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This is the author's manuscript

Original Citation:

Availability:

This version is available http://hdl.handle.net/2318/103902 since 2016-10-04T12:19:09Z

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(Article begins on next page)

12 October 2024

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Photodegradation of naphthalene sulfonic compounds in the presence of a bio-waste derived sensitizer

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Abstract

Soluble substances of biological origin (SBO) isolated from urban bio-wastes (UBW) are shown to be efficient photosensitizers for the abatement of naphthalene sulfonates from water solutions. Depletion of 70-80 % of the investigated mono and disulphonated probe substrates was demonstrated to occur after 24 h irradiation of solutions containing 20 mg L^{-1} probe substrates in the presence of 150 mg L^{-1} SBO. Mineralization of the probe substrates' organic C was evaluated at 40-45 % level. The residual organics in solution did not show any potential acute toxicity Photodegradation of SBO occurred together with the photodegradation of the probe substrates. The implications of these results for the development of products obtained by UBW are discussed. It would seem that these bio-wastes have greater potential as a renewable, sustainable source of chemical auxiliaries than studies published up to now have led to believe.

Keywords

bio-organics; bio-wastes; photosensitizers; photodegradation; aromatic sulfonates

1.Introduction

Soluble substances of biological origin (SBO) isolated from urban bio-wastes (UBW) of different composition and ageing conditions have been reported [1] to perform promisingly as chemical auxiliaries for a number of technological applications in the chemical industry and in environmental remediation: i.e. textile dyeing; detergent manufacture; hydrocarbon-contaminated soil washing; light-induced oxidation processes for environmental remediation of waste waters; oil in water

emulsification and metal oxide flocculation; and templates for the synthesis of porous materials with tailored morphology [2-5]. These results, coupled with the easy, virtually no cost, availability of UBW offer scope to develop sustainable products and processes from bio-refuse at industrial and commercial level.

However, while the above-mentioned applications for this technology exemplify the rather novel and appealing aspect of UBW as a potential source of revenue, rather than as an added cost for society, the effective achievement of such applications through technological transfer of results obtained in the laboratory to production scale requires more in-depth study. An analysis of the above results, indicated that product performance should still be made the priority of any further research, Moreover, such research should not only evaluate the full potential of UBW as a sustainable source of chemicals to replace or reduce the use of synthetic chemicals but also rate products based on the economic and environmental benefits expected from their applications. Accordingly, any specific process development should fulfil these two criteria. In this context, photodegradation of organics in polluted water streams seemed a worthwhile application to be further investigated due to its high industrial and social relevance.

Work reporting the photosensitizing properties of SBO was started based on their chemical similarities [5] to natural organic matter (NOM) present in soil and water and on the fact that NOM is known to be light-absorbing matter capable of promoting photochemical transformation of organics of anthropogenic origin [7-14]. The above SBO are described [15] as mixtures of macromolecules with weight average molecular weight (Mw) values ranging from 67 to 463 kg mol^{-1}. Chemical composition data also show that these macromolecules contain several functional groups and C types of different polarity. They appear to be formed by long aliphatic C chains substitued by aromatic rings and several functional groups such as COOH, CON, C=O, PhOH, O-alkyl, OAr, OCO, OMe, and NRR', with R and R' being alkyl C or H. These organic moieties are the likely memory of the main constituents of the sourcing bio-organic refuse matter which are not completely mineralized during ageing under aerobic fermentation conditions. For this reason, SBO may be considered to be the pristine material of natural soil organic matter formed under longer ageing conditions. Thus, the structural similarities between SBO and NOM are not surprising.

The question at this point might be: why use SBO rather then NOM? Although one might reasonably hypothesise that SBO, compared to NOM, might be effective for different or for a wider number of organic probes, in fact, one main reason for the development of SBO rather than NOM is that as photosensitizers at industrial/commercial level SBO appear more feasible based on product source sustainability. Indeed, while NOM in soil and water is present in low concentration (< 3 %),

composted UBW may contain up to 40–60 % SBO. In addition, as a result of the increased production due to population urbanization, UBW are concentrated in confined areas by municipal collection.

