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Abstract

Water pollution by wastewater containing dyes is an environmental issue that can be mitigated by the use of advanced oxidation processes (AOP). Pulsed light (PL) is an emerging food processing technology that uses eco-friendly lamps and can potentially be adapted as light source of an UV-based AOP. In the present work, a PL/H_2O_2 process was tested for the decolourization of two azo dyes, and a pulsed light/H_2O_2/ferrioxalate process was tested for the decolourization of one azo dye. The efficiency of the PL/H_2O_2 process in a batch reactor under different parametric values: dye concentration, pH, H_2O_2 and salt doses was followed by spectrophotometry and fitted to first-order kinetics; and several degradation products were detected. In the PL/H_2O_2 process, decolourization rates increased at low dye concentrations and high H_2O_2 doses, were pH-dependent and were inhibited by the addition of NaCl, Na_2SO_3 or Na_2CO_3. More than 50 % decolouration was achieved with the PL/H_2O_2 process for both dyes after applying 54 J/cm^2 (25 light pulses). The PL/H_2O_2/ferrioxalate process achieved > 95 % decolouration for Methyl orange when applying 21 J/cm^2 (10 pulses); that level of energy can be supplied by PL commercial systems in nine and four seconds respectively. No known toxic degradation products were detected. Results show that a PL/H_2O_2 process has potential to be used for the efficient degradation of dyes from wastewater. Furthermore, the efficacy of this process can be improved by the use of ferrioxalate. PL technology could become an alternative light source to contribute to decrease the environmental impact of wastewater produced by the dyeing industry.

Keywords: pulsed light; advanced oxidation process; azo dye; wastewater remediation; ferrioxalate.

1. Introduction

The disposal of effluent dyes from the textile industry in the environment is an ecological concern due to their toxicity and low degradability. Moreover, dyes are also used for other applications beyond coloration such as in high-technology (optical data storage, light-emitting diodes, etc.), medicine and biomedicine (Singh and Arora, 2011). Arora (2014) estimates that 100,000 tons of dyes are discharged directly in aqueous effluent. It is widely agreed that the disposal of dyes to the environment is a very important problem and that there is an urgent need to develop efficient treatments that decrease water pollution (May-Lozano et al., 2017).

The common biological processes of degradation and discoloration on modern dyes are ineffective because of the high degree of aromatic groups in dye molecules. The traditional physical methods such as using active carbon, filtration, reverse osmosis and coagulation are costly; moreover, these methods do not degrade the dye and just change its phase (Janus and Morawski, 2007; Kaur and Singh, 2007).

Advanced oxidation process (AOP) is a group of technologies that uses hydroxyl radicals for oxidation of target molecules; it has deserved attention in the last years as a mean to degrade dyes. Among the different types of AOPs, the simplest is the generation of hydroxyl radicals from hydrogen peroxide using UV light. The use of novel irradiation sources has been identified as one of the possible ways to improve the efficacy of AOPs (Lachheb et al., 2002). For example, Congo red has been used to test the efficacy of new light sources such as XeBr, KrCl and Cl_2 excilamps emitting maximum UV radiation at 283, 222 and

259 nm, respectively (Murcia et al., 2011) and an indium gallium nitride light emitting diode (LED) radiating in the range 390-410 nm (Natarajan et al., 2011). Pulsed light (PL) is a photonic technology mainly studied for microbial inactivation, especially in the food technology field, but it is not restricted to it. It consists in the application of pulses of high-intensity broad-spectrum light that includes UV light (Gómez-López et al., 2007). The main feature of PL technology is the production of high photon fluxes. The intermittence of the light emission has not any advantage as such, it is just a consequence of the way the photon flux is generated, which uses a pulsed power energization technique (PPET). A PL system takes energy from the electric main during a relatively long time (milliseconds/seconds), stores it in condensers and then releases it in a short time (microseconds) to one or several lamps. While conventional systems can work at powers of the order of 100-1000 W, PPET can deliver powers of the order of MW, without requiring excessive energy consumption. For example, a PPET system developed 20 years ago was already able to provide 3 MW of electric energy to a lamp while consuming only 3 W from the electric main (MacGregor et al., 1998). Part of the lamp emission is constituted by UV light in different proportions depending on the system manufacturer and operating conditions, these short wavelengths provide high energy photons required by AOPs based on UV light.

One of the characteristics of PL technology is the short treatment time required to attain effects because of the massive generation of photons. Short treatment times can offer an advantage for the degradation of dyes in textile effluents in terms of speeding up treatments or treating large volumes of wastewater in compact reactors. Additionally, the technology uses eco-friendly lamps filled with

Xenon, therefore, it is mercury free, in opposition to the widely used low pressure and medium pressure mercury lamps.

Therefore, PL used as a new light generating technology looks worth investigating due to the possibility of working at high photon fluxes using eco-friendly lamps with modest energy requirements; which may become an interesting alternative for integration in AOPs for the textile industry aimed to reduce the environmental impact caused by its effluents

The incorporation of ferrioxalate complex to an UV/H_2O_2 system enhances dye degradation (Arslan et al., 2000; Monteagudo et al., 2008; Doumic et al., 2015). When ferrioxalate is irradiated in the presence of H_2O_2, Fe^{2+} is produced, which generates hydroxyl radicals (Hislop and Bolton, 1999). An UV-vis/ferrioxalate/H_2O_2 system is more efficient than an UV/H_2O_2 system because of a higher quantum yield and wider absorption spectrum (Safarzadeh-Amiri et al., 1997). The ferrioxalate complex has a much higher molar absorption coefficient than H_2O_2 and absorbs light up to 500 nm (Safarzadeh-Amiri et al., 1997), while PL has a significant emission in the 200-500 nm range (Cudemos et al., 2013); therefore, coupling the ferriolaxate complex to a PL/H_2O_2 AOP may lead to enhanced dye degradation.

Consequently, a series of experiments were designed in order to assess the effectiveness of this new photonic technology as UV light source of an AOP on decolourization of two model azo dyes. The decolourization of Congo red and Methyl orange solutions was assayed by studying the effect of relevant factors: dye concentration, H_2O_2 concentration, pH and potential inhibitors. Furthermore,

the possibility that the ferrioxalate complex accelerates even more dye degradation was tested on Methyl orange.

2. Materials and methods

2.1. Reagents.

Congo red (C. I. 22120; MW: 696.67 g/mol) CAS nº 573-58-0 (fig. 1A) was purchased from Prolabo (Fontenay-sous-Bois, France) and Methyl orange (C. I. 13025; Acid orange 52; MW: 327.33 g/mol), CAS nº 547-58-0 (fig. 1B) was purchased from Sigma-Aldrich (St. Louis, USA). Dyes were used as received. NaCl and $Fe(NO_3)_3 \bullet 9H_2O$ were acquired from Scharlab (Barcelona, Spain), $Na_2C_2O_4$ from VWR (Fontenay-sous-Bois, France) and Na_2CO_3 from Sigma-Aldrich. Ethanol was purchased from Panreac (Barcelona, Spain). Other chemicals were purchased from Merck (Darmstadt, Germany). Solutions were prepared by dissolving the required quantity in milli-Q water >0.2 MΩ. For identification of transformation products (TPs), LC-MS grade acetonitrile (ACN) (≥99.9%), methanol (MeOH) (≥99.9%) and HPLC water were purchased from Merck. Formic acid, ammonium acetate and ammonium fluoride (≥96%, ACS reagent) were supplied by Sigma-Aldrich.

