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Bio-organics isolated from urban bio-refuse for the photodegration of azo-dyes in aqueous solutions

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ABSTRACT

A bio-organic substances (BOS) was isolated from urban bio-refuse undergoing aerobic biodegradation. The isolated BOS was characterized for chemical composition and performance as sensitizers for the photodegradation of azo-dyes in solution. Three commercial sulphonated azo-dyes, i.e., ethylorange (EO), Orange I (OI) and Orange II (OII), were selected as probe molecules. For these molecules high abatement rates (60–100%) were obtained within few hours of irradiation in the presence of BOS, whereas almost no abatement was observed in the absence of BOS. A delay in the color bleaching was observed, in comparison to the dyes degradation; coloured intermediates were identified. Acute toxicity tests showed a low toxicity for the samples at the end of the degradation process.

Keywords: Urban refuse; Azo-dye baths; Industrial effluents; Photodegradation; Bio-surfactants Refuse bio-photosensitizers

1.Introduction

The wastewater purification is of great worldwide concern due to the continuous increase of water consumption for domestic, agricultural and industrial use. The traditional treatments such as adsorption on activated carbon, ultrafiltration, reverse osmosis, etc., even when efficient do not represent an ultimate solution of this problem, since they are non-destructive processes. They mainly consist in a phase transfer of the pollutants and a successive waste treatment is therefore needed. Biological treatments are finalized to achieve pollutant mineralization but, unfortunately, many organic compounds are recalcitrant to biodegradation. For these reasons, in the last decades, great attention has been devoted to the study of the so-called advanced oxidation processes (AOPs) [1,2]. These techniques (e.g., UV photolysis, heterogeneous photocatalysis, UVperoxide hydrogen or UV-ozone) are based on the generation (often using light energy), of highly reactive radical species, as •OH radicals, able to promote the destruction of organic substrates, including recalcitrant compounds. Hopefully, the pollutants should be transformed to non-toxic or less toxic products, and ultimately mineralized. Natural organic matter (NOM) in terrestrial waters and soils contains light-absorbing species which are able to promote photochemical reactions and therefore allow water auto-remediation [3–5] from organic pollutants originating from human

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activities. Natural organic matter has other properties which may affect in many ways the fate of organic pollutants and inorganic matter present in the environment. Structural information [6] suggests NOM constituted by polymeric substances comprising a C framework of aliphatic C chains bonded to more or less fused cycloaliphatic and aromatic rings and substituted by several functional carboxylic, phenol, ether, ammine and amide groups. Consistently with their chemical nature, these substances perform as complexing agents, ion exchangers and surfactants, and may therefore bind and transport organic and inorganic pollutants from soil to plants and waters. The available information indicates therefore that NOM, by virtue of its chemical nature, might allow a wide number of applications in fields actually dominated by the use of commercial products obtained from fossil sources by chemical synthesis. However, large scale production of bio-products isolated from NOM would require the availability of sources containing high concentration of NOM in order to be economically feasible. Such sources are rare and their intensive exploitation would lead to adverse environmental impact caused by their depletion.

Urban wastes (UR) have become nowadays rather attractive potential sources of bio-organic substances (BOS) for several reasons. These substances bear basic structural similarities with BOS isolated from NOM. As result of increased production due to population urbanization, UR 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-based products fitting a wide range of uses [7,8]. On this basis, in 2007 the authors undertook a R&D project funded by Regione Piemonte [9] in Italy and devoted to the promotion and commercialization of new bio-based products and processes from organic residues. This paper addresses the specific topic of aqueous industrial effluents treatments taking as case study the photodegradation of azo-dyes assisted by BOS. The importance of these compounds in water treatment studies stems from the fact that actually the textile industry uses more than 3,000 dyes, and it is estimated that about 15% of the world dyes production is lost in the environment during the dyeing process [10,11]. 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 [12]. This poses the problem of their removal from industrial wastes or polluted natural water streams. Azo-dyes are recalcitrant to aerobic degradation in municipal sewerage systems [13] and the common water treatments (precipitation, flocculation, adsorption on active carbon) do not solve the problem by themselves, but require further sludge treatment or carbon regeneration [14]. In the present study, aiming to investigate photodegradation assisted by BOS as alternative solution for the remediation of industrial dyes effluents, three typical commercial sulphonated azo-dyes (Fig. 1), i.e., ethylorange (EO), Orange I (OI) and Orange II (OII), have been taken as probe molecules. In previous work BOS have been shown efficient auxiliaries for dyeing textiles with azo-dyes [8]. Thus, a further intriguing motivation for the present study was the perspective to use BOS at two stages in the dyeing process, i.e. to improve the dyeing process efficiency and to help removal of the residual dye from the exhaust dye bath.

