



HAL
open science

The use HPTLC and Direct Analysis in Real Time-Of-Flight Mass Spectrometry DART-TOF-MS for rapid analysis of degradation by oxidation and sonication of an azo dye

Hayet Djelal, Carole Cornée, Ronan Tardivel, Olivier Lavastre, Abdeltif Amrane

► To cite this version:

Hayet Djelal, Carole Cornée, Ronan Tardivel, Olivier Lavastre, Abdeltif Amrane. The use HPTLC and Direct Analysis in Real Time-Of-Flight Mass Spectrometry DART-TOF-MS for rapid analysis of degradation by oxidation and sonication of an azo dye. *Arabian Journal of Chemistry*, 2017, 10 (Supplement 2), pp.S1619-S1628. 10.1016/j.arabjc.2013.06.003 . hal-00840315

HAL Id: hal-00840315

<https://hal-univ-rennes1.archives-ouvertes.fr/hal-00840315>

Submitted on 5 Jul 2013

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

The use of HPTLC and Direct Analysis in Real Time-Of-Flight Mass Spectrometry (DART-TOF-MS) for rapid analysis of degradation by oxidation and sonication of an azo dye

Hayet Djelal^{1*}, Carole Cornée², Ronan Tartivel³, Olivier Lavastre³, Abdeltif Amrane⁴

¹Ecole des Métiers de l'Environnement, Campus de Ker Lann, 35170 Bruz, France.

²CITRENNES Platform, Université de Rennes 1, Campus de Beaulieu, CS 74205, 35042 Rennes Cedex, France.

³IETR UMR CNRS-Université Rennes1 6164, Campus de Beaulieu, CS 74205, 35042 Rennes Cedex, France.

⁴Université Rennes 1, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France.

*Corresponding author: Tel.: (+33) 2 99 05 88 00; Fax: (+33) 2 99 05 88 09;

E-mail: hayetdjelal@ecole-eme.com

Abstract

Advanced oxidation processes are efficient for the removal of recalcitrant compounds, like azo-dyes. However, the intermediates produced during their degradation can be more toxic than the parent compounds. Improving the knowledge concerning the degradation pathways may be therefore helpful to optimize the process. In this aim, HPTLC and Direct Analysis in Real Time-Of-Flight Mass Spectrometry (DART-TOF-MS) were considered and applied to analyze the sono-oxidation of an azo dye, methyl red sodium salt (MRSS) as a model compound. Initial and final UV-Vis spectra showed a clear disappearance of the maximum absorption peak, but shows limit since it cannot allow by-products identification. MRSS degradation was confirmed by HPTLC, which also confirmed that MRSS degradation was mainly due to oxidation, while in the considered experimental conditions the sonication effect appeared negligible. The analysis by DART-TOF-MS of the MRSS is characterized by a peak at $m/z = 279.137$. Three major peaks were observed after the MRSS oxidation: $m/z=139.002$, $m/z=223.073$ and $m/z=279.137$. Relative abundance of $m/z=139.002$, which was much higher after oxidation, tends to prove that a large proportion of initial oxydized MRSS was fragmented. The coupling of HPTLC and DART-TOF-MS may be subsequently considered to identify the oxidation reaction products.

Keywords: HPTLC, DART-TOF-MS, Azo dyes, MRSS, sono-oxidation

1. Introduction

Organic dyes constitute one of the larger groups of pollutants in wastewater. These effluents may cause environmental, visual and chemical pollution. Amongst the 10^6 tons per year of dyes annually produced, about 60-70 % were azo-dyes (Neamtu et al., 2002), which constitute therefore the largest group of dyes used in industry, and about 15 % are released in the environment. This class of dyes is characterized by an azo linkage $N=N$, a visible light chromophore. They are potentially toxic, as well as their by-products, including aromatic amines (Arslan et al., 2000. Dominguez et al., 2005); they can also perturb aquatic life since some azo-dyes and their degradation products are highly carcinogenic (Brown and De Vito, 1993). For instance, the anionic dye, Methyl red, is used in paper printing and textile dyeing (Lachheb et al., 2002), as well as in the food industry (Muthuraman and Teng, 2009. Kucharska and Grabka, 2010); its impact on human health is irritation of eye, skin and digestive tract if inhaled or swallowed (Robinson et al., 2001).

