Degradation of an azo dye by a fast and innovative pulsed light/H₂O₂ advanced oxidation process

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A B S T R A C T

Pulsed light (PL) is a food processing technology initially intended for microbial inactivation that can potentially be applied in other UV-light based processes. PL lamps emit high intensity broad spectrum light from UV to infrared. This research tested the use of PL as part of an advanced oxidation process (AOP) for degrading polluting dyes. Experiments were performed in a batch reactor, and the efficiency of the AOP under different parametric values: dye concentration, pH and H₂O₂ doses on Direct yellow 106 decolourization was followed by spectrophotometry. Effects on chemical oxygen demand and electrical efficiency were also determined. Decolourization process follows a pseudo-first order kinetic. It was improved by increasing H₂O₂ concentrations and low pH; while there was little influence of dye concentration, perhaps due to the reactor configuration. The highest constant rate observed was 0.0410 cm²/J. The decolourization by PL/H₂O₂ fits to a typical mechanism of a conventional UV/H₂O₂ process; since no direct photolysis or thermal effects were observed. Mineralization was incomplete likely due to the highly resonant structure of the dye. An electrical energy per order of 1009 kWh/m³/order was calculated. Ninety % of colour removal was reached at 40 J/cm², which is achievable in less than 30 s by most of PL systems existing in the market. The PL/H₂O₂ process seems to be useful for decolourization of wastewater and could offer the advantage of a very fast degradation.

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1. Introduction

From the past few decades the extensive use of pesticides, industrial chemicals and different types of dyes in cosmetic, paper and leather is well known. A large amount of pollutants are disposed continuously into water bodies from the above sources, leading to undesirable accumulation of toxic compounds that entail serious environmental problems [1]. The textile industry is considered the most polluting industrial sector due to the quantity and constituents of the effluents produced [2]. Therefore, it is logical to look for an economical and feasible technique for remediation of such hazardous environmental effluents [3]. In fact, about 1–20% of world dye products enter into textile wastewater during the dying process. Due to their good properties, azo dyes are the most widely used. It is estimated that their total production exceed 7,000,000 ton per year, representing over 60% of the total dye production, followed by the anthraquinone group [4–7]. The main adverse effects of azo dyes in the environment are their inhibitory effect on aquatic photosynthesis, ability to deplete dissolved oxygen and toxicity to flora, fauna and humans. Also, if the dyes are broken down anaerobically, aromatic amines are generated, which are very toxic, carcinogenic, genotoxic and mutagenic compounds [8].

One of the strategies to reduce the disposal of dyes into water bodies is directed to recover them from wastewater and reuse them as raw material in new dyeing steps, as well as obtaining less contaminated wastewater that can be reused. Following this strategy, our research group has recently developed a method based on the use of cyclodextrins for the encapsulation of different dyes, such as Direct yellow 106 [9]. Since dye retention is incomplete, an additional strategy to eliminate the remaining dye from wastewater is required.

In recent years, advanced oxidation processes (AOPs) have been proved as an excellent method for the degradation of environmentally hazardous material [1]. Among these methods,
homogeneous chemical oxidation using ultraviolet radiation (UV) in the presence of H$_2$O$_2$ has been widely studied. The UV/H$_2$O$_2$ process involves the photolysis of hydrogen peroxide to generate hydroxyl radicals (·OH), which are very effective in the oxidation and mineralization of most organic pollutants [10].

