Degradation of malachite green by a pulsed light/H$_2$O$_2$ process

Patricia Navarro, Jean Pier Zapata, Gemma Gotor, Rafael Gonzalez-Olmos and Vicente M. Gómez-López

ABSTRACT

Pulsed light (PL) is a type of photonic technology characterized by intense short light pulses that enhance the speed of photochemical reactions, and which might be useful as light source in advanced oxidation processes. This work aimed to test PL as light source for the degradation of the dye malachite green (MG) by combining PL with H$_2$O$_2$. To this end, the effect of dye and H$_2$O$_2$ concentrations and pH on the degradation rate of MG was studied and a degradation pathway was proposed. Dye degradation followed a pseudo-first order kinetics; it increased with low initial dye concentration, high H$_2$O$_2$ concentration and low pH. Complete decolourization was achieved after 35 light pulses (75 J/cm^2), with a degradation rate of 0.0710 cm^2/J. The degradation was initiated by the attack of hydroxyl radicals to the central carbon of MG generating 4-(dimethylamino)benzophenone (DLBP) followed by the addition of hydroxyl radicals to the non-amino aromatic ring of DLBP and the demethylation of the amino group. Results indicate that PL technology has potential to be implemented to decrease the environmental impact of dyeing industries.

Key words | advanced oxidation process, malachite green, pulsed light, textile dye, wastewater

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INTRODUCTION

Pulsed light (PL) is a method initially developed for microbial inactivation based on the use of xenon lamps that emit wide spectrum light pulses of very high intensity and short duration, with a continuous spectrum ranging from ultraviolet light to infrared radiation (Gómez-López et al. 2007). PL technology was initially adopted by the food industry, but its application fields have been diversified in recent years. New developments in the application of PL to water treatment include pesticide abatement (Baranda et al. 2017) and disinfection of municipal wastewater (Uslu et al. 2016). The main advantage of PL technology is the production of very fast effects in comparison with other photon-based technologies because it works under extremely high photon fluxes. Standard light sources can provide light in the order of some tens or hundreds of watts (Modirshahla & Behnajady 2006), while PL technology works at emitting radiant powers in the order of millions of watts (Pellicer & Gómez-López 2017).

Water pollution is one of the most important environmental problems nowadays. The dyeing industry uses huge amounts of water, and in consequence generates high volumes of wastewater. Approximately 200 L of water are used to produce 1 kg of textile (Ghaly et al. 2014). There is a proportion of dye that remain unfixed to the fabrics after the dyeing process and it is washed out, reaching the wastewaters. The magnitude of this environmental issue has been recently revised (Fazal et al. 2018). According to these authors, between 10 and 60% of the dyes used in the dyeing industry is discharged into wastewater, which amounts to 280,000 t of dyes released per year. It has been estimated that about 2% of the dyes produced is discharged directly to the environment, and 10% is later lost during the textile colouration process (Arora 2014). Dyes are toxic substances to humans and some are carcinogenic. When wastewater from the textile industry is discharged to the environment, it blocks the transmission of sunlight in water ecosystems and increases the biological oxygen demand; consequently the photosynthesis and reoxygenation processes are inhibited (Ghaly et al. 2014).

Malachite green (MG) is a triarylmethane dye extensively used for dyeing of cotton, wool, silk and leather (Bhavani & Sivasamy 2016). Furthermore, it is used as an antimicrobial in aquaculture and for staining in microbiological laboratories. It is one of the most controversial dye because of toxicity issues related to teratogenicity, mutagenesis, carcinogenesis, multi-organ tissue injury, etc. (Srivastava et al. 2004). MG can reach foods for human consumption, and it is a subject of concern for US and EU authorities.

Several strategies can be implemented to eliminate residual dyes in wastewaters. Separation processes such as filtration, coagulation and biosorption can be effective but do not degrade the dye – they only transfer the dye to another phase. Biological treatments have limited efficiency since many dyes are not biodegradable and this kind of wastewater often contains metals that are toxic to microorganisms (Ghaly et al. 2014). Advanced oxidation processes (AOPs) are a group of techniques based on the generation of reactive radicals to oxidize water contaminants. The most used AOP is based on the generation of hydroxyl radicals by splitting hydrogen peroxide molecules by UV light. Different light sources can be used in AOPs. While the current trend in the treatment of water pollutants is the design of more efficient photocatalysers, the investigation of new light sources should not be neglected because it is complementary to the first. Several types of light sources have been assayed in AOPs for dye degradation, such as low-pressure mercury lamps ($\lambda_{max} = 254$ nm) (Modirshahla & Behnajady 2006), high-pressure mercury lamp (largely infrared radiation, several emission lines from UV to visible ranges) (Fischer et al. 2011), light emitting diodes (Natarajan et al. 2011), microwave-powered electrodeless discharge lamp (several emission lines between 250 and 600 nm, $\lambda_{max} = 254$ nm) (Ju et al. 2013), continuously operated Xenon lamp ($\lambda = 400\text{--}1{,}000$ nm) (Yong et al. 2015) and tungsten lamp ($\lambda > 410$ nm) (Kulsi et al. 2017).