So far, the photosensitizing properties of SBO have been demonstrated for the photodegradation of azo-dyes [16] and phenols [3]. To extend the investigation to other substrate classes, the present work focused on naphthalene sulfonics as probe molecules. Sulfonic acids are compounds frequently found in aqueous industrial effluents. They contribute dissolved organic sulfur (DOS) in water [17], a frequently-used water quality control parameter. Within this class of compounds, 60 % DOS originates from linear sulfonates, used as detergents, while 40% stems from aromatic sulfonates. However, while the environmental impact of linear alkylbenzene sulfonates (LAS) has been widely investigated, little research has been dedicated to benzene and naphthalene sulfonates [18]. In contrast to readily biodegradable LAS and benzene sulfonic acid, polycyclic aromatic sulfonates are reported to be rather recalcitrant [19,20], to persist in wastewater effluents [21], surface waters, [22,23] and landfill leachates [24]. Specifically, naphthalene sulfonates are currently used in several industrial processes as dispersants, stabilizers, suspending and wetting agents and intermediates in the production of textile dyes. These compounds do not show significant toxicity, but their degradation processes is worth studying due to their widespread use, high stability and high solubility in water which causes their transport and accumulation even at considerable distances from the effluent source.

In the present work, four different naphthalene sulfonates, 1-Naphthalenesulfonic sodium salt (1-NS), 2-Naphthalenesulfonic sodium salt (2-NS), 1,5-naphthalenedisulfonic acid (1,5-NdS) and 2,6-Naphthalenedisulfonic disodium salt (2,6-NdS), have been used as probe molecules.

2. Experimental Section

2.1 Materials

The specific SBO used in this work, hereinafter referred to as AC8, was sourced from UBW supplied by ACEA Pinerolese S.p.a., a waste treatment plant operating in the province of Torino (Italy). The UBW material was the product of the aerobic digestion of a 2:1 food/green residue mixture aged for 110 days. The AC8 SBO was isolated in 10 % w/w yield according to a previously reported procedure [1] comprising the ACEA UBW digestion in aqueous alkali followed by precipitation at pH < 1.5 with HCl. The product, characterized according to a known analytical protocol [1], was found to contain C types and functional groups in the relative ratios represented in

the virtual molecular fragment shown in Figure 1. This representation is only meant to fit the analytical data. The product in reality is a mix of polymeric molecules according to the description given in the Introduction section.

As AC8 is not a synthetic polymer, the fragment in Figure 1 cannot be taken as the only repeating unit in the polymer. In reality, to account for the biological origin and the wide molecular weight distribution, a range of different molecular fragments and molecules with greater and lower molecular weight is more likely to compose AC8. However, even if other structures could be drawn based on the experimental data, the graphical, although virtual, representation of C types' and functional groups' relative concentrations, as shown in Figure 1 is felt to communicate to the reader in an uncomplicated way the nature of the investigated material..

Before use, AC8 was solubilized in Milli-Q^{TM} water adding aqueous KOH up to pH 8-9 and treated in an ultrasound bath to complete dissolution of the suspended matter. The solution was then filtered through a cellulose acetate 0.45 μm pore diameters filter (Millipore) to remove residual insoluble matter. All other materials were used as received analytical-grade reagents purchased from Aldrich, except for Fluka 2-NS and KOH, Merck tetra-n-butyl ammonium hydroxide (TBAH), and Millipore ultra pure (Milli-Q^{TM}) water.

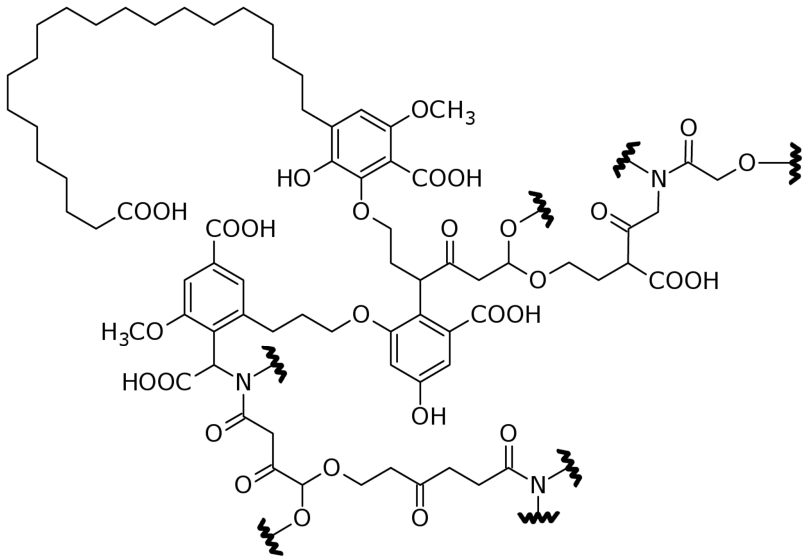

Figure 1. Virtual molecular fragment representing the analytical relative ratios of C types and functional groups.

