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Toxic effect of H_2O_2 in H_2O_2/UV, photo-Fenton and heterogeneous photocatalysis (TiO_2/H_2O_2/UV) systems to treat textile wastewater

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ABSTRACT

The application of H_2O_2/UV, photo-Fenton and heterogeneous photocatalysis (TiO_2/H_2O_2/UV) processes for the treatment of a highly polluted coloured wastewater was analysed. The experiments were carried out with different H_2O_2 concentrations (0.25, 0.5, 1, 2 and 5 g/L). The toxic properties of different H_2O_2 concentrations in textile wastewater were tested by the use of a Microtox bioassay with *Vibrio fischeri.* The efficiency of the process was checked by assessing the physicochemical parameters, total organic carbon (TOC) and colour. The use of TiO_2 as a catalyst with UV photolysis was the most effective method to remove toxins, organic material and colour using the five concentrations of H_2O_2 tested. By using 5 g/L of H_2O_2, 94% TOC removal was achieved. In relation to colour removal, this was greater than 99% with 5 g/L of H_2O_2 in all three processes. The use of a catalyst allowed us to reduce the hydraulic retention time of the process to 30 min with Fe^{2+} and 45 min with TiO_2. Controlling the amount of H_2O_2 used as the oxidant in an advanced oxidation process (AOP) is important since it was found to increase the toxicity of the influent with the addition of H_2O_2 by 4.99 ± 1.48%, 27.4 ± 3.24%, 39.16 ± 5.64%, 53.40 ± 4.15% and 59.39 ± 4.67% with 0.25, 0.5, 1, 2 and 5 g/L H_2O_2, respectively. Therefore, under the studied conditions, an H_2O_2 concentration greater than 1 g/L is not recommended for an AOP in order to avoid an excess of H_2O_2 in the effluent.

Keywords: AOP; Catalyst; Toxicity; Colouring

1. Introduction

The textile industry is an important consumer of water resources in the manufacturing process and consequently one of the largest groups of industries causing intense water pollution [1,2]. Textile wastewater contains a wide variety of dyes and chemicals. The chemical composition of textile industry effluents has an important environmental impact [3], and the

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removal of dye from wastewaters represents a major environmental concern [4].

Within the textile industry, various types of synthetic dyes and pigments, such as azo, anthraquinone, triarylmethane and phthalocyanine (PC) groups are used [5]. Dyes and pigments are generally non-biodegradable and are chemically stable molecules. Moreover, dyes show a high resistance to microbial degradation in wastewater treatment systems [6]. These characteristics make synthetic dyes very recalcitrant chemicals capable of inducing toxicity in aquatic organisms and, in some cases, humans [7]. Over 50% of all the dyes used in the industry are azo dyes, which contain one to four azo groups, usually attached to two radicals of which at least one, but usually both, are aromatic groups [8,9].

Wastewater from the textile industry is produced during raw material cleaning and in many flushing steps throughout production [3]. Textile manufacturing involves several processes that generate large quantities of wastewaters that are highly variable in composition with relatively low biological oxygen demand and high chemical oxygen demand and suspended solids contents; dyes also impart intense colour and contain other soluble substances [9–11]. Given the complex and bioresistant character of textile effluents, their effective treatment usually requires a combination of physical, chemical and biological technologies [12].

Physicochemical methods such as advanced oxidation can be very effective for the removal of colour in wastewaters [13]. Advanced oxidation processes (AOPs) have been used extensively for the degradation of a broad range of contaminants [14]. AOPs can be defined as aqueous-phase oxidation methods based primarily on the intermediacy of hydroxyl radicals employing mechanisms that lead to the destruction of the target compound [9]. These processes have been proposed as a potential alternative approach for the treatment of bio-recalcitrant organic pollutants [15] due to their ability to convert contaminants into less harmful chemicals. Consequently, to increase the treatment efficiency, they are usually combined with biological processes [16,17].

One of the most common AOPs studied combines ultraviolet photolysis with hydrogen peroxide (UV/H_2O_2); this is one of the most appropriate AOP technologies for removing toxic organics from water because it may occur in nature itself [18]. H_2O_2/UV involves the production of reactive and non-selective hydroxyl radicals ($OH^{\cdot}$) and can initiate decolourisation reactions by reacting with dye molecules [19]. These radicals are produced from oxidising agents such as hydrogen peroxide (H_2O_2), often combined with metallic or semiconductor catalysts and UV radiation [20]. The effect of toxicity using H_2O_2 is important to consider. The toxicity of hydrogen peroxide in oxidation processes has been studied by other authors. At low concentrations of H_2O_2, i.e. 3 mM H_2O_2 [21] or below 50 mg/L [22], and using UV irradiation, no toxicity was detected in the treated water; however, H_2O_2 toxicity has not been studied at higher concentrations. Many dyes have been studied in this process, such as sulphonated diazo dye Reactive Green 19, C·I. Acid Blue 113, Acid Blue 74, Acid Black 24 and Vat Green 01 [18,23–26]. Shu et al. [24] investigated the decolourisation of Acid Blue 113 dye with 23.27 mM H_2O_2, obtaining 93.5% colour removal in 20 min. With prolonged treatment time (over 200 min), Aleboyeh et al. [25] achieved 100% decolourisation of Acid Blue 74 dye with 35 mM H_2O_2.

Another popular AOP is the photo-Fenton process, which is a very effective process for many industrial wastewater treatment processes [27,28], especially for textile wastewaters that contain high levels of dye, recalcitrant organic compounds and suspended solids [29]. Fenton oxidation is a homogeneous oxidation process, and it is considered to be a metal-catalysed oxidation reaction, in which iron acts as the catalyst [30,31], including reactions of peroxides (usually H_2O_2) with iron ions to form active oxygen species ($OH^{\cdot}$) that oxidise organic or inorganic compounds when they are present [32]. Several researchers have studied the decolourisation of wastewater under different