The aim of this work was to test the use of PL as a novel photonic technology for dye degradation within the frame of an AOP, studying some operational parameters and elucidating the degradation pathway of the concerned dye.

MATERIALS AND METHODS

Chemicals

MG oxalate (Basic Green 4, C. I. 42000, CAS 2437-29-8) (Figure 1) and other chemicals were purchased from Scharlab (Barcelona, Spain) except for catalase (Sigma Aldrich,
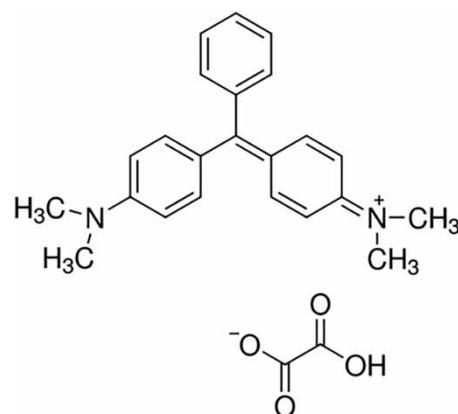

Figure 1 | Molecular structure of MG oxalate.

St Louis, MO, USA) and ethanol (Panreac, Barcelona, Spain). Solutions were prepared by dissolving the required quantity in Milli-Q water >0.2 MΩ.

Pulsed light experimental set-up

The PL system XeMaticA-Basic-1 L (Steribeam, Kehl, Germany) was used for the experiments. It is represented in Figure 2. The system consists of a treatment chamber with a xenon lamp placed at the top, which emits light pulses of 200 μs of duration. The emission is a broad-spectrum light from UV to infrared. The fluence of the pulse and its spectral characteristics depends on working voltage. The system was operated at 2.5 kV, giving place to a flash of 500 J (2.5 MW) whose spectrum has been reported before (Cudemos et al. 2013). Samples were placed in a 90 mm-diameter Petri dish without a cover located 7.1 cm below the lamp and supported by a magnetic stirrer (Topolino, IKA, Staufen, Germany) that homogenized the sample between pulses. The fluence incident on the sample was 2.14 J/cm^2 with 21% of UV emission. The fluence of the
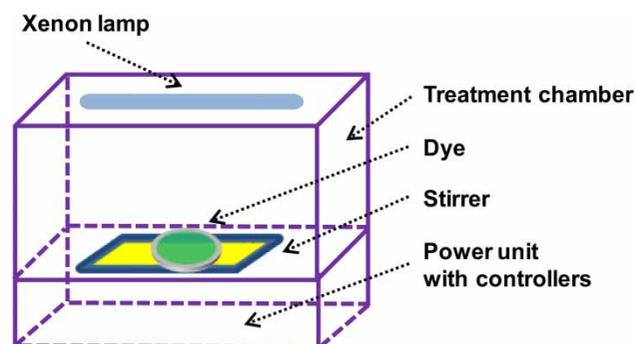

Figure 2 | Schematic representation of a pulsed light system.

pulse was determined by analysis of in-built photodiode signals using a virtual oscilloscope (PC-Lab 2000 LT PC, Velleman Instruments, Gavere, Belgium) and performance charts provided by the manufacturer of the PL system. Fluence was increased by applying multiple pulses. Sample temperature was monitored by an infrared thermometer (ScanTemp 410, TFA Dostmann, Wertheim, Germany) according to a standardized procedure (Pellicer & Gómez-López 2017).

Experimental procedure

The experiments were carried out with a 20 mL mixture of dye solution in water and H_2O_2; the sample had a liquid depth of 27 mm. The effect of different operational parameters was studied by changing dye concentration (5.0–12.5 mg/L; 13.7–34.3 µM), H_2O_2 concentration (50–400 mg/L; 1.5–11.8 M) or pH (3.4–7.1) adding concentrated H_2SO_4 or NaOH, changing one variable at a time while keeping the others constant. The experiment with 10 mg/L of dye, 200 mg/L of H_2O_2 and pH 5.10 (natural pH of this mixture) was used as base case. H_2O_2 concentrations were at least 400 times higher than dye concentration on a molar basis, so that H_2O_2 concentration could be considered constant during the whole experiment. A higher dye concentration (250 mg/L) was used in the experiments carried out to determine the degradation pathway in order to enable the detection and identification of by-products. In this case, 7,500 mg/L of H_2O_2 was used to keep it in excess and catalase was used to quench the oxidant residues. Treatments were carried out up to 96 J/cm^2 (45 pulses). The control of the effect of H_2O_2 alone on the degradation of MG was carried out under darkness conditions in parallel with PL tests. Samples were withdrawn at five pulse intervals and dye concentration was determined by measuring the absorbance of the dye solution.