Pulsed light technology is a kind of photonic technology where electrical energy is stored in capacitors over a relatively long time, and then released in a shorter time to a xenon lamp, which emits pulses of a high intensity broad spectrum light, that includes UV light [11]. PL can deliver high fluences in a significantly shorter time than UV continuous (CW UV) processes, producing more rapid effects both in time and fluence. This technology has been mainly developed and applied for inactivation of microorganisms on food, food contact surfaces and transparent liquids, and it is currently applied at industrial level for decontamination of caps and cups used in food packaging. In recent years, the scope of potential applications of PL technology has been extended to other fields such as protein modification [12], inactivation of enzymes [13] or enrichment of food vitamin content [14], the latter currently applied at industrial scale. Since PL has an important UV component, a brand new application of this technology could be its use as part of an AOP for degradation of polluting dyes. Therefore, the aim of this research has been to assess the performance of PL as part of an AOP, for the degradation of polluting dyes, studying specifically the effect of H$_2$O$_2$ and dye and concentrations and pH on the rate of decolourization. Moreover, dye mineralization and electrical efficiency of the process was evaluated.

2. Materials and methods

2.1. Chemicals

C. I. Direct yellow 106 (DY106) (CAS: 12222-60-5) was kindly provided by Comercial Química Massó (Barcelona Spain). As can be observed in Fig. 1 [15], the chemical structure of DY 106 is a challenge for its degradation by an AOP since is a stable molecule, including in its structure an azo link, an ethylene group and benzene-sulphonic moieties. Also, the presence of naphthalene groups sharing carbons with 1,2,3-triazole groups give this dye a high conjugation degree. Hydrogen peroxide solution (30%) and other compounds such as HCl and NaOH, were purchased from Merck (Germany). Work solutions were prepared by dissolving the required quantity in demineralized water.

2.2. Apparatus

Pulsed light treatment was performed in a XeMaticA-Basic-1L system (Steribeam, Kehl, Germany). The system produces a broad-spectrum pulsed light spanning from infrared to ultraviolet light with a pulse width of 200 µs The treatment chamber has dimensions of 20 cm wide, 14 cm high, 10 cm deep, and it is equipped with one 19-cm long xenon lamp placed at the top of the chamber. A stirrer (Topolino, IKA, Staufen, Germany) was incorporated to the chamber for inter-pulse sample homogenization. The system applied a discharge voltage of 2.5 kV, which generates 500 J/pulse. Samples received an incident fluence of 2.14 J/cm$^2$ pulse, which was determined by analysis of in-built photodiode readings using a PC-Lab 2000 LT PC oscilloscope (Velleman Instruments, Gavere, Belgium), and manufacturer performance charts. At this discharge voltage, the UV fraction of the spectrum is 21%. Different fluencies were obtained by increasing the number of pulses.

2.3. Experimental procedure

A Petri dish without cover with 15 mL of sample was placed on the stirrer below the centre of the lamp. This volume (2.7 mm height) was selected as the minimum required to fully covering the plate bottom. The distance between the lamp and the sample surface was 6.7 cm. Tests were performed based in a reaction mixture consisting in 20 mg/L of dye and 600 mg/L H$_2$O$_2$ dissolved in demineralized water, at the natural pH of this mixture (9.15); this solution was adjusted to the different pHs by addition of HCl or NaOH.

Spectrophotometric measurements were carried out by using a UV−Vis spectrophotometer (UV−1700, Shimadzu, Japan). A 400 nm wavelength was selected to monitor decolourization because the dye solution exhibits its highest absorbance at this wavelength in the visible range (Fig. 2). The absorbance was linearly correlated
(R² = 0.999) to dye concentration over the studied range. COD was determined by the closed reflux colorimetric method using Lovibond (Dortmund, Germany) ampoules and a Lovibond MultiDirect tintometer. Also, pH was measured by a Crison pH meter (Basic 20, CRISON, Barcelona, Spain). Temperature through treatments was monitored by an infrared thermometer (ScanTemp 410, TFA Dostmann, Wertheim, Germany). Amperage during the capacitor charging process was measured by a HT73 Digiclamp ammeter (HT Instruments, Barcelona, Spain).

2.5. Calculations

Absorbance at 400 nm vs. fluence data were regressed for the pseudo-first order kinetic using Eq. (1):

$$\ln \frac{A}{A_0} = -k F$$  \hspace{1cm} (1)

where A is the absorbance at fluence F(J/cm²), A₀ the initial absorbance and k the constant rate (cm²/J).