2. Materials and methods

All materials and reagents were Aldrich products, unless otherwise specified. Experimental details, other than those reported hereinafter, were as in previous work [6].

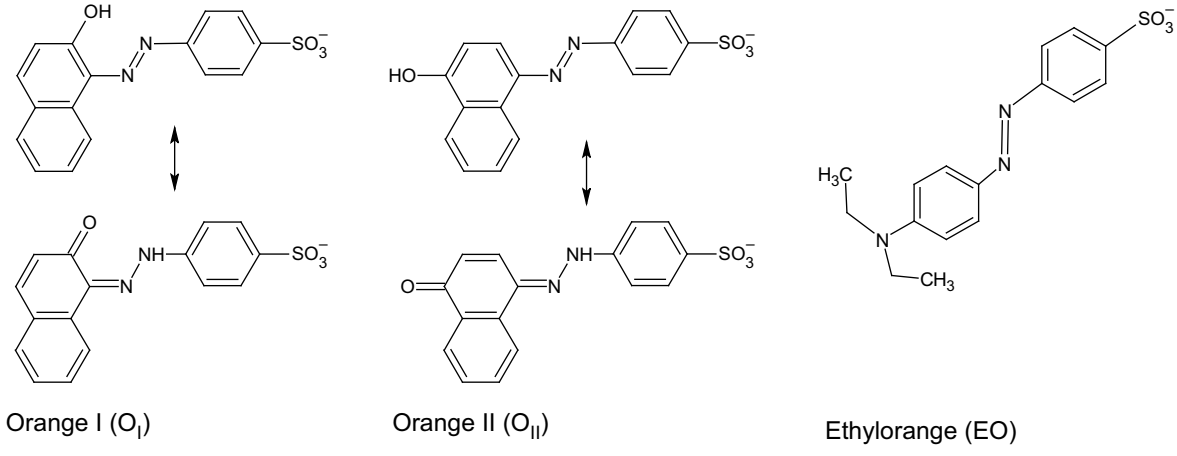

Fig. 1. Structure of the investigated azo-dyes.

2.1. Isolation of BOS

The investigated BOS were isolated from urban bio-waste facilities located in Piemonte, Italy, performing aerobic bio-degradation. The starting refuse was a mature compost obtained from a mix of kitchen and gardening-park trimming residues. The collected refuse sample was treated 4 h at 65°C with 1 mol L^{-1} NaOH. The resulting suspension was centrifuged for 20 min and the supernatant liquid phase acidified with 37% HCl to pH < 1.5 to yield the final BOS product.

2.2. Chemical characterization of BOS

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 [6]. The functional groups composition reported in Table 1 was calculated from the above NMR signals area ratios, and from the total C and N microanalytical and acid groups concentration 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.

2.3. Irradiation experiments

A stock 1 g L^{-1} BOS aqueous solutions was prepared by taking up solid BOS with MilliQ® water at 250–200 V/w ratio, stirring 1 h, then adding aliquots 0.2 M KOH 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 solution containing the organic substances to be photodegraded at 5 mg L^{-1} concentration and variable amounts of BOS. The degradation trials were performed by irradiating 5 ml of the above solutions in a closed Pyrex® cell with a Xenon (1,500 W) lamp (Solarbox) and a cut-off filter for wavelengths below 340 nm.