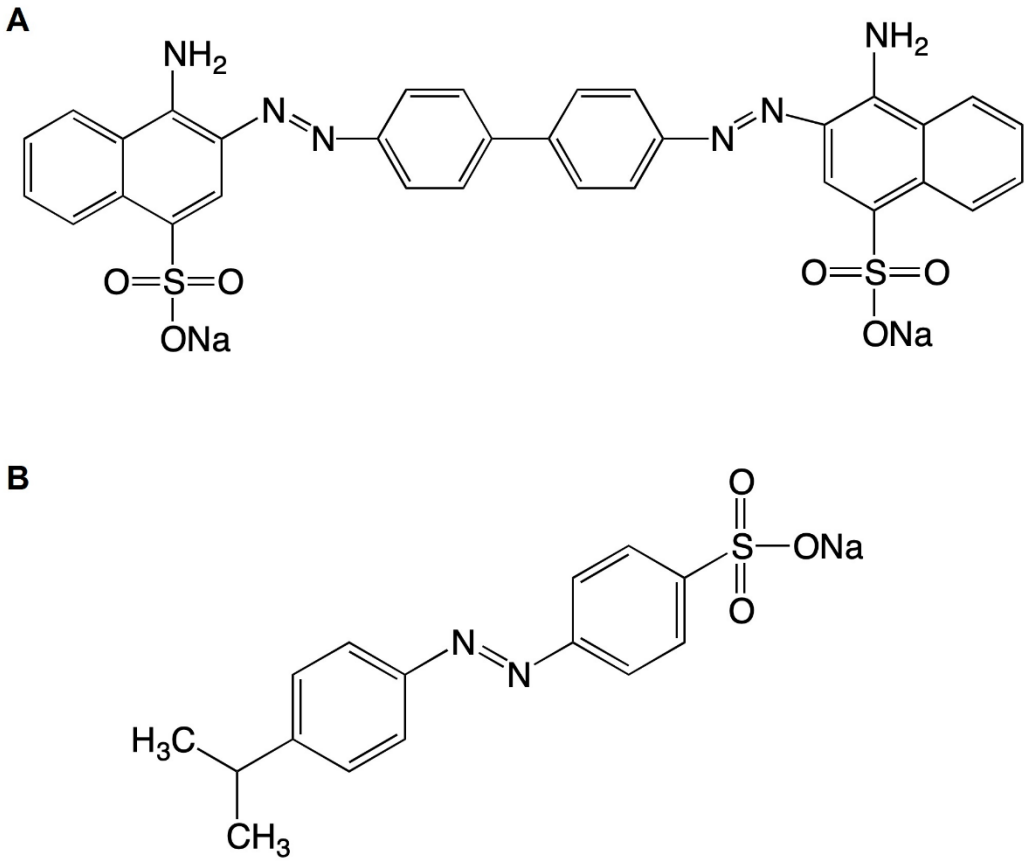


Fig. 1. Molecular structure of Congo red (A) and Methyl orange (B).

2.2. Apparatus

Experiments were performed in a pulsed light system XeMaticA-Basic-1L system (Steribeam, Kehl, Germany). The system has a 19-cm long xenon lamp placed at the top of the reactor and was worked at 2.5 kV.

The light pulse consists in flash with a duration of 200 µs, an energy of 500 J that contained 21 % of UV light and a broad-spectrum emission which composition has been previously reported (Cudemos et al., 2013).

The dye sample was placed in a Petri dish without cover centred at 7.1 cm below the lamp. The Petri dish was positioned at top of a magnetic stirrer (Topolino, IKA, Staufen, Germany) that was used to homogenize the sample between pulses (fig. 2). The fluence incident on the sample was 2.14 J/cm^2. Dosimetry was carried out by the analysis of in-built photodiode readings registered by a PC-Lab 2000 LT PC oscilloscope (Velleman Instruments, Gavere, Belgium) and PL system manufacturer performance charts. Fluence was increased by applying multiple pulses.

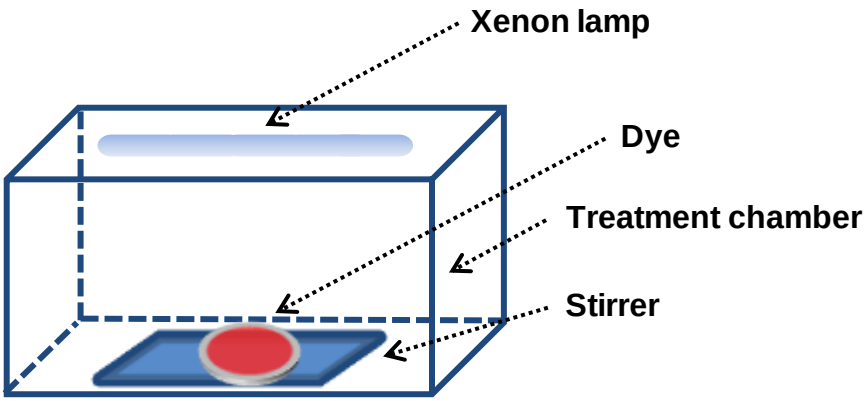


Fig. 2. Schematic representation of a pulsed light system. (For colour reproduction on the web and in black-and-white in print).

2.3. Experimental procedure

The experimental design was based in a reaction mixture of 20 ml volume containing Congo red or Methyl orange, mixed with hydrogen peroxide and water. Treatments were carried out up to 45 light pulses. Samples were withdrawn every five pulses and then samples were poured back into the reaction mixture in order to keep its volume and the distance lamp-sample surface constant.

Colour degradation was monitored by measuring the absorbance at specific wavelengths. Absorbance was measured at 465 nm for Methyl orange. Congo red decolouration was measured at 566 nm for pH 1.0, 540 nm for pH 3.5 and 498 nm for pH ≥ 6.0 since absorption spectra at different pHs did not show a clear isosbestic point (Fig. S1). The change in absorbance was linearly proportional to dye concentration within the measuring range. Tests were run at least per duplicate. Control tests were also performed replacing H_2O_2 for water (photolysis control), or without applying light pulses (H_2O_2 effect control). The H_2O_2 control was run for the same duration of the PL treatment.

Different tests were carried out changing the concentration of H_2O_2 or dye, or adjusting pH; one variable at a time while keeping the others constant. The concentrations of dye and H_2O_2 were selected for every dye independently according to preliminary tests in order to have initial absorbances high enough to enable monitoring colour changes. Typical concentrations were 15 mg/L (22 mM) for Congo red and 10 mg/L (31 mM) for Methyl orange; H_2O_2 concentrations were > 350 times higher than dye concentration on molar basis so that H_2O_2 concentration could be considered constant during the whole experiment. pH was adjusted by adding minimal amounts of concentrated NaOH or HCl. The effect of potential inhibitors was tested by addition of NaCl, Na_2SO_3 or Na_2CO_3 to a final concentration of 1 g/L. Generation of hydroxyl radicals was assessed by the incorporation of different amounts of ethanol, a well-known hydroxyl scavenger, to the reaction mixture.

The effect of the incorporation of the ferrioxalate complex to the dye/H_2O_2 mixture was also assayed. To this, different concentrations of sodium oxalate and iron

nitrate were combined (2.17-12.99 mg/L and 9.69-58.16 mg/L final concentrations respectively) keeping a molar ratio iron:oxalate of 1:3.2 (Hislop and Bolton, 1999). The pH was adjusted to 2, and the mixture was kept 30 min in darkness before use in order to allow the generation of the ferrioxalate complex. The ferrioxalate solution was added to a Methyl orange/H_2O_2 mixture with final concentrations of 10 mg/L Methyl orange and 400 mg/L H_2O_2 respectively and treated with PL.

2.4. Analytical methods

Spectrophotometric determinations were performed using a UV-vis spectrophotometer (UV-1700, Shimadzu, Japan). pH was measured by a Crison pH meter (Basic 20, CRISON, Barcelona, Spain). Temperature was monitored by an infrared thermometer (ScanTemp 410, TFA Dostmann, Wertheim, Germany).

2.5. Detection of intermediaries

For detection of intermediaries, a 300 µL aliquot of a water-based colorant solution, 600 µL of 5 mM ammonium acetate in water and 100 µL of MeOH were transferred to a 2-mL vial for the analysis (90:10, v/v).

2.5.1. Liquid chromatography separation

Liquid chromatography separation was performed using a SCIEX ExionLC™ AD system (Sciex, Redwood City, CA, U.S.) with a Hibar® HR Purospher® STAR RP-C18 column (100 mm x 2.1 mm i.d., 2 µm particle size, Merck), maintained at 40 °C in the column oven. Chromatography for high-throughput qualitative analysis employed a fast gradient with a 10 minute run time composed of 2 mM

ammonium fluoride in water (A) and ACN (B) for negative electrospray ionization and 5 mM ammonium acetate and 0.1% of formic acid in water (A) and ACN (B) for positive mode. The flow rate was of 0.5 mL/min, the injection volume was 10 µL, and the auto-sampler temperature was maintained at 8 °C. A blank sample (MeOH) was injected after each sample to reduce carryover and to clean the column from any residue of colorant.

2.5.2. MS and MS/MS conditions

Qualitative TP samples were acquired using information dependent acquisition (IDA). Samples were analyzed using a SCIEX X500R QTOF system (Sciex, Redwood City, CA, USA) with Turbo V™ source and Electrospray Ionization (ESI) and operating in negative/positive polarity.

