^a$
304.0747	 $R = -\text{NHEt}$ or $-\text{NMe}_2$	17.5
320.0694	 $R = -\text{NHEt}$ or $-\text{NMe}_2$	16.5
320.0945	 I	12.0 ^b
	 II	12.9 ^c
348.1006	 $R = -\text{N(CH}_3\text{)CH}_2\text{CH}_3$	13.3 16.0 17.9 20.3

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^aMultiple 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. ^bAssigned to compound I. ^cAssigned to compound II.

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- 11

1 **Figure captions**

2

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

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

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9 **Fig. 3.** Dye % abatement and $\ln C_{ir}/C_o$ (C_{ir} and C_o = concentrations at time $t > 0$ and $t = 0$
10 respectively) vs. irradiation time in Solarbox for 5 mgL^{-1} starting EO solutions at 75 w/w cHALi (i = 3
11 or 6)/EO ratio.

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13 **Fig. 4.** Color (o) and dye (●) % abatement vs. irradiation time in closed cells operating with 5 mgL^{-1}
14 starting EO solutions at 75 w/w cHAL3/EO (lower plots) or cHAL6/EO (upper plots).

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

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20 **Fig. 6.** ESI-HRMS spectra for product A in Fig. 5.

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2 **Fig. 7.** ESI-HRMS spectra for product B in Fig. 5.

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4 **Fig. 8.** ESI-HRMS spectra for product C in Fig. 5.

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6 **Fig. 9.** ESI-HRMS spectra for product D in Fig. 5.

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