Physical techniques can be used to remove these recalcitrant pollutants (Vandevivere et al., 1998; Chaudhuri and Sur, 2000) among them: adsorption, flocculation, electro-flocculation, reverse osmosis, ultrafiltration, coagulation have been applied. The main drawback is the frequent need for expensive regeneration and post-treatment processes, owing to the non destructive characteristic of these processes. Indeed, the pollutant is only transferred to another phase (Arslan et al., 2000; Stock et al., 2000; Comninellis et al., 2008). Advanced Oxidation Processes (AOP) appear as an interesting way for the treatment of this pollution (Bizani et al., 2006; Brosillon et al., 2008. Chebli et al., 2010; Kayan et al., 2010). An alternative method is the sonocatalytic degradation in the presence of $Fe^{2+}/H_2O_2/ S_2O_8^{2-}$ (Grcic et al., 2010) or in the presence of CeO_2/TiO_2 (Wang et al., 2010).

Several analytical methods have been published for the determination of azo-dyes and their degradation by-products based on UV (Brosillon et al., 2008. Muthuraman and Teng, 2009), HPLC (Scarpi et al., 1998. Kucharska and Grabka, 2010; Kayan et al., 2010), capillary electrophoresis (Borros et al., 1999) and HPTLC (Kucharska and Grabka, 2010).

Thin Layer Chromatography Technique is the easiest one, because there is no need to expensive and complex apparatus (Somsen 1995; Lavastre et al., 2003). HPTLC is a powerful analytical technique because of its reliability, simplicity, reproducibility and rapid measurement. This method is economical as it requires small amounts of solvents with minimum sample clean up, and its main advantage is that a large number of samples can be simultaneously analyzed (Kotiyani and Vavia, 2000; Neamtu et al., 2002; Chopra et al., 2006). Choosing the appropriate mobile and stationary phases is the sole difficult of the method. For a qualitative determination of a mixture of dyes, the TLC method is the best solution (Kucharska and Grabka, 2010).

High Performance Thin-Layer Chromatography is a derivative of TLC. This method is based on the use of appropriate plates, which ensures a better separation of the analyzed compounds, leading to satisfactory results on the shortest developing distance. In addition, Direct Analysis in Real Time-Of-Flight Mass Spectrometry DART-TOF-MS was introduced in 2005 (Cody, 2005). This method is interesting because of its ability to analyse very different samples with minimal destructive sampling and without sample preparation and chromatography (Hajslova and Zrostlikova, 2003; Morlock and Ueda, 2007; Cajka et al., 2008; Curtis et al., 2009). DART-MS technique is an emerging tool for diverse application, as food quality and safety control (Hajslova et al., 2011; Kim et al., 2011; Chernetsova and Morlock, 2012), biological fluids and tissues, drugs, narcotics (Cody, 2005; Navare et al., 2010; Chernetsova et al., 2011; Zeng et al., 2012; Shena et al., 2012), printing and writing paper (Adams, 2011) and phtalic acid ester in poly(vinyl chloride) samples (Kuki et al.,

2011). The results show DART-MS to be a very promising tool for the rapid analysis of important markers in crude products (Shena et al., 2012).

The aim of the present work was to use HPTLC and Direct Analysis in Real Time (DART) for study chemical degradation of organic compounds. HPTLC and DART were considered and applied to analyze the sono-oxidation of an azo dye, methyl red sodium salt (MRSS) as a model compound. Like for other oxidative processes, the intermediates produced during the photocatalytic degradation of dyes with or without addition of H_2O_2 and $\text{K}_2\text{S}_2\text{O}_8$ can be more toxic than the parent compounds (Bizani et al., 2006). Improving the knowledge concerning the degradation pathways may be therefore helpful to optimize the process by identification of the by-products and hence help in the determination of the metabolic degradation pathways

2. Materials and methods

2.1 Chemicals and reagents

The chosen azo dye, methyl red sodium salt (MRSS) (Colour Index Number 13020), was purchased from Sigma Aldrich (Isle d'Abeau Chesnes, France) and used without further purification, owing to its high purity, at least 99%. The molecular structure of the dye is given in Fig.1. Purified water (Elix Millipore equipment, Guyancourt, France) was used to prepare the colored solution.

Hydrogen peroxide 100 volumes and potassium peroxydisulfate were purchased from Merck (Darmstadt, Germany) and VWR (Fontenay sous Bois, France), respectively.

Dichlormethane, ethyle acetate, acetonitrile, toluene, heptane, n-hexane, chloroform, 1,4-dioxane and methanol were of analytical-reagent grade. Plate prewashing was performed with methanol of HPLC-grade (Carlo Erba, Val de Reuil, France).

As stationary phases, the following plate (Merck) was used: silica gel glass HPTLC plate 60 F₂₅₄ (10×10cm).

