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Short title: pulsed light advanced oxidation process

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Abstract

Pulsed light (PL) is a type of photonic technology characterized by intense short light pulses that enhance the speed of photochemical reactions and might be useful as light source in advanced oxidation processes (AOPs). This work aimed to test PL as light source for the degradation of the dye malachite green by combining PL with H_2O_2. To this, the effect of dye and H_2O_2 concentrations and pH on the degradation rate of malachite green 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_2O_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 mechanism was initiated by the attack of hydroxyl radicals to the central carbon of malachite green 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.

Keywords: pulsed light; advanced oxidation process; wastewater; malachite green; textile dye.

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 teens 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 are discharged into wastewater, which amounts 280,000 t dyes released per year. It has been estimated that about 2 % of the dyes produced are 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, its used as antimicrobial in aquaculture and 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 a 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 wastewaters often contain metals that are toxics to microorganisms (Ghaly *et al.* 2014). Advanced oxidation process (AOP) is a group of techniques based in the generation of reactive radicals to oxidize water contaminants. The most used AOP is based in 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 photocatalyzers, the investigation on 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 (λ_{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, λ_{max}=254 nm) (Ju *et al*. 2013), continuously operated Xenon lamp (λ=400-1000 nm) (Yong *et al*. 2015) and tungsten lamp (λ>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) (fig. 1) and other chemicals were purchased from Scharlab (Barcelona, Spain) except for catalase Sigma Aldrich (St. Louis, MO, USA) and ethanol (Panreac, Barcelona, Spain). Solutions were prepared by dissolving the required quantity in mili-Q water >0.2 MΩ.
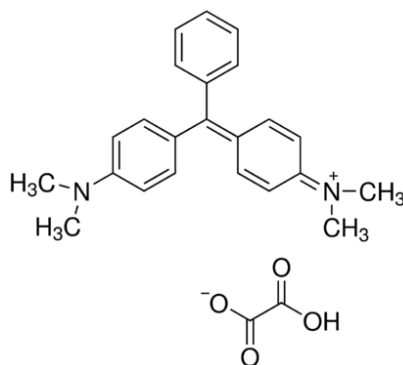
Fig. 1. Molecular structure of MG oxalate

Pulsed light experimental set-up

A PL system XeMaticA-Basic-1L system (Steribeam, Kehl, Germany) was used for the experiments. It is represented in fig. 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) which spectrum has been reported before (Cudemos *et al.* 2013). Samples were located in a 90 mm-diameter Petri dish without cover placed 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 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).
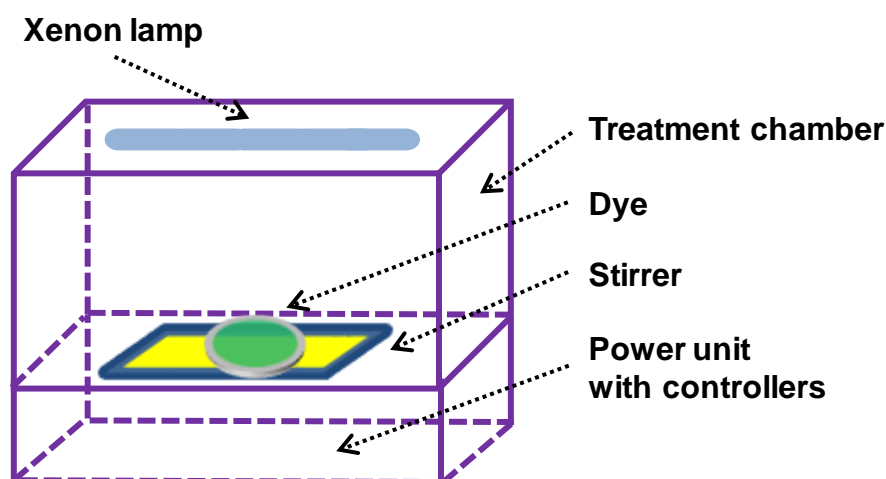
Fig. 2. Schematic representation of a pulsed light system.

