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Oxidative degradation of food dye E133 Brilliant Blue FCF Liquid chromatography–electrospray mass spectrometry identification of the degradation pathway

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Abstract

This paper is devoted to the evaluation of the degradation pathway of the E133 Brilliant Blue FCF (C.I. 42090) that is largely used in the food industry. The degradation is studied in oxidation conditions obtained by addition of potassium persulfate at different persulfate to dye molar ratios under natural sunlight irradiation. The degradation pathway of the dye passes through a species coloured in dark blue and then gives rise to uncoloured species. Due to the low volatility and the poor thermal stability of the dye, reversed-phase liquid chromatography associated to mass spectrometry and tandom mass spectrometry was employed to follow the kinetics of degradation and identify some intermediates. The identification of organic species still present in the decoloured dye and the value of COD obtained in these conditions show evidence that complete decolorization does not correspond to complete mineralisation. No direct information of toxicity is available for the uncoloured degradation products but the further formation of aromatic amines can not be excluded.

Keywords: Triphenylmethane dyes; Degradation; Persulfate oxidation; HPLC–MS

1. Introduction

Triphenylmethane dyes, extensively used in textile, paper, leather and the plastics industry, also find large applications in food industry to colour food and beverages.

The problem to choose a suitable treatment to decolour industrial wastewaters is old and not yet definitively solved. When, already about 30 years ago, River Tyne (England) [1] waters acquired red colour from the industrial effluents discharged there, chlorination methods were firstly employed to decolour wastes. But the identification of up to 17 chlorinated organic species formed during the treatment, suggested that chlorination processes cause greater danger than the colour itself. Anyway, since environmental regulations in most of the countries made it mandatory to decolour industrial wastewaters prior to discharge, other strategies have been developed based on absorption, sedimentation, flotation, flocculation, ultrafiltration [2–7], as well as treatments based on chemical reactions of reduction [7–9], oxidation [12], ozonation [10,11], and photoreaction [13,14]. The use of ozone, which is a strong non-selective oxidizer as chlorine, appears to be a cleaner process but the chemical instability of ozone requires its generation on site with particularly high costs.

The use of all these techniques, a part the large quantity of sludge formed, the high costs, and the long time required, does not give any information on the nature of the products formed. The removal of colour is due to reactions that transform chromophoric groups into non chromophoric ones, but it does not assure for a complete mineralisation of the organic structure. This result is reported to be achievable in some cases by the use of biological methods able to completely degrade the dye molecule, but the method works only when a biological system is able to metabolise the structure of the dye [15]; the conventional biological treatments used for industrial and municipal wastewaters are not effective [16].

It is reported that some dyes are naturally decoloured as a consequence of prolonged exposure to sunlight: but in this case too the loss of colour does not mean complete mineralisation [17].

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For both natural or induced decolorization processes, in order to guarantee for a sure discharge, it is necessary to know the composition of the treated effluent streams and the nature of the intermediate degradation products.

Literature reports the study of the fading products of the dye Basic Yellow-2 that, in moist of acetonitrile containing amount of water lower than 1%, was irradiated for 96 h in a photolytic chamber containing 16 lamps emitting at 300 nm. By HPLC–MS and GC–MS the main degradation products identified in the faded dye were the Michler's ketone, formed in the hydrolysis reaction of $C{=}NH_2^+$ group to C=O and demethylation products [17]. Some authors report the formation of aromatic amines by exposure to natural light of some dyes [18–25], but this hypothesis must be discussed because aromatic amines are reported to be already present as impurities in many dye standards [18], as for example naphthylamine in amaranth [21] and *p*-cresidine and aniline in FD&C Red n. 40 [22].

Examples of degradation patterns that employ photocatalysis with TiO_2 as the catalyst are reported [16]. A characterization of methyl orange and its photocatalytic degradation products is reported by the use of HPLC–MS^n techniques [26]. MS, MS^2, and MS^3 fragmentation permitted the authors to collect information about the bonds that more easily break from collisions of suitable energy. Moreover the use of HPLC interfaced to both mass spectrometry and diode-array detectors permitted to discuss and propose a structure of the intermediates formed in the sulfonated dyes synthesis [27,28].

This paper considers the degradation of the E133 Brilliant Blue FCF (C.I. 42090) that is largely used in food industry to colour beverages, dairy products, powders, and syrups. The information about the degradation pattern and about the conditions of temperature and wavelength that preferentially favour the degradation process is of paramount importance for food dyes, since the results could suggest the best storage conditions of the commercial product, to avoid natural degradation processes and the formation of potentially toxic species.

The interest to follow the degradation pattern of this dye is related to its high absorptivity in UV–vis range and to the need to individuate a remediation strategy that not only gives uncoloured wastes but also could guarantee for the absence in the faded dye of species more toxic than the original dye. No information is available in literature about the degradation strategy of this dye and about its degradation products.

To study the degradation pathway, tuning the different procedures suggested in literature and based on both reduction and oxidation reactions, preliminary experiments suggested the use of persulfate associated to the irradiation at natural sunlight. Under these conditions the degradation process is low enough to make it possible to appreciate the formation of differently coloured species and to follow the degradation kinetics and identify the intermediates. This choice, that presents advantages in terms of cost, could be applied as a remediation strategy of wastewaters containing the largely used triphenylmethane dyes, at least in countries and seasons in which sunlight is disposable.

Due to the low volatility and the poor thermal stability of the dye, RP-HPLC techniques associated to MS and MS–MS spectrometric detection were employed [27,28].