In order to detect hydroxyl radicals during the degradation process, experiments with the standard reaction mixture were conducted with and without the addition of different concentrations of ethanol (Behnajady *et al.* 2004).

Analytical methods

Absorbance was measured spectrophotometrically (UV-1700 spectrophotometer, Shimadzu, Japan) at 617 nm. Temperature was monitored by an infrared thermometer (ScanTemp 410, TFA Dostmann, Wertheim, Germany). pH was measured by a Hanna Edge pH-meter (Hanna, USA).

A high resolution gas chromatography–mass spectrometer (HRGC-MS) (Agilent 6890/5973) equipped with a non-polar HP5 MS (5% phenyl methyl siloxane) 30 m × 0.25 m × 0.25 µm was used in order to separate and identify the by-products produced during the oxidation of MG in scan mode from a range of m/z = 50 to m/z = 500. Helium was used as carrier gas. A temperature ramp from 50 °C to 300 °C was used. Samples from experiments with 0, 20 and 60 pulses were directly injected without dilution in duplicate. The identification of by-products was carried out by comparing the obtained mass spectra with the NIST14 database.

Data processing

Data were analysed to determine pseudo-first order constants regressing concentration vs. fluence data according to Equation (1):

$$\ln C/C_0 = -kF \qquad (1)$$

where C is the absorbance at fluence F (J/cm^2), C_0 the initial absorbance and k the pseudo-first order rate constant (cm^2/J).

RESULTS AND DISCUSSION

Advanced oxidation process

Firstly, the direct photolytic action of PL was tested in order to assess if this technology can be used alone for the degradation of MG. A low dye degradation was observed under PL in these experiments (Figure 3(a)), with a first-order degradation rate of only 0.0008 cm^2/J (R^2 = 0.925). In contrast, Modirshahla & Behnajady (2006) have reported no evidence of degradation by the direct photolytic action of a low-pressure mercury lamp used for 2 hours. The difference between both findings could be associated with the different spectral outputs of these lamps. Low-pressure mercury lamps emit at 254 nm and this wavelength is poorly absorbed by MG. On the other hand, PL emits a broadband light that includes wavelengths that can be absorbed by MG very efficiently, including 200–230 nm photons, which are very energetic. Likewise, limited efficiency of direct photolysis of MG under simulated and natural irradiation has been reported, with 83% of the dye still remaining after 40 hours of treatment (Yong *et al.* 2015). The combined effect of PL and H_2O_2 brings about a higher degradation rate (0.071 cm^2/J), which is more than
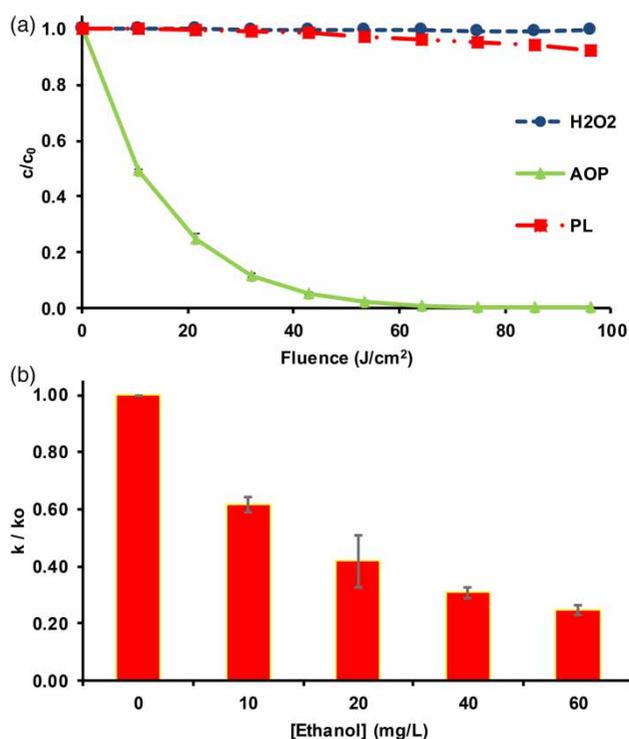
Figure 3 | (a) Effect of pulsed light, H_2O_2 (200 mg/L) and a pulsed light/H_2O_2 advanced oxidation process on the degradation of MG (10 mg/L) with the progress of the treatment. (b) Effect of hydroxyl radical scavenger concentration on the degradation rate of MG by a PL/H_2O_2 process. [MG]: 10 mg/L, [H_2O_2]: 200 mg/L.