2.2 Sono-oxidation

Ultrasonic apparatus (Vibra cell, Sonics & Materials Inc., Danbury, CT., USA) was adopted to irradiate the MRSS solution. It was carried out at an ultrasonic frequency of 20 KHz and an output power of 40 W through manual adjustment according to the available related literature (Hajslova et al., 2011); pH (Eutech Instruments, Thermo-Fisher Scientific, Illkirch, France) and temperature were monitored during experiments.

Dye solutions were prepared at 100 mg L⁻¹ and stored at 4°C, in the dark. The sonocatalytic degradation of MRSS (100 mL) was performed using hydrogen peroxide (30% w/w) and potassium peroxydisulfate, each at 10 mmol.L⁻¹ final concentration during 2 hours at room temperature under magnetic stirring (250 rpm). Before analysis, oxidation samples were filtered through a Millipore filter (Millex[®]-HV-0.45 µm) to avoid particles entering the analytical apparatus.

The study is based on four conditions: MRSS in ultrapure water (condition n°1), MRSS in ultrapure water after sonication treatment (condition n°2), MRSS with K₂S₂O₈ + H₂O₂ before sonication treatment (condition n°3) and MRSS with K₂S₂O₈ + H₂O₂ after treatment by sonication (condition n°4).

2.3 Sample analysis

2.3.1 Spectrophotometer

MRSS oxidation was followed by means of a UV–Vis Thermospectronic Helios 8 spectrophotometer (Bioblock scientific, Illkirch, France) at the maximum absorption or isobestic wavelength of MRSS.

2.3.2 HPTLC

HPTLC plates were prewashed with methanol and dried in a current air under the extractor hood for 20 min.

Narrow bands of 8 mm in length were sprayed using the Automatic TLC sampler 4 (ATS4, CAMAG). Pre-recorded application parameters for water and nozzle temperature of 40 °C were employed.

15 µL of each MRSS conditions were sprayed on the plate. After drying the starting zones for 1 min, the silica gel plate was developed with each solvent according to the CAMAG method, in order to find the best eluent. Development was performed in the Twin Trough Chamber (TTC 20×10 cm, CAMAG) up to a migration distance of 70 mm measured from the lower plate edge. After drying for 10 min, densitometry was performed via absorbance measurement at wavelength 466 nm corresponding to the isobestic point, the point at which the spectra recorded for various pH cross each other, and wavelength 501 nm corresponding to the maximum absorbance, with TLC Scanner 3 (CAMAG); evaluation was performed via peak height. Owing to the pH effect on the absorbance previously observed for MRSS (Chebli et al., 2010), the isobestic point was mainly considered in this work instead of the maximum absorption point.

For digital documentation, the Digistore 2 Documentation System (CAMAG) consisting of illuminator Reprostar 3 with digital camera Baumer optronic DXA252 was applied in the reflectance mode at UV 254 nm. Exposure time was set for 400 ms and gain at 1. Data obtained were processed with WinCATS software, version 1.4.2 (CAMAG). The exact zone positions were marked.

For calibration curves of MRSS, two solutions of MRSS ($0.1 \mu\text{g } \mu\text{L}^{-1}$ and $1 \mu\text{g } \mu\text{L}^{-1}$) were prepared in ultrapure water. Different volumes of the two stock solution were sprayed on three HPTLC plates to obtain masses of 0.1, 0.5, 1.5, 10, 15, 20, 25 $\mu\text{g spot}^{-1}$ of MRSS. The data of peak areas at 466 nm plotted against the corresponding concentrations were treated by a polynomial analysis.

2.3.3 DART-MS

Samples were automatically introduced into the excited gas stream of DART (IonSense, Danvers, MA, USA) which was installed on a JMS-T100LC (AccuTOF-LC) [Jeol (Europe), Croissy sur Seine, France]. Helium was used as gas with a flow rate of 2.5 L/min and the gas heater was set to 250°C. The distance between the first orifice lens and the exit of the DART gas flow was fixed to 15 mm. The needle voltage of the dart was 2 kV. For positive-ion detection the potentials of the second perforated electrode and the grid electrode were biased to positive potentials of 11 V and 250 V, respectively. The first orifice lens, that is, the interface for atmospheric pressure state, was set to 35 V, the spectra recording interval was 0.5 s. The mixture solution of polyethylene glycol PEG 600 was used as calibrant for the mass scale. The resolution of mass spectrometer (AccuTOF CS) was 6000 DA at full width of the peak at half its maximum height. For the data acquisition and processing, MassCenter 1.3

software was used. When a sample was introduced in the DART gas stream, the peaks of the target compound appeared immediately on the TIC or mass chromatograms.

3. Results and discussion

3.1 Oxidation study of MRSS by UV-vis absorption spectra

MRSS UV-VIS spectrum is displayed in Fig.2. As shown, maximum absorption wavelength was observed at 501 nm, in agreement with a previous report (Chebli et al., 2010).