2. Experimental

2.1. Reagents

Ultrapure water from a Millipor Milli-Q system (Milford, MA, USA) was used for the preparation of all the solutions. HPLC-grade methanol from Merck (Darmstadt, Germany) was filtered before use through a 0.45 μm membrane (Millex, Millipore). Brilliant Blue FCF (C.I. 42090—E133), ammonium iron (II) sulfate hexahydrate 98% and ferroin-indicator 0.1% water solution were purchased from Aldrich (Milwakee, WI, USA), potassium dichromate and sulfuric acid 96% were purchased from Carlo Erba (Milan, Italy). Potassium peroxydisulfate, acetic acid, triethylamine (TEA), barium hydroxide, tetrabutylammonium bromide (TBA), and dichloromethane were Merck (Darmstadt, Germany) analytical grade chemicals.

2.2. Instrumentation

The analyses were carried out by a Finnigan Mat Spectra System equipped with a Degaser SCM1000, a gradient pump Spectra System P4000, an Autosampler Spectra System AS3000, interfaced by the module SN4000 to a diode-array detector Spectra System UV6000LP and to ESI-MS ion trap detector Finnigan LCQ Duo.

A microprocessor pH meter (Hanna Instrument, Portugal), equipped with a combined glass-calomel electrode, was employed for pH measurements. The spectrophotometric analyses were carried out with a spectrophotometer Jasco V-550.

2.3. Samples preparation and pre-treatment

The 1000 mg/L standard solution of food-dye Brilliant Blue FCF was prepared in ultrapure water and kept in dark glass bottle at 4 °C. For the degradation studies three solutions were prepared 0.13 mM in dye and respectively, 0.13, 1.26, and 12.60 mM in potassium persulfate (molar dye/persulfate ratios 1/1, 1/10, and 1/100). The solution containing dye/persulfate in molar ratio 1/1 was diluted 1/20 (v/v) in ultrapure water prior the LC–MS analysis; that containing 1/10 molar ratio was diluted 1/50 (v/v). The solution with dye/persulfate ratio 1/100 must be pre-treated before the LC–MS analysis: 10.0 mL were added with 3.0 mL of 0.13 mM barium hydroxide solution of the solution in order to precipitate the excess of persulfate and sulfate produced during the degradation reaction. After centrifugation, the precipitate was removed, and 40.0 μL of tetrabutylammonium (TBA) bromide 100.0 mM were added to the solution to

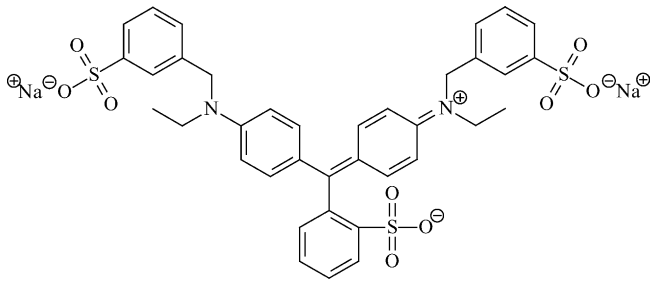

Fig. 1. Molecular structure of dye Brilliant Blue FCF (E133—C.I. 42090).

form an ion pair with the dye that was extracted in 3.0 mL of dichloromethane. The extract was treated in Rotavapor and the residue collected in 5.0 mL of ultrapure water. The sample was diluted 1/100 (v/v) before the LC–MS analysis.

2.4. Degradation experiments

To study the degradation mechanism of the dye, oxidative conditions of degradation were simulated. Preliminary experiments showed that the rate of the oxidation reaction obtained for addition of Fenton reagent is too fast and it does not permit to follow the intermediate steps.

Also in the presence of persulfate as the oxidising agent and UV lamp irradiation (wavelength 254 nm), the degradation process is too quick, while the use of persulfate and natural sunlight permitted to follow the kinetics and to identify some intermediates.

Solutions containing dye/persulfate ratios, respectively 1/1, 1/10, and 1/100 were exposed in sealed glass vials for 2 months (May and June) at full sunlight with a strong solar irradiation. The colour variations as a function of time, that could be appreciated also with naked eye, were followed spectrophotometrically and the solutions were analyzed as a function of time by LC–MS to follow the concentration of the dye still present and the possible formation of new species along the degradation process.

2.5. Chemical oxygen demand (COD) determination method

In a distillation flask, we added to 5.0 mL of the degraded colourless solution containing a dye/persulfate 1/100 molar ratio, 5.0 mL of $K_2Cr_2O_7$ 0.25N and 7.0 mL of H_2SO_4 (96%, w/w). This solution was kept thermostatised at 20 °C in order to avoid the possible loss of volatile species. The acid solution was then boiled for 2 h in reflux conditions, cooled and added with three drops of ferroin-indicator. The dichromate excess was titrated by a 0.25N solution of ammonium iron (II) sulfate hexahydrate until the solution colour changed from blue–green to dark red.

Under the same degradation conditions as the sample, we carried out a blank experiment on 5.0 mL of 12.60 mM persulfate solution.