80 times higher than the rate of the direct photolysis. The hydrolytic effect of H_2O_2 alone showed negligible effects (Figure 3(a)). The latter tests were carried out to control the potential effect of individual factors. Yong *et al.* (2015) also assessed the effect of H_2O_2 alone, reporting only 8% degradation after 40 hours of hydrolysis. Even though a direct photolytic effect was measured, this was small and the degradation of MG by combining PL and H_2O_2 can be assumed to be fundamentally a UV/H_2O_2 AOP.

In order to support the hypothesis that the degradation of MG by this process is due to the generation of hydroxyl radicals, experiments were conducted with the addition of ethanol, which is a hydroxyl scavenger. Results (Figure 3(b)) show evidence of the production of hydroxyl radical during the PL/H_2O_2 process, since a progressive retardation in the degradation rate of MG was observed with increasing concentrations of ethanol, likely due to a competitive effect between dye and scavenger for hydroxyl radicals (Behnajady *et al.* 2004).

Heating is a side-effect occurring during PL processes and sometimes the temperature of the treated samples can

become very high, as for example in the case of barley grains (Zenklusen *et al.* 2018). Hence, temperature was monitored during treatment in order to assess a possible contribution of heat to dye degradation and also a potential effect on kinetic parameters due to treatments run under non-isothermal conditions. However, temperature at the end of treatments increased less than 5 °C; this small variation has no significant effect on dye degradation because photochemically induced reactions often have a low activation energy (Galindo & Kalt 1998).

The advantage of using PL over conventional UV light sources is a faster dye degradation. Under our assay conditions, complete decolourization of the dye could be achieved with the application of only 35 light pulses (75 J/cm^2), which can be supplied by common PL systems in 12 seconds (Uslu *et al.* 2016; Zenklusen *et al.* 2018). In contrast, Kulsi *et al.* (2017) have recently compared the degradation time of 15 different photocatalysts under visible and UV light; the fastest method achieved 100% degradation after only 5 minutes. A strict comparison among different reported results is not possible because of differences in experimental approaches. Results are sensitive to reactor configurations, where variables such as light paths, dye concentration and turbulence have an impact on the speed of dye decomposition. However, the difference in time scale to achieve total dye degradation is noteworthy, where PL works in a scale of a few seconds, while others have the same efficacy in minutes or hours, even using advanced photocatalyst.

The use of PL as light source in light-driven processes for wastewater treatment applications may increase the environmental sustainability of AOPs. Foteinis *et al.* (2018) have recently compared, using actual life cycle inventory data, seven light-driven processes applied to degrade water contaminants. They concluded that the UV-C/H_2O_2 process, which is similar to a PL/H_2O_2 process, is one of the eco-friendliest among those analysed. They also realized that the environmental sustainability of the processes was inversely proportional to treatment time, because of the large energy input per unit time, and identified electricity consumption as the main environmental hotspot. It is important to notice that the extremely high light intensity characteristic of PL technology is not necessarily associated with high energy consumption. PL technology generates light using a pulse power energization technique (MacGregor *et al.* 1998), where electricity is stored in capacitors during a fixed time and then released to the lamp in a shorter time. Indeed, the lamp is off during most of the duty cycle (>99.99% of the cycle). The eco-friendly character of
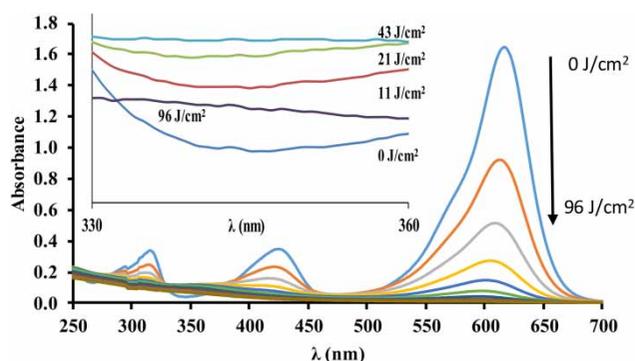
Figure 4 | Evolution of the UV-Vis absorption spectrum of MG during the course of a pulsed light/H_2O_2 advanced oxidation process. [MG]: 10 mg/L, [H_2O_2]: 200 mg/L.