Both sonication and oxidation, as well as their combination, were tested for MRSS degradation.

Ultrasound has been therefore combined to oxidation involving H_2O_2 and $\text{S}_2\text{O}_8^{2-}$. Dye sono-oxidation was carried out for 2 h, but did not allow to improving the degradation yield (30 %) at 501 nm, if compared to the direct oxidation. Initial and final UV-Vis spectra showed a clear disappearance of the maximum absorption peak, at 501 nm (Fig.2), which corresponded most likely to the main chromophore, the azo-linkage. The peak recorded at 300 nm corresponded most likely to the naphthalene ring, as well as the benzene ring peak observed at 221 nm (Chebli et al., 2010) (Fig.2).

3.2 Oxidation study of MRSS by HPTLC

The spectrophotometric method (UV-Vis) shows limit, since it cannot allow by-products identification. To improve the identification of sono-oxidation by-products, more fine analytical techniques should be considered. In this aim HPTLC has been considered.

Development of the optimum mobile phase

The first step consisted in the development of the method. The HPTLC procedure was optimized according to the “Camag method”. It consists in developing plates with each pure solvent. The most appropriate protocol is to test one or two solvents from eight classes of the Snyder triangle. The solvents that move the compounds onto the plate were selected; and then mixtures of solvents were tested until the best eluent was found.

15 μL of the MRSS dye (condition n°1) was sprayed on fourteen silica gel HPTLC plates and they were developed with the following solvents (Table 1). Finally, the mobile phase consisting of chloroform (100 %) gave a sharp and well-defined peak at $R_f = 0.10$ (Fig.3). Well-defined spots were obtained when the chamber was saturated with the mobile phase for 30 min at room temperature. Diffuse spots were obtained with others solvents.

Calibration curves

The developed HPTLC method for the determination of MRSS showed a correlation coefficient $r^2 = 0.9896$ in a mass range of 0.1- 25 $\mu\text{g spot}^{-1}$ with respect to the peak area at 466 nm (Fig.5), showing an easy and quantitative monitoring of the target compound removal.

3.3 Oxidation study of MRSS

In a first step, 15 μL of the MRSS dye were also sprayed (condition n°3 – MRSS with oxidants before sonication) on the same type of plates in order to confirm if 100 % chloroform is an appropriate eluent in both conditions. Unfortunately, MRSS dye (condition n°3) did not migrate with chloroform 100 %. Therefore, the same pure solvents were tested in

order to select the most appropriate eluent for this experimental condition. However, none of the tested solvents appear really relevant; and hence chloroform 100 % was considered for the four experimental conditions.

In a second step, the four conditions were sprayed on the HPTLC plate, showing that the sonication had no effect on the MRSS dye. Indeed, on one hand pure MRSS (condition n°1) and sonicated (condition n°2) led to similar spots (Fig.5), while on the other hand MRSS oxidated (condition n°3) and sono-oxidated (condition n°4) led to similar spots (Fig.5). Two conditions were then considered: MRSS in ultrapure water (condition n°1) and MRSS with $K_2S_2O_8 + H_2O_2$ (condition n°3). HPTLC analysis allowed to characterize MRSS degradation after the addition of $K_2S_2O_8 + H_2O_2$. Indeed, the Rf value for the condition n°1 was 0.10, while no migration was shown for the plate corresponding to the condition n°3, which stayed at the start zone.

The above results clearly showed that in our experimental conditions, there is no clear impact of the sonication, which was also confirmed for decreasing working volumes (in the range 100 to 25 mL – data not shown). Indeed, to remain economically relevant low output power (40 W) and frequency (20 kHz) was considered. In addition, a partial degradation may be expected from the use of a low energy level, leading to a significant residual organic content available for a subsequent biological treatment (Chebli et al., 2010). Obviously in these conditions, there is no acoustic cavitation or the short lifetime of $\cdot OH$ radicals did not allow to react with polar organic compounds like the considered azo dye; a large fraction of the formed radicals recombine at the interface of the bubble before reacting with hydrophilic substances (Torres et al., 2008). Some authors advocate the combination of sonication and advanced oxidation processes (Stock et al., 2000; Grcic et al., 2010; Wang et al., 2010). In

this early study, to avoid a too complex and energy consuming process, only oxidants (Grcic et al., 2010) were added in combination with sonolysis.