The figure-of-merit electric energy per order $E_{EO}$ (kWh/m³/order) was used to calculate the electric efficiency of the process using Eq. (2) [16]:

$$E_{EO} = \frac{Pt}{mV \log \frac{C_0}{C_t}}$$  \hspace{1cm} (2)

where P is the power (kW) of the system, t (h) is the duration of the current input to the PL system, V (m³) is the treated volume, and C₀ and Cᵣ the initial and final dye concentrations (mg/L) respectively, obtained from the calibration curve; a factor of 1000 was used to convert litres in m³. The power was estimated taking into account the Spanish electrical network voltage (220 V), and amperemetric measurements.

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

3. Results and discussion

3.1. PL direct photolysis and PL/H₂O₂ process

Firstly, the effect of PL alone on the decolourization of DY 106 was tested. As can be seen in (Fig. 3), the results obtained showed that PL not cause a direct photolytic effect on colour solution, maybe as explained before, due to the highly stable chemical structure of this dye. The use of H₂O₂ alone, which was tested to control its possible individual effect, has no influence on the decolourization process. However, when used as a part of a H₂O₂ AOP, PL is effective for decolourization. The PL/H₂O₂ process reaches nearly 90% of colour removal, showing faster initial colour degradation up to 40 J/cm² and a progressive declining of decolouration rate, which is typical of a first-order reaction commonly observed in the decomposition of dyes by an UV/H₂O₂ process. In this sense, the decolourization of the dye by the PL/H₂O₂ AOP can be described according to the widely known mechanism of generation of hydroxyl radicals upon photolysis of H₂O₂ according to Eq. (3) [17]; where the UV part of the PL emission provides the required photons for the generation of hydroxyl radicals. The hydroxyl radical show a high oxidation potential and can attack both the dye and the products of photolysis [18], by abstracting hydrogen atoms or by adding to double bonds [17].

$$\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2\cdot\text{OH}$$  \hspace{1cm} (3)

An unwanted side effect of PL is sample heating [11], therefore temperature is usually monitored during PL treatments to assess potential thermal effects. The temperature rise at the end of all tests was lower than 3 °C, thus ruling out any heat contribution to the process.

The UV–visible absorption spectrum of DY 106 has peaks at wavelengths of 400 nm and 204 nm (Fig. 2). The peak at 400 nm corresponds to the azo linkage [19] and the UV peak includes both the aromatic groups together with the background absorbance of H₂O₂. The change in absorption spectrum with the progress of the treatment, shows the progressive disappearance of the peak at 400 nm, which can be ascribed to the attack of OH radical to the azo group leading to the opening of the –N=N– double bond [20]. No hypsochromic or bathochromic shifts have been observed, which may indicate limited changes in the generation of degradation products; although it can also be noticed that, the original dye exhibits a minimum absorbance in the UV range at 316–319 nm, that increases without forming a peak, with the progress of the treatment, becomes stable between 21 and 43 J/cm² and then decreases. The formation of new peaks or absorption bands in photolytic degradation of dyes is due to formation of the intermediate products [21].

3.2. Effect of dye concentration

The results of decolourization obtained at different initial dye concentrations are shown in Fig. 4. As can be seen in Table 1, pseudo-first order rate constants show that the decolourization rate under different dye concentrations are quite similar in the range of 5–15 mg/mL, decreasing at concentrations of 20 mg/mL.
It is known that higher dye concentrations produce slow decolourization rates, due to the lower light penetration [18]. However, the relative insensitivity of this process at low dye concentrations can be attributed to the thin sample film used in the experiments, just 2.4 mm thick, which allows a high light transmission through the sample. For example, according to the Beer-Lambert law, at 400 nm between 72 and 91% of light that penetrates the sample just 2.4 mm thick, which allows a high light transmission through the sample depend on dye concentration.

