

Development and comparison of advanced oxidation processes (AOPs) for the mineralization of azo-dyes from wastewaters

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The Dystar's Levafix Brilliant Red E-6BA dye was tested as model molecule and treated through three different Advanced Oxidation Processes (AOPs): H₂O₂/UV, Fenton and Photo-Fenton reactions.

Amount of oxidant, quantity of Fe catalyst, type of light source were evaluated and optimized to complete the degradation in the shortest time. The best performances were observed when using a low-power UV lamp directly immersed into the solution. The time required to degrade 100 ppm solution of dye (pH 7, 25 °C, 36 mg/L of catalyst, 1 equivalent of oxidant) was ca. 10 minutes for both Photo-Fenton and UV/H₂O₂ processes, compared with 160 minutes required to complete the degradation in dark conditions. The reaction time almost doubled when employing an external UV lamp, while both visible LED and solar light sources were comparable in terms of results (ca. 50 min), but the latter strictly depended on the weather conditions.

To check the possible formation of harmful intermediates *in vivo* acute toxicity tests of treated samples were carried out using *Daphnia magna* specimens. Results of toxicity test showed the importance to minimize the residual amount of H₂O₂ into the treated solution, as it was individuated as the main cause of toxicity.

1. Introduction

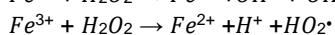
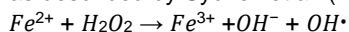
Nowadays, textile and clothing industries represent a big part of the market, with, according to Eurostat 2017, a turnover of 181 billion of euro in Europe and a constant growth over the past twenty years. It has been roughly estimated that the production of 1 kg of clothes requires about 800 liters of water for the whole process, of which 16% is used for dyeing (Raja et al., 2019) and it cannot be disposed after the usage due to the presence of several pollutants in different concentration: mainly bleach, dyes, detergent and other harmful chemicals. In fact, more than 10,000 different types of dyes and pigments are available on the market and up to 200,000 ton per year are lost in the effluents due to the inefficiency of the dyeing processes (Drumond Chequer et al., 2013).

The effects of the residual dyes into the effluents have been widely studied. The precursor and the dyes usually are toxic for the aquatic organisms and so influence the food chain (Puvaneswari et al., 2006). Moreover, they affect the photosynthesis hindering the passage of sunlight through water and they increase significantly the BOD, limiting the growth of plants, fish and microbes. In addition, the usage of redox agents like hypochlorous acid and sodium hydrosulphite in combination with azo-dyes can form 2-Phenylbenzotriazole (PBTA) derivatives and highly mutagenic aromatic amines, often more hazardous than the original dye. Furthermore, dyes and pigments are designed to resist biodegradation and daily usage, so it is difficult to remove them through conventional biodegradation and they persist for a long time.

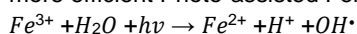
In this work, we compared different Advanced Oxidation Processes (AOPs) to find an efficient and sustainable process in order to fully degrade a model dye to non-harmful products: CO₂, H₂O, N₂ and complete mineralization for chlorine, fluorine and sulphur. All the proposed AOPs promote the generation of hydroxyl radicals into the polluted water at ambient temperature and pressure (Sievers 2011). The radicals subsequently

act as strong oxidising agents, reacting with both dissolved organic and inorganic compounds. The reaction rate depends on the concentration of the pollutant, the radicals and the oxygen present in the surrounding, but it may be enhanced in presence of H_2O_2 , Fe^{2+} , O_3 , TiO_2 and UV (Al-Kdasi et al., 2004). Dystar's Levafix Brilliant Red E-6BA belongs to the class of the azo-dye and was used here as model dye molecule. Three homogeneous processes like Photo-oxidation ($H_2O_2 + UV$), Fenton ($Fe^{2+} + H_2O_2$) and Photo-Fenton ($Fe^{2+} + H_2O_2 + UV$) were taken into consideration. In the former case, the UV radiation below 300 nm is used to cleave the O-O bond in order to convert the peroxide into two hydroxyl radicals. This step is kinetically slow if compared to the oxidation reaction (milliseconds), moreover, the advantages of H_2O_2/UV process is that no sludge is generated during any stage of the treatment and the peroxide is quite easy to handle (Galindo et al., 1999).