Experimental procedure

The experiments were carried out with 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 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 have enable the detection and identification of by-products. In this case, 7500 mg/L of H_2O_2 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).

An HRGC-MS (Agilent 6890/5973) equipped with a non-polar HP5 MS (5% phenyl methyl siloxane) 30 m x 0.25 m x 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 between m/z= 50 to m/z= 500. Helium was used as carrier gas. A temperature ramp from 50ºC to 300 ºC was used. Samples from experiments with 0, 20 and 60 pulses were directly injected without dilution by duplicate. The identification of by-products was carried out by comparing the obtained mass spectra with NIST14 database.

Data processing

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

$$\ln C/C_o = - k F \qquad (1)$$

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 (fig. 3A), 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 two hours. The difference between both findings could be associated to 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, while PL emits a broad-band 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 80 times higher than the rate of the direct photolysis. The hydrolytic effect of H_2O_2 alone showed negligible effects (fig. 3A). 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 an UV/H_2O_2 advanced oxidation process.
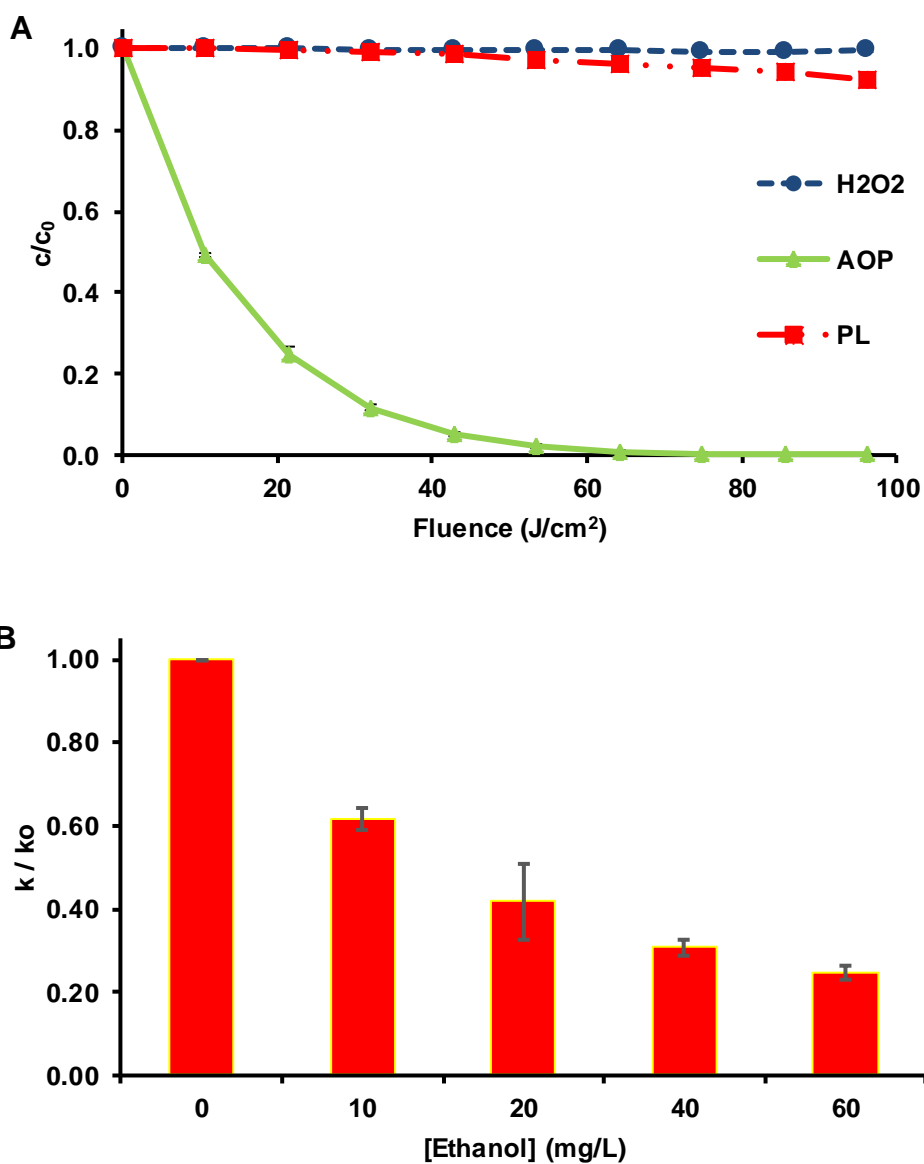