Table 1
MS^n characterization of Brillant Blue FCF

m/z	MS	Fragment
373	MS	$[M–2Na]^{2-}$
769	MS	$[M–Na]^-$
689	MS^2	$[M–NaSO_3]^-$
495	MS^3	$[M–2\ NaSO_3{-}CH_3$ $]^-$
453	MS^4	$[M–2\ NaSO_3{-}CH_3$ $-CH_3NCH_3]^-$
424	MS^5	$[M–2\ NaSO_3{-}CH_3$ $-CH_3NCH_3{-}CH_2CH_3]^-$
747	MS	$[M–2Na + H]^-$
667	MS^2	$[M–2\ NaSO_3 + H]^-$
587	MS^3	$[M–2\ NaSO_3]^-$
558	MS^4	$[M–2\ NaSO_3 + H{-}CH_2CH_3]^-$
529	MS^5	$[M–2\ NaSO_3 + H{-}2CH_2CH_3]^-$

The chemical oxygen demand was calculated through the following formula:

$$\frac{(v_1 - v_2)\, N\, 8000}{v}$$

where v_1 and v_2 are the volumes (mL) of ammonium iron (II) sulfate hexahydrate solution, respectively used in the blank titration and in the sample titration, N is the normality of the ammonium iron (II) sulfate hexahydrate used solution; v is

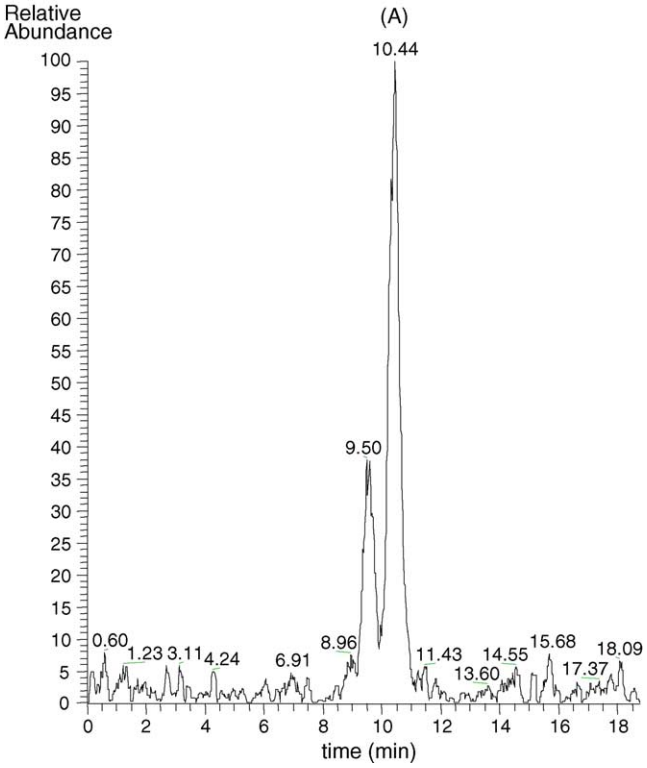

Fig. 2. LC–MS chromatogram of 2.0 mg/L Brillant Blue FCF. Stationary phase: Lichrospher 100 RP-18 column (250 mm × 4 mm, 5 μm) with a (15.0 mm × 4 mm) Lichrospher RP-18 (5 μm) guard precolumn. Mobile phase: methanol/triethylamine 5.00 mM and acetic acid 5.00 mM aqueous solution at pH 6.50 (45/55 (v/v)); flow rate 0.30 mL min^{-1} and injection volume 20 μl. Detector MS. Peak identification: 10.44 min dye major peak (the others peaks are due to undocumented impurities in standard dye).

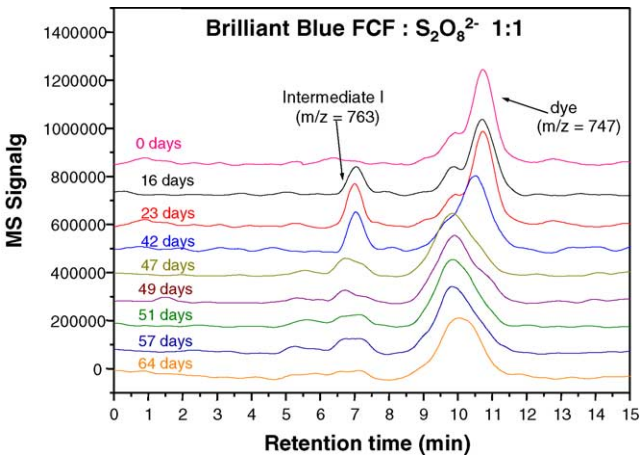

Fig. 3. Chromatograms of the separation between the dye and its degradation product in the solution 1/1 dye/persulfate ratio. Chromatographic conditions as in Fig. 1.

the volume (mL) of the sample solution; 8000 is the oxygen equivalent weight multiplied for 1000, to report the COD value at the volume of 1 L.

2.6. Chromatographic conditions

Two stationary phases were used and namely an end-capped Lichrospher 100 RP-18 column (250 mm × 4 mm, 5 μm) (Merck, Darmstadt, Germany) with a (15.0 mm × 4 mm) Lichrospher RP-18 (5 μm) guard precolumn and a Polaris C18-Ether column (150 mm × 4.6 mm, 5 μm) (Varian, CA, USA).

For the solution containing a dye/persulfate ratio 1/1, chromatographic analysis was performed under isocratic conditions using a RP-C18 stationary phase and a mobile phase composed of 45% methanol and 55% aqueous solution of triethylamine 5.00 mM and acetic acid 5.00 mM, pH 6.50; flow rate was 0.30 mL min^{-1} and the injection volume 20.0 μL.

For the solutions containing molar dye/persulfate ratios of 1/10 and 1/100, the chromatographic analysis was performed under isocratic conditions using a Polaris C18-Ether stationary phase and a mobile phase 45/55 (v/v) methanol–water pH 5.00 (acetic acid); flow rate was 0.30 mL min^{-1} and the injection volume 20.0 μL.