The Fenton reaction is mainly employed when wastewaters are characterized by a high UV absorbance and high concentration of pollutants. Small amounts of Fe^{2+} are employed to decompose catalytically the peroxide, as described by Sychev et al. (1995):



Several other reactions may occur. The regeneration of Fe^{2+} is the rate-determining step, so to fasten it, the more efficient Photo-assisted Fenton process was introduced, summarized by the following reaction:



Both Fenton and Photo-Fenton processes do not require expensive apparatus or hazardous chemicals and they are very effective in most cases, for instance to treat highly polluted wastewaters where UV rays cannot reach the depth of the solution due to opacity of the dye containing solution. This is one of the main limiting features during scale up. On the other hand, when the oxidation is completed, the excess of hydrogen peroxide can be decomposed with production of molecular oxygen and water.

The single reactions have been previously applied to different dyes, but, to the best of our knowledge, a comprehensive comparison of their effectiveness and of toxicity of by-products was never carried out under similar conditions and the same substrate, preventing a safe decision on the most appropriate approach. Thus, to fill this gap, we compared the three degradation processes for this model azo-dye. Moreover, in order to check for its full mineralization to innocuous by-products, in vivo acute toxicity tests were carried out using the freshwater crustacean *Daphnia magna*. Finally, different light sources have been compared for effectiveness. All these aspects are particularly relevant for a scale up and achieve industrialization of the process.

2. Experimental

To the reactor filled with 250 mL solution of dye in the selected concentration, were added in order the powder of iron salt ($Fe_2(SO_4)_3$, $FeSO_4$ or Fe_2O_3 , 99.9% purity, Sigma Aldrich) in the (Photo)Fenton case and, after complete dissolution, the hydrogen peroxide (35% v/v, Sigma Aldrich). Concentrated sulphuric acid (95-98%, Sigma Aldrich) or 5 mol/L solution of sodium hydroxide (NaOH pellets, 97%, Sigma Aldrich) is added to the reaction vessel in order to adjust the pH. In the case of Fenton process, the reaction was performed in dark conditions and started when the H_2O_2 was added. For UV/ H_2O_2 and Photo-Fenton processes, the reaction started when the UV/LED lamp was switched on or the reactor was exposed to the sunlight.

Tests with Fenton and Photo-Fenton reactions that were carried out under natural sunlight and with an external UV lamp (Jelosil HG 200W L, maximum emission at 365 nm) in a cylinder-type top-opened reactor with a flat bottom made of transparent glass. The internal volume was about 600 mL. The distance between the lamp and the surface of the liquid was 150 mm and the irradiance measured with a photo radiometer (delta OHM HD2102.2) was 116 W/m².

Photo-Fenton tests with LED lamp (white light, 30 W, 2700 lm) were performed with a round bottom cylinder-type glass reactor open to air of about 300 mL capacity. The distance between the lamp and the surface of the solution was 100 mm.

Additional Photo-Fenton reactions were performed with a lower power immersion UV lamp (Jelosil HG 100 AS, 125 W, maximum emission at 365 nm), coupled with a 350 mL round bottom cylinder-type glass closed reactor equipped with a cooling jacket where water can circulate. Two lamps of that type were employed: one with a measured irradiance at the height of the bulb and on lamp surface that was on average 60 W/m² (low irradiance UV-lamp) and a higher intensity one with a measured irradiance of 260 W/m² (high irradiance UV-lamp).

UV-Vis analysis was performed to determine the conversion of the dye by means of a double-beam spectrometer (Perkin Elmer Lambda 35) and two quartz cuvettes with 10 mm of light path. The reference sample was distilled water. Two calibration curves in the range of 0.02 – 60 ppm were obtained at wavelength of 530 and 550 nm and by dilution of a mother solution of dye (240 ppm) into 9 samples.