Table 1
Solvent mix composition versus elution time for the analysis of dyes concentration after irradiation

t (min)	EO		OI		OII	
	% A	% B	% A	% B	% A	% B
0	72	28	80	20	75	25
10	72	28	80	20	75	25
25	10	90	10	90	10	90
30	10	90	10	90	10	90

2.4. Analyses of the irradiated solutions

The dye abatement was calculated from the starting dye concentration (Co) and the found dye concentration (*C*) after irradiation. The *C* value was determined by HPLC-DAD-UV-VIS (Surveyor, Thermo Scientific) analysis performed on Lichrospher 5-μm C-18 column (125 × 4.0 mm) at 1 ml min^{-1} flow rate of 5.0 mM ammonium acetate (eluent A) and acetonitrile (eluent B).

Different gradients (Table 1) were adopted depending on the dye, in order to optimize the elution time of the dye and of the corresponding photodegradation products through the HPLC column. The products detection was performed at 467 nm.

The matrix effect of BOS was assessed by comparing the HPLC results obtained from the analysis of different dye solutions, containing the same dye amount and increasing BOS amounts, up to 600 mg L^{-1}. Since a not negligible matrix effect was observed, the calibration standards were prepared by adding to the dyes aqueous solutions the same amount of BOS present in the irradiated solutions to be analyzed.

The analysis of the dye 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 (vs. calculated) was ±15 ppm (without internal calibration). The chromatographic separations were performed on a Phenomenex Synergi C18 column, 150 × 2.0 mm, 3 μm particle size. Injection volume was 20 μl and flow rate 200 μl min^{-1}. Gradient mobile phase composition was adopted: acetonitrile/ammonium acetate 0.1 mM 5/95 to 100/0 in 30 min.

Color bleaching in the irradiated solutions was quantified by means of a double beam CARY 100 SCAN-VARIAN, UV-VIS spectrophotometer by measuring the absorbance at 467 nm where the dyes irradiated solutions exhibit the maximum absorptivity. The absorbance was corrected for the BOS contribution.

Correction of absorbance readings at 467 nm for BOS contribution were obtained as follows. Dyes and BOS UV-VIS absorption spectra were recorded to yield the patterns shown in Fig. 2. The contribution of BOS to the dye maximum absorbance at 467 is clearly not negligible. Thus, in parallel to the irradiation of the dye in the presence of BOS, also a solution containing BOS alone was irradiated and its absorbance contribution was taken into account to calculate the net colour due to BOS and/

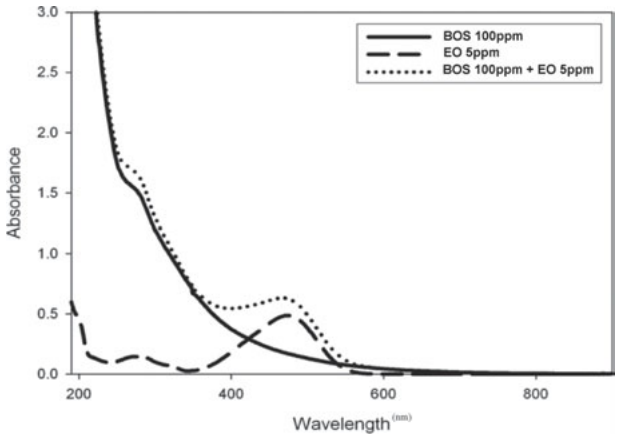

Fig. 2. UV-VIS spectra of BOS, EO and their mixture.

or its degradation products in the irradiated solutions. This procedure was adopted under the assumption that any photodegradation of BOS would not be influenced by the presence of the dissolved dye.

3. Results and discussions

The investigated BOS was isolated from a typical refuse available in metropolitan areas. The sourcing material was a mix of kitchen and gardening residues obtained by separate source collection which was piled and periodically turned in order to promote aerobic biodegradation of the bio-organic matter. In waste treatment installations this procedure is normally continued until the pile reaches a peak temperature and cools down to ambient temperature. At this time, the biomass volume is reduce to 1/3 of the initial one. Indeed, during this bio-degradation treatment part of the refuse organics is complete mineralized, while lignin and other recalcitrant biopolymers undergo structural modifications becoming soluble in alkali. The composted sourcing material was characterized by 35.2% humidity and 46.0% w/w (referred to dry matter) volatile solids content. The BOS, extracted from the residual pile refuse as described in the experimental section, was characterized by a 1–3 × 10^5 D weight average molecular weight (MW) and by the C types and functional groups distribution reported in Table 2. The data demonstrate the presence of many organic moieties representing the memory of the main constituents of the refuse starting organic matter which are not completely mineralized by biodegradation. Use of these data for structure assignments is a rather complex task, as already reported for similar substances [6], and is part of foregoing work to be reported in future papers. Nevertheless, the lipophilic and hydrophilic C types and aromatic moieties in Table 2 may suggest many potential applications of the isolated BOS as biosurfactants, sequestering agent and photosensitizer. Whereas a number of these applications have been already reported [7–9] for similar BOS isolated from urban refuse, for the specific topic of industrial water treatments the results obtained in the photodegradation of the three commercial azo-dyes assisted by BOS are reported hereinafter.