2.2 Photodegradation and analytical procedures

Photodegradation of the probe naphthalene sulfonate substrate was performed by irradiating, under continuous stirring, 5 mL AC8-substrate aqueous solution in a closed Pyrex® cell with a Xenon (1500W) lamp (Solarbox) and a 340 nm cut-off filter (Figure 1 in supplementary file), allowing only light with wavelength above 340 nm to irradiate the sample. The substrates degradation was followed by HPLC, employing a Merck-Hitachi instrument, equipped with Lichrospher RP-C18 (125 mm x 4 mm i.d., d.p. 5 μm, from Merck), L-6200 pumps and UV-VIS L-4200 detector. The elution was carried out with aqueous TBAH 2.5 mM (eluent A)/ methanol (eluent B) fed at 1.0 mL min^{-1} flow rate, applying a linear gradient changing from 30 to 80 % eluent B over 30 min. The detection was performed at 225 nm.

A CARY 100 SCAN-VARIAN spectrophotometer was used to follow the AC8 photobleaching.

The sulfate evolution was followed by a suppressed ion chromatography, employing a Dionex DX 500 instrument equipped with a Dionex IonPac® AS9-HC column (200 mm x 4 mm i.d.), GP40 pump (Dionex), an electrochemical detector ED40 (Dionex) and an Anion Self-Regenerating Suppressor-Ultra (ARSR®-ULTRA, 4-mm, Dionex). Elutions were performed in isocratic conditions with 90% of aqueous solution of K_2CO_3 12 mM and $NaHCO_3$ 5 mM and 10% of water, at 1.0 mL min^{-1} flow rate. Total organic carbon (TOC) was measured by a Shimadzu TOC-5000 analyser (catalytic oxidation on Pt at 680 °C), previously calibrated with standard solutions of potassium hydrogen phthalate, sodium carbonate and sodium hydrogen carbonate.

The Microtox® system was used to determine short-term biotoxicity of AC8-substrate solution. This test is a powerful tool for screening the toxic properties of multicomponent samples, employing. the *Vibrio Fischeri* bacterium as a probe organism. This bacterium is bioluminescent, characterized by peak light emission at 490 nm in the presence of oxygen. When the bacterium comes into contact with toxic substances, the cell metabolism is inhibited, and a relative light emission decrease (inhibition effect E %) is observed. The amount of light emitted, corrected for the light decrease physiologically occurring in the absence of toxicity, is proportional to the toxic effect of compounds present in the samples. The test must be performed in controlled experimental conditions (pH, T and salinity); for coloured or turbid samples, a correction factor, calculated from the sample absorbance at 490 nm, is needed.

3. Results and Discussion

3.1 Substrate photodegradation

Preliminary experiments performed on the aqueous solutions of the four investigated naphthalene sulfonates at 20 mg L^{-1} irradiated for three hours in the absence of AC8, showed that direct photolysis of the substrates, as evaluated by the direct HPLC concentration measurements of these molecules, was not relevant. Viceversa, under the same experimental conditions, but in the presence of AC8, substrate degradation was found to increase upon increasing AC8 concentration and to reach a 20-25 % plateau value at about 150 mg L^{-1} AC8. A similar trend has also been reported for the photodegradation of azodyes performed in the presence of other AC8 similar SBO [16]. The following plausible explanation of the experimental results is based on considering the photodegradation of AC8 itself. Due to its rather complex nature, the degradation rate of AC8 could not be evaluated by direct concentration measurement as in the case of naphthalene sulfonates. However, indirect evidence was obtained by UV-VIS spectroscopic measurements. Indeed, Figure 2 shows a significant decrease of the UV-VIS absorbance recorded for the 150 mg L^{-1} AC8 solution upon increasing the irradiation times up to 24 h; at 280 nm the decrease of the absorbance value reached about 40 % after 24 h of irradiation. The UV absorbance at 280 nm has been used by previous investigators to characterize NOM [25], or for monitoring its photodegradation [26]. In the specific case of AC8 and the proposed fragment in Figure 1, it is certainly possible that several functional groups could be responsible for the absorption around 280-300 nm. This absorbance arises from p–p* electron transition occurring for phenolic arenes, benzoic acids, aniline derivatives, polyenes and polycyclic aromatic hydrocarbons with two or more rings. The ^{13}C NMR data for AC8 have, however, indicated aromatic moieties as major molecular components of this material. To produce the transformation of the above aromatic moieties, it is not strictly necessary that they absorb the radiation employed. Indeed, since irradiation was performed using a cut-off filter at 340 nm, and radiation below this wavelength is not able to reach the system, moieties absorbing at 280 nm cannot be directly photodegraded. Nevertheless, for AC8 to undergo photo degradation, it is sufficient that other groups absorbing radiation above 340 nm promoted the formation of reactive species, and that these species were able to react further with aromatic moieties, thus causing an absorbance decrease at 280 nm as reported in Figure 2.