Total Organic Carbon (TOC) was used to determine the mineralisation of the dye after the treatment.

The *Daphnia* sp. acute toxicity test was applied to verify if the degradation path leads to more toxic compounds than the starting dye. Adult *Daphnia magna* specimens were cultured (30 individuals/L) in a commercial mineral

water (San Benedetto®) according to the procedure previously described (De Felice et al. 2019). Toxicity of five concentrations (10, 30, 50, 70 and 100 mg/L) of each tested solutions (native dye and after different advanced oxidation processes), as well as a control (mineral water only), was tested for 48 hrs at 20 ± 0.5 °C under a 16 h light: 8 h dark photoperiod. The results were analysed in order to calculate the Lethal Concentration 50 (LC₅₀) at 48h using the Toxicity Relationship Analysis Program (TRAP, Version 1.30a) developed by US EPA.

3. Results and discussion

3.1 Fenton/Photo-Fenton processes

The degradation rate (Figure 1) depends on dye concentration, as intuitive, so the higher is its concentration, the longer the process will be, but with quite similar profiles. Every sample reached 100% of conversion after different reaction times, increasing with increasing the dye concentration. We then selected 100 ppm concentration of the substrates for further screening to allow for sufficiently long reaction time for comparative purposes. Exposure to visible light improved the reaction rate, though less significantly than UV radiation, that is required to break the O-O bond in H₂O₂.

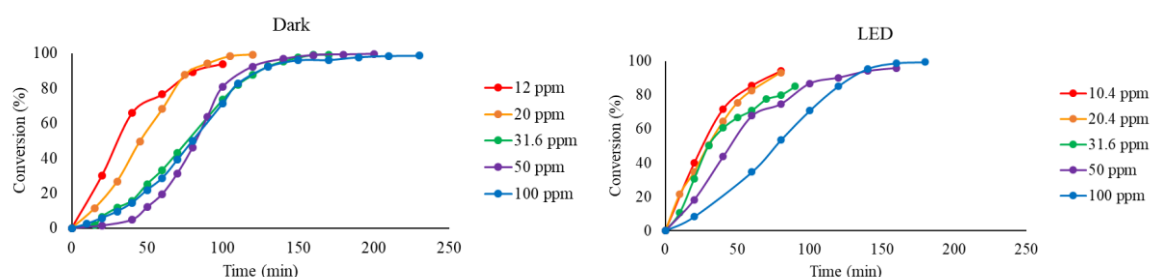


Figure 1: Degradation of Levafix Brilliant through Fenton (Dark) and Photo-Fenton (LED) reactions at pH = 3, excess of H₂O₂ and 9 mg of Fe₂(SO₄)₃

An induction time is sometimes evident when using Fe (III) as in the examples of Figure 1 especially at the highest concentration of dye, needed to form a significant amount of Fe²⁺ reacting species.

The effect of pH on the reaction kinetics was tested working under LED irradiation in acid (pH = 3), neutral (pH = 7) and basic (pH = 12) environment while keeping constant the amounts of dye, iron catalyst, hydrogen peroxide and volume of solutions. The reaction at basic pH did not occur. A possible explanation is that the ferric ions converts from the hydrated form to the colloidal one. Furthermore, H₂O₂ spontaneously decomposes under alkaline condition and ferric hydroxide may assist the reactions, but without forming any hydroxyl radicals. A degradation kinetic strongly enhanced at neutral pH, with a 90% conversion of the target molecule in ca. 50 minutes, to be compared with the 150 minutes required at pH 3. These results are in contrast with literature, which reports that even at neutral pH Fe should precipitate as hydroxide, but we did not detect any precipitate under the adopted conditions. Due to the better efficiency, we decided to operate in neutral conditions for the next steps. It would be a great advantage from an industrial point of view, as the degradation process results less expensive and can occur in environmental-friendly conditions.