2.7. Mass spectrometry conditions

The MS experiments were conducted by means of Thermoquest LCQ DUO ion trap mass spectrometer from Finnigan (San Jose, CA, USA) equipped with an atmospheric pressure ionization (API) interface and an electrospray (ESI) ion source. High purity nitrogen was used as nebulizer (operating pressure at 60 of the arbitrary scale 0–100 of the instrument), and helium (>99.999%) served as quenching agent. The ESI probe tip and capillary potential were set at 4.50 kV and −30.00 V, respectively. The heated capillary was set at 300 °C and ion optics parameter were optimized to the following value: tube lens offset, 10.00 V; first octapole voltage, 4.75; inter octapole lens voltage, 30.00; second octapole voltage, 6.00.

The mass to charge range was 200–1000 *m/z*. The mass spectrometer was operated in negative ion full-scan

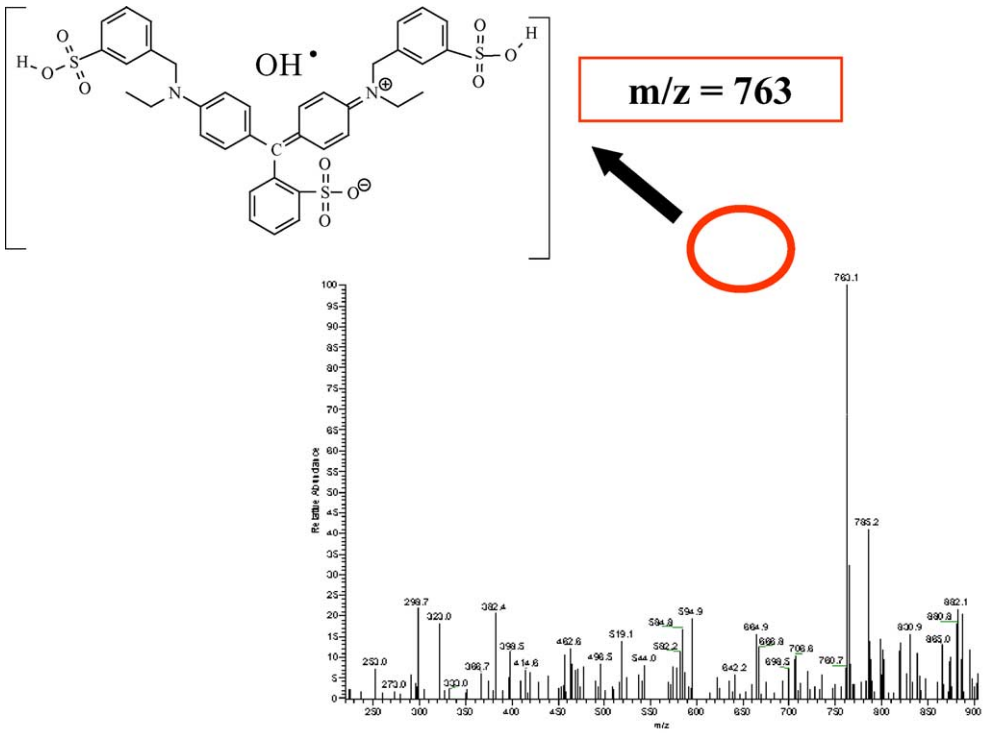

Fig. 4. Mass spectrum of the degradation intermediate I and relating proposed structure.

mode (three micro scans, 50 ms inlet time) and in MS^n mode.

3. Results and discussion

3.1. Characterization of Brilliant Blue FCF with mass spectrometry and liquid chromatography

As the first step in this study, the mass characterization of the dye was performed through the identification of the major product-ions that form in the collisional sequential fragmentations of MS^n analysis. This study could be useful for the degradation study, since it could suggest the presence of possible degradation products characterized by structures comparable with those obtained in the MS–MS fragmentation process.

ESI mass spectra profiles (MS, MS^2, MS^3, MS^4, MS^5) were obtained by direct infusion in ESI ion source of 10.0 mg/L methanolic solution of the standard (at flow rate of 20.0 μL min^{-1}). The dye structure shows three negative sulphonated groups saturated with Na^+, and one protonable positive aminic group (Fig. 1). Due to the presence in the molecule of three anionic groups the characterization study was carried out in negative ion-mode.

The molecular mass of the dye is 792 amu; the molecule provides well recognizable signals corresponding to three negative ions at *m*/*z* 373, 747, and 769. The peak at *m*/*z* 373 is due to the $[M–2Na]^{2-}$, whereas the peaks at *m*/*z* 747 and 769 represent $[M–2Na + H]^-$ and $[M–Na]^-$, respectively. In the characterization study performed as a function of temperature it was observed that the peaks corresponding to monocharge structures prevail at higher temperatures, whereas the peak corresponding to bi-charge structure prevails at lower temperatures. Each precursor ion peak was then fragmented with MS^n analysis and the characteristic product ions are summarized in Table 1.

Fig. 2 reports the LC–MS chromatogram obtained for a 2.0 mg/L standard solution of the dye and shows the presence of three peaks, as already observed by other authors [18]. The major peak A is considered. The mobile phase is a 45/55 (v/v) methanol–water mixture pH 6.50 (acetic acid) and 5.00 mM in triethylamine, that behaves as a ion-pairing reagent towards the polar analytes and at same time presents chemical properties suitable for mass analysis [29].