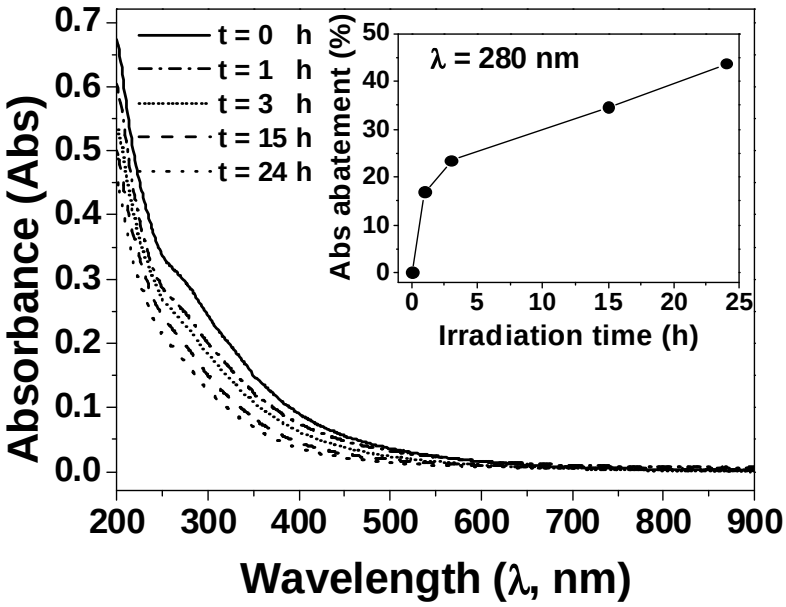

Figure 2. UV-vis spectra of 150 mgL^{-1} AC8 aqueous solution at variable irradiation time (t, h) recorded after 10x sample dilution. Insert: absorbance (Abs) abatement % at 280 nm vs. irradiation time.

Previous work [6-14] on the photochemical reactions promoted by soil and water NOM as a photo sensitizer focuses on the photodegradation of probe substrates (S), without considering the degradation of the photosensitizer itself as a possible competitive process. The authors suggest a possible reaction mechanism involving the generation of the NOM excited triplet state (^{3}NOM*) upon light absorption, followed either by the formation of reactive oxygenated species (ROS) [12] or by the interaction between ^{3}NOM* and S yielding substrate degradation products (SDP) [7]. This mechanism in the presence of AC8, as a photosensitizer in place of NOM, is represented by reactions 1-4. However, under the experimental conditions of the present work, we also consider the photodegradation of AC8 (reaction 5) with the formation of its degradation products (AC8DP). In this case, the ROS species formed in reaction 2 might be able to promote the photodegradation of both the substrate (reaction 4) and the photosensitizer (reaction 5). As a result, competition between AC8 and the substrate for ROS could be a plausible explanation for the substrate degradation increasing with AC8 concentration up to the plateau value observed at about 150 mg L^{-1} AC8. In essence, all excess ROS produced in reaction 2 by increasing AC8 concentration above 150 mg L^{-1} would be engaged in reaction 5 and none would be available for reaction 4.