Under LED light and without catalyst the reaction did not proceed at an appreciable rate. Once more, the LED lamp emits mainly in the visible spectrum, so without a catalyst it is impossible to promote the formation of hydroxyl radicals. In contrast, increasing the concentration of iron salt, ca. 20 mg of Fe₂(SO₄)₃, improves the degradation reaction as almost 90% of the dye was converted in less than 30 min. However, this would imply working with large excess of both oxidant and catalyst and may be anti-economic and not sustainable even though effective, also leading to a higher amount of residuals to be removed after treatment.

Four solutions of dye were treated through LED-Photo-Fenton process with increasing amount of H₂O₂. The results (Figure 2) clearly shown that over 60% of conversion is reached in the early stage of the degradation process, independently of the magnitude of the oxidant excess. Moreover, after 20 min the reaction slowed down until it did not proceed with an appreciable rate, reaching a plateau (ca. 70% conversion). However, it was observed that in the late stage of the reaction, when the solution is almost discoloured, an orange sludge starts forming, probably due to the large excess of iron catalyst with respect to the dye. The sludge interferes with the spectrophotometric measurement. The same effect is not noticed when using 100 ppm of dye as the absorbance of the inorganic salt was just a little contribute. Overall, an excess of oxidant does not affect the reaction rate, at least under this illumination.

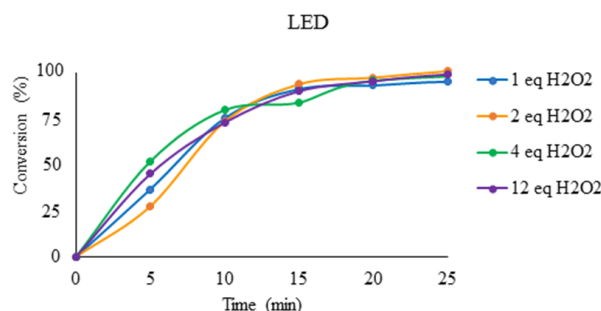


Figure 2: Degradation of Levafix Brilliant through LED-Photo-Fenton reaction and different amounts of H₂O₂, with 100 ppm of dye, 10 mg of Fe₂(SO₄)₃ and pH 6.8-6.4

On the other hand, the results are quite different if looking at both Solar-Photo-Fenton and UV-Photo-Fenton. In the case of UV immersed lamp, it was observed that the conversion is complete in ca. 30 minutes for almost all the experiments, even if under-stoichiometric amounts of oxidant significantly reduces the rate of the reaction. Indeed, UV radiation is able to cleave the O-O bond of H₂O₂ and leads to the formation of two hydroxyl radicals. Concerning the experiments under sunlight, the environmental conditions such as temperature and irradiance are reported in Table 1. The average irradiance was measured through a photo-radiometer (delta OHM HD 2102.2). We expected results more similar to the one of the LED lamp due to the composition of the sunlight spectrum. In fact, most UV is filtered by the atmosphere and the small part which reaches the earth's surface is mainly composed of UV-A (400 – 315 nm) and 5% of UV-B (315 – 280 nm). We observed a full discoloration of all the samples under solar irradiation with longer reaction times than with the UV lamp. In addition, the weather conditions affected widely the degradation time as the test performed with highest amount of oxidant under solar light (*i.e.* 3.5 equivalents of H₂O₂) was even the slower one, with a reaction time almost doubled due to the low radiance of that day and the colder temperature (Table 1).

Overall, it can be stated that the concentration of H₂O₂ should be at least the stoichiometric value, while oversizing this parameter does not improve the reaction rate.

Table 1: Environmental condition measured for the tests performed under natural sunlight

Test	H ₂ O ₂ (eq.)	ΔT (°C)	Irradiance (W/m ²)
#1	1	22-29	3.26
#2	2	22-29	3.26
#3	3.5	14-17	1.04
#4	0.5	22-29	4.05
#5	0.3	24-31	4.26

The tests performed under solar light were strongly depending on the daily variance of irradiation, but accordingly, offer a picture of the expected results under natural illumination. The temperature was very similar, except for the test #3, also characterised by the lowest irradiance. Tests #1 and #2 were carried out with similar irradiance and temperature and the reaction rate almost doubled by doubling the amount of H₂O₂. The reactivity decreased when decreasing the concentration of the peroxide, even by increasing the irradiance by ca. 20-25% (tests #4 and #5). By contrast, comparing test #3 with test #5 one may notice that when the irradiance decreased by ca. 4 times, the same conversion was approximately reached by adding 10 times more oxidant. This first evidence can be used as a tool for the possible tuning of the oxidant addition to the photoreactor depending on the daily and seasonally variable irradiance when exploiting sunlight.

