

Degradation and toxicity evaluation of azo dye Direct red 83:1 by an advanced oxidation process driven by pulsed light



Ana Serrano-Martínez^a, María Teresa Mercader-Ros^a, Isabel Martínez-Alcalá^b,
Carmen Lucas-Abellán^a, José Antonio Gabaldón^a, Vicente M. Gómez-López^{c,*}

^a Molecular Recognition and Encapsulation Research Group (REM), Health Sciences Department, Universidad Católica de Murcia (UCAM), Campus de los Jerónimos 135, Guadalupe, 30107, Spain

^b Department of Civil Engineering, Universidad Católica de Murcia (UCAM), Campus de los Jerónimos, 135, 30107, Guadalupe, Murcia, Spain

^c Cátedra Alimentos para la Salud, Universidad Católica de Murcia (UCAM), Campus de los Jerónimos 135, Guadalupe, 30107, Murcia, Spain

ARTICLE INFO

Keywords:

Pulsed light
Azo dye
Advanced oxidation process
Wastewater
Textile

ABSTRACT

Water contamination by dyes is an ecological problem that can be alleviated by advanced oxidation processes (AOPs). A common AOP uses hydroxyl radicals generated by splitting H₂O₂ using UV light. Pulsed light (PL) technology can be used as light source in AOPs having the advantage of producing fast effects. Direct red 83:1 (DR) is an azo dye that is being used to study the elimination of dyes from wastewaters but details about its degradation by a PL/H₂O₂ process are missed. In this work, the effect of H₂O₂ and dye concentrations, pH and salts on the decolourization of DR were determined by spectrophotometry. The PL/H₂O₂ process was able to degrade nearly 80 % of the dye after 45 light pulses. Absence of photolysis and inhibition by hydroxyl scavenging indicate that the degradation was due to oxidation hydroxyl radicals. The decolouration was higher at low dye concentration, high H₂O₂ concentration and alkaline conditions, and was inhibited by salts. These results are useful for the further use of DR as model dye to study the potential of PL as an alternative light source in AOPs for dye degradation. Further studies are recommended to estimate the treatment conditions required for enhancing toxicity abatement.

1. Introduction

Minimizing water pollution is one of the most challenging problems that humanity is facing nowadays. The reduction of the disposal of contaminants in water requires of methods to separate them from wastewaters or the implementation of technologies to destroy them before its disposal to the environment. One of the most contaminants industries of the world is the textile dyeing industry. Dyeing fabrics alone can require 150 liters of water per kilogram [1]. Part of the dyes are not fixed to the fabrics and gets washed up. It has been estimated that 100,000 tons of dyes are disposed directly in aqueous effluents every year [2] and that textile treatment and dyeing accounts for 20 % of the fresh water pollution [3]. The most common type of dyes is azo dyes. Azo dyes released to the environment have important effects on human health, water, soil, flora and fauna as recently revised by Hasaan and El Nembr [4].

One of the existing alternatives to degrade azo dyes present in wastewaters is the use of advanced oxidation processes (AOPs), in which dyes are degraded by attack of hydroxyl radicals. A common and

simple way of generate these radicals is the photolytic split of H₂O₂ using UV light. Low-pressure mercury lamps are the most common type of light source used in AOPs and also in the industry of water and food decontamination. However, alternative light sources for disinfection are being actively assessed to overcome some disadvantages of low-pressure mercury lamps such as potential mercury leakage; although the bulk of the research is being devoted to a single light source, light emitting diodes [5]. Several of the desired features of the new light sources are: being mercury-free, suffer no damage from repeated on/off cycles, reach full power instantaneously and implementation in diverse designs [6]. Pulsed light (PL) technology is a microbial inactivation method used by the food industry in which high-power short-time pulses of wide-spectrum UV-rich light are applied to foods or food-contact surfaces using mercury-free xenon lamps [7]. It has the advantage over low-pressure mercury lamps that produces similar effects in much shorter times and as per fluence basis [8]. The emission spectrum of PL systems has a significant amount of UV-C light and the molar absorption coefficient of H₂O₂ increases at wavelengths < 260 nm; therefore, PL systems are *a priori* suitable for use in AOPs.

* Corresponding author.

E-mail address: vmgomez@ucam.edu (V.M. Gómez-López).

<https://doi.org/10.1016/j.jwpe.2020.101530>

Received 24 February 2020; Received in revised form 26 May 2020; Accepted 10 July 2020

2214-7144/ © 2020 Elsevier Ltd. All rights reserved.