The time-of-flight (TOF) acquisition covered m/z 100-1200. While high resolution product ions collected with IDA acquisition in both positive and negative ion mode occurred over the mass range m/z 50-1150. TOF and high resolution product ion extraction widths were 10 mg/L for positive and negative ion data. An inclusion list with the parent compounds and the most probable candidate ions was included. The source conditions for the system were optimized as follow. Ion Spray Voltage was set to 5500 V. Source temperature and nitrogen gas flows (Atomizing gas, GS1 and Auxiliary gas, GS2) were set to 300° C and 50 psi, respectively. Curtain gas was set to 30 psi, Declustering Potential (DP) was set to 50 V (-50 V for negative). Collision Energy (CE) was set to 35V (-35V) with a collision energy spread of ±15V.

Any drift in the mass accuracy of the SCIEX Q-TOF was automatically corrected and maintained throughout batch acquisition by infusion of Reserpine reference standard ($C_{33}H_{40}N_2O_9$, m/z 609.28066) for positive ionization, and a cluster of trifluoroacetic acid (5(TFA-Na)+TFA-, m/z 792.85963) for negative mode. Calibration was running every 5 samples during the batch acquisition making use of the Calibrant Delivery System (CDS).

Qualitative data sets were processed with SCIEX OS 1.4.1 and MarkerView 1.3.1. (Sciex, Redwood City, CA, U.S.).

2.6. Kinetic data processing

Pseudo-first order constants were calculated by regressing absorbance vs. fluence plots according to Eq. (1):

$$\ln A/A_o = - k F \qquad (1)$$

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

Data was processed by using Excel 2010 (Microsoft, USA).

3. Results and discussion

3.1. PL/H_2O_2 process

The efficacy of a PL technology to be used as part of an AOP was studied in this work. Each one of the factors, PL and H_2O_2, applied alone, was unable to

decolour the dyes significantly (fig. 3). Even though the dyes absorb in the UV range (fig. 4) and PL lamp emits a significant portion of UV light (Cudemos et al., 2013), the effect of direct photolysis was negligible. Direct photolytic effects have been reported for other light sources but no attempt was made in this research to reach similar decolourization levels because they required energy and treatment times considered too long for the goals of the present work. As examples, a direct photolytic effect on Congo red was observed by Murcia et al. (2011) using a KrCl excilamp, but one hour of treatment was needed to reach 75 % decolourization. The direct photolysis using a low-pressure mercury lamp has resulted less efficient, requiring two hours to reach 50 % decolouration of a 10 mg/L Congo red solution (Kamel et al., 2009).

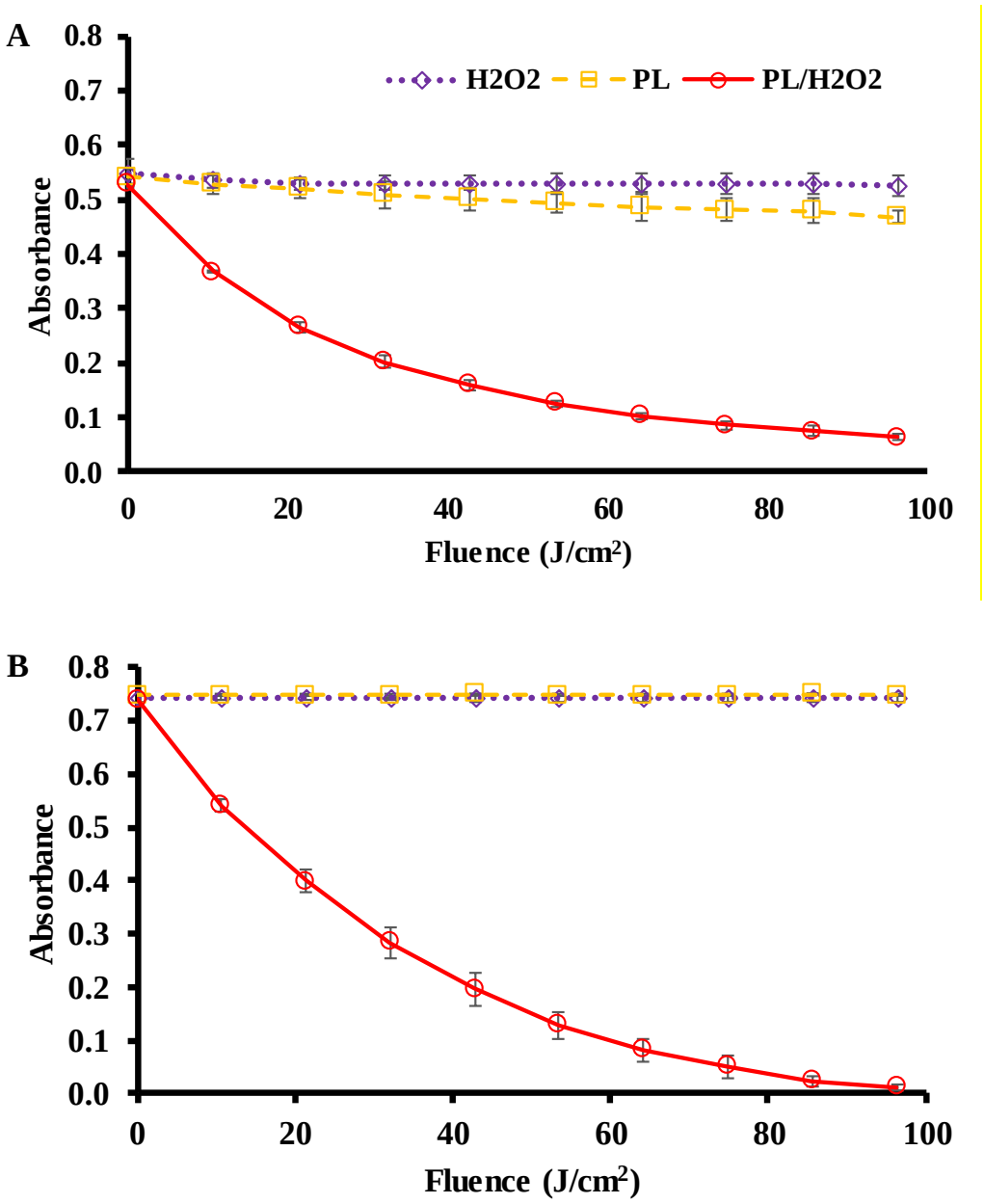


Fig. 3. Decolourization of Congo red (A) and Methyl orange (B) under a PL/H_2O_2 process. Congo red: [dye] = 15 mg/L, [H_2O_2] = 450 mg/L, pH = 6.0. Methyl orange: [dye] = 10 mg/L, [H_2O_2] = 400 mg/L, pH = 8.6. Bars represent standard deviation. (For colour reproduction on the web and in black-and-white in print).