Again, when testing under sunlight the irradiance was variable from day to day. If the tests with 1 and 2 eq. of H₂O₂ we carried out under very comparable conditions, the one with the addition of 3.5 eq. of oxidant was performed at much higher irradiance. Therefore, the effect of the highest oxidant loading is likely overestimated. Yet, it demonstrates the possibility to complete the conversion in less than 30 min.

3.2 H₂O₂/UV process

This option does not employ Fe salts as activator, so UV illumination must be used in order to promote directly the H₂O₂ dissociation. The results reported in Figure 3 show that also, in this case, an increasing concentration of oxidant slightly improves the reaction, but the magnitude of its effect is even lower than what was observed

with the Fenton and Photo-Fenton reactions. Probably, the degradation rate is limited by the penetration of photons into the solution. This is in accordance with the results obtained with external UV lamp, where a significant part of the irradiance is waste in the environment and the reaction does not occur significantly. Furthermore, the reactor used with external UV lamp was not provided with a cooling system and an overheating of the solution may lead to direct decomposition of H_2O_2 into water and oxygen. In addition, the tests performed under LED irradiation and dark conditions showed a null conversion.

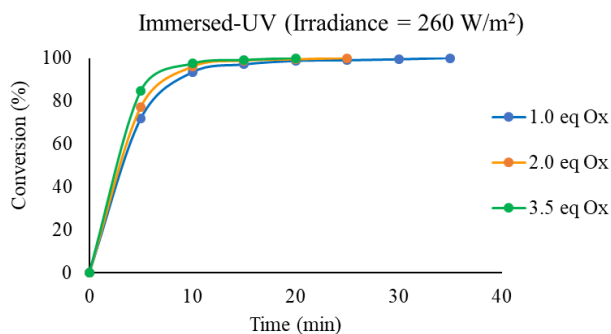


Figure 3: Degradation of Levafix Brilliant Red through H_2O_2 treatment under UV light with various amounts of H_2O_2 , 100 ppm of dye, 9 mg of $FeSO_4$ and pH 7

Looking at all the tests, the H_2O_2 /UV and Fenton/Photo-Fenton processes are comparable in terms of performance, at least if looking at the results obtained with the immersion UV lamp. The main drawback of the Fenton reaction is that it may form sludges at the end of the process that should be separated and recovered. On the contrary, with H_2O_2 /UV may be directly discharged after the discoloration, provided a full conversion of H_2O_2 is achieved. On the other hand, one is forced to use UV lamps (higher cost respect to sunlight) without an astonishing shortening of reaction times with respect to the other alternatives. Moreover, the Photo-Fenton and H_2O_2 /UV approaches with immersion UV lamp at high irradiance allowed to fully converting the dye in less than 10 min. However, the use of sunlight for Photo-Fenton also proved effective, with full conversion in less than one hour in spite of the considerable performance variability depending on the available irradiance. However, the variation of the Fe and H_2O_2 concentration may be a tool to tune the reactivity when irradiance is low.

3.3 Acute toxicity

AOPs should bring to the full mineralization, but stable intermediates may form and the analysis of the possible products is very challenging, being possibly hundreds intermediates of partial oxidation/decomposition. Therefore, besides following the conversion of the dye through spectrophotometry, we checked for the material balance by TOC analysis and, more importantly, we investigated the toxicity of the treated solutions.

In order to understand if the degradation mechanism of Levafix Brilliant Red lead to toxic intermediates or products, *Daphnia magna* acute toxicity tests were performed. First of all, 100 ppm solution of untreated dye and several diluted samples were used as a benchmark. The value of 48h-LC₅₀ reported in literature for this compound is 117 mg/L, but our test was carried out with a lower concentration and after 48h of exposure, no mortality occurred at all the tested dilutions. For this reason, a 48h-LC₅₀ could not be calculated.