Fig. 3. (A) Effect of pulsed light, H_2O_2 (200 mg/L) and a pulsed light/H_2O_2 advanced oxidation process on the degradation of MG (10 mg/L) with the progress of the treatment. (B) Effect of hydroxyl radical scavenger concentration on the degradation rate of MG by an PL/H_2O_2 process. [MG]: 10 mg/L, [H_2O_2]: 200 mg/L.

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 (fig. 3B) 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 of 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 ran 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 faster method achieved 100 % degradation only after five 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, it is noteworthy the difference in time scale to achieve total dye degradation, where PL works in a scale of 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 this process is enhanced by the use of H_2O_2, which discomposes fast in water and specially 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 the need of mercury

disposal at the end of their useful life. This inconvenient 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 fig. 4. It can be observed that the spectrum disappears progressively as 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 330-360 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.
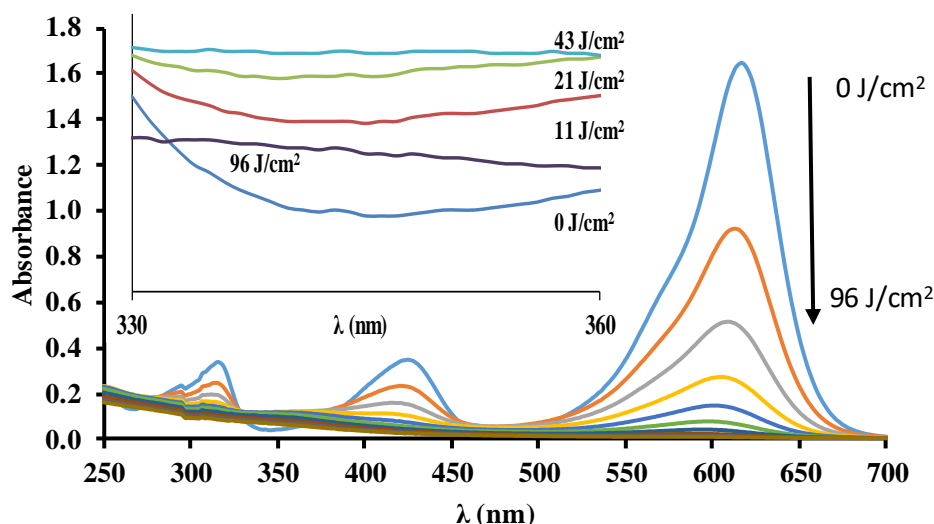
Fig. 4. Evolution of the UV-Vis absorption spectrum of MG during the course of a pulsed light/H$_2$O$_2$ advanced oxidation process. [MG]: 10 mg/L, [H$_2$O$_2$]: 200 mg/L.

Effect of operational parameters.

The effect of initial H$_2$O$_2$ concentration on the decolourization of MG is shown in fig. 5A. The degradation rate increased with increasing H$_2$O$_2$ concentrations from 50 to 200 mg/L, then it reaches a plateau (Table 1). This means that the PL/H$_2$O$_2$ process acts similarly to a conventional UV-C/H$_2$O$_2$ process from the chemical point of view. In this kind of process, the generation of hydroxyl radicals is increased with higher H$_2$O$_2$ concentrations. But increasing too much the H$_2$O$_2$ concentration will make hydroxyl radicals react with the excess of H$_2$O$_2$ molecules according to equation 2. This unwanted reaction competes with dye degradation (Galindo & Kalt 1998).