3.4 Oxidation study of MRSS by DART-TOF-MS

The use of DART-TOF-MS appears as a first insight to the MS analysis of the phenomena occurring during experiments. Indeed, the DART method allows an easy check of target compound degradation owing to its direct, rapid and gentle characteristics (Morlock and Ueda, 2007; Navare et al., 2010; Chernetsova et al., 2011). The purpose was to assess this analytic method for the monitoring of any modification occurring during sonication and/or oxidation of MRSS; at this stage of the study the objective was not to present a comprehensive scheme of the reaction or the fragmentation induced by the method. Preliminary results are presented here, and further study will be subsequently conducted.

We considered as a reference the spectrum of MRSS in water, which is presented in Fig. 6a. We got only one peak of high intensity at $m/z = 270.078$, and a lower one at $m/z = 271.074$. The molecular weight of MRSS is $291.28 \text{ g}\cdot\text{mol}^{-1}$, but since the salt was dissolved in water, Na^+ cation cannot be considered in DART; indeed, alkali metal cation attachments are never observed by this method (NIST Mass Spectrometry Data Center Collection, 2008). Hence the molecular weight to take into account was $268.29 \text{ g}\cdot\text{mol}^{-1}$. Our peak at 270.069 could consequently be interpreted as $[\text{M}+2\text{H}]$. After sonication, the spectrum remains almost unchanged, which may mean that the sonication did not provoke any major fragmentation of MRSS (data not shown), in agreement with the above results recorded by means of UV and HPTLC analysis.

Concerning the spectra obtained from oxidized MRSS, the scheme is totally different; it confirmed that MRSS was not any more in its original state after oxidation, even without sonication. Indeed, the three major peaks observed, $m/z=139.002$, $m/z=223.064$ and $m/z=279.127$ respectively, (Fig.6b) do not lead to obvious assignation neither regarding MRSS structure nor the products of the oxidation reaction. Relative abundance of $m/z=139.002$, which was much higher after sono-oxidation, tends to prove that a large proportion of initial oxidized MRSS was fragmented. However, sonication seems to increase the recombination process within the solution or induced by the DART ionization method. That may be an interpretation for the high m/z peaks exhibited by sono-oxidated MRSS ($m/z=371.19$, $m/z=415.224$, $m/z=459.248$ and $m/z=503.272$ respectively). Indeed, the results recorded by the DART method differ significantly from other ionization processes, like Electron Ionization (EI-MS) for instance. Examination of the spectrum of Methyl Red (*i.e.* MRSS with bonding hydrogen instead of the Na^+ counterion) obtained by EI (NIST Mass Spectrometry Data Center Collection, 2008) leads to two remarks (Fig.7): the spectrum possess a larger number of peaks and most of these peaks match the masses of fragments classically observed in MS, as shown in Table 2

Sonication induces radical formation as follows (Sivasankar and Moholkar, 2009):



Direct sonication of MRSS did not show significant dye removal. Indeed, sonochemical reactions are not always quite efficient for the degradation of organic compounds, since in most cases total mineralization is not achieved. This might be attributed to the higher polarity of the organic compounds, the low availability of OH^\bullet radicals or a lack of power dissipation.

To overcome these disadvantages, the sonochemical treatment can be combined with oxidation or advanced oxidation (Grcic et al., 2010; Joseph et al., 2009).

In this aim, hydrogen peroxide and potassium peroxydisulfate have been tested as oxidants for direct azo-dye degradation or in advanced oxidation process (Kayan et al., 2010). The main purpose was to combine two oxidants in order to achieve better mineralization extent due to consequent generation of various non-selective radicals, like OH^\bullet , $\text{SO}_4^{\bullet-}$ (Huang et al., 2002; Bizani et al., 2006; Grcic et al., 2010; Kayan et al., 2010).

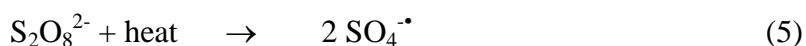
The persulfate has a high oxidation potential as seen in equation (4); however, the reaction is irreversible and proceeds at low rate.



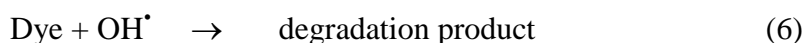
$E = 2.0 \text{ eV}$ versus NHE.

Hydrogen peroxide has a smaller oxidation potential than persulfate ($E = 1.77 \text{ eV}$ versus NHE).

Free radicals are formed in aqueous solution after heating the persulfate solution:



Hydroxyl radical and sulphate radical anion are powerful oxidants, which can degrade dye (Dhananjeyan et al., 2000):

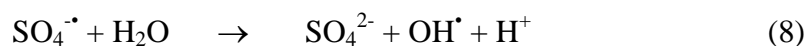


Hydroxyl radical OH^\bullet ($E^\circ = 2.80 \text{ eV}$) is the main responsible for initial breakdown of dye molecules into several differentiated substituted aromatic compounds (Grcic et al., 2010).