Preliminary photodegradation experiments were performed by irradiating for 3 h aqueous solutions containing 5 mg L^{-1} of azo-dye and BOS in the concentration range from 120 up to 600 mg L^{-1}. The results are reported in Fig. 3; data in the absence of BOS are omitted since the degradation percentage was not higher than 5%.

It may be clearly observed that, increasing the BOS/dye ratio, leads to higher dye % abatement. Further experiments were performed at the BOS concentration at which the % abatement rate was nearly quantitative to assess photodegradation kinetics for the three dyes. The results reported in Fig. 4 demonstrate that in all cases nearly quantitative dyes abatement can be achieved with kinetics following a first-order law. The highest reactivity observed for OI has already been reported in a previous paper were the azo-dyes photodegradation was studied in the presence of TiO_2 suspension [15]. TiO_2 photocatalysis is well known to occur through reaction of the substrate and photogenerated holes and/or OH radicals on or close to the TiO_2 surface, respectively. On the basis of the same kinetic order one might expect a similar mechanism operating in both TiO_2 and AC8 systems. However, TiO_2 catalyzed system are heterogeneous, whereas the AC8-dyes

Table 2
BOS C types and functional group distribution

C and Functional group[a]	Cal	OMe	NC	OR	ROCOR	C=C	PhOH	PhOX	COOH	CON	C=O
Concentration/ meq g^{-1}	17.1	0.0	2.9	4.0	1.3	6.8	1.3	2.5	3.8	0.0	1.6

[a]Aliphatic C (Cal), O-Me, ammine C (NC), O-alkyl C (OR), di-O-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 (C=0).

systems investigated in this work are homogenous. Thus, for the latter ones mass transfer kinetics do not need to be taken into account in order to explain the different reactivity of the investigated dyes. In the AC8-aqueous dye solutions the photodegradation trials were performed in the presence of 0.01 M of hydrogen peroxide. Based on the same dyes reactivity order observed for the TiO_2 and AC8 systems, it may reasonably be assumed that, regardless of mass transfer kinetics, the dyes photodegradation rate depends mainly on the kinetics of the chemical reaction of the dyes with OH radicals. A detailed kinetic study was however beyond the scope of the present work and further speculations are not warranted.

Additional experiments were then performed in order to verify the solution bleaching. Fig. 5 shows different UV-VIS spectra obtained after irradiating for different times OI solutions in the presence of 360 mg L^{-1} of BOS. A trend for absorbance to decrease over 4 h irradiation time can be appreciated. Analogous behaviour was observed for the other two investigated dyes. The quantitative data reported in Fig. 6 are consistent with the observed absorbance versus irradiation time trend.

Three processes are compared in Fig. 6 for their % advancement versus irradiation time, i.e., the OI abatement rate, the solution bleaching and the sulphate

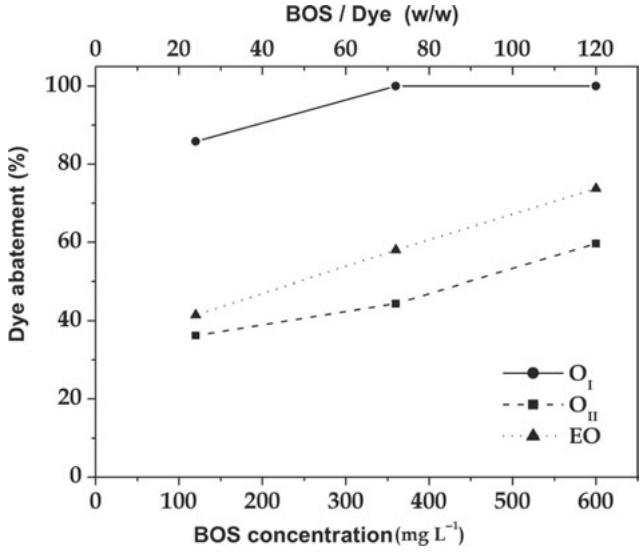

Fig. 3. Dye abatement % upon 3 h irradiation versus BOS concentration and BOS/dye w/w ratio in solution.