Direct red 83:1 (DR) is being used as a model compound for studying sequential cyclodextrin- or chitosan-AOP to eliminate azo dyes from simulated wastewater from the dyeing industry [9,10]. In this process, cyclodextrins are used to entrap dyes, and once saturated; the dye is eluted for further reutilization. This process, as well as other processes considered by the European Commission to achieve the same goal such as reverse osmosis or ion exchange [11] is not 100 % efficient in the extraction of dye from the wastewater, therefore, a novel AOP is under investigation as complementary alternative to degrade the remaining dye [10,12]. In this method, hydroxyl radicals are generated by the photolytic split of hydrogen peroxide using the high photon flux lamp characteristic of PL technology. The efficacy of PL as light source in AOPs aimed to dye degradation has been shown for some azo dyes [12,13] and malachite green [14], but to the best of our knowledge, no reports about its potential to reduce the eco-toxicity of dyes have been published. The results reported so far did not study how the different operational factors affect the efficacy of this novel AOP on DR degradation. The degradation of this dye has only been previously reported using electrolysis [15]. Consequently, the effect of relevant factors in the degradation of DR by AOPs were determined, namely: dye concentration, H₂O₂ concentration, pH and potential inhibitors.

2. Materials and methods

2.1. Reagents

Direct red 83:1 (C. I. 29225; MW: 992.77 g/mol, CAS n° 90880-77-6) (Fig. 1) was kindly provided by Comercial Química Massó (Barcelona, Spain). Ethanol was purchased from Panreac (Barcelona, Spain), NaCl from Scharlab (Barcelona, Spain) and Na₂CO₃ and catalase from Sigma-Aldrich (St. Louis, MO, USA). The rest of the chemicals were from Merck (Darmstadt, Germany). Milli-Q water > 0.2 MΩ was used to prepare the solutions.

2.2. Apparatus

Tests were carried out in a bench-top pulsed light system XeMaticA-Basic-1 L system (Steribeam, Germany). The system has a treatment chamber with a 19-cm long xenon lamp positioned at the top. When operated at 2.5 V, the lamp emits flashes 200 μs long of a broad-spectrum light containing 21 % of UV light, which characteristic spectrum has been previously reported [16]. The dye was placed in an uncovered Petri dish centred 7.1 cm below the lamp and stirred between pulses with a magnetic stirrer (IKA, Staufen, Germany). Under these conditions, the incident fluence provided by each pulse was 2.14 J/cm², according to data registered by an in-built photodiode coupled with a PC-Lab 2000 L T PC oscilloscope (Velleman Instruments, Belgium) and

performance charts provided by the manufacturer of the PL system. Fluence was increased by applying multiple pulses.

2.3. Experimental procedure

A 20 mL reaction mixture was prepared mixing DR and hydrogen peroxide solutions at different concentrations depending on the test, with or without pH adjustment or addition of scavengers. A typical reaction mixture consisted in 30 mg/L (30.22 μM) of dye and 900 mg/L (26.46 mM) of H₂O₂. pH was adjusted using concentrated NaOH or HCl (pH meter Basic 20, CRISON, Spain). The effect of potential inhibitors was assayed by adding Na₂CO₃, NaCl or Na₂SO₃ (1 g/L, final concentration). Generation of hydroxyl radicals was assessed by adding different amounts of ethanol to the reaction mixture.

Tests consisted in applying 45 light pulses and samples were withdrawn every five pulses. Dye degradation was monitored by measuring absorbance at 530 nm or UV-vis spectra (UV-1700, Shimadzu, Japan) and samples were returned to the mixture after measurements in order to keep the same volume of the reaction mixture along the treatments. The concentration/absorbance relationship fulfilled the Beer-Lambert law. Sample heating, which is a potential side effect of PL treatment) was monitored by an infrared thermometer (ScanTemp 410, TFA Dostmann, Germany). Experiments were run at least per duplicate. Tests without addition of H₂O₂ or without applying light pulses were also carried out in order to assess the possible occurrence of a direct photolytic effect and to control the effect of H₂O₂ without light pulses. The H₂O₂ control was run for the same duration of the PL treatment.

2.4. Kinetic data processing

Data were processed to find the pseudo-first order constants (k , cm²/J) according to Eq. (1):

$$\ln A/A_0 = -k F \quad (1)$$

where A and A_0 are the absorbance at fluence F (J/cm²) and the initial absorbance respectively. Data was processed using Excel 2010 (Microsoft, USA).