The pH of MRSS in ultrapure water was 6.0, while in presence of oxidative reactants, namely $\text{K}_2\text{S}_2\text{O}_8$ and H_2O_2 , it decreased to 3.8. Indeed, in agreement with the following relations (7,8), the addition of these oxidants causes a significant pH decrease (Kayan et al., 2010):



(M represents organic compounds)



It is in agreement with the low direct degradation of another azo-dye, Acid Red 97, using 5 mM of H_2O_2 and $\text{S}_2\text{O}_8^{2-}$ each, after 60 minutes treatment at room conditions (Kayan et al., 2010).

To complete this study using DART-TOF-MS, further investigations are needed which are in progress to fully understand the consequences of the sono-oxidation process and that of the ionization method, and to discriminate between both. However, at this stage, we can only conclude that effects of none of the two processes can be neglected.

To complete this study using DART-TOF-MS, further investigations are needed which are in progress to fully understand the consequences of the sono-oxidation process and that of the ionization method, and to discriminate between both. However, at this stage, we can only conclude that effects of none of the two processes can be neglected.

4. Conclusions

The above results showed that in the tested experimental conditions there was no clear impact of the sonication; the azo-dye degradation resulted mainly from oxidation after addition of H_2O_2 and $\text{K}_2\text{S}_2\text{O}_8$. Indeed, pure and sonicate MRSS led to similar results on one hand, while oxidated and sono-oxidated MRSS led to similar results on the other hand, as confirmed from UV spectra and HPTLC analysis.

These results were confirmed by DART-TOF-MS analysis, since three major peaks were observed after MRSS oxidation, $m/z=139.002$, $m/z=223.073$ and $m/z=279.137$, while pure MRSS led to a peak at $m/z = 270.078$. The results show DART-MS to be a very promising tool for the rapid analysis. Further experiments are however needed to identify the fragments and propose a degradation pathway.

This work showed that the considered analytical tools appeared relevant for a fast control and monitoring of target compounds degradation; this would be especially helpful in case of experiments on real effluents.

References

- Adams J, 2011. Analysis of printing and writing papers by using direct analysis in real time mass spectrometry. *International Journal of Mass Spectrometry* 301:109–126.
- Arslan I, Bacioglou IA, Tuhkanen T, Bahnemann D, 2000. H₂O₂/UV-C and Fe²⁺/H₂O₂/UV-C versus TiO₂/UV-A treatment for reactive dye wastewater. *Journal of Environmental Engineering* 126:903-911.
- Bizani E, Fytianos K, Poulios I, Tsiridis V, 2006. Photocatalytic decolorization and degradation of dye solutions and wastewaters in the presence of titanium dioxide. *Journal Hazardous Materials* 136:85-94.
- Brosillon S, Djelal H, Merienne N, Amrane A, 2008. Innovative integrated process for the treatment of azo dyes : coupling of photocatalysis and biological treatment. *Desalination* 22:331-339.
- Borros S, Barbera G, Biada J, Agullo N, 1999. The use of capillary electrophorèse to study the formation of carcinogenic aryl amines in azo dyes. *Dyes and Pigments* 43:189-196.
- Brown MA, De Vito SC, 1993. Predicting azo dye toxicity. *Critical Reviews in Environmental Science and Technology* 23:249–324.
- Cajka T, Hajslova J, Lacina O, Mastovska K, Lehotay SJ, 2008. Rapid analysis of multiple pesticide residues in fruit-based baby food using programmed temperature vaporiser injection–low-pressure gas chromatography–high-resolution time-of-flight mass spectrometry. *Journal of Chromatography A* 1186:281-294.

Chaudhuri SK, Sur B, (2000) Oxidative Decolorization of Reactive Dye Solution Using Fly Ash as Catalyst. *Journal of Environmental Engineering* 126:583-594.

Chebli D, Fourcade F, Brosillon S, Nacef S, Amrane A, 2010. Supported photocatalysis as a pre-treatment prior to biological degradation for the removal of some dyes from aqueous solutions, Acid Red 183; Biebrich Scarlet; Methyl Red Sodium Salt; Orange II. *Chemical Technology and Biotechnology* 85:555-563.

Chernetsova ES, Ovcharov MV, Khomyakov YY, Bochkov PO, Varlamov AV, 2011. The use of DART mass spectrometry for express confirmation of empirical formulas of heterocyclic compounds. *Russian Chemical Bulletin, International Edition* 59:2014—2015.