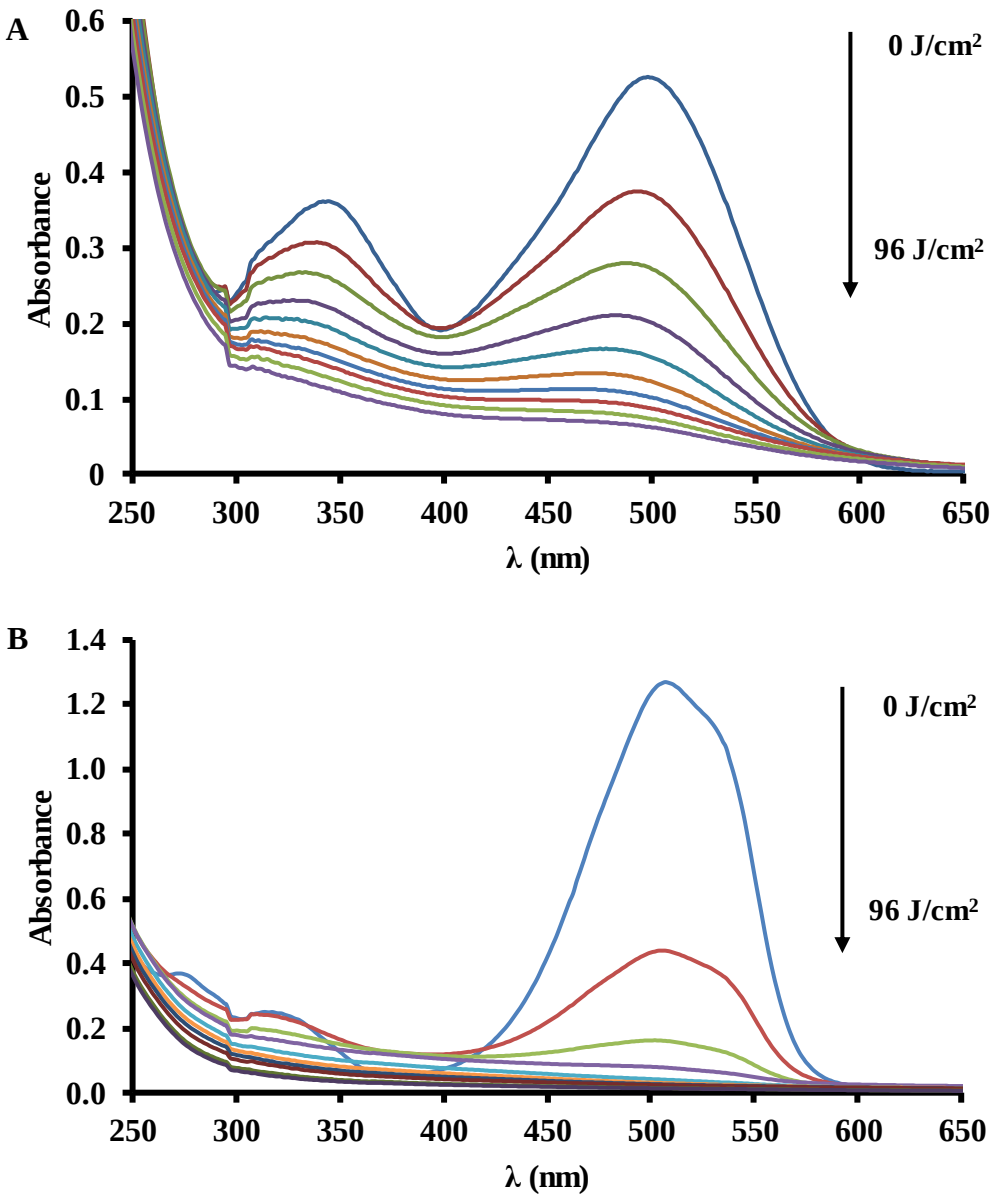


Fig. 4. Evolution of the absorption spectrum of Congo red (A) and Methyl orange (B) with the progress of a PL/H_2O_2 process. Congo red: [dye] = 15 mg/L, [H_2O_2] = 450 mg/L, pH = 6.0. Methyl orange: [dye] = 10 mg/L, [H_2O_2] = 400 mg/L, pH = 8.6. (For colour reproduction on the web and in black-and-white in print).

When both factors, PL and H_2O_2, were combined to give place to a PL/H_2O_2 process, the decolourization markedly improved (fig. 3). This process can be consequently described as following a typical UV/H_2O_2 AOP, where light splits

H_2O_2 molecules in hydroxyl radicals that will later attach the dye, as represented in equations 3 and 4:

$$H_2O_2 + hv \longrightarrow 2 \cdot OH \qquad (3)$$

$$\text{Dye} + \cdot OH \longrightarrow \text{Degradation products} \qquad (4)$$

This suggestion is supported by tests carried out adding ethanol to the reaction mixture (fig. 5), where the degradation rate of the dyes was decreased by more than 35 %. This is consequence of the scavenger action of ethanol on hydroxyl radicals, which leaves less radicals to attack dye molecules (Mahmoodi et al., 2018).

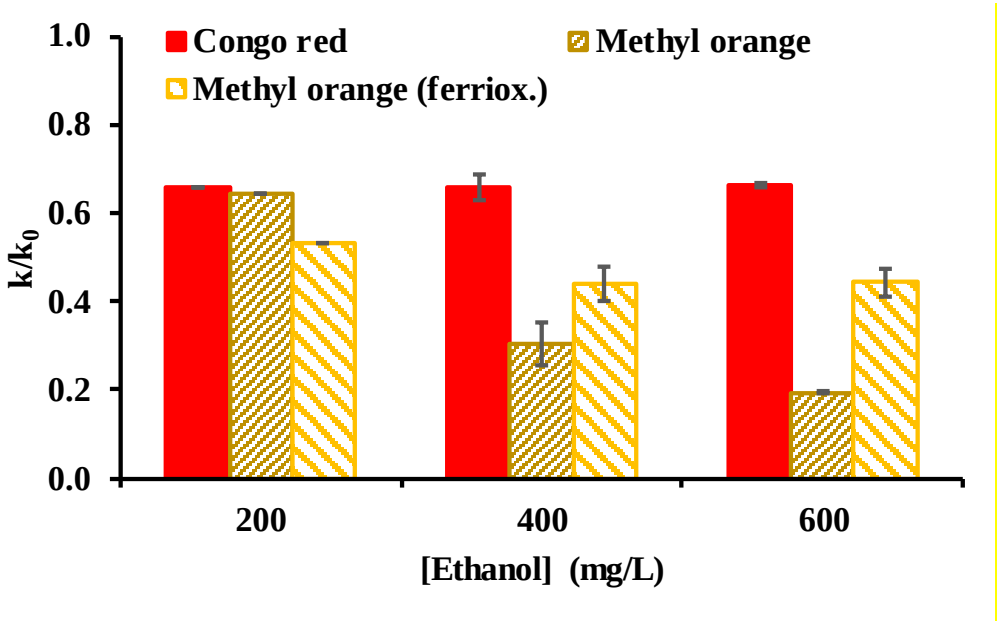


Fig. 5. Inhibition of decolourization rate by the action of a hydroxyl scavenger. *Congo red: [dye] = 15 mg/L, [H_2O_2] = 450 mg/L, pH = 6.0. Methyl orange: [dye] = 10 mg/L, [H_2O_2] = 400 mg/L, pH = 8.6. Methyl orange (ferrioxalate): [dye] = 10 mg/L, [H_2O_2] = 400 mg/L, pH = 2.0, [$Fe(NO_3)_3 \cdot 9H_2O$]=39 mg/L, [$Na_2C_2O_4$]=8.7 mg/L.* (For colour reproduction on the web and in black-and-white in print).

The PL/H_2O_2 process has typical characteristics of other UV/H_2O_2 processes, but could provide faster effects, yet, any comparison is rough because results depend on experimental set-ups, specially reactor configuration. It can be observed (fig.

3) that more than 50 % decolouration of both dyes has been achieved after applying 25 light pulses. Typical commercial PL systems can work at pulse repetition rates of 3 Hz (Wang et al., 2016), therefore, they are able to provide the energy required by this AOP in about 9 seconds. This treatment is significantly faster than AOP driven by other light sources, which can last several minutes or hours, even though.

The interval between light pulses is not expected to have a significant effect on dye degradation. The generation of hydroxyls is a photochemical process, and as such, it depends on fluence. Once generated, hydroxyl radicals are expected to disappear during the interval between pulses because of their very fast reaction rates. Rate constants of reaction with organic molecules are usually in the order of 10^6-10^9 1/M s (Andreozzi et al., 1999).

The use of H_2O_2 was initially selected for this research as the simplest example to test the effect of PL technology as part of an AOP, but it can be thought that PL could yield even better results if combined with appropriated photocatalyst selected among the wide variety of them currently existing (Ma et al., 2018; Sacco et al., 2018; Sharma et al., 2018).

In spite of PL has been classified as a non-thermal method, it can warm up samples as a collateral effect due to the infrared portion of its spectrum. Consequently, temperature is usually monitored during its application (Gómez-López et al., 2007). The increase in temperature in these tests has been < 3 ºC; which allows considering that they were run under isothermal conditions. It has been demonstrated that this kind of reactions are not sensitive to small

temperature changes in the range 22-45 ºC due to their low activation energy (Galindo and Kalt, 1998).

3.2. Changes in spectral characteristics during the decolourization process

Fig. 4 shows the absorption spectrum of the two dyes measured at the natural pH's of its respective reaction mixtures. Both spectra exhibit an absorption band in the visible range due π→π* transitions in the azo bonds. The weaker absorption bands of Methyl orange to the π→π* transitions located in the benzene rings. The bands fade with increasing fluence as consequence of the AOP. Hypsochromic shifts observed during degradation of Congo red and Methyl orange are associated with degradation products having spectral characteristics different from the parent molecule.

Dye decomposition was incomplete since there was still some absorbance at the end of the treatment under the assay conditions, especially in the UV region. For example, 12 % of the absorbance of Congo red still persisted at 96 J/cm^2, therefore, complete mineralization is not expected under the experimental conditions used in this research. This is not a peculiar weakness of the assayed process but a characteristic of azo dye degradation, which is related to the generation of recalcitrant by-products. The complete mineralization of Congo red is relatively difficult in comparison with that of other dyes. Lachheb et al. (2002) tested the mineralization of five dyes by using UV/TiO_2, Congo red was the only dye that was not fully mineralized after 180 min of treatment; while Thomas et al. (2016) achieved only 80 % mineralization after four hours using a nanocomposite hydrogel under direct sunlight irradiation. Full mineralization of Methyl orange is also difficult; only 67 % reduction of the chemical oxygen demand of a MO

solution was achieved by Jiang et al. (2012) using a non-thermal plasma AOP for 20 min of treatment, and Li et al. (2014) reported 80 % chemical oxygen demand abatement in a MO solution after three hours of treatment with sodium persulfate activated with zero-valent zinc.