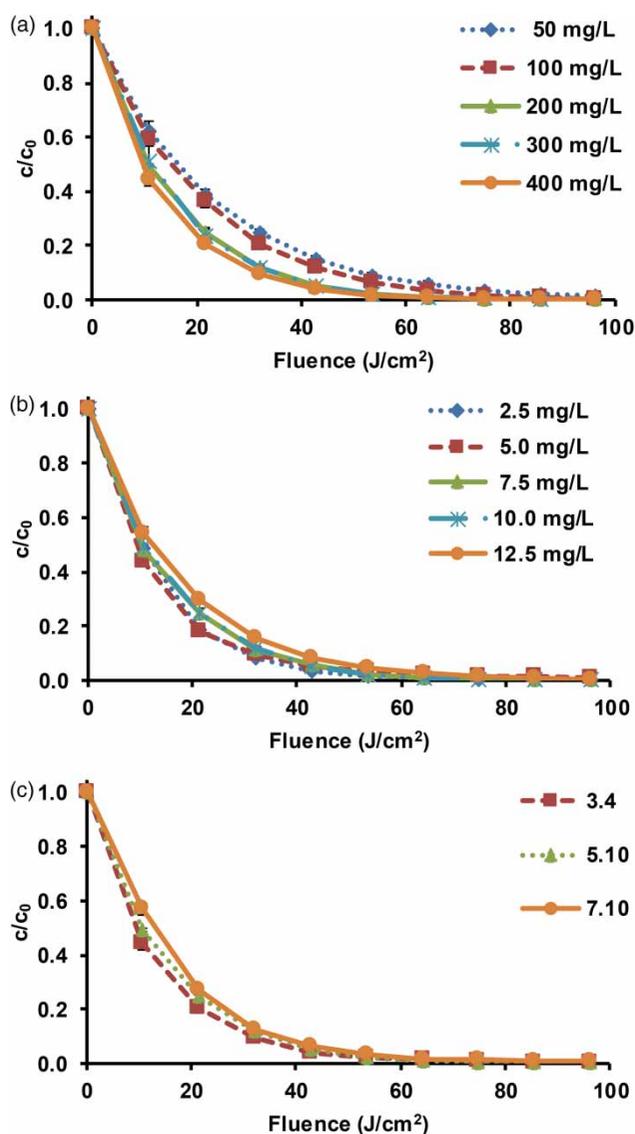**Figure 5** | Effect of (a) H_2O_2 concentration, (b) MG concentration or (c) pH on the degradation of MG during the course of a pulsed light/H_2O_2 advanced oxidation process. When fixed, parameters were: [MG] = 10 mg/L, [H_2O_2] = 200 mg/L, pH 5.10.

this process is enhanced by the use of H_2O_2, which decomposes fast in water and especially due to the use of xenon lamps. Low-pressure and medium-pressure mercury lamps, which are the standard light sources of AOPs, pose an environment problem because of the need for mercury disposal at the end of their useful life. This inconvenience is absent in PL technology, which uses lamps filled with a noble gas.

Spectral changes

The evolution of the spectrum of MG during the AOP is shown in Figure 4. It can be observed that the spectrum disappears progressively as a consequence of dye degradation. The three characteristic peaks of the absorbance spectrum of MG are shown, with a maximum at 617 nm. This peak experiences a hypsochromic shift during the course of the degradation process, which has been attributed to the non-selective attack of reactive oxygen species at C-N bonds (Ju *et al.* 2013). The decrease of the peaks at 316 and 425 nm indicates the destruction of the whole conjugated chromophore structure of the dye (Yong *et al.* 2015). A small increase in the absorbance between 330 and 360 nm up to 43 J/cm^2 indicates the formation of 4-(dimethylamino)benzophenone (DLBP) (Ju *et al.* 2013; Yong *et al.* 2015), while a further decrease points towards its transformation to other products. These features in the evolution of the absorption spectrum match some of the routes of the degradation pathway proposed below.

Table 1 | Pseudo-first rate constants for decolourization of MG by a pulsed light/H_2O_2 process under different dye and H_2O_2 concentrations and pHs with fluence up to 96 J/cm^2

[H_2O_2] (mg/L)	[MG] (mg/L)	pH	k (cm^2/J)	R^2
50	10.0	5.1	0.0458	0.999
100	10.0	5.1	0.0569	0.996
200	10.0	5.1	0.0710	0.998
300	10.0	5.1	0.0697	0.997
400	10.0	5.1	0.0701	0.997
200	2.5	5.1	0.0778	0.996
200	5.0	5.1	0.0745	0.997
200	7.5	5.1	0.0737	0.995
200	10.0	5.1	0.0710	0.998
200	12.5	5.1	0.0592	0.999
200	10.0	3.4	0.0747	0.999
200	10.0	5.1	0.0710	0.998
200	10.0	7.1	0.0664	0.998