2.5. Short-term toxicity

The effect of the PL/H₂O₂ process on the ecotoxicity of the dye solution was assessed by measuring the survival of the crustacean *Thamnocephalus platyurus*. The assay was carried out using the commercial test Thamnotoxkit F (MicroBioTest Inc., Nazareth, Belgium) and performed according to ISO 14380 (2011) using larvae hatched from cysts during 20–22 h before the assay in a standard freshwater (dilution 1:8 with deionized water) at 25 °C under continuous

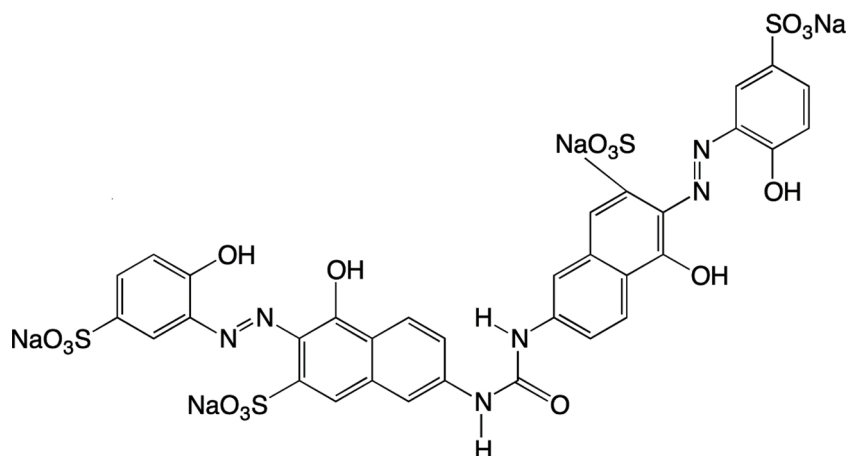


Fig. 1. Molecular structure of Direct red 83:1.

illumination (3000–4000 lx). To this, dye solutions were treated with 0, 15, 30 and 45 pulses and then 0.1 mL catalase solution (5 mg/mL) was added to eliminate the residual H_2O_2 . Afterwards, 10 mL samples were taken after 0, 15, 30 and 45 pulses and dilution series of 100, 50, 25, 12.2 and 6.25 % were prepared (each dilution was made by diluting the previous concentration by half). Samples were transferred to 24-well plates with 10 crustaceans/well (1.0 mL of test solution), in three replicates. Results are presented as toxicity units (TU) according to Eq. (2):

$$TU = \left(\frac{1}{LC50} \right) \times 100 \quad (2)$$

where LC50 means 50 % of test reaction-survival and were assessed according to the following toxicity scale: < 1: non toxic, $1 \leq TU < 10$: toxic, $10 \leq TU < 100$: acute toxic and $100 \leq TU$: very toxic [17,18].

3. Results and discussion

3.1. PL/ H_2O_2 process

Firstly, the capability of the PL AOP to degrade the azo dye DR was assayed. The process was able to decrease almost 80 % of dye colour after applying 45 pulses (Fig. 2A). No direct photolytic effect on the dye molecule was observed in spite of having a strong absorption in the UV range (Fig. 2B) and that the emission spectrum of the lamp used in the current study has a strong UV component [16]. Matching the emission spectrum of the light source with the absorption spectrum of the target compound is an absolute requisite to achieve photolysis, however, it is not the only one because the absorbed photons must have energy enough to break at least the weakest covalent bond. This is not the case for the current target compound/light source pair. Likewise, the simple addition of H_2O_2 to the dye solution without applying light treatment