3.3. Effect of H_2O_2 concentration

The rate of decolourization of the two dyes increase with the concentration of H_2O_2 (fig. 6, tables 1-2), which is a consequence of a bigger generation of hydroxyl radicals for attacking dye molecules. A higher availability of H_2O_2 increases the amount of hydroxyl radicals generated by the process, which accelerates degradation rates. However, this trend stops at relatively high H_2O_2 concentrations where a further increase in H_2O_2 concentration does not affect decolourization rates. This is result of hydroxyl self-quenching at high H_2O_2 concentrations as shown in equations 5 and 6 (Wang and Xu, 2012):

$$\cdot OH + H_2O_2 \longrightarrow H_2O + HO_2\cdot \qquad (5)$$

$$\cdot OH + HO_2^- \longrightarrow HO_2\cdot + OH^- \qquad (6)$$

$HO_2\cdot$ radicals are less reactive than $\cdot OH$, therefore, its increasing concentration has a negligible contribution to dye degradation (Daneshvar et al., 2008) and can even decrease dye degradation at very high concentrations of H_2O_2 (Zuorro and Lavecchi, 2013).

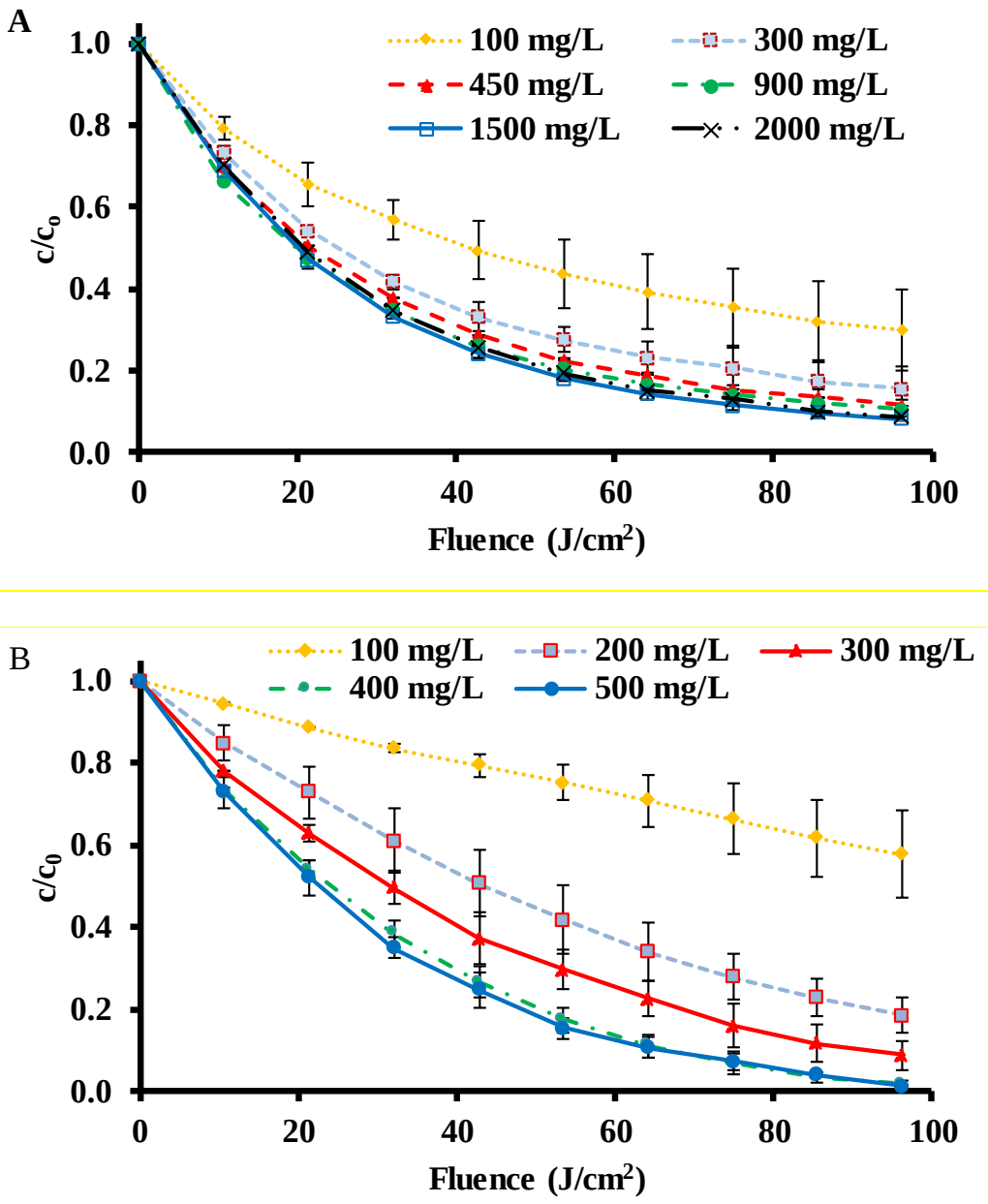


Fig. 6. Effect of H_2O_2 concentration on the decolourization of Congo red (A) and Methyl orange (B) subjected to a PL/H_2O_2 process. Congo red: [dye] = 15 mg/L, pH = 6.0. Methyl orange: [dye] = 10 mg/L, pH = 8.6. Bars represent standard deviation. (For colour reproduction on the web and in black-and-white in print).

Table 1. Pseudo-first rate constants for decolourization of Congo red 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]	[Dye]	pH	k (cm^2/J)	R^2
100	15	6.0	0.0125	0.98
300	15	6.0	0.0194	0.98
450	15	6.0	0.0223	0.98
900	15	6.0	0.0233	0.97
1500	15	6.0	0.0262	0.98
2000	15	6.0	0.0256	0.98
450	2.5	6.0	0.0372	0.99
450	5.0	6.0	0.0295	0.99
450	15.0	6.0	0.0230	0.98
450	25.0	6.0	0.0222	0.99
450	30.0	6.0	0.0199	0.99
450	15	1.0	0.0026	1.00
450	15	3.5	0.0050	0.95
450	15	6.0	0.0220	0.99
450	15	9.0	0.0237	0.99
450	15	12.0	0.0230	1.00

Table 2. Pseudo-first rate constants for decolourization of Methyl orange 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]	[Dye]	pH	k (cm^2/J)	R^2
100	10	8.57	0.0057	1.00
200	10	8.57	0.0178	1.00
300	10	8.57	0.0258	0.99
400	10	8.57	0.0419	0.98
500	10	8.57	0.0424	0.96
400	2.5	8.57	0.0508	0.99
400	5.0	8.57	0.0470	1.00
400	10.0	8.57	0.0419	0.98
400	15.0	8.57	0.0235	1.00
400	20.0	8.57	0.0191	0.98
400	10	2.03	0.0563	0.99
400	10	4.01	0.0427	0.99
400	10	5.99	0.0323	0.99
400	10	8.57	0.0419	0.98
400	10	10.0	0.0276	0.99

3.4. Effect of initial dye concentration

It is important from an appplication point of view to study the dependence of dye decolouration on the initial concentration of dye. The effect of the initial concentration of Congo red and Methyl orange on their decolourization rates was studied. Initial dye concentration plays a major role and significantly influence the degradation rate (fig. 7). The decolourization declined at increasing dye concentrations (tables 1-2), for example, the pseudo first reaction rate of Congo red gets reduced 47 % when initial dye concentration changes from 5 to 30 mg/L. This finding is caused by the attenuation of light through the dye solution, which increases with dye concentration. Therefore, lower amounts of hydroxyl radicals can be formed because less photons can reach H_2O_2 molecules. The presence of intermediate products may also play a role in the observed effect by consuming more hydroxyl radicals (Bali, 2004).