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \qquad (2)$$
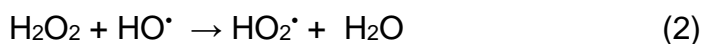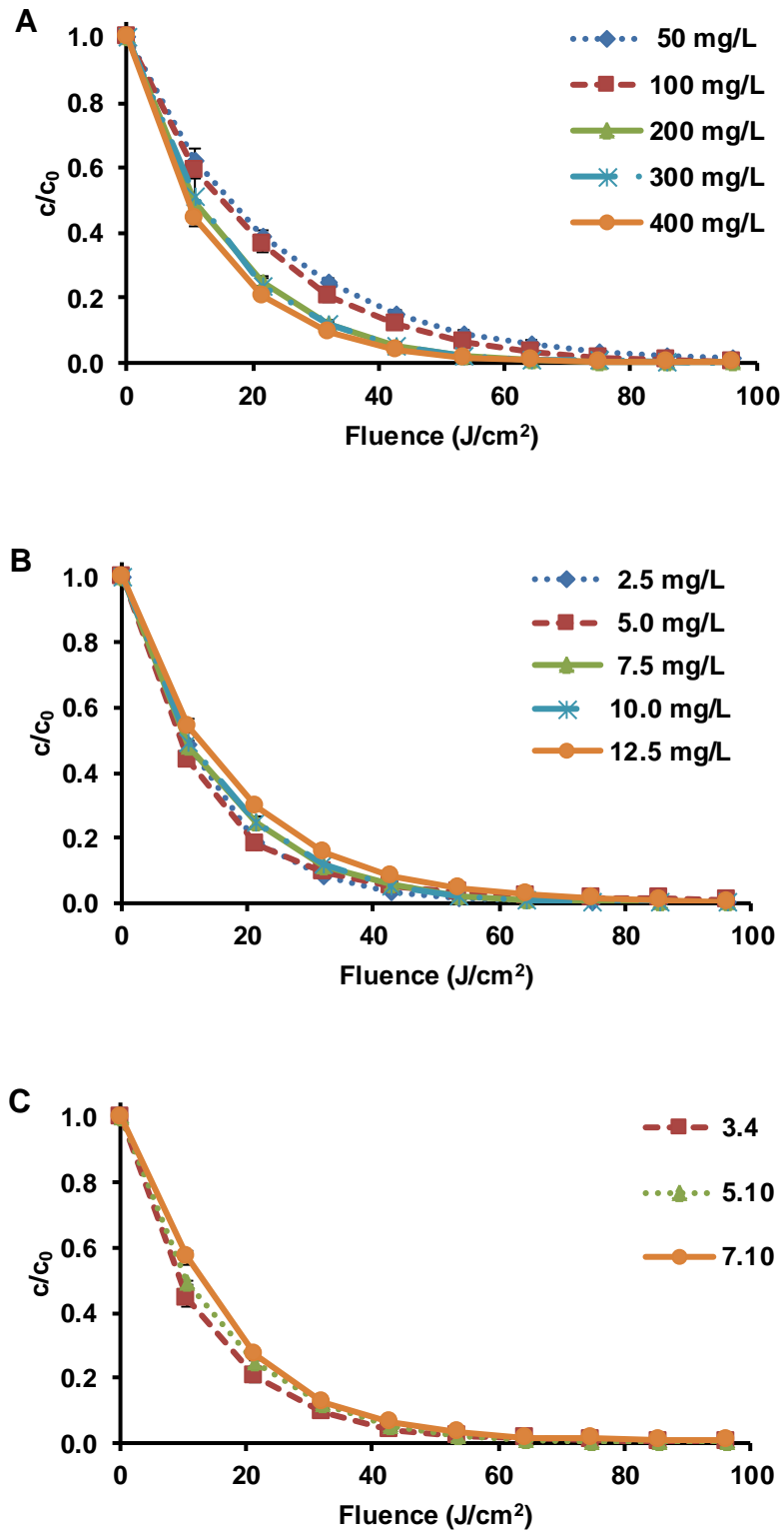
Fig. 5. Effect of (A) H_2O_2 concentration, (B) MG concentration or (C) pH on the degradation of MG during the course of a pulsed light/H_2O_2 advanced oxidation process. When fixed, parameters were: [MG]= 10 mg/L, [H_2O_2]= 200 mg/L, pH 5.10.