$$AC8 + h\nu \rightarrow {}^{3}AC8^{*} \qquad (1)$$

$$^{3}AC8^{*} \xrightarrow{O_2/H_2O} AC8(H) + ROS \qquad (2)$$

$$^{3}AC8^{*} + S \rightarrow AC8 + SDP \qquad (3)$$

$$S + ROS \rightarrow SDP \qquad (4)$$

$$AC8 + ROS \rightarrow AC8DP \qquad (5)$$

Further work was carried out by irradiating the probe naphthalene sulfonates 20 mg L^{-1} solutions in the presence of 150 mg L^{-1} AC8 to investigate the effect of the irradiation time. In this case both the substrate and sulfate concentration were monitored as indicators of the substrate degradation rate. The results are reported in Figures 3 and 4. The data based on substrate concentration depletion in solution indicate that after 24 hours' irradiation, a 65-80% degradation rate can be achieved, being slightly higher for NS than NdS compounds. The lower reactivity of the disulfonates might result from the lower electron density of the aromatic nuclei and thus from the lower electron availability for the electrophilic ROS in reaction 4.

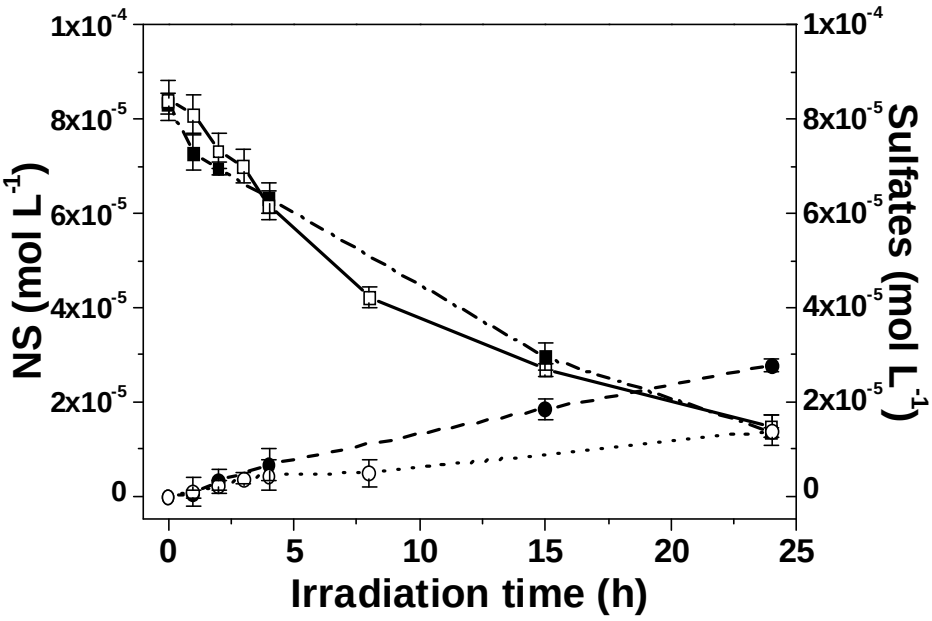

Figure 3. Naphthalene sulfonates (NS) and sulfates concentration (mol L^{-1}) vs. irradiation time (h) in the presence of 150 mg L^{-1} AC8: data for 1-NS (■) and 2-NS (□) substrates and for the sulfates released from 1-NS (●) or 2-NS (○) degradation.