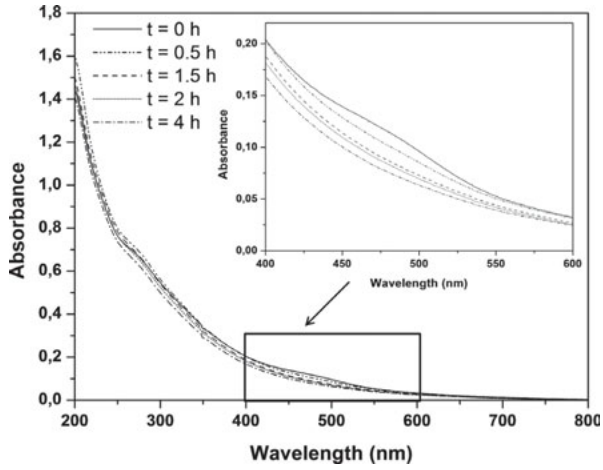

Fig. 5. UV-VIS spectra of 5 mg L^{-1} OI samples containing 360 mg L^{-1} BOS at different irradiation time; all samples were diluted 1:10 with water before recording the spectra.

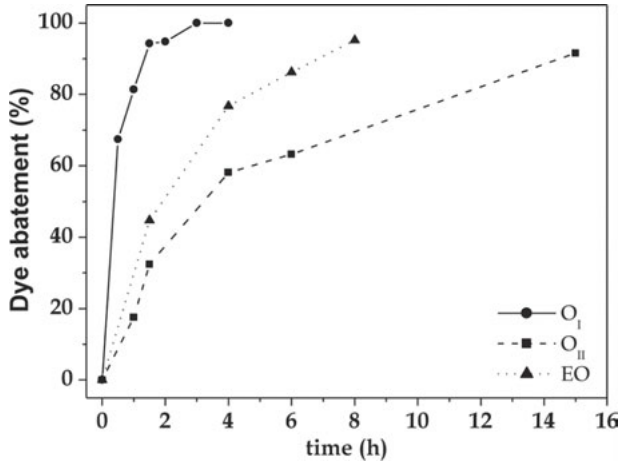

Fig. 4. Abatement % versus irradiation time for azo-dyes at 5 mg L^{-1} starting concentration in the presence of BOS a t 360 mg L^{-1} concentration.

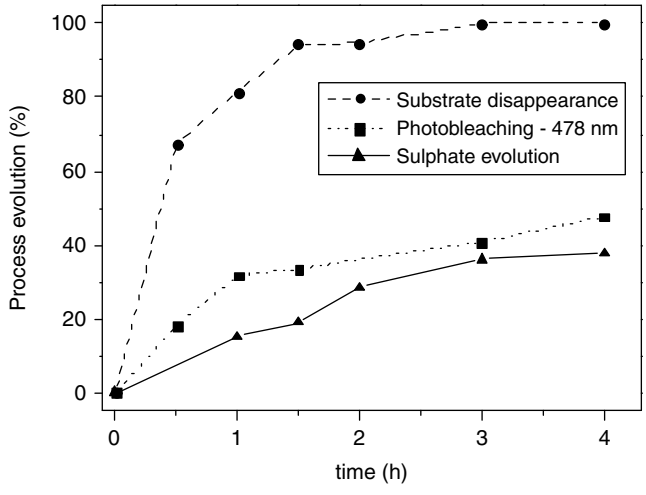

Fig. 6. Degradation of OI at 5 mg L^{-1} starting concentration in the presence of BOS (360 mg L^{-1}) versus irradiation time: dye disappearance, photobleaching and sulphate evolution.