Chernetsova ES, Morlock GE, 2012. Assessing the capabilities of direct analysis in real time mass spectrometry for 5-hydroxymethylfurfural quantitation in honey. *International Journal of Mass Spectrometry* 314:22– 32.

Chopra S, Ahmad FI, Khar RK, Motwani SK, Mahdi S, Iqbal Z, Talegaonkar S, 2006. Validation high-performance thin-layer chromatography method for determination of trigonelline in herbal extract and pharmaceutical dosage form. *Analytica Chimica Acta* 577: 46-51.

Cody RB, Laramée JA, Durst HD, 2005. Versatile new ion source for the analysis of materials in open air under ambient conditions. *Analytical Chemistry* 77:2297-2302.

Comninellis C, Kapalka A, Malato M, Parsons SA, 2008. Poullos I and Mantzavinos D, Advanced oxidation processes for water treatment. *Journal of Chemical Technology and Biotechnology* 83:769-776.

Curtis ME, Jones PR, Sparkman OD, Cody RB, 2009. Determination of the Presence or absence of Sulfur Materials in Drywall Using Direct Analysis in Real Time in Conjunction with an Accurate-Mass Time-of-Flight Mass Spectrometer. *Journal of the American Society for Mass Spectrometry* 20:2082-2086.

Dhananjeyan MR, Fine E, Kiwi J, 2000. Synthetic polymer delivery system. Sustained release of persulfate during the photo-oxidation of an azo-dye. *Journal of Photochemistry and Photobiology* 136:125-131.

Dominguez JR, Beltran J, Rodriguez O, 2005. Vis and UV photocatalytic detoxification methods (using TiO_2 , $\text{TiO}_2/\text{H}_2\text{O}_2$, TiO_2/O_3 , $\text{TiO}_2/\text{S}_2\text{O}_8^{2-}$, O_3 , H_2O_2 , $\text{S}_2\text{O}_8^{2-}$, $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{C}_2\text{O}_4^{2-}$) for dyes treatment. *Catalysis Today* 101:389-395.

Kucharska M, Grabka J, 2010. A review of chromatographic methods for determination of synthetic food dyes. *Talanta* 80:1045-1051.

Grcic I, Vujevic D, Koprivanac N, 2010. Modeling the mineralization and discoloration in colored systems by (US) $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$ processes: A proposed degradation pathway. *Chemical Engineering Journal* 157:35-44.

Hajslova J, Zrostlikova J, 2003. Matrix effects in (ultra)trace analysis of pesticide residues in food and biotic matrices. *Journal of Chromatography A* 100:181-197.

Hajslova J, Cajka T, Vaclavik L, 2011. Challenging applications offered by direct analysis in real time (DART) in food-quality and safety analysis. *Trends in Analytical Chemistry* 30:204-218.

Huang KC, Couttenye RA, Hoag GE, 2002. Kinetics of heat-assisted persulfate oxidation of methyl *ter*-butyl ether (MTBE). *Chemosphere* 49:413-420.

Joseph CG, Puma GL, Bono A, Krishnaiah D, 2009. Sonophotocatalysis in advanced oxidation process: A short review. *Ultrasonics Sonochemistry* 16:583-589.

Kayan B, Gözmen B, Demiret M, Gizir AM, 2010. Degradation of acid red 97 dye in aqueous medium using wet oxidation and electro-Fenton techniques. *Journal Hazardous Materials* 177:95-102.

Kim HJ, Baek WS, Jang YP, 2011. Identification of ambiguous cubeb fruit by DART-MS-based fingerprinting combined with principal component analysis. *Food Chemistry* 129:1305–1310.

Kotiyan PN, Vavia PR, 2000. Stability indicating HPTLC method for the estimation of estradiol. *Journal of Pharmaceutical and Biomedical Analysis* 22:6676-671.

Kuki A, Nagy L, Zsuga M, Kéki S, 2011. Fast identification of phthalic acid esters in poly(vinyl chloride) samples by Direct Analysis In Real Time (DART) tandem mass spectrometry. *International Journal of Mass Spectrometry* 303:225–228.

Lachheb H , Puzenat E, Houas A, Ksibi M, Elaloui E, Guillard C, Herrmann JM, 2002. Photocatalytic degradation of various types of dyes (Alizarin S, Crocein Orange G, Methyl Red, Congo Red, Methylene Blue) in water by UV-irradiated titania. *Applied Catalysis B. Environmental* 39:75-90.

Lavastre O, Touzani R, Garbacia R, 2003. Thin Layer Chromatography for the detection of unexpected reactions in organometallic Combinatorial Catalysis. *Advances Synthesis and Catalysis* 345:974-977.