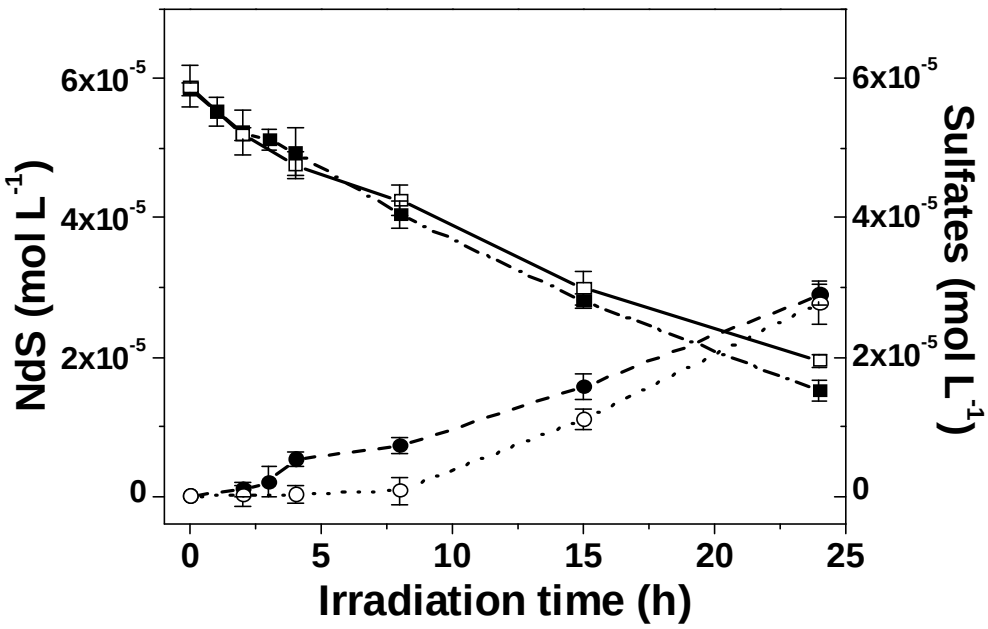

Figure 4. Naphthalene sulfonate (NdS) and sulphate concentration (mol L^{-1}) vs. irradiation time (h) in the presence of 150 mg L^{-1} AC8: data for 1,5-NdS (■) and 2,6-NdS (□) substrates and for the sulfates released from 1,5-NdS (●) or 2,6-NdS (○) degradation.

Among several possible different ROS species formed upon AC8 irradiation (reaction 2), previous work has evidenced the formation of OH radicals and singlet oxygen [3]. At AC8 concentration close to the one used in the present work, singlet oxygen formation was considered negligible, whereas a significant signal corresponding to the presence of OH radical was detected, thus allowing to hypothesize a relevant role for the OH radical in the photodegradation of a probe substrate.

To verify the hypothesis in the present case, that is in the photodegradation of naphthalene sulfonates, irradiation experiments were performed in the presence of 2-propanol OH radicals scavenger [27]. Solutions containing 2-NS or 1,5-NdS at 20 mg L^{-1} were irradiated for two hours in the presence of 150 mg L^{-1} of AC8 and 0.01 M of 2-propanol. The results are reported in Table 1:the significant decrease in the degradation % observed for both substrates in the presence of 2-propanol confirms the relevant role played by the electrophilic OH radicals in the herewith investigated photodegradation process and supports the argument for a lower reactivity order of the NdS compared to the NS compounds.

Table 1. Effect of the addition of 2-propanol (0.01 M) on the photo degradation rate of 2-NS and 1,5-NdS (20 mg L^{-1}) in the presence of AC8 (150 mg L^{-1}).

Compound	Degradation w/w % in the absence of 2-propanol	Degradation w/w % in the presence of 2-propanol
2-NS	15.9	4.5
1,5-NdS	10.7	1.2

The data based on sulfate concentration increase (Figures 2 and 3) add further insight into the investigated photodegradation process. It may be observed that for all the examined substrates, the sulfate release rate in solution is much less than that expected from the substrate depletion rate. After 24 hours' irradiation, only 15 and 30 % organic S is mineralized for NS and NdS compounds respectively, compared to the rates of depletion of the starting molecules (about 80 % for NS and 70 % for NdS) calculated from their direct concentration measurements depletion. This suggests that both desulfonated and sulfonated intermediate products are formed during photodegradation of the probe substrates. The delayed release of inorganic S relatively to the substrate depletion rate does not necessarily imply that the process is not capable of achieving complete mineralization of the organic substrate. A similar situation has already been reported for the photodegradation of sulfonates in the presence of TiO_2 [28], where complete mineralization of both organic C and S was

demonstrated to occur later than the complete abatement of the probe substrate starting molecule. Detailed investigation of the degradation path of the probe substrates was beyond the scope of this work. Such investigation appeared rather difficult since the photosensitizer itself was also organic and could, in principle, release degradation products according to reaction 5. Nevertheless, total organic C (TOC) measurements were performed to appreciate the mineralization rate of the starting organic load. The TOC measurements were designed in order to distinguish the probe substrates and the AC8 organic C contributions. This was achieved by performing parallel irradiation trials of solutions containing both the probe substrates and AC8, and of solutions containing AC8 only, and then subtracting the TOC measured in the latter solutions from the TOC detected in the probe substrates-AC8 solutions. Under these experimental conditions, the estimated mineralized C for the probe substrates was 40-45 %.

