



Degradation and mineralization of antipyrine by UV-A LED photo-Fenton reaction intensified by ferrioxalate with addition of persulfate



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ABSTRACT

The intensification of the degradation of antipyrine in aqueous solution by using a UV-A-LED-photo-Fenton reaction intensified by ferrioxalate complexes and with addition of persulfate anions was studied. The efficiency of the reaction was evaluated in terms of antipyrine degradation and mineralization degree at different initial concentrations of hydrogen peroxide, ferrous ion, oxalic acid and persulfate anion. The reaction was carried out using a lab-scale photoreactor irradiated with artificial UV-A-LED light emitting at 365 nm. Artificial neural networks (NNs) were implemented for modelling the degradation process. Under optimal conditions, complete degradation of antipyrine and 93% mineralization was reached in 2.5 and 60 min, respectively. The contribution of HO· radicals in this system was evaluated running the reaction in the absence and presence of appropriate quenchers such as *tert*-butyl alcohol and methanol. In the last step of reaction, possibly different intermediates such as 2-butenedioic acid, butanedioic acid, 4-oxo-pentanoic acid, acetate and formate can be generated which cannot be degraded by HO· radicals or their reaction is very slow. This ferrioxalate-mediated system reduces the amount of H₂O₂ needed (100 mg L⁻¹) for antipyrine degradation and persulfate was not necessary because it could not be activated with UV-A LED nor with Fe²⁺ since it is quickly converted to Fe³⁺ forming ferrioxalate complexes.

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1. Introduction

The consumption of pharmaceuticals compounds in last years has increased considerably leading to the increase in their concentration in urban wastewaters [1–3]. These compounds are known to be recalcitrant to biodegradation because of their aromatic structure and their low solubility in water. So, they are only slightly degraded in sewage wastewater treatment plants [4,5]. For instance, antipyrine is a pharmaceutically active compound detected in various natural environments [6,7]. The percentage of removal of antipyrine in effluents from conventional wastewater treatment plants is only about 30% [8]. Therefore, an effective tertiary treatment for the removal of antipyrine would be necessary.

Advanced Oxidation Processes (AOPs) are being proposed as valuable approaches for pharmaceuticals pollutants wastewater treatment. It is well-known that the efficiency of AOPs is based on the generation of highly reactive free radicals such as hydroxyl radicals (HO·, E_o = 2.8 V) or sulfate radicals (SO₄⁻, E_o = 2.6 V). HO·

can be generated by various combinations such as UV/H₂O₂, Fenton, photo-Fenton, ferrioxalate-based systems, UV/TiO₂, UV/O₃ or these processes in conjunction with ultrasound. Sulfate radicals can be formed in AOPs based on systems with activated S₂O₈²⁻ by UV light, transition metals, hydrogen peroxide or ultrasound [9].

Several processes including direct photolysis and UV/H₂O₂ [10,11], Sono-photo-Fenton [12], ferrioxalate-assisted solar photo-Fenton [12–14] have been investigated for the removal of antipyrine.

Oxidation of antipyrine aqueous solution by UV-C/S₂O₈²⁻ [11] or by heat activated persulfate [15] has also been reported in the scientific literature. The effectiveness of these studies was examined in terms of antipyrine removal, but they have not reported data about mineralization.

However, until now, UV-A LED lamps have not been used for the degradation of antipyrine in AOPs. LEDs offer potential advantages over conventional UV lamps like high efficiency, compactness, lower energy consumption, robustness, not overheating, long life times, no disposal problems and no warm-up time [16,17]. LEDs are semiconductor p-n junction diodes, which, when activated, emit light due to electrons and holes recombination (i.e. electrolu-

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minescence). Recombined electrons and holes become more stable and release excess energy by emitting photons of the same frequency. A key advantage of LEDs is that almost all electrical energy can be converted into monochromatic light energy [16]. The light output is linearly proportional to the current within its active region, so the light output can be precisely modulated to send an undistorted signal through a fiber optic cable. A LED is a directional light source, with the maximum emitted power in the direction perpendicular to the emitting surface [18].

The main objective of the present work was to optimize the degradation and mineralization of an antipyrine aqueous solution by using a UV-A LED photo-Fenton system using a LED lamp with a light peak emission wavelength at 365 nm. The intensification of this photo-Fenton system with ferrioxalate was studied as it is a photo-sensitive complex being 320–400 nm irradiation favorable for the ferrioxalate photochemistry [19,20].

Additionally, the photolysis of ferrioxalate generates more H_2O_2 which, with Fe(II), yields more HO^\bullet radicals through the well-known Fenton reaction mechanism [21,22], improving the degradation process. The addition of persulfate was also studied to test the synergistic effect of its possible activation with ferrous ion and hydrogen peroxide in this UV-A LED photo-Fenton process.