evolution (as indicator of the dye mineralization). It can be noticed that the photobleaching is delayed compared to the dye disappearance and this can be due to the formation and accumulation of coloured intermediates. The evolution of an amount of sulphate lower than the stoichiometric value suggests that the intermediates are steel bearing the sulphonic group. Analogous results were obtained also for OII and EO. The irradiated solutions were thus analysed by HPLC-MS for the presence of intermediates formed by the dyes photodegradation. Figs. 7–9 report the compounds which were identified in the irradiated solutions of each dye. It may be observed that these compounds result from hydroxylation of the parent molecule to the aromatic ring in all cases and/or EO N dealkylation or OI and OII azo-group reduction. The fact that the same compounds have been reported in the case of the degradation of these dyes in the presence of TiO_2 suspension [15] is a further argument in favour of a similar photodegradation mechanism induced by both TiO_2 and BOS.

Due to the presence of the intermediate compounds in Figs. 7–9 at degradation times corresponding to the complete dyes disappearance, acute toxicity in the irradiated solutions was evaluated by measuring the Vibrio Fischeri luminescence inhibition [16]. This test is a powerful tool for screening the toxic properties of a set of samples containing a multitude of chemical compounds. It allows to obtain a preliminary classification of the overall toxicity based on the % luminescence inhibition effect. The results obtained for the irradiated solutions containing the dyes and AC8 before and after irradiation are reported in Table 3. All values are below 20% inhibition and do not indicate any important toxicity concern. Thus further tests to determine E50 levels were not performed.

The experimental data prove that BOS are efficient sensitizers in the photolysis of azo-dyes. The observed kinetic order and the type of intermediates generated by the dyes photolysis assisted by BOS are similar to those reported in the photolysis of the same dyes assisted by TiO_2. This fact may suggest similar mechanism in both cases and warrants a specific investigation on the photodegradation mechanism induced by BOS.

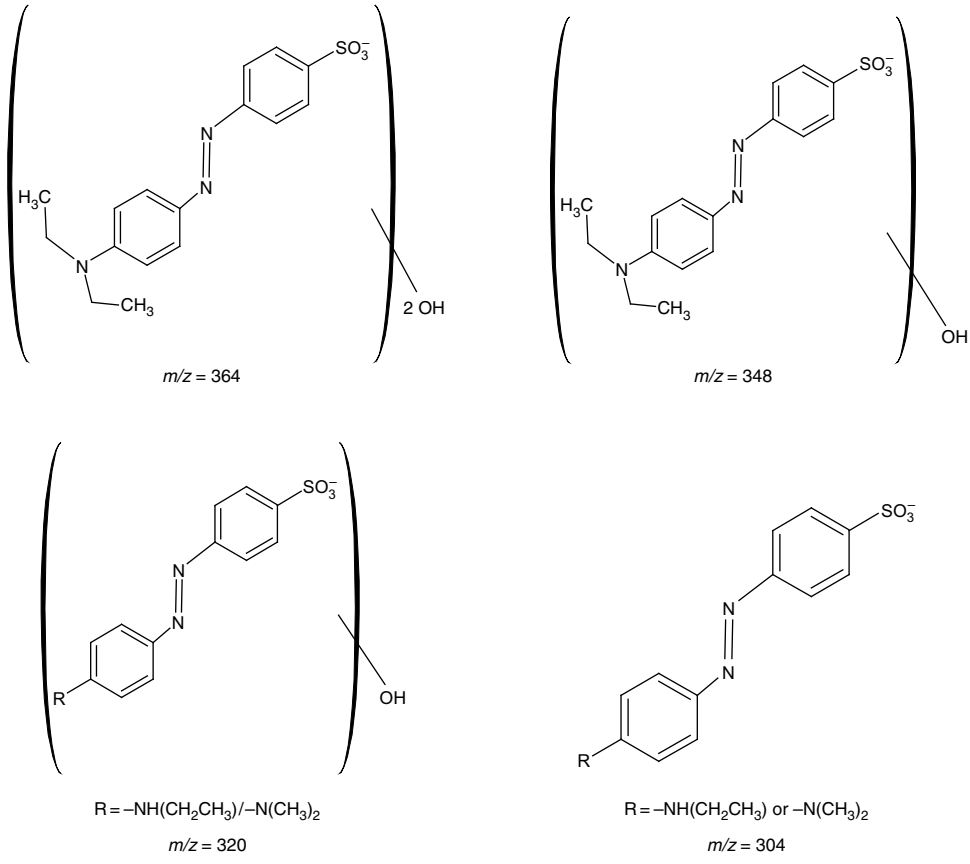

Fig. 7. Ethylorange intermediates formed during photodegradation in the presence of BOS; m/z = mass to charge ratio.