3.2 Toxicity evaluation.

The above results, indicating the presence of photodegradation intermediates formed by irradiation of the probe substrates, posed the need for further studies to evaluate the potential toxicity of the residual organic solutes (SDP in reactions 3 and 4). These also included AC8 and/or its degradation products (AC8DP in reaction 5). One approach to achieve the above objective might have been a detailed study for the identification of the above degradation organic intermediates followed by a dedicated toxicity study. Due to the complex nature of the systems investigated in the present work, this research strategy was momentarily postponed. A simpler approach was the direct evaluation of the potential global toxicity of the investigated AC8-substrate solutions before and after irradiation. This appeared an easy way to assess if it was worthwhile to undertake the more complex, detailed, chemical characterization work. Toxicity was therefore evaluated by the Microtox® test which yields the percentage of bioluminescence inhibition (E %) value for the *Vibrio Fischeri* bacterium by the investigated solutions (see Experimental section). To understand the significance of the experimental data, it must be considered that the higher the inhibition effect (E %), the higher the toxicity level. In more detail, E % < 20% corresponds to the absence of toxicity, whereas a higher E % value, between 20 and 50, indicates weak toxicity.

The data reported in Table 2 indicated the following results: (i) no toxicity caused by the neat 150 mg L^{-1} AC8 solution before and after irradiation; and for the solutions containing both AC8 and NS or NdS (ii) no toxicity (E < 20%) for 1,5-NdS and 2,6-NdS solutions before irradiation, (iii) weak toxicity for 1-NS and 2-NS solutions before irradiation, (iv) a marked decrease of the E % values for the irradiated AC8/NS and AC8/NdS samples, except for the AC8/2,6-NdS showing E %

increase up to 41. It can thus be concluded that the degradation process is essentially producing intermediates which are not significantly toxic. Further analytical effort to identify degradation products did not appear strictly necessary.

Table 2. Inhibition effect (E %) measured by biotoxicity Microtox® test, after 30 minutes contact with *Vibrio Fischeri* bacterium. AC8 = 150 mg L^{-1} and naphthalene sulfonates = 20 mg L^{-1}.

Investigated solution	Irradiation time, h	E %
AC8	0	4.6
AC8	24	9.4
AC8 / 1-NS	0	27
AC8 / 1-NS	24	17
AC8 / 2-NS	0	29
AC8 / 2-NS	24	18
AC8 / 1,5-NdS	0	18
AC8 / 1,5-NdS	24	-33
AC8 / 2,6-NdS	0	17
AC8 / 2,6-NdS	24	41

4. Conclusions.

A soluble substance of biological origin, namely AC8, isolated from urban bio-wastes has been shown to be an efficient photosensitizer for the abatement of naphthalene sulfonates from water solutions. Depletion of 70-80 % of the investigated mono and disulfonated probe substrates has been demonstrated to occur after 24 h irradiation of solutions containing 20 mg L^{-1} probe substrates in the presence of 150 mg L^{-1} AC8. Complete mineralization of the probe substrates was not observed. However, the residual organics in solution after irradiation have potentially been shown to be not toxic according to the Microtox® test. This result, coupled with previous data obtained on the photodegradation of azo-dyes and phenols, widens the range of probe substrates that may be handled in waste waters where photodegradation is assisted by soluble substances of biological origin.

It has also been found in this study, that increasing the AC8/naphthalene substrate ratio above 7.5 does not yield any increase of the probe substrate abatement rate. This result, undoubtedly

important from a practical application viewpoint, has allowed a novel mechanism to be proposed (reaction 1-5) whereby AC8 acts at the same time as photosensitizers for the production of reactive oxygenated species (ROS) and as substrates undergoing photodegradation. In this second role, it may compete with the intended probe substrates for ROS and end up by inhibiting any further photodegradation of the probe substrates.

5. Acknowledgements

This work was carried out with the contribution of Cipe 2006 and MISEICECRUI 2007 funds. The authors are grateful to Acea Pinerolese Industriale in Pinerolo, TO (Italy) for supplying the sourcing UBW material. The authors also wish to thank 7thFP IRSES-2010-269128-EnvironBos Marie Curie Action.

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