Experimental tests based on a Factorial Design were analyzed and results were fitted using neural networks (NNs), which allowed the value of the Response Functions (degradation of antipyrine or mineralization degree (mg L^{-1} TOC removed)) to be estimated within the studied range as a function of the operating variables (1: initial concentration of hydrogen peroxide, 2: initial concentration of Fe^{2+} , 3: initial concentration of oxalic acid, 4: initial concentration of persulfate). The effects of the variables on Response Functions were also determined.

Finally, the reaction kinetics and hydroxyl and sulfate radical contribution on the mineralization reaction were also studied.

2. Experimental

2.1. Materials and chemicals

Antipyrine, $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}$ (99%) (Fig. 1) was obtained from Acros. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, sodium persulphate ($\text{Na}_2\text{S}_2\text{O}_8$, 98%), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, 99.5%) and *tert*-butyl alcohol were purchased from Pan-reac. Hydrogen peroxide (30% w/v) was obtained from Merck. Methanol was obtained from Sigma-Aldrich. All chemicals were used as received without further purification.

The initial concentration of antipyrine was always 50 mg L^{-1} ($\text{TOC} = 35 \text{ mg L}^{-1}$). For experimental runs focused on the evaluation of radical mechanism, *tert*-butyl alcohol and methanol were added to the system as radical scavengers [23].

2.2. UV-light emitting diodes (UV-A LED)

The UV LED photosystem was developed with an indium gallium nitride (InGaN) LED lamp (LZ4-00U600 LED ENGIN, USA) with a light peak emission wavelength at 365 nm (see Fig. S1, Supplementary Material). The nominal consumption of the LED lamp was 1.80 W, for an applied current of 700 mA. The photon flux emission of UV-A-LED was determined by potassium ferrioxalate actinometer and found to be $3.32 \times 10^{-6} \text{ Einstein s}^{-1}$.

2.3. UV-A LED photocatalytic reactor

The schematic diagram of the experimental system employed in this research is shown in Fig. 2. A quartz protective plate is placed between the reactor and the UV-LED lamp emitting at 365 nm. The volume of the reactor is 150 mL.

All experiments were carried out in a batch mode lab-scale photoreactor illuminated with a UV-A LED lamp.

2.4. Experimental procedure

The experiments were carried out in the batch UV-A LED photoreactor indicated above. The pH was adjusted to 2.8 with H_2SO_4 and NaOH solutions to avoid iron precipitation. Then, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, oxalic, hydrogen peroxide and persulfate were directly added to the photoreactor at the beginning of each experiment. All the experiments were run at room temperature between 24 and 26 °C. For the duration of the tests, the samples were periodically withdrawn from the reactor to obtain the residual concentrations of antipyrine, total organic carbon (TOC), ferrous iron, hydrogen peroxide, persulfate and dissolved oxygen.

Hydroxyl radical scavenging was accomplished using 1 M *tert*-butyl alcohol or methanol to determine the contributions of the radical reactions to mineralization. Before analysis, all samples were withdrawn from the reactor to determine their H_2O_2 contents and were immediately treated with excess Na_2SO_3 (in solution) to prevent further oxidation (this procedure was performed to avoid overestimating degradation).

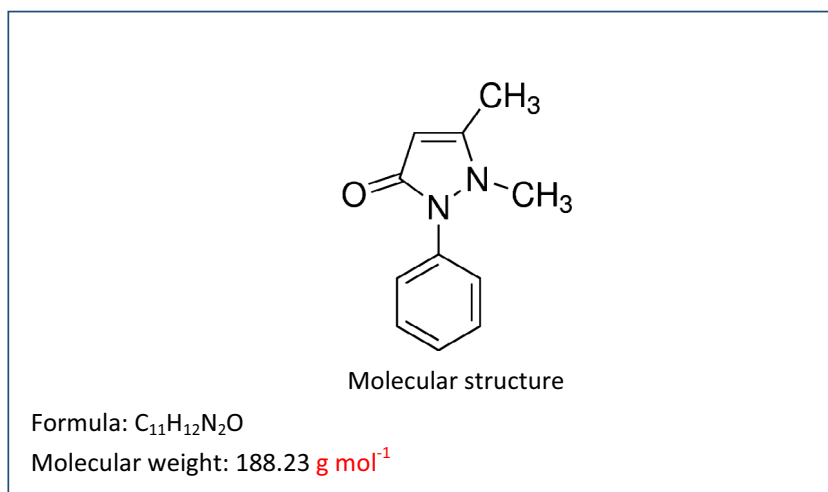


Fig. 1. Structure and properties of antipyrine.

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