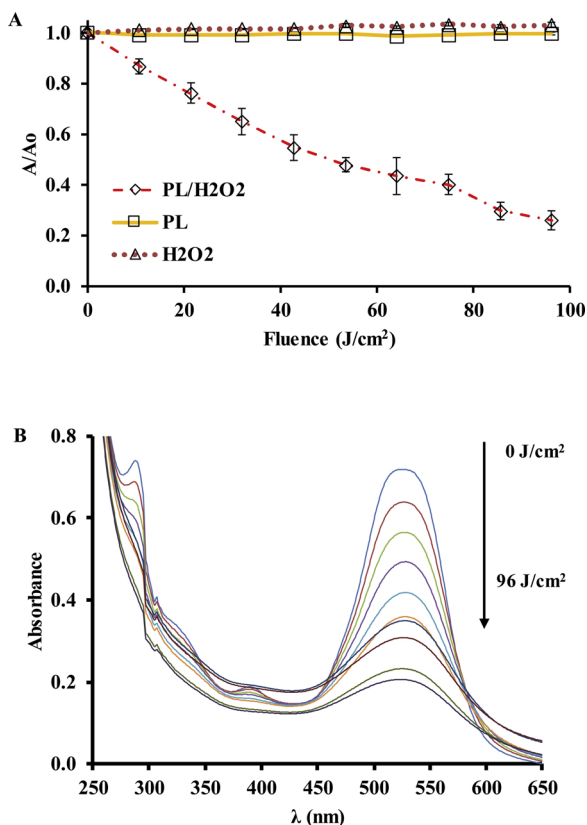


Fig. 2. Effect of H_2O_2 , PL and a PL/ H_2O_2 process on the decolourization of Direct red 83:1. [dye] = 30 mg/L, [H_2O_2] = 900 mg/L, pH = 7.8. A: degradation kinetics (bars represent standard deviation). B: absorption spectra.

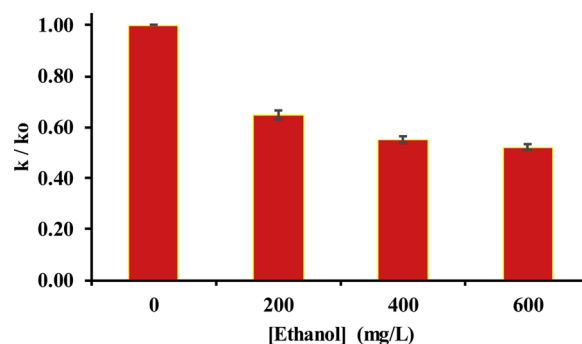


Fig. 3. Effect of a hydroxyl scavenger on the decolourization rate of Direct red 83:1. [dye] = 30 mg/L, [H_2O_2] = 900 mg/L, pH = 7.8.

has no effect on dye degradation. Therefore, the degradation can be attributed to the oxidation of the dye by hydroxyl radicals generated by the photolysis of the H_2O_2 molecule, as happens in many usual AOPs. This hypothesis is supported by tests using ethanol as hydroxyl scavenger (Fig. 3), where a progressive decrease of the dye degradation rate can be observed at increasing concentrations of the scavenger. The inhibition effect of ethanol on DR degradation can be explained by hydroxyl radical competitive reactions between dye and scavenger [19,20].

The PL/ H_2O_2 process is just another version of the well-known UV/ H_2O_2 process but it has an important advantage, it can give place to a very fast dye degradation. In the current case, 74 ± 4 % decolourization is achieved after applying 45 pulses (Fig. 2A). Since commercial PL systems are able to operate at pulse repetition rates of 3 Hz [21], a similar decolourization could be reached in just 15 s, yet, the actual outcome would also depend on reactor configuration. Heat did not contribute to dye degradation since temperature increase was lower than 3 °C during treatments; this kind of reaction are not affected by small changes of temperature in the range 22–45 °C due to their low activation energy [22].

3.2. Absorption spectrum

Fig. 2B shows the evolution of the absorption spectrum of DR with the progress of the PL/ H_2O_2 process. The spectrum of the untreated dye shows an absorption band in the visible range due $\pi \rightarrow \pi^*$ transitions in the azo bonds. The weaker absorption bands in the UV range can be attributed to $\pi \rightarrow \pi^*$ transition in the naphthalene part of the molecule. The bands progressively decrease with increasing fluence as consequence of the cleavage of azo groups and disintegration of aromatic moieties. No spectral shifts were observed during DR degradation; this dye has a rather flat peak at 522–529 nm, therefore small shifts are harder to detect. A remaining absorbance can be observed at the end of the treatment, which indicates that full mineralization was not attained under the assay conditions.

3.3. Operational parameters affecting the degradation of Direct red 83:1 by a PL/ H_2O_2 process

The effect of H_2O_2 concentration on the decolourization of DR can be observed in Fig. 4A. The dye degradation increases with the concentration of H_2O_2 due to a higher generation of hydroxyl radicals available for reacting with the dye molecule. The pseudo-first order reaction rates (Table 1) linearly increases with fluence, and this change can be described by the following equation: $y = 0.007 \cdot 10^{-3} x + 7.5 \cdot 10^{-3}$, $R^2 = 0.98$. The equation is valid only for the range of H_2O_2 concentrations between 300 and 1500 mg/L.