Morlock G, Ueda Y, 2007. New coupling of planar chromatography with direct analysis in real time mass spectrometry. *Journal of Chromatography A* 1143:243-251.

Muthuraman G, Teng TT, 2009. Extraction of methyl red from industrial wastewater using xylene as an extractant. *Progress in Natural Science* 19:1215-1220.

Navare AT, Mayoral JG, Nouzova M, Noriega FG, Fernández FM, 2010. Rapid direct analysis in real time (DART) mass spectrometric detection of juvenile hormone III and its terpene precursors. *Anal Bioanal Chem* 398:3005–3013.

Neamtu M, Siminiceanu I, Yediler A, Kettrup A, 2002. Kinetics of decolorization and mineralization of reactive azo dyes in aqueous solution by the UV/H₂O₂ oxidation. *Dyes and Pigments* 53:93-99.

NIST Mass Spectrometry Data Center Collection, 2008.

Robinson T, McMullan G, Marchand R, Nigam P, 2001. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technology* 77:247-255.

Scarpi C, Ninci F, Centini M, Anselmi C, 1998. High-performance liquid chromatography determination of direct and temporary dyes in natural hair colourings. *Journal of Chromatography A* 796:319-325.

Shena Y, van Beeka TA, Claassena FW, Zuilhofa H, Chenb B, Nielen MWF, 2012. Rapid control of Chinese star anise fruits and teas for neurotoxic anisatin by Direct Analysis in Real Time (DART) high resolution mass spectrometry. *Journal of Chromatography A*, doi:10.1016/j.chroma.2012.03.058.

Sivasankar T, Moholkar VS, 2009. Mechanistic approach to intensification of sonochemical degradation of phenol. *Chemical Engineering Journal* 149:57-69.

Somsen GW, 1995. Planar chromatography coupled with spectroscopic techniques. *Journal of Chromatography A* 703:613-665.

Torres RA, Nieto JI, Combet E, Périer C, Pulgarin C, 2008. Influence of TiO₂ concentration on the synergistic effect between photocatalysis and high-frequency ultrasound for organic pollutant mineralization in water. *Applied Catalysis B: Environmental* 80: 168-175.

Stock NL, Peller J, Vinodgopal K, Kamat PV, 2000. Combinative sonolysis and photocatalysis for textile dye degradation. *Environmental Science Technology* 34:1747-1750.

Vandevivere PC, Bianchi R, Verstraete W, 1998. Treatment and reuse of wastewater from the textile wet-processing industry: Review of emerging technologies. *Journal of Chemical Technology and Biotechnology* 72:289-302.

Wang J, Lv Y, Zhang L, Lin B, Jiang R, Han G, Xu R, Zhang X, 2010. Sonocatalytic degradation of organic dyes and comparison of catalytic activities of CeO₂/TiO₂, SnO₂/TiO₂ and ZrO₂/TiO₂ composites under ultrasonic irradiation. *Ultrasonics Sonochemistry* 17:642-648.

Zeng S, Lu Wang L, Teng Chena T, Yuefei Wang Y, Moc H, Qua H, 2012. Direct analysis in real time mass spectrometry and multivariate data analysis: A novel approach to rapid identification of analytical markers for quality control of traditional Chinese medicine preparation. *Analytica Chimica Acta* 733:38–47.

Figure captions

Fig. 1 Chemical structure of the Methyl Red Sodium Salt.

Fig. 2 UV-VIS spectroscopic analysis of the MRSS solutions before (a) and after oxidation using H_2O_2 and $\text{S}_2\text{O}_8^{2-}$ (b).

Fig. 3 Chromatogram of MRSS (15 μL i.e. 1,5 μg) : peak 3 ($R_f = 0,09 \pm 0,03$) mobile phase: chloroform 100 % ; detection wavelength : 466 nm, silica gel glass HPTLC plate 60 F₂₅₄ (10×10cm)

Fig. 4 Calibration curve for pure MRSS

Fig. 5 HPTLC plate of sonication and sono-oxidation of MRSS, mobile phase: chloroform 100 % ; detection wavelength : 466 nm, silica gel glass HPTLC plate 60 F₂₅₄ (10×10cm)

Legend: 1: condition n° 1, 2: condition n° 2, 3: condition n° 3, 4: condition n° 4

Fig. 6 Spectra obtained by Direct Analysis in Real Time-Of-Flight Mass Spectrometry (DART-TOF-MS) of the MRSS before (a) and after oxidation using H_2O_2 and $\text{S}_2\text{O}_8^{2-}$ (b).

Fig. 7 Methyl Red spectrum obtained by Electron Ionization – Mass Spectrometry method (NIST – [36]).