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

The effect of MG concentration on the performance of the PL/H_2O_2 process can be seen in fig. 5B 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_2O_2 absorbs light. Lower light penetration into the liquid dye mixture means less photons being able to attack the H_2O_2 molecule, therefore, less 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 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_2O_2 process was studied over a limited pH range since extreme pH's conduct to its rapid spontaneous decolourization (El Hajj Hassan *et al.* 2011). Results are shown in fig. 5C and its corresponding kinetic analysis in table 1. The degradation was faster at acidic pH. A similar pattern was observed 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's generation. Low pH favors MG decolourization because at high pH, H_2O_2 deprotonates forming HO_2^-, which reacts with H_2O_2 yielding dioxygen and

water; this reduces the availability of hydroxyl radicals to attack the dye molecule (Daneshvar *et al.* 2008).

Degradation pathway

The GCMS spectrum of the untreated and treated samples is shown in fig. 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 identity was tried to identify by using HRGC-MS (EI/SCAN) (fig. 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=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 in 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.
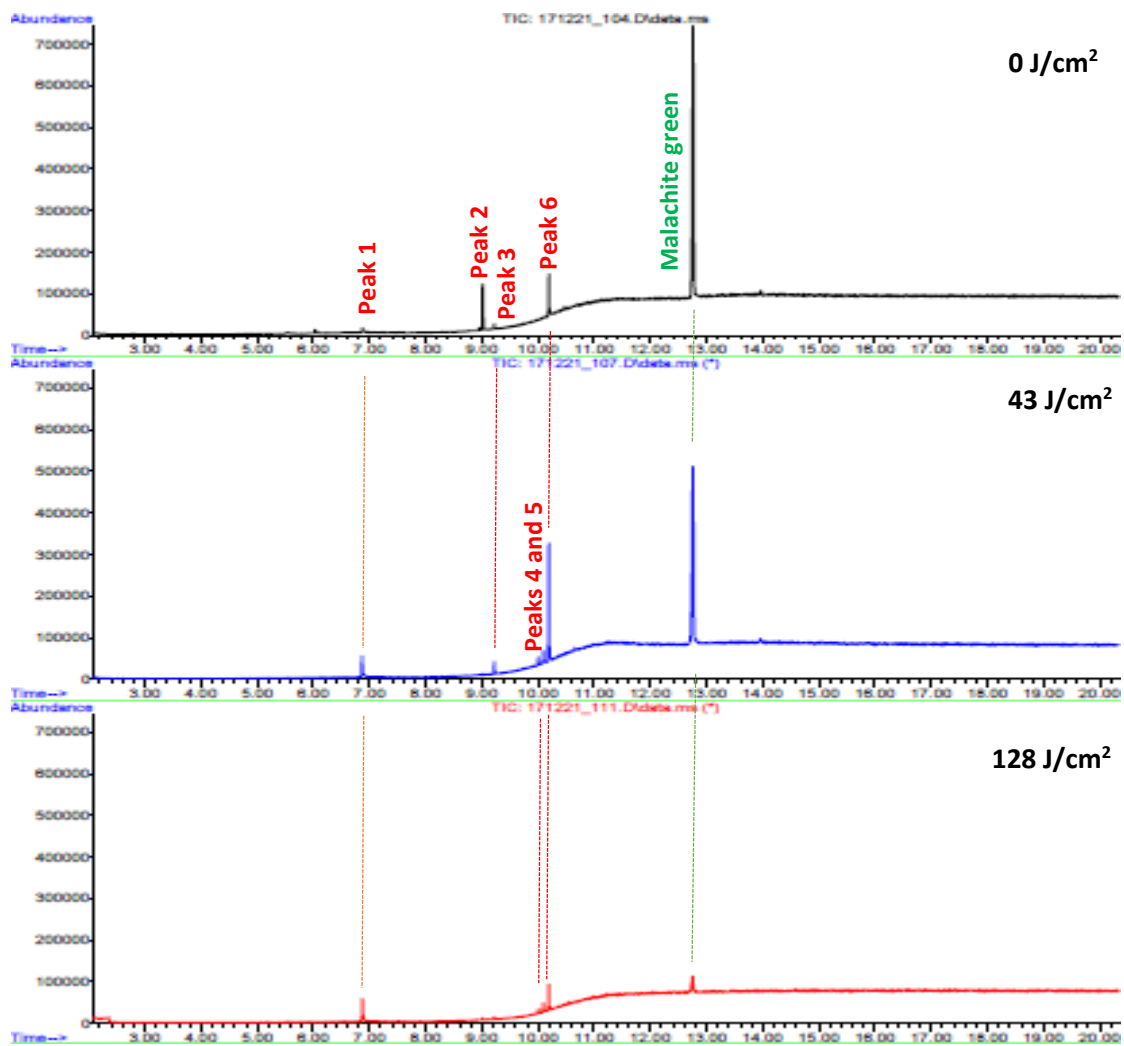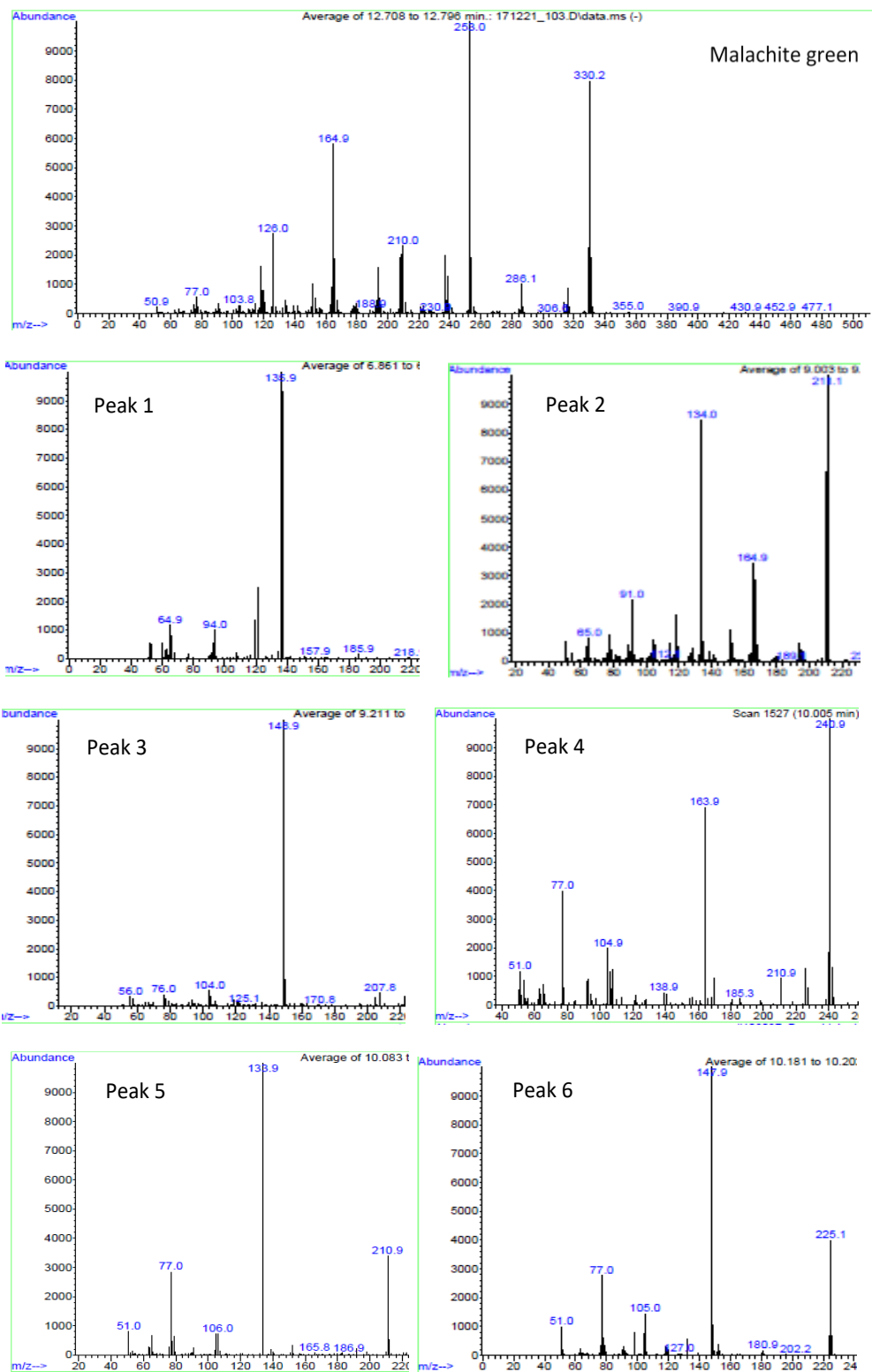
Fig. 6. GCMS overall spectrum of MG and their degradation products during the course of the pulsed light/H₂O₂ advanced oxidation process.