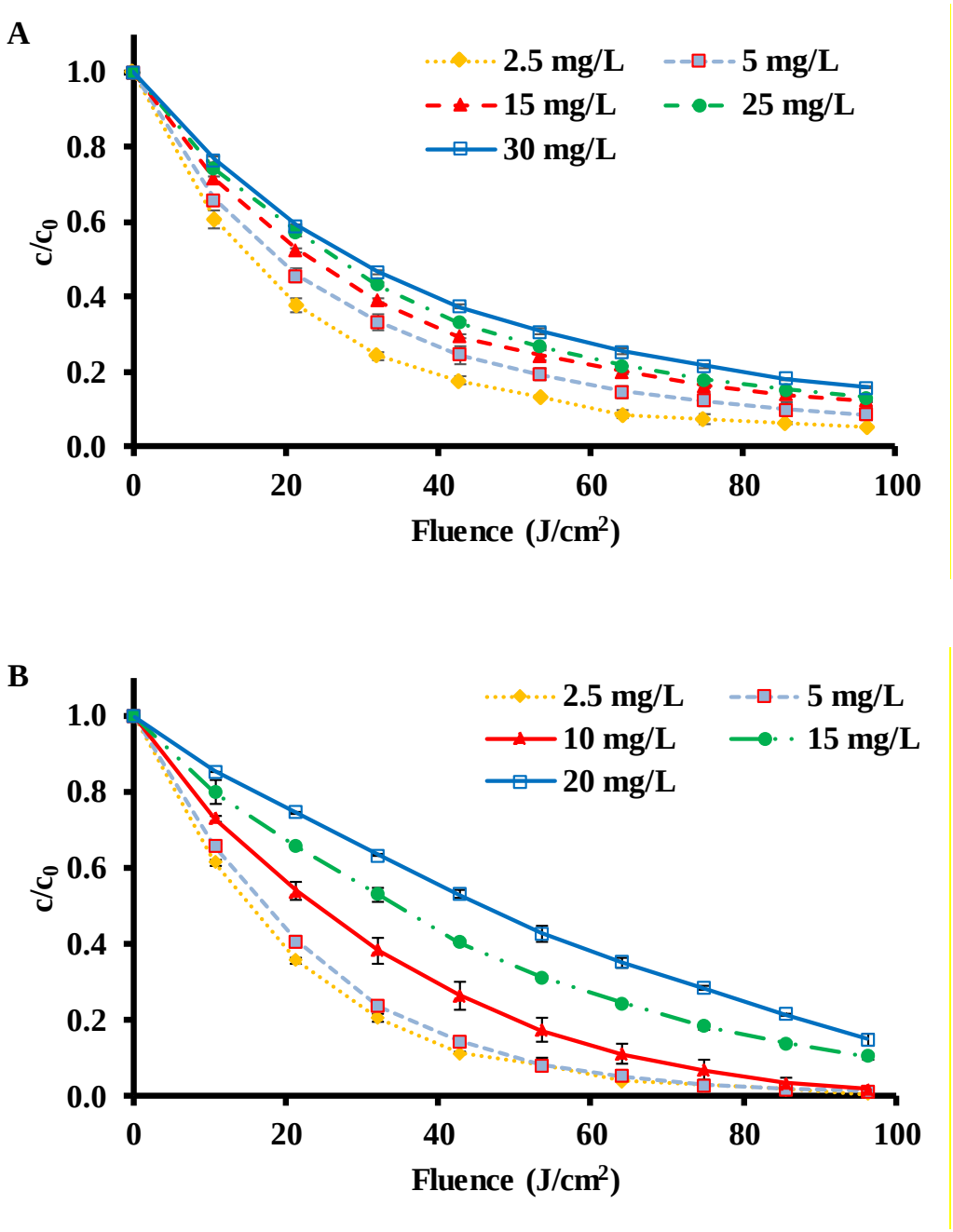


Fig. 7. Effect of dye concentration on the decolourization of Congo red (A) and Methyl orange (B) subjected to a PL/H_2O_2 process. Congo red: [H_2O_2] = 450 mg/L, pH = 6.0. Methyl orange: [H_2O_2] = 400 mg/L, pH = 8.6. Bars represent standard deviation. (For colour reproduction on the web and in black-and-white in print).

3.5. Effect of initial pH

The effect of the pH of the dye solution on decolourization of dyes depends on both, hydroxyl radical and dye properties. Generally, the decolourization of dyes by AOP is slower at high pH because under alkaline conditions H_2O_2 is converted to its less reactive conjugated base (Buxton et al., 1988). However, the results found in the current research show that the decolourization of Congo red is faster at high pH. In fact, the results can be clustered into two very distinct groups, a group of high decolourization rates at mildly acidic to alkaline conditions and another group of low decolourization rates at highly acidic conditions (fig. 8). This kind of results can be attributed to dye structure. At pH > 5.3, Congo red exists with an azo structure. When the pH is decreased the dye protonates giving place to forms with at least two tautomeric quinoid structures, an ammonium and an azonium form (where one proton is added to the α-azo nitrogen). These structures render a stable chelate ring with the azo group and the amino group and the oscillation of a proton between them (Pigorsch et al., 1994).

It has also been postulated that dyes containing two sulfonic groups, such as Congo red, can produce aggregates of several molecules that are less accessible to hydroxyl radicals than single molecules (Galindo et al., 2001). Actually, the aggregation of Congo red molecules upon acidification was observed in the fundamental studies by Pigorsch et al. (1994).

From the point of view of hydroxyl radical stability to pH, given that HCl was used to decrease pH, it is possible that the chloride ion reacts with hydroxyl radicals according to eq. 7 (Jayson et al., 1973) leading to inorganic radical ion, which

shows lower reactivity than hydroxyl radicals, so that they do not take part in the dye decolourization (Aleboyeh et al., 2005).

$$Cl^- + OH\cdot \rightarrow HOCl\cdot^- \qquad (7)$$

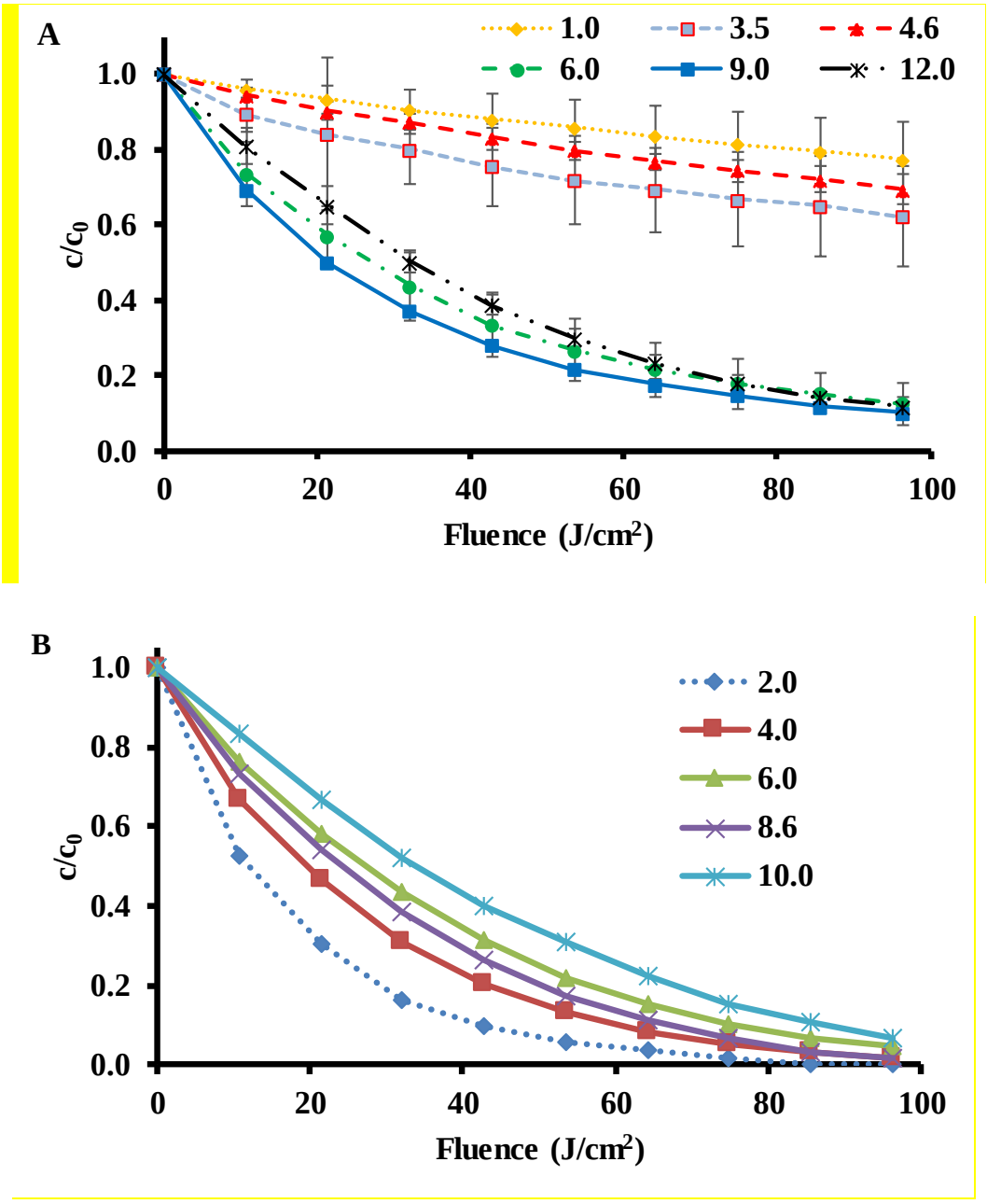


Fig. 8. Effect of initial pH on the decolourization of Congo red (A) and Methyl orange (B) subjected to a PL/H_2O_2 process. Congo red: [dye] = 15 mg/L, [H_2O_2] = 450 mg/L. Methyl orange: [dye] = 10 mg/L, [H_2O_2] = 400 mg/L. Bars represent standard deviation. (For colour reproduction on the web and in black-and-white in print).