The effect of the initial concentration of DR on their decolourization rates was studied (Fig. 4A). The rate of decolourization linearly decrease with dye concentration in the range 10–40 mg/L ($y = -0.3 \cdot 10^{-3} x +$

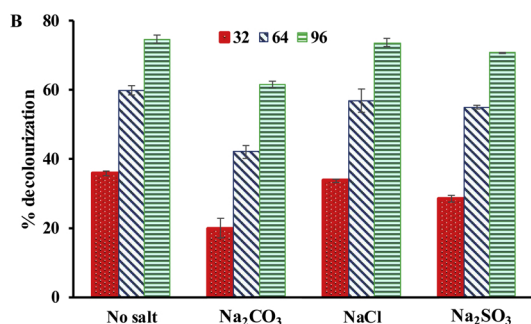
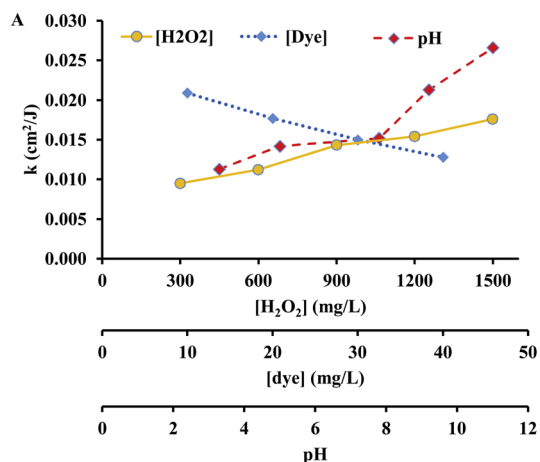


Fig. 4. Effect of operational parameters on the decolourization of Direct red 83:1 by a PL/H₂O₂ process. A: [H₂O₂], [dye] and initial pH; B: salts. Bars represent standard deviation.

Table 1

Pseudo-first rate constants for the decolourization of Direct red 83:1 by a pulsed light/H₂O₂ process under different conditions with fluence up to 96 J/cm².

[H ₂ O ₂]	[Dye]	pH	k (cm ² /J)	R ²
300	30	7.8	0.0095	1.00
600	30	7.8	0.0112	1.00
900	30	7.8	0.0143	0.99
1200	30	7.8	0.0154	1.00
1500	30	7.8	0.0176	0.99
900	10	7.8	0.0209	1.00
900	20	7.8	0.0177	1.00
900	30	7.8	0.0150	1.00
900	40	7.8	0.0128	1.00
900	30	3.3	0.0113	1.00
900	30	5.0	0.0142	1.00
900	30	7.8	0.0152	1.00
900	30	9.2	0.0213	1.00
900	30	11.0	0.0266	0.99

$23.4 \cdot 10^{-3}$, $R^2 = 0.99$). As the concentration of dye increases the light penetration into the sample gets lower, therefore, less hydroxyl radicals are produced to attack the dye molecule.

The degradation of DR under a PL/H₂O₂ process gets favoured under alkaline conditions (Fig. 4A). It is thought that acidification of solutions of dyes containing two sulfonic groups promote aggregation of dye molecules, which would render them less accessible to hydroxyl molecules. Additionally, the ion chloride coming from the HCl added to regulate pH can react with hydroxyl radicals producing the less reactive

$\text{ClOH}^{\bullet-}$ [23,24].

Several types of salts are used in the textile industry to improve the dyeing process [25]. However, they can impair the efficacy of AOPs by reacting with OH[•] giving place to radicals with lower reactivity [26]. Consequently, the effect of Na₂SO₃, NaCl and Na₂CO₃ on decolourization of DR by the PL/H₂O₂ process was tested (Fig. 4B). The order of inhibitor efficacy was Na₂CO₃ > Na₂SO₃ > NaCl. Muruganandham & Swaminathan [27] also observed that Na₂CO₃ had a stronger retarding effect on decolouration than NaCl. Na₂CO₃ and NaCl inhibit dye degradation by the hydroxyl scavenging activity of the carbonate and chloride ions according to Eqs. (3) and (4) respectively Muruganandham & Swaminathan [27].



The inhibition effect is higher at low fluences, however, the PL/H₂O₂ process seems able to overcome the inhibition at higher fluences.