The eluent from the chromatographic column firstly enters the UV–vis diode-array detector, then in the ESI interface and in the ion trap mass analyzer. The method conditions used in

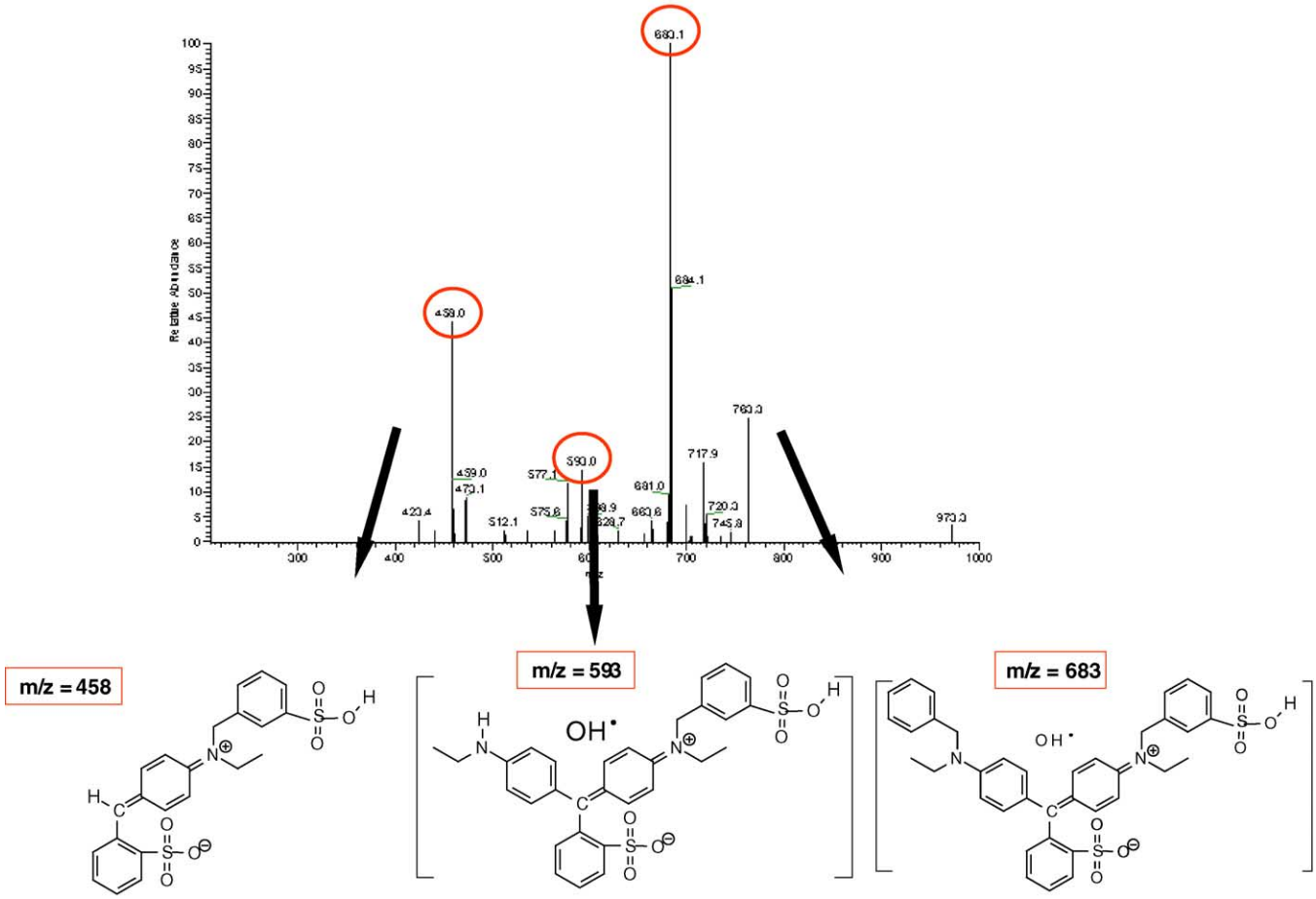

Fig. 5. MS/MS spectrum of the 763 *m*/*z* peak (collision energy 30 eV) of intermediate I and relating proposed structures.

the MS analysis make use of the tuning method optimized for the peak at 747 amu.

3.2. Degradation studies of the dye

As mentioned, a degradation study of the dye was performed under oxidative conditions obtained by addition of sodium persulfate and irradiation with sunlight. In order to evaluate if and how much the degradation extent is affected by persulfate to dye ratio, solutions containing persulfate to dye molar ratios of 1, 10, 100 were studied.

3.2.1. Dye/persulfate 1/1

A solution containing a mixture of the dye and persulfate in molar ratio 1/1 was exposed to solar irradiation and the behaviour was followed as a function of time by HPLC analysis under the chromatographic conditions previously described. The solution colour observed at naked eye changed from the Brilliant Blue FCF colour to dark blue in about 16 days and to dark green colour after 40 days of exposition. Fig. 3 illustrates the variation of the chromatographic response along time. At time = 0 we can observe the presence of the peak of the dye at 10.70 min together with a peak at about 9.80 min that corresponds to the not declared impurities contained in the standard. After 16 days of exposure to sunlight we can observe a decrease of the peak area of the dye and the presence of a new peak (labelled I) that can be ascribed to the formation of a degradation product.

Along time the peak area of the dye (*m*/*z* 747) progressively decreases while the peak area of intermediate I firstly increases and then progressively decreases till to become not detectable after irradiation times of about 64 days. As concerns the impurities contained in the standard, their absolute areas practically do not vary along time (the chromatograms of Fig. 3 are reported with different full scale unities).