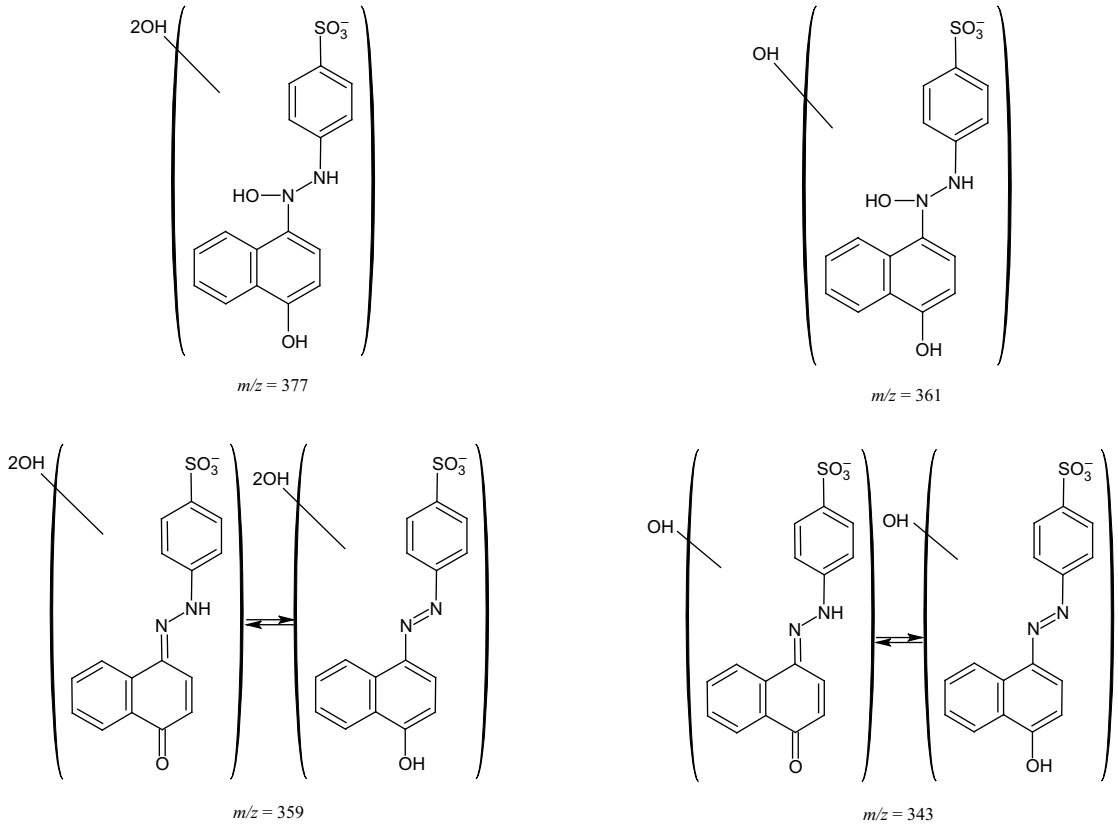

Fig. 8. OI intermediates formed during photodegradation in the presence of BOS; m/z = mass to charge ratio.