Effect of operational parameters

The effect of initial H_2O_2 concentration on the decolourization of MG is shown in Figure 5(a). The degradation rate increased with increasing H_2O_2 concentrations from 50 to 200 mg/L, then it reaches a plateau (Table 1). This means that the PL/H_2O_2 process acts similarly to a conventional $UV-C/H_2O_2$ process from the chemical point of view. In this kind of process, the generation of hydroxyl radicals is increased with higher H_2O_2 concentrations. But increasing too much the H_2O_2 concentration will make hydroxyl radicals react with the excess of H_2O_2 molecules according to
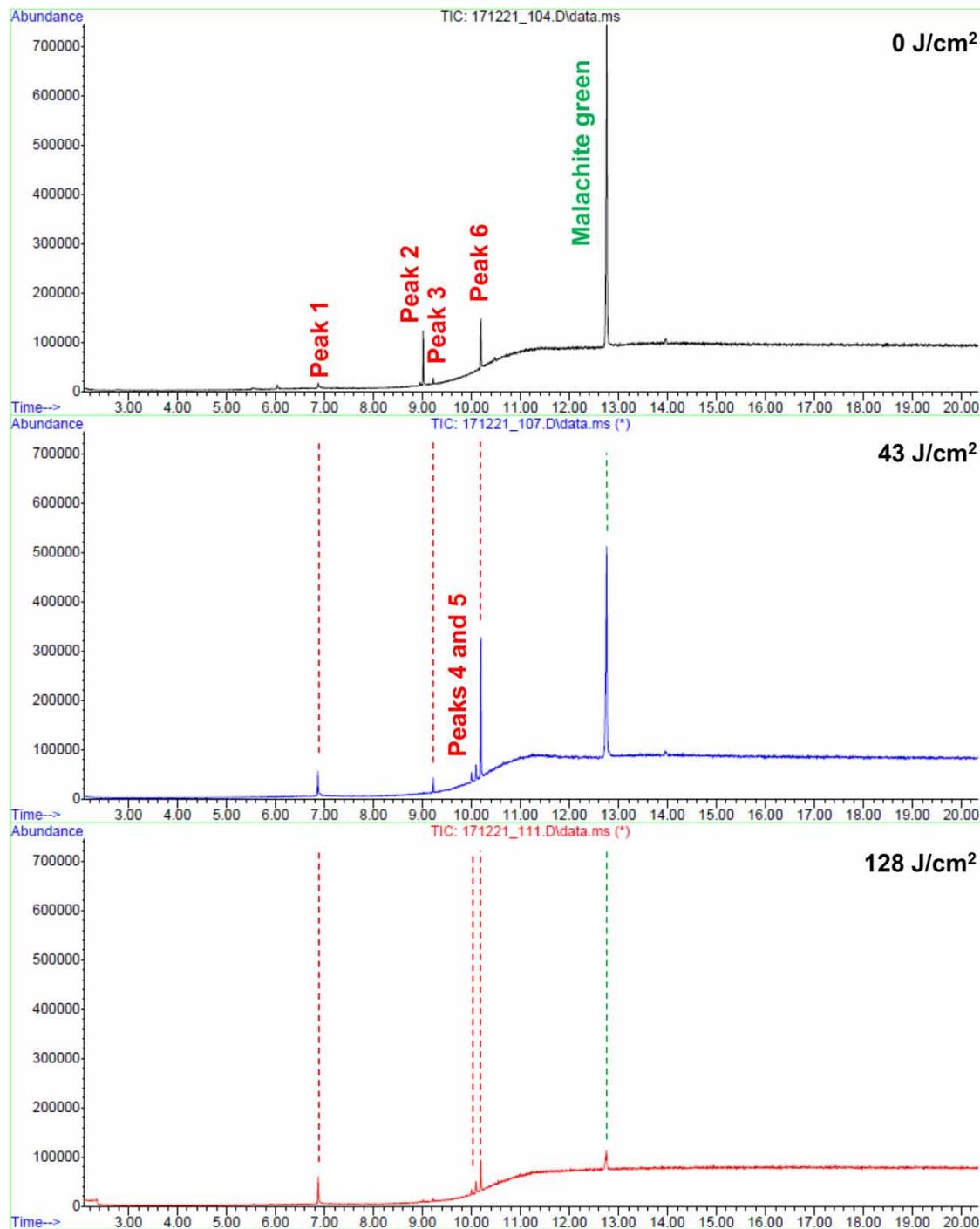