Fig. 7. ESI mass spectra of intermediaries of the degradation of MG by the pulsed light/H₂O₂ advanced oxidation process. Each peak is characterized by its m/z value.

According to the compounds detected during the HRGC-MS analysis of samples of the PL/H_2O_2 experiment with MG, it was proposed in Fig. 8 the initial steps of the degradation pathway. Unlike the results obtained by Yong *et al.* (2015) in photolysis experiments, it was only observed an initial mechanism. 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_2O_2 clearly MG reacted with the generated hydroxyl radicals by the combination of H_2O_2 with the PL through the first pathway, generating DLBP, which presence was already apparent in the absorption spectra, and DAMP. A benzophenone has also been identified as 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.
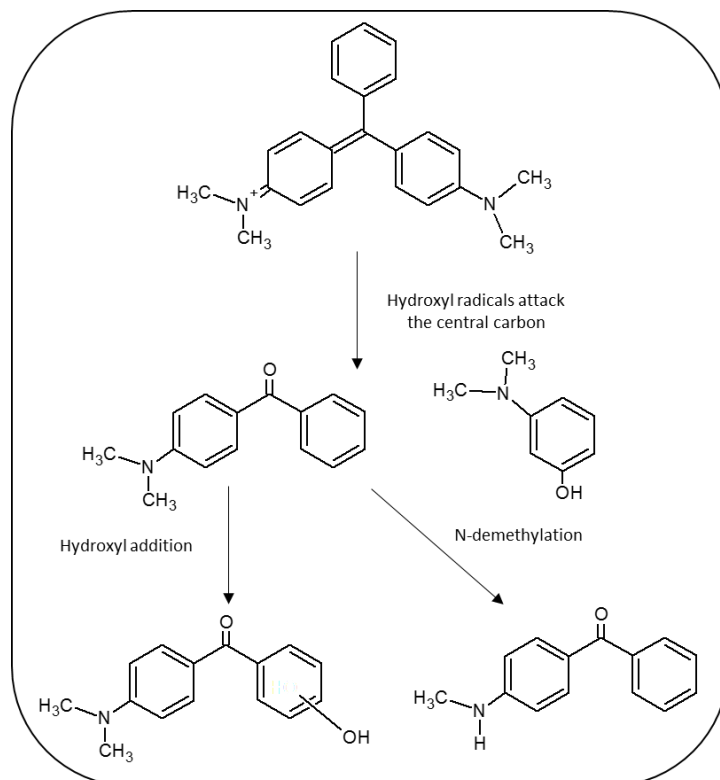
Fig. 8. Degradation mechanisms of MG during pulsed light/H$_2$O$_2$ advanced oxidation process.

CONCLUSIONS

The operational parameters for the application of PL as a novel light source in AOP were studied for dye degradation. Dye degradation followed a pseudo-first order kinetic. Increasing dye concentration decreased decolourization rate; while higher H$_2$O$_2$ 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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