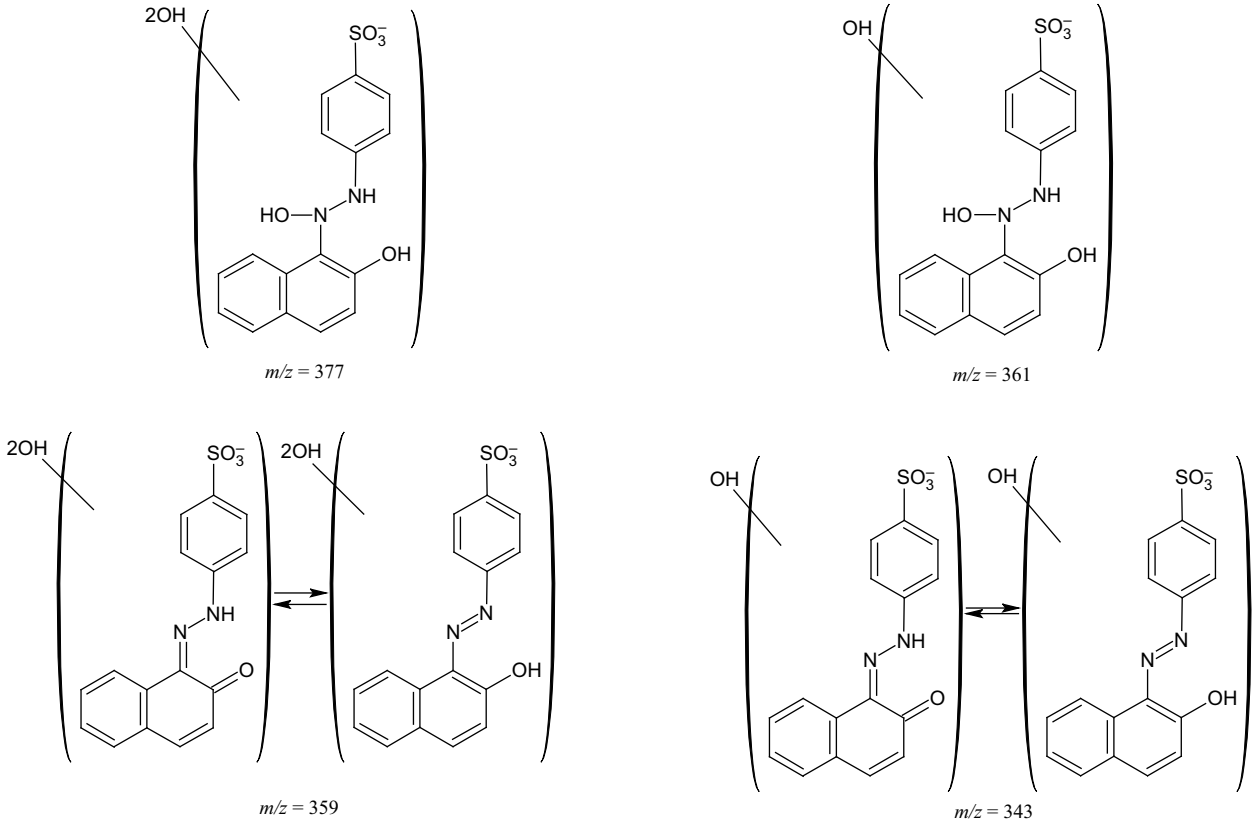

Fig. 9. OII intermediates formed during photodegradation in the presence of BOS; m/z = mass to charge ratio.

Table 3
Inhibition effect versus irradiation time for the investigated AC8-dyes

Dye/irradiation time (h)		Inhibition effect (%)
EO	0	–5.398
	8	5.049
OI	0	–11.6
	4	17.76
OII	0	17.66
	15	10.32

4. Conclusions

The experimental data in this work demonstrate that photodegradation of solutions containing 5 mg L^{-1} azo-dyes performed in the presence of BOS allows complete removal of azo-dyes in relatively short irradiation time. The reaction has been found to yield some intermediate compounds deriving from aromatic hydroxylation and/or N dealkylation and reduction of azo-groups. These compounds however do not seem to contribute any significant toxicity increase in the irradiated solutions. Nor the authors expect any adverse environmental impact coming from the BOS themselves upon use in the photoremediation of industrial effluent, due to their biological origin and structural similarities with NOM substances. These results, coupled to previous work [8] reporting BOS as efficient auxiliaries for textile dyeing, propose a unique intriguing scenario envisioning the use of the same substance to improve the dyeing process and then help the removal of the residual dye from the exhaust dye bath. Further work is encouraged in this direction.

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