On the other hand, the decolourazation of Methyl orange is higher at low pH. This effect has been attributed to protonation of the dye at low pHs, where a labile hydrogen atom makes the dye more vulnerable toward attack of hydroxyl radicals (Galindo & Kalt, 1998).

3.6. Effect of salts

Various salts are added in the bath of textile industries as auxiliaries of the dying process, which can act as radical scavengers. The radical scavenging activity of inorganic salts is generally attributed to the generation of new radicals with lower reactivity than OH·, even though some cases have been reported where certain anions can enhance degradation efficiency (Aleboyeh et al., 2012). Therefore, the effect of NaCl, Na_2SO_3 and Na_2CO_3 on decolourization of Congo red and Methyl Orange by the PL/H_2O_2 process was tested (fig. 9). In general, the inhibitory effect was stronger for SO_3^{2-} and weaker for NaCl. SO_3^{2-} was also the strongest inhibitor of Congo red decolourization among eight salts tested by Sun et al. (2009). It is known that sulphite reacts with hydroxyl radicals with very high constant rates, near the diffusion-controlled limit (Neta and Huie, 1985).

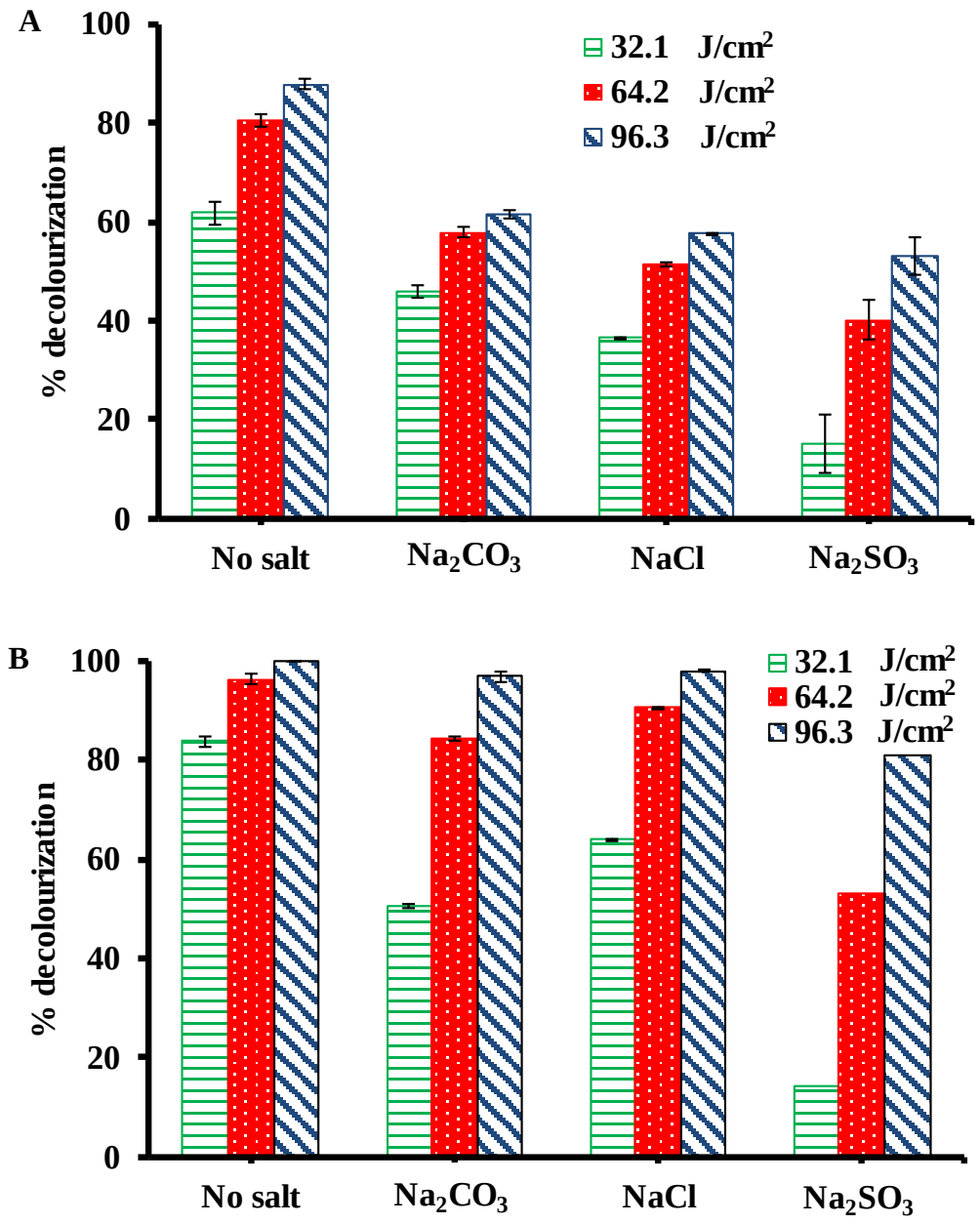


Fig. 9. Effect of different salts on the decolourization of Congo red (A) and Methyl orange (B) subjected to a PL/H_2O_2 process. Congo red: [dye] = 15 mg/L, [H_2O_2] = 450 mg/L, pH = 6.0. Methyl orange: [dye] = 10 mg/L, [H_2O_2] = 400 mg/L, pH = 8.6. Bars represent standard deviation. (For colour reproduction on the web and in black-and-white in print).

NaCl inhibits dye degradation because Cl^- reacts with OH· according to Eq. 7 and carbonate acts as a radical scavenger by producing the much less reactive $CO_3^{\cdot -}$ according to the Eq. 8 (Andreozzi et al., 1999).

$$CO_3^{2-} + OH\cdot \rightarrow CO_3\cdot^{-} + OH^{-} \quad (8)$$

The inhibitory effect of these salts occurs as long as hydroxyl radicals exist in dye solution. It starts during the pulse, when hydroxyl radicals are generated, and will persist until these are depleted. The depletion should occur very fast given the high constant rates of the reaction between hydroxyls and salts, which are 5.5 x 10^9, 4.3 x 10^9 and 3.9 x 10^8 1/M s for SO_3^{2-} (Neta and Huie, 1985), Cl^- (Jayson et al., 1973) and CO_3^{2-} (Buxton et al., 1988) respectively.

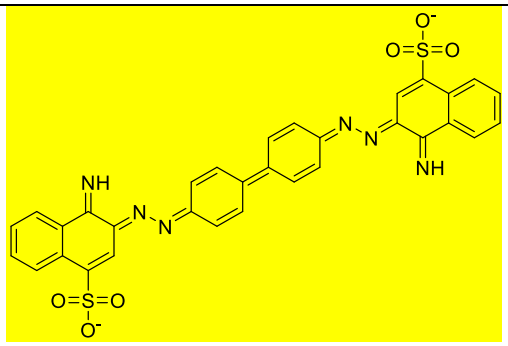
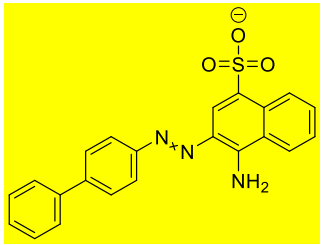
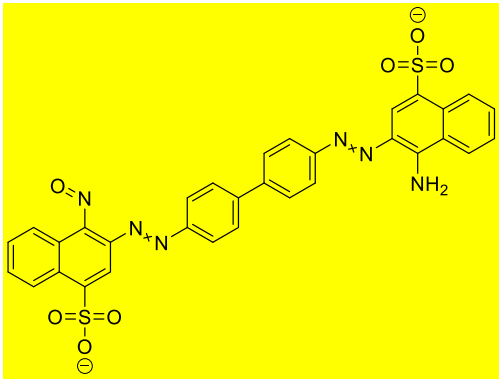
In order to overcome the inhibitory effects of inorganic salts in a real-life scenario, several strategies are possible, the separation of those salts from the effluent before proceeding with AOP process, or the use of higher fluences.