Figure 6 │ GC-MS overall spectrum of MG and the degradation products during the course of the pulsed light/H_2O_2 advanced oxidation process.
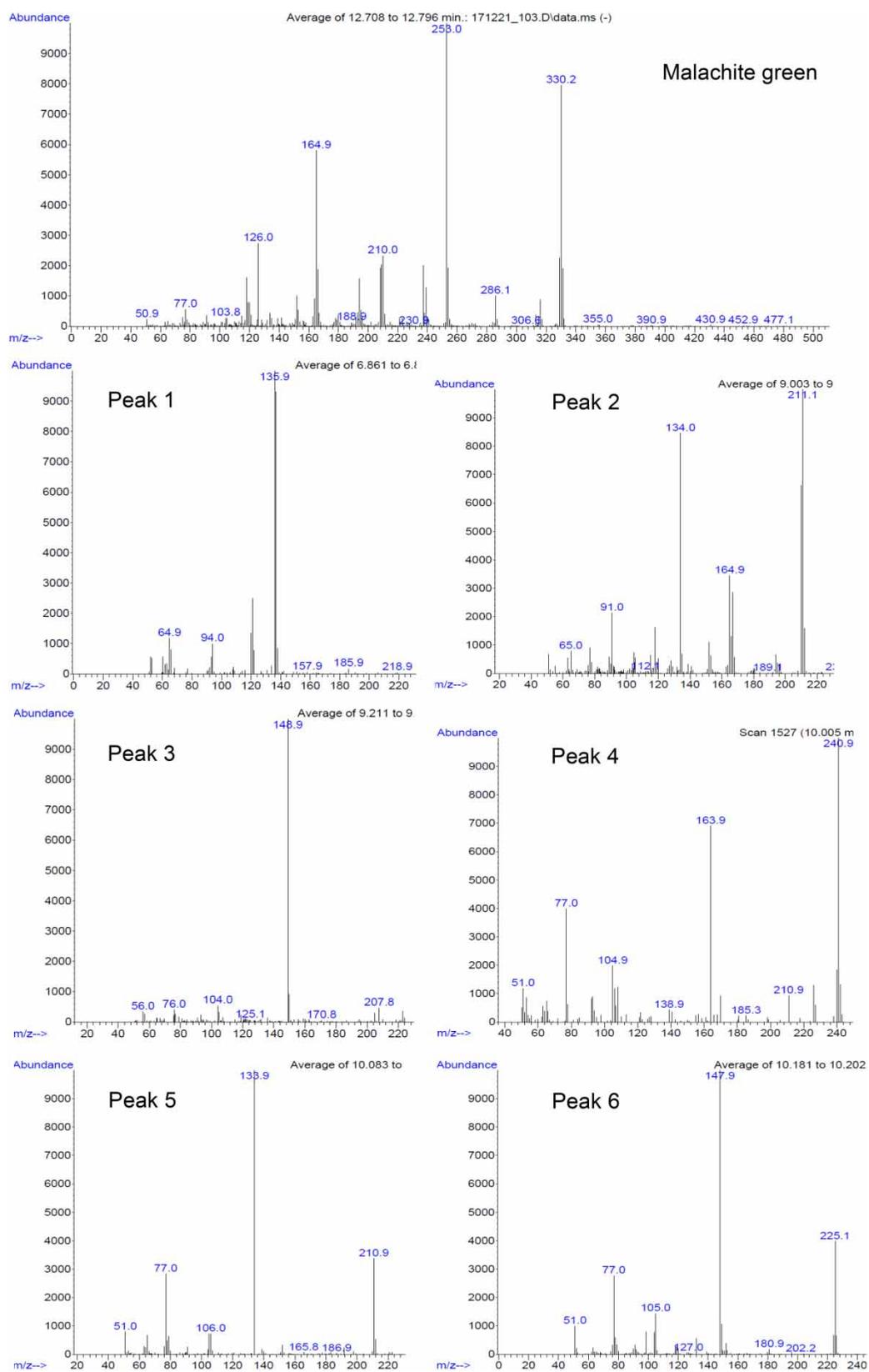
Figure 7 │ ESI mass spectra of intermediaries of the degradation of MG by the pulsed light/H_2O_2 advanced oxidation process. Each peak is characterized by its m/z value.

Equation (2). This unwanted reaction competes with dye degradation (Galindo & Kalt 1998).

$$H_2O_2 + HO^\bullet \rightarrow HO_2^\bullet + H_2O \tag{2}$$

The effect of MG concentration on the performance of the PL/H$_2$O$_2$ process can be seen in Figure 5(b) and the corresponding kinetic constants in Table 1. The decreased efficiency of the process with higher dye concentrations is due to the increased absorbance of the liquid, taking into consideration that MG has a considerable absorbance below 300 nm, which is the range where H$_2$O$_2$ absorbs light. Lower light penetration into the liquid dye mixture means fewer photons being able to attack the H$_2$O$_2$ molecule; therefore, fewer hydroxyl radicals that can degrade the dye molecule can be formed. However, the effect of dye concentration on dye degradation rates is not linear; a linear fitting of degradation rates vs dye concentration yields a low correlation ($R^2 = 0.78$). This could be a consequence of two opposite effects. On one side, there is the lower light penetration. On the other side, a higher concentration of the dye increases likelihood of collisions between hydroxyl radical and MG molecules (Galindo *et al.* 2001).

The effect of initial pH on the degradation of MG by the PL/H$_2$O$_2$ process was studied over a limited pH range since extreme pH values lead to rapid spontaneous decolourization (El Hajj Hassan *et al.* 2011). Results are shown in Figure 5(c) and the corresponding kinetic analysis in Table 1. The degradation was faster at acidic pH. A similar pattern was noted by Yong *et al.* (2015), who observed a faster degradation of MG at pH 5 within the assayed range (pH 5–8), and by Rauf *et al.* (2016). This trend can be related to the effect of pH on hydroxyl radical generation. Low pH favours MG decolourization, because at high pH, H$_2$O$_2$ deprotonates forming HO$_2^-$, which reacts with H$_2$O$_2$ yielding dioxygen and water; this reduces the availability of hydroxyl radicals to attack the dye molecule (Daneshvar *et al.* 2008).