The peak of species I shows a mass spectrum characterized by a signal at *m*/*z* 763, that corresponds to a hydroxylation of the parent molecule. Fig. 4 reports the mass spectrum of the intermediate I and the proposed structures. The structure assigned to the *m*/*z* 763 peak corresponds to an electrophilic addition reaction of hydroxyl group on aromatic ring, indicated in the figure as a general position, since five similar aromatic rings are present [30]. Another peak is clearly recognizable at *m*/*z* 785 accounting for the sodium adduct of the molecule.

The MS/MS analysis of the *m*/*z* 763 peak of the intermediate I produces the spectrum reported in Fig. 5, which shows three signals corresponding respectively, to a loss of *m*/*z* 80,

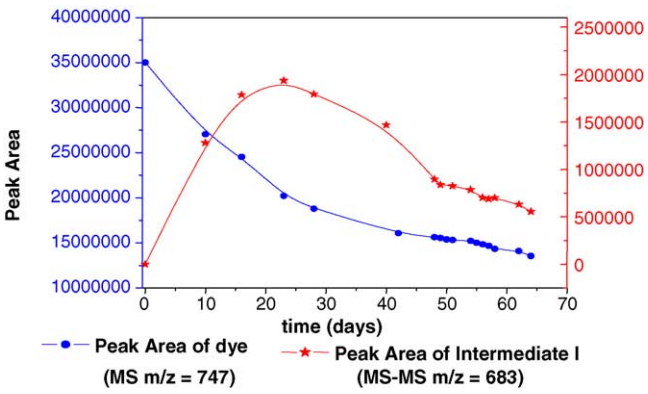

Fig. 6. Peak areas of the dye (747 *m*/*z*) and of the intermediate I (683 *m*/*z*) in the solution 1/1 dye/persulfate ratio as a function of time.

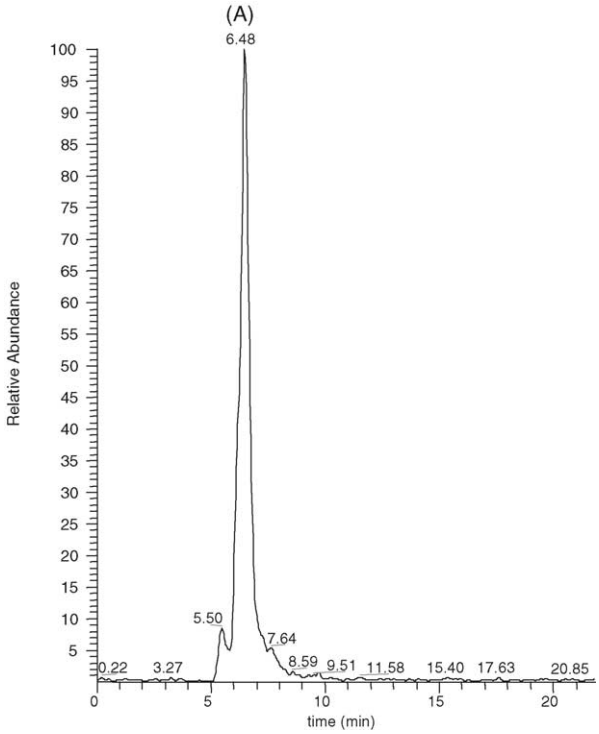

Fig. 7. LC–MS chromatogram of 2.0 mg/L Brillant Blue FCF. Stationary phase: Polaris C18-Ether column (150 mm × 4.6 mm, 5 μm). Mobile phase: methanol/water pH 5.00 for acetic acid 45/55 (v/v); flow rate 0.30 mL min^{-1} and injection volume 20 μl. Detector MS. Peak identification: 6.48 min: dye (the other peaks are due to undocumented impurities in the standard dye).

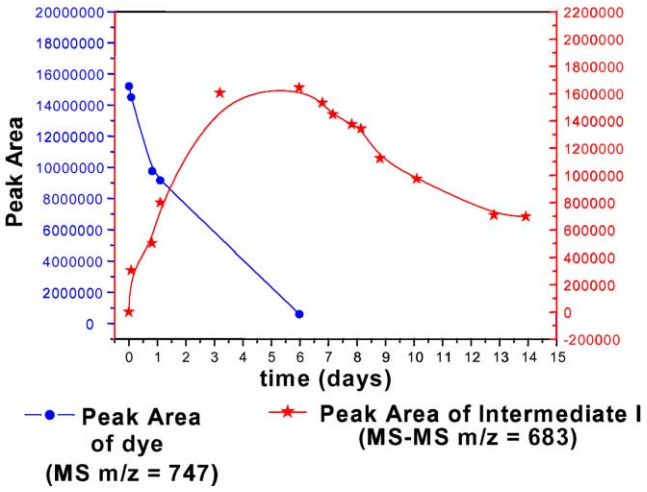

Fig. 8. Peak areas of the dye (747 *m*/*z*) and of the intermediate I (683 *m*/*z*) in the solution 1/10 dye/persulfate molar ratio as a function of time.