3.4. Short-term eco-toxicity

In spite of the efficacy of the PL/H₂O₂ process on the degradation of Direct red 83:1, the treatment was unable to decrease the short-term toxicity of the dye mixture (Table 2). The mixture was toxic to the crustacean *Thamnocephalus platyurus* and was still toxic after a treatment of 96 J/cm². This result is likely due to the generation of oxidation products that still have toxic effects. Therefore, new tests using the PL/H₂O₂ process at higher fluences should be carried out in order to estimate the fluence necessary to abate the toxicity of the dye. Fluence can be increased by several ways: prolonging treatment time, increasing the fluence per pulse or applying higher voltage to the lamp. Therefore, a longer treatment time may provide the energy required for toxicity abatement thanks to the degradation of toxic intermediates. This solution is not new, since an increased toxicity at early stages of the treatment followed by a decrease in toxicity has been reported during the treatment of azo dyes by diverse treatments. For example, the ozonation of the azo dye Remazol Black 5 caused an increase in toxicity during the first 120 min of treatment, which declined below the toxicity of the parent compound only after 360 min of treatment [28]. An increased electrolysis time was enough to reduce the toxicity of the azo dye Acid Orange 7, which increases during the first 10 min of treatment [29]. A prolonged treatment time also yielded positive results for the electro-Fenton treatment of Acid Orange 7, which toxicity sharply raised almost instantaneously at the beginning of the treatment and only decreased below the toxicity of the parent compound after 30 min of treatment [30]. Another possibility to decrease the toxicity of the degraded dye is the use of other methods to complement the action of the PL AOP or enhance it. For example, the degradation of methyl orange by a PL/H₂O₂/ferrioxalate AOP can be about three times faster than a PL/H₂O₂ AOP [13]. Notwithstanding, it should be bore in mind that some oxidation by-products can be recalcitrant and still toxic. There is evidence that an UV/H₂O₂/ferrioxalate process can decrease the toxicity of an azo dye, although the treatment also included the use of a fungi [31].

Table 2

Toxicity of water containing Direct red 83:1 against the crustacean *Thamnocephalus platyurus* at different fluences during a PL/H₂O₂ process.

Fluence (J/cm ²)	EC ₅₀	TUs	Toxicity
0	52	1.9	Toxic
32	29	3.4	Toxic
64	22	4.6	Toxic
96	21	4.8	Toxic

TU < 1 (non toxic); 1 ≤ TU < 10 (toxic); 10 ≤ TU < 100 (acute toxic); 100 ≤ TU (very toxic).

4. Conclusions

Several factors affecting the efficacy of an advanced oxidation process driven by pulsed light on the degradation of the azo dye Direct red 83:1 were studied. The decolorization of the dye is due to the oxidation of dye molecules typical of an AOP as evidenced by radical scavenging by ethanol. The degradation follows the pseudo-first order kinetic and it was higher at low dye concentration, high H₂O₂ concentration and alkaline conditions. Several salts inhibit the process, but its effect can be overcome at high fluences. The use of pulsed light in the frame of an advanced oxidation process may allow the design of compact and fast reactors, and could be an alternative for alleviating the environmental impact of the dyeing industry but needs more studies to estimate the treatment conditions required to decrease the toxicity of dyes.

Funding source

This work was supported by Universidad Católica San Antonio de Murcia [grant number PMAFI/29/14].