3.7. Generation of degradation products

The generation of degradation products during the PL/H_2O_2–based dye treatment was monitored by LC-HRMS which allowed to detected and tentatively identify several compounds. The three degradation products observed for Congo red are listed in Table 3. The TP403 at m/z 402 corresponds to the loss of the azonaphthalene moiety. TP 666, in turn, is proposed to be formed from Congo red by oxidative conversion of one of the amino group to the nitroso derivative. The third product, the TP650 with an m/z of 324 is attributed to dehydrogenation upon formation of an extended conjugated system. It worth noting that no benzidine, a known carcinogen (IARC, 2012), was detectable during the catalytic breakdown of Congo red. Additionally, the conservation of the azo group at this stage of the oxidation as it has been reported to occur for Congo red degraded

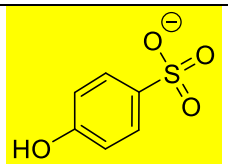
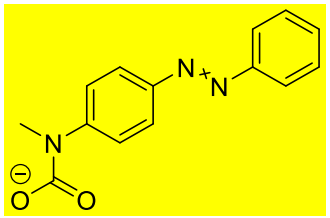
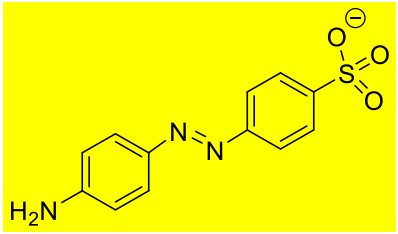
by other AOPs such as TiO_2 photocatalysis (Erdemoğlu et al., 2008) and a photo Fenton like process (Devi et al., 2009).

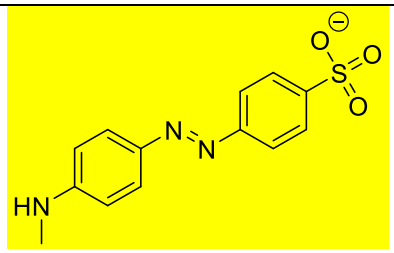
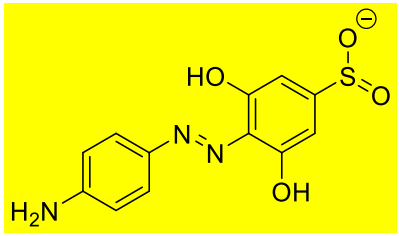
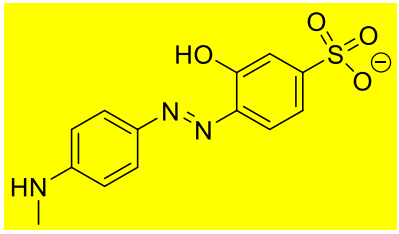
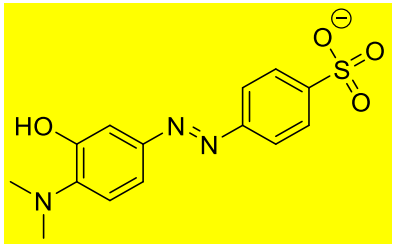
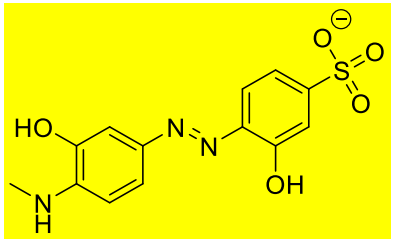
Table 3. Transformation products (TP) identified during the degradation of Congo red by a PL/H_2O_2 process.

m/z of $[M-H]^-$	Structure	TP name
324.0448		TP650
402.0918		TP403
664.0846		TP666

A larger number of degradation products was observed in the experiments with Methyl orange (Table 4). The parent compound gave rise to a desulfonated and N-demethylated compound (TP255), three hydroxylated and demethylated compounds (TP293, TP307 and TP323), two demethylated compounds (TP277 and TP291), an hydroxylated compound (TP 321) and an hydroxylated compound with cleavage of the bond between the azo group and one benzene ring. Compounds corresponding to TPs 277, 291, 321 and 323 have also been reported for the TiO_2 photocatalytic degradation of Methyl orange (Baiocchi et al., 2002).

Table 4. Transformation products (TP) identified during the degradation of Methyl orange by a PL/H_2O_2 process.

m/z of $[M-H]^-$	Structure	TP name
172.9914		TP173
254.0935		TP255
276.0448		TP277

290.0605		TP291
292.0398		TP293
306.0554		TP307
320.0711		TP321
322.0503		TP323

3.8. Effect of ferrioxalate complex on Methyl orange decolourization

The effect of PL as a light source in the frame of an AOP was firstly studied in a very basic system, an UV/H_2O_2 process. It can be thought that using system that is a bit more advanced could yield better results. Therefore, the incorporation of ferrioxalate to the PL/H_2O_2 was studied. The ferrioxalate complex was added to the combination of variables that produced the best results for Methyl orange

degradation, that is, 400 mg/L H_2O_2 at pH 2. This has the advantage that the ferrioxalate complex works better at acidic pH (Jeong and Yoon, 2005).

It can be observed in table 5 that the addition of ferrioxalate complex to the PL/H_2O_2 system accelerated the decolouration rate of MO. Increasing ferrioxalate concentration accelerates the decolourization up to certain concentration beyond which the decolourization rate starts to decline, likely due to excessive hydroxyl generation. The results demonstrate that the PL/H_2O_2/ferrioxalate process is able to increase almost 3-fold the decolourization rate of MO. This conclusion is derived from the comparison of the rate constant of the treatment using 38.8 mg/L Fe^{3+} and 8.7 mg/L $C_2O_4^{2-}$ (0.1477 cm^2/J) with that of the treatment with no ferrioxalate (0.0523 cm^2/J). Less than 5 % of colour remained after applying just 21 J/cm^2 (10 light pulses) when using 38.8 mg/L Fe^{3+}, 8.7 mg/L $C_2O_4^{2-}$ and 400 mg/L H_2O_2 for 10 mg/L of dye.

Table 5. Pseudo-first rate constants for decolourization of Methyl orange by a pulsed light/H_2O_2 process under different ferrioxalate concentrations with fluence up to 96 J/cm^2. [dye] = 10 mg/L, [H_2O_2] = 400 mg/L, pH = 2.0.

[Fe^{3+}] (mg/L)	[$C_2O_4^{2-}$] (mg/L)	k (cm^2/J)	R^2
0	0	0.0523	1.00
9.7	2.2	0.0689	0.99
19.4	4.3	0.0996	1.00
29.1	6.5	0.1112	1.00
38.8	8.7	0.1477	0.99
48.5	10.8	0.0877	1.00

Even though a direct comparison between our results and those that can be found in the literature reporting on different dye degradation methods should not done because of differences in experimental approaches, a gross comparison can reveal the main advantage of including PL in an AOP for dye degradation. The time needed to achieve 95 % decolouration of MO solutions is 19 min as the best (Devi *et al*. 2009; Wang and Bai 2016; Lee *et al*. 2016; Chen *et al*. 2017; Ljubas *et al*. 2015). In comparison, 21 J/cm^2 is required to attain the same effect on a MO solution when using the PL/H_2O_2/ferrioxalate process, that level of energy can be supplied by PL commercial systems in four seconds. The comparison supports our statement that PL can provide very fast dye degradation, which would allow the implementation of fast/compact wastewater treatment reactors that would yield cleaner dying industries.

4. Conclusions

Fast decolourization of two azo dyes by a PL AOP was demonstrated in this research. The decolourization follows the pseudo-first order kinetic with high rates at low dye concentration or increasing H_2O_2 concentrations up to a maximum. The efficacy of the process is affected by pH in a different way depending on the dye. SO_3^{2-}, Cl^- and CO_3^{2-} ions inhibit dye decolourization. No known toxic intermediaries were identified. The incorporation of the ferrioxalate complex to form a pulsed light/H_2O_2/ferrioxalate process increase more than twice the decolourization rate of Methyl orange. This result also shows, beyond the enhanced efficacy of the system, that pulsed light integrated as light source in AOP systems other than a simple pulsed light/H_2O_2 process can accelerate

dye degradation. It is hypothesized that the use of PL coupled to state-of-the-art photocatalyzers may yield even better results. PL technology could become an alternative light source to contribute to decrease the environmental impact of wastewater produced by the dyeing industry.

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