Subsequently, the samples obtained after treatment of 100 ppm of dye solution with Fenton and Photo-Fenton processes were tested. The degradation was performed with 36 mg/L of $FeSO_4$, 1 equivalent of H_2O_2 , at pH 7 and respectively under dark, LED and UV illumination.

The calculated 48h-LC₅₀ for all the solutions analysed was 77.10 ± 5.59 mg/L. Four scenarios are possible:

- The intermediates of the degradation reaction are more toxic than the dye itself, stable radicals may be formed or smaller more bio-toxic molecules, products of degradation formed
- The unreacted H_2O_2 is hazardous for daphnids
- The $FeSO_4$ is hazardous for daphnids
- This particular mix of substances is hazardous for daphnids.

The third point may not be the cause of the toxicity, as the 48h-LC₅₀ value of $FeSO_4$ is about 152 mg/L, according to safety data sheet. Thus, in order to better understand what causes the toxicity, other tests were performed.

The 100 ppm solution treated with the H_2O_2 /UV process was characterized by a mortality even higher than that previously reported. In fact, the calculated 48h-LC₅₀ was 13.52 ± 5.33 mg/L. A sample of the same solution was

analysed through TOC technique, which unveiled that all the starting carbon was fully mineralized. Thus, it is reasonable that the daphnids suffered from the residual hydrogen peroxide, which has not been decomposed. In fact, the 48h-LC₅₀ value of H₂O₂ for *Daphnia magna* is 5.6 mg/L, so few traces of oxidant may be extremely toxic for the cladoceran. Thus, the acute toxicity is mainly attributed to residual H₂O₂ that must be carefully removed after treatment for the industrial application of all these processes

4. Conclusions

Firstly, the reaction parameters were tuned in order to fully degrade this pollutant in a fast and efficient way, achieving in every case the full conversion of the dye within few hours in the worst case, few minutes for the best ones. It was found that the pH of the solution influences the performance and the best results were obtained at pH 7, with a reaction time of 80 min under LED lamp and selected conditions, compared with the 140 min required when the pH of the solution is 3. Conversely, the rate of the reaction did not increase proportionally to the amounts of oxidant and Fe catalyst.

The oxidant and Fe concentration are critical parameter when using sunlight as a source of photons, because the latter is not constant. On the other hand, the amount of catalyst seems to speed up the treatment just in the early stage but does not affect the time necessary to complete the degradation.

Regarding the processes, it is possible to state that the degradation rate is related to the type of light source used, which follows the trend UV>Sunlight>LED>Dark. Therefore, the Photo-Fenton treatment is much better than Fenton the more intense is the light and the shorter the wavelength, even though inexpensive LED lamp of just 30 W seems to be a good compromise between the efficiency, constancy of operation and the operative costs. Although the presence of iron catalyst allows to operate with highly polluted wastewater, the major limitation of both processes is still the filtration of the iron sludges from the treated effluents. In order to overcome that, we successfully tested the H₂O₂/UV treatment, whose performance using the low power UV immersed lamp were comparable with the Photo-Fenton (nearly 10 minutes with 3.5 eq of oxidant). The best process to adopt probably depends on the characteristic of the effluents to treat.

Anyway, toxicity tests performed exposing *Daphnia magna* to the dye solutions treated with different processes have given shown an increase of the mortality of the daphnids in the treated water. Indeed, the EC₅₀ value after 48h of exposure was respectively 76 mg/L and 17 mg/L for solutions treated with (Photo-)Fenton and H₂O₂/UV, whereas the Levafix Brilliant Red show its noxious effect at 117 mg/L. The acute toxicity is attributed to incompletely decomposition during the exposure to the lamp. The results of TOC analysis are in accordance with this thesis, since they showed that the dye is fully mineralized rather than converted into partially oxidized products.

Acknowledgments

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