CRedit authorship contribution statement

Ana Serrano-Martínez: Investigation. **María Teresa Mercader-Ros:** Investigation. **Isabel Martínez-Alcalá:** Investigation, Formal analysis. **Carmen Lucas-Abellán:** Investigation. **José Antonio Gabaldón:** Funding acquisition. **Vicente M. Gómez-López:** Conceptualization, Methodology, Formal analysis, Resources, Writing - original draft, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- [1] GFA-TBCG (Global Fashion Agenda & The Boston Consulting Group), Pulse of the Fashion Industry, (2017) Accessed 19 February 2020 https://globalfashionagenda.com/wp-content/uploads/2017/05/Pulse-of-the-Fashion-Industry_2017.pdf.
- [2] S. Arora, Textile dyes: its impact on environment and its treatment, *J. Bioremed. Biodegrad.* 5 (2014) 3, <https://doi.org/10.4172/2155-6199.1000e146>.
- [3] D. Maxwell, L. McAndrew, J. Ryan, State of the Apparel Sector Report – Water, A Report for the Global Leadership Award in Sustainable Apparel, Aug 2015. <https://ceowatermandate.org/resources/glasa-state-of-the-apparel-sector-report-2015/>. Accessed 19 February 2020 (2015).
- [4] M.A. Hassaan, A. El Nemr, Health and environmental impacts of dyes: mini review, *Am. J. Environ. Sci. Eng.* 1 (3) (2017) 64–67, <https://doi.org/10.11648/j.ajese.20170103.11>.
- [5] W.K. Jo, R.J. Tayade, Recent developments in photocatalytic dye degradation upon irradiation with energy-efficient light emitting diodes, *Chin. J. Catal.* 35 (2014) 1781–1792, [https://doi.org/10.1016/S1872-2067\(14\)60205-9](https://doi.org/10.1016/S1872-2067(14)60205-9).
- [6] N.M. Hull, K.G. Linden, Synergy of MS2 disinfection by sequential exposure to tailored UV wavelengths, *Water Res.* 143 (2018) 292–300, <https://doi.org/10.1016/j.watres.2018.06.017>.
- [7] V.M. Gómez-López, P. Ragaert, J. Debevere, F. Devlieghere, Pulsed light for food decontamination: a review, *Trends Food Sci. Technol.* 18 (2007) 464–473, <https://doi.org/10.1016/j.tifs.2007.03.010>.
- [8] K.G. Linden, J. Thurston, R. Schaefer, J.P. Malley Jr., Enhanced UV inactivation of adenoviruses under polychromatic UV lamps, *Appl. Environ. Microbiol.* 73 (2007) 7571–7574, <https://doi.org/10.1128/AEM.01587-07>.
- [9] J.A. Pellicer, M.I. Rodríguez-López, M.I. Fortea, J.A. Gabaldón, C. Lucas-Abellán, et al., Removing of Direct Red 83:1 using α - and HP- α -CDs polymerized with epichlorohydrin: kinetic and equilibrium studies, *Dyes Pigments* 149 (2018) 736–746, <https://doi.org/10.1016/j.dyepig.2017.11.032>.
- [10] J.A. Pellicer, M.I. Rodríguez-López, M.I. Fortea, C. Lucas-Abellán, M.T. Mercader-