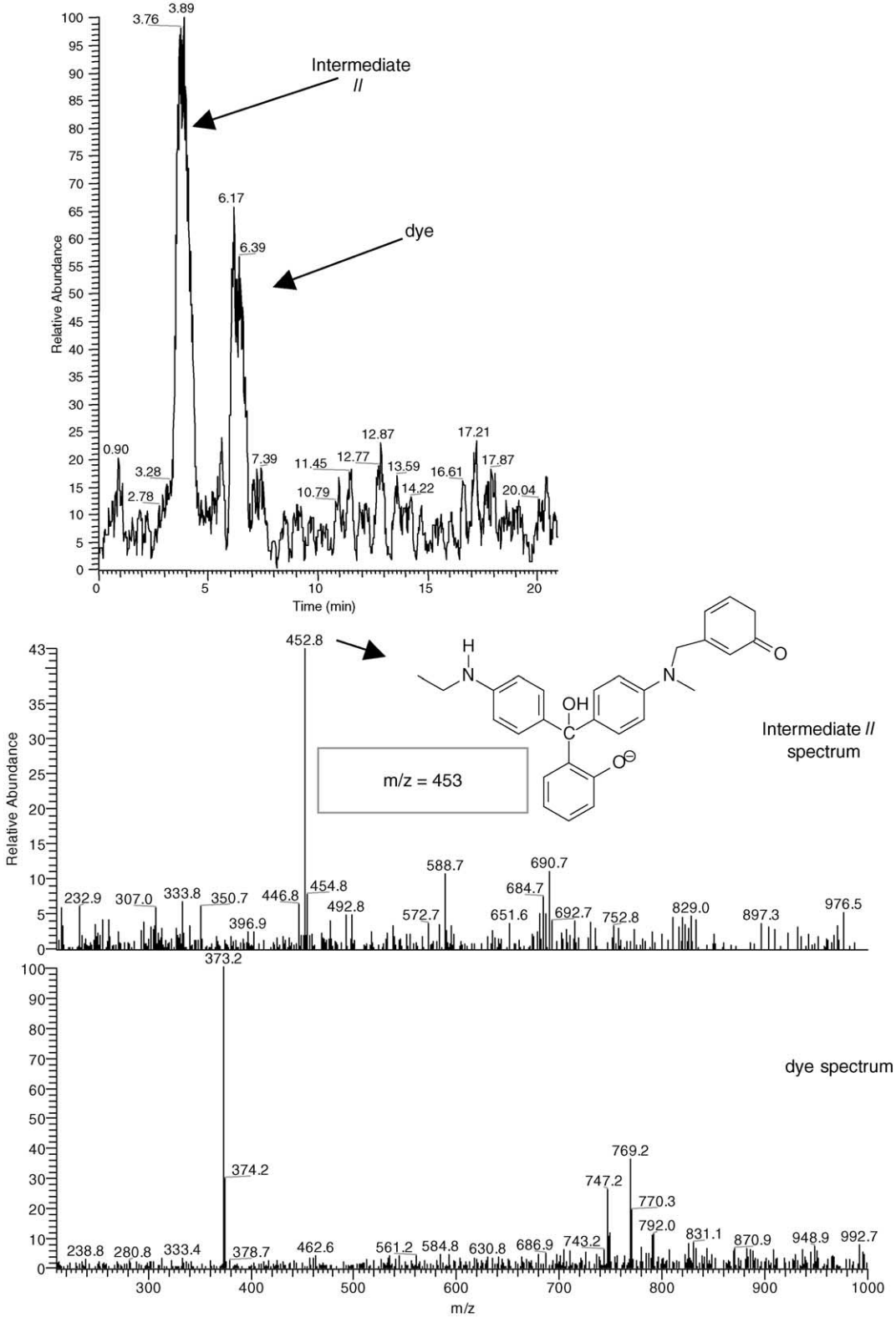

Fig. 9. TIC chromatogram of the solution containing a 1/100 dye/persulfate molar ratio recorded after 5.0 min from the addition of persulfate. Chromatographic conditions as in Fig. 6.

170, and 305 with respect to the precursor ion. These mass losses can be explained with the structures reported in Fig. 5, that are compatible with the structure proposed for I.

In order to follow the kinetics of the degradation process of the dye and the behaviour of the degradation product I, we recorded the peak areas of the dye (*m/z* 747) and of the product ion at *m/z* 683 formed by MS/MS experiments performed on *m/z* 763 signal (collision energy 30 eV) as a function of time. The areas, plotted in Fig. 6 as a function of time, show that the signal due to the intermediate I progressively increases and reaches its maximum in about 23 days, afterwards it decreases. In the same time window, the dye progressively decreases reaching a stable non null value at about 50 days. After about 60 days no further significant change seems to occur in the solution: in these conditions the signal given by the unreacted dye is about 28% of the signal recorded at time = 0.

3.2.2. Dye/persulfate 1/10

The solution containing a molar persulfate to dye ratio equal to 10 was diluted 1/50 prior the injection, in order not to damage the MS system. The stationary phase used in the chromatographic separation is a Polaris C18-Ether reversed-phase column, specifically built to present some polar proprieties. The use of this stationary phase did not require the addition to the mobile phase of ion pairing agent to separate the dye and its degradation products.

Fig. 7 reports the chromatogram recorded with a 45/55 (v/v) methanol/water mobile phase for a solution containing 2.0 mg/L of dye in the presence of persulfate (molar ratio dye/persulfate 1/10). The chromatogram shows, as already observed for solutions containing a 1/1 dye/persulfate ratio, beside the major peak (A) also the presence of other two peaks.

The degradation process produces the same intermediate I obtained in solutions containing a molar dye/persulfate ratio of 1/1, but it is much faster. In fact, in Fig. 8 the areas of the peaks of the dye (*m/z* 747) and of the degradation intermediate I (*m/z* 683) reported as a function of elapsed time show that the peak area of the intermediate reaches its maximum in only 5 days. The signal of the dye is progressively decreasing up to become undetectable in about 6 days. On the contrary the intermediate after 14 days still shows a detectable signal that is (about 43% of its maximum).