Degradation pathway

The GC-MS spectrum of the untreated and treated samples is shown in Figure 6. It can be observed that the MG peak, with a retention time (RT) of 12.7 min, gradually disappears. Six other peaks were also detected, which we tried to identify by using HRGC-MS (EI/SCAN) (Figure 7) and mass spectra comparison with the NIST14 database. The identity of the peaks was: peak 1 (RT = 6.9 min, m/z = 136), 3-dimethylaminophenol (DAMP); peak 2 (RT = 9.0 min, m/z = 211), 1-dimethylamino-4-phenylmethyl-benzene; peak 3 (RT =
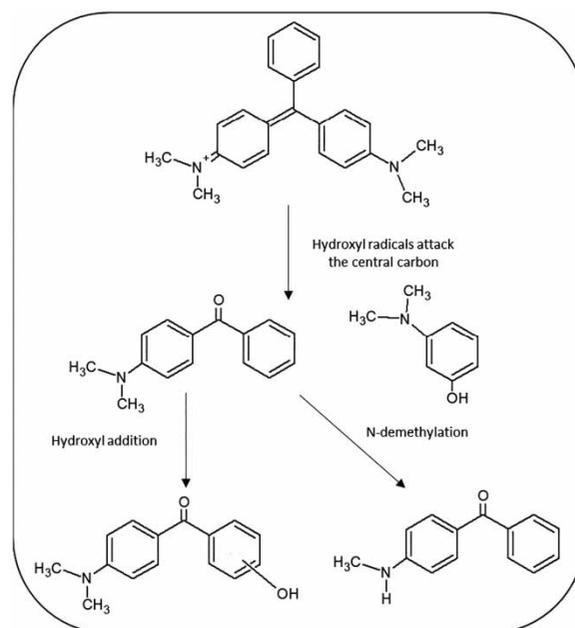

Figure 8 | Degradation mechanisms of MG during pulsed light/H$_2$O$_2$ advanced oxidation process.

9.1 min, m/z = 149), isobutyl isopropyl phthalate and peak 6 (RT = 10.4 min, m/z = 148), DLBP. The identity of peaks 4 (RT = 10.0 min) and 5 (RT = 10.1 min) could not be firmly established. Nevertheless, peak 4 (m/z = 241) corresponds to a compound that has one nitrogen atom and two benzene rings. The comparison of peaks 4 and 2 indicates that they could have the same base but the mass difference between both (m/z = 30) could point to the presence of a ketone and an additional methyl group. Likewise, peak 5, with m/z = 134, differs from peak 6 by 14 m/z units; therefore, both can correspond to similar structures but the compound corresponding to peak 5 could have one methyl group less than DLBP.

According to the compounds detected during the HRGC-MS analysis of samples of the PL/H$_2$O$_2$ experiment with MG, the initial steps of the degradation pathway are proposed in Figure 8. Unlike the results obtained by Yong *et al.* (2015) in photolysis experiments, only an initial mechanism was observed. Yong *et al.* observed that the degradation of MG could be initiated with two different degradation mechanisms: (1) the attack of hydroxyl radicals to the central carbon of MG or (2) N-demethylation or deamination of MG. In the experiments with PL/H$_2$O$_2$, clearly MG reacted with the generated hydroxyl radicals by the combination of H$_2$O$_2$ with the PL through the first pathway, generating DLBP, whose presence was already apparent in the absorption spectra, and DAMP. A benzophenone has also been identified as a degradation

compound of the photocatalytic degradation of another triarylmethane dye, namely, gentian violet (Saquib & Muneer 2003). None of the compounds related to the second mechanism proposed by Yong et al. (2015) were found with the current analysis. Afterwards, in the next degradation steps two different mechanisms were observed: (1) hydroxyl radicals were added to the non-amino aromatic ring of DLBP forming DLBP + OH or (2) the demethylation of the amino group started.

CONCLUSIONS

The operational parameters for the application of PL as a novel light source in an AOP were studied for dye degradation. Dye degradation followed a pseudo-first order kinetic. Increasing dye concentration decreased decolourization rate, while higher H_2O_2 concentrations promoted faster dye degradation up to a certain concentration. Acidic conditions favoured decolourization. The degradation mechanism was initiated by the attack of hydroxyl radicals to the central carbon of MG, generating DLBP and DAMP. In the next degradation steps two different mechanisms were observed: (1) addition of hydroxyl radicals to the non-amino aromatic ring of DLBP forming DLBP + OH or (2) the demethylation of the amino group.

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DECLARATION OF INTEREST

None.

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