- Ros, S. López-Miranda, Adsorption properties of β - and HP- β -CDs cross-linked with epichlorohydrin in aqueous solution. A sustainable recycling strategy in textile dyeing process, *Polymers* 11 (2019) 252, <https://doi.org/10.3390/polym11020252>.
- [11] EC (European Commission), Environmental Improvement Potential of Textiles (IMPRO Textiles), (2014) Accessed 19 February 2020 http://publications.jrc.ec.europa.eu/repository/bitstream/JRC85895/impro%20textiles_final%20report%20Dedited_pubsy%20web.pdf.
- [12] A. Murcia-Salvador, J.A. Pellicer, M.I. Fortea, V.M. Gómez-López, M.I. Rodríguez-López, et al., Adsorption of Direct Blue 78 using chitosan and cyclodextrins as adsorbents, *Polymers* 11 (2019) 1003, <https://doi.org/10.3390/polym11061003>.
- [13] S. Martínez-López, C. Lucas-Abellán, A. Serrano-Martínez, M.T. Mercader-Ros, N. Cuartero, P. Navarro, et al., Pulsed light for a cleaner dyeing industry: azo dye degradation by an advanced oxidation process driven by pulsed light, *J. Clea. Prod.* 217 (2019) 757–766, <https://doi.org/10.1016/j.jclepro.2019.01.230>.
- [14] P. Navarro, J.P. Zapata, G. Gotor, R. González-Olmos, V.M. Gómez-López, Degradation of malachite green by a pulsed light/H₂O₂ process, *Water Sci. Technol.* 79 (2019) 260–269, <https://doi.org/10.2166/wst.2019.041>.
- [15] M.J. Kupferle, A. Galal, P.L. Bishop, Electrolytic treatment of azo dyes containing o,o'-dihydroxyazo complexation sites, *J. Environ. Eng. Sci.* 3 (2004) 223–229, <https://doi.org/10.1139/s04-007>.
- [16] A. Izquier, V.M. Gómez-López, Modelling the pulsed light inactivation of microorganisms naturally occurring on vegetable substrates, *Food Microbiol.* 28 (2011) 1170–1174, <https://doi.org/10.1016/j.fm.2011.03.010>.
- [17] R. Kalinowski, M. Zaleska-Radziwill, Ecotoxicological assessment of freshwater sediments, *Pol. J. Environ. Stud.* 20 (2011) 1181–1191.
- [18] G. Persoone, B. Marsalek, I. Blinova, A. Torokne, D. Zarina, L. Manusadzianas, A practical and user-friendly toxicity classification system with microbiotests for natural waters and wastewaters, *Environ. Toxicol.* 18 (2003) 395–402, <https://doi.org/10.1002/tox.10141>.
- [19] N. Daneshvar, M.A. Behnajady, M.A.M. Mohammadi, M.S. Seyed, UV/H₂O₂ treatment of Rhodamine B in aqueous solution: influence of operational parameters and kinetic modeling, *Desalination* 230 (2008) 16–26, <https://doi.org/10.1016/j.desal.2007.11.012>.
- [20] N.M. Mahmoodi, B. Karimi, M. Mazarji, H. Moghtaderi, Cadmium selenide quantum dot-zinc oxide composite: synthesis, characterization, dye removal ability with UV irradiation, and antibacterial activity as a safe and high-performance photocatalyst, *J. Photochem. Photobiol. B* 188 (2018) 19–27, <https://doi.org/10.1016/j.jphotobiol.2018.08.023>.
- [21] D. Chen, P. Chen, Y. Cheng, P. Peng, J. Liu, Y. Ma, et al., Deoxyribose decontamination in raw and germinating barley treated by plasma-activated water and intense pulsed light, *Food Bioprocess Technol.* 12 (2019) 246–254, <https://doi.org/10.1007/s11947-018-2206-2>.
- [22] C. Galindo, A. Kalt, UV-H₂O₂ oxidation of monoazo dyes in aqueous media: a kinetic study, *Dyes Pigments* 40 (1998) 27–35, [https://doi.org/10.1016/S0143-7208\(98\)00027-8](https://doi.org/10.1016/S0143-7208(98)00027-8).
- [23] E. Pigorsch, A. Elhaddaoui, S. Turrell, Spectroscopic study of pH and solvent effects on the structure of Congo red and its binding mechanism to amyloid-like proteins, *Spectrochim. Acta Part A: Mol. Spectrosc.* 50 (1994) 2145–2152, https://doi.org/10.1007/978-94-011-1934-4_59.
- [24] C. Galindo, P. Jacques, A. Kalt, Photochemical and photocatalytic degradation of an indigo dye: a case study of Acid blue 74 (AB74), *J. Photochem. Photobiol. A-Chem.* 141 (2001) 47–56, [https://doi.org/10.1016/S1010-6030\(01\)00435-X](https://doi.org/10.1016/S1010-6030(01)00435-X).
- [25] S.M. Burkinshaw, G. Salihu, The role of auxiliaries in the immersion dyeing of textile fibres: part 6 analysis of conventional models that describe the manner by which inorganic electrolytes promote reactive dye uptake on cellulosic fibres, *Dyes Pigments* 161 (2019) 595–604, <https://doi.org/10.1016/j.dyepig.2017.09.028>.
- [26] C. Zhang, Y. Dong, B. Li, F. Li, Comparative study of three solid oxidants as substitutes of H₂O₂ used in Fe (III)-oxalate complex mediated Fenton system for photocatalytic elimination of reactive azo dye, *J. Clean. Prod.* 177 (2018) 245–253, <https://doi.org/10.1016/j.jclepro.2017.12.211>.
- [27] M. Muruganandham, M. Swaminathan, Photochemical oxidation of reactive azo dye with UV-H₂O₂ process, *Dyes Pigments* 62 (2004) 269–275, <https://doi.org/10.1016/j.dyepig.2003.12.006>.
- [28] C. Wang, A. Yediler, D. Lienert, Z. Wang, A. Kettrup, Ozonation of an azo dye C.I. Remazol Black 5 and toxicological assessment of its oxidation products, *Chemosphere* 52 (2003) 1225–1232, [https://doi.org/10.1016/S0045-6535\(03\)00331-X](https://doi.org/10.1016/S0045-6535(03)00331-X).
- [29] Y. Xia, G. Wang, L. Guo, Q. Dai, X. Ma, Electrochemical oxidation of Acid Orange 7 azo dye using a PbO₂ electrode: parameter optimization, reaction mechanism and toxicity evaluation, *Chemosphere* 241 (2020) 125010, <https://doi.org/10.1016/j.chemosphere.2019.125010>.
- [30] T.X. Huong Le, T.V. Nguyen, Z.A. Yacoubia, L. Zougrana, et al., Toxicity removal assessments related to degradation pathways of azo dyes: toward an optimization of Electro-Fenton treatment, *Chemosphere* 161 (2016) 308–318, <https://doi.org/10.1016/j.chemosphere.2016.06.108>.
- [31] S. Barkaat, M. Zuber, K.M. Zia, A. Noreen, S. Tabasum, UV/H₂O₂/Ferrioxalate based integrated approach to decolorize and mineralize reactive blue dye: optimization through response surface methodology, *Zeitschrift für Physikalische Chemie* (2020), <https://doi.org/10.1515/zpch-2019-1388> In press.