A remarkable finding that can be observed in Fig. 4 and others is that a high level of decolourization can be attained at 66 J/cm²; this fluence is achieved by 31 light pulses. The PL system used in the current work has an important difference with others, is manually fl...
mineralization level cannot be associated with a PL technology, since this is just a different way to generate hydroxyl radicals from H$_2$O$_2$. Similar results have been reported for other chemicals subjected to similar or different AOP, such as Acid orange 52 [28], Acid yellow 23 [21] and for a triazole [29].

Taking into account the variation of absorption spectra with the progress of AOP and incomplete mineralization (50%) achieved in this work, similar results have been reported by Neamtu et al. [30] for Reactive yellow 84 and Behnajady et al. [21], for Acid yellow 23 degradation with ZnO photocatalyst.

It is also possible that in addition to the aromaticity of the structure, its sulfonic moiety contributes to its stability, since it is known that the sulfonate group has a high electron withdrawing capacity that could help to stabilize aromatic species. No attempts to test mineralization under other conditions were done because complete mineralization would not be expected based on the findings that the mineralization degree observed for the standard reaction mixture was relatively low, the decolourization was not complete under any condition, and it is known that mineralization rates are always lower than decolourization rates [10,18,28,31].

3.6. Electric energy per order

The figure-of-merit $E_{EO}$ was used to evaluate the electrical efficiency of the process. This figure was developed by an expert panel of the International Union of Pure and Applied Chemistry [16] for direct comparison of electric efficiency of AOPs, independently of their nature. The figure-of-merit $E_{EO}$ is seldom reported for PL process, therefore it worth explaining how it was calculated in the current case. The original equation define its variables for a continuous process, where $P_t$ is the energy billed by the power company and $t$ the time invested to treat a volume $V$ [16]. However, PL systems work in a discontinuous mode, where the electricity is taken from the mains during a relatively long time, to be stored in capacitors and then released to the lamp in a shorter time. Therefore, the time that the PL system takes electricity from the mains and the treating time are not neither simultaneous nor the same. In the current case, the duration of the light pulse is 200 μs but it takes 4 s to charge the capacitors to the desired voltage, this is the time ($t$) that must be used to calculate the $E_{EO}$. Since the measured amperage has been 1.43 A, the energy consumption is 0.011 kWh and the $E_{EO}$ of this process for 20 mg/mL dye with 600 mg/mL H$_2$O$_2$ at pH 9.15 is 1009 kWh/m$^3$/order. This value is similar or smaller than those reported for other photolytic processes. For example, the $E_{EO}$ for diazinon by a photocatalysis with ZnO nanocrystals is 1075–1389 kW h/m$^3$/order [31] and for the more complex dyes rhodamine B and methylene blue are 1500 and 3000 kWh/m$^3$/order, respectively [32].

The electric efficiency of this process can be improved by more than 30% to less than 700 kWh/m$^3$/order by either using a higher concentration of hydrogen peroxide (Table 2) or a lower pH (Table 3), both factors decrease the electrical energy necessary to decolourize DY 106 by the same magnitude. Using another type of system configuration such a flow-through reactor should render a higher energy efficiency because it will allow make profit of all photons generated by the lamp.

4. Conclusions

Pulsed light technology used alone has not effect on Direct yellow 106 degradation. However, when PL was used together H$_2$O$_2$ in an advanced oxidation process, it can degrade very fast the dye. The effects of this AOP can be explained by the formation of hydroxyl radicals as any other UV/H$_2$O$_2$ process, and follow a pseudo-first order kinetics. Decolourization increases with concentration of oxidant agent. While a faster decolourization rate was observed at low pH, the concentration of dye showed a weak influence due to the thin film reactor configuration. A PL/H$_2$O$_2$ process may offer a much faster dye degradation rate than conventional CW UV/H$_2$O$_2$ processes, which should allow treating higher volume of wastewater. Additional tests including other dyes should be performed to further assess the potential of PL for dye degradation.

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