3.2.3. Dye/persulfate 1/100

To evaluate if the degradation process continues and to further verify the effect of the excess of persulfate, we increased the persulfate concentration until to reach a 1/100 dye/persulfate ratio. The high concentration of the non-volatile salt, that could damage the mass spectrometer and suppress and perturbate the mass signal, firstly suggested to dilute the solution 1/600 (v/v) prior the injection in the LC–MS system. Since in these conditions the mass signal was not sensitive enough, the following cleaning procedure was developed for the chromatographic analysis. As described in detail in Section 2, barium hydroxide was added to separate for precipitation the persulfate unreacted and the sulfate formed. The dye was extracted from the aqueous filtered solution in dichloromethane as ion pair with tetrabutylammonium. The dichloromethane extract was evaporated, collected with 5.0 mL of ultrapure water, diluted 1/100 by ultrapure water and injected in the LC–MS system.

The chromatogram obtained for a solution collected 5.0 min after the addition of persulfate shows (Fig. 9) the presence of a new peak eluting at about 3.80 min and characterized by a signal at *m/z* 453 in the mass spectrum. This species likely corresponds to another degradation product of the dye (intermediate II), that likely forms (Fig. 10) by the loss of a methyl group in the chain, of two $-SO_2$ groups from the sulphonates groups and of a fragment of molecule bound to the aminic group. In this structure the –OH group is hypothesized to be bound to the central carbon atom. The absence for this structure of a possible resonance effect is in agreement with its absence of colour in UV–vis wavelength range. Its behaviour as a function of time is shown in Fig. 11:

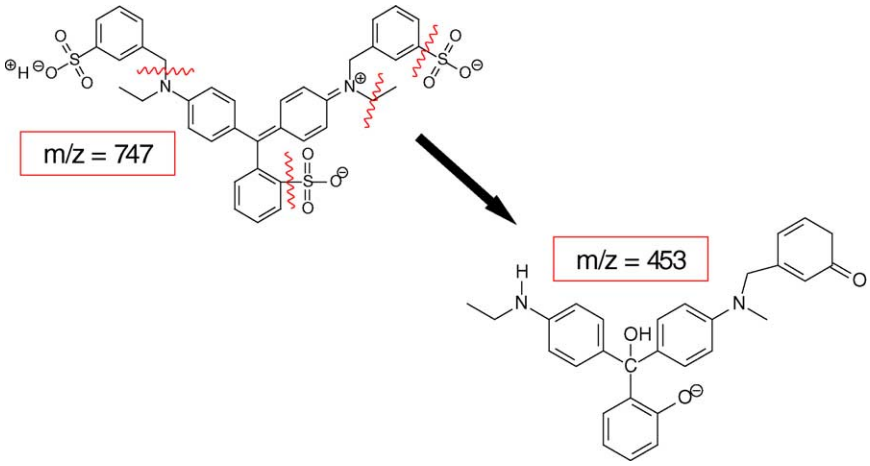

Fig. 10. Dye structure and degradation pathway suggested for the formation of the intermediate II (*m/z* 453).

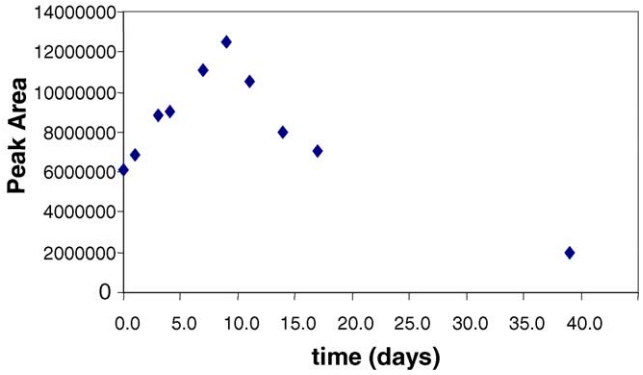

Fig. 11. Peak area of the intermediate II (*m/z* 453) in the solution 1/100 dye/persulphate ratio as a function of time.

the peak area of the compound corresponding to the signal at *m/z* 453 reaches its maximum in 8 days and afterwards decreases, to become about 14% of its maximum for times of about 35 days.

In order to estimate the extent of oxidative degradation of the species present in the colourless solutions obtained after 6 days, the chemical oxygen demand was also measured according to the method IRSA-CNR n. 5110 [31].

The COD value at time = 0 is 280.0 mg/L, whereas when the solution is colourless, the COD value reduces until 80 mg/L. The 71% decrease in COD that accompanies decolorization indicates that the organics species are being oxidatively decomposed.

Therefore, we hypothesized that the predominant species present in the colourless degraded solution is the intermediate II. The COD titration performed on the colourless solution obtained with the same concentration of persulfate and UV lamp irradiation gives similar results.

Up to now, the conditions inducing a further degradation have not been envisaged.

4. Conclusion

The use of HPLC–MS technique allows to identificate some degradation intermediates of the food colour Brilliant Blue FCF obtained by the oxidative treatment with persulfate addition and sunlight irradiation. The structural information concerning the degradation achieved by MS and MS–MS studies are compatible with oxidative degradation pathway reported in literature for similar dyes [32].

It was shown that persulfate excess heavily affects the velocity of the degradation process. Anyway, also in the presence of a molar persulfate to dye ratio = 100, both HPLC–MS analysis and COD evaluation showed that the faded dye still contains relevant concentration of organic matter, predominantly identified as the intermediate II.

No information is available about the direct or the potential toxicity of this species, since a further degradation step can not be excluded leading to the possible formation of aromatic amines, as suggested by many degradation studies of different dyes reported in literature [18–25].

These results underline the importance of this kind of studies in order to develop remediation strategies for industrial effluents not only addressed to decolour wastes but also assuring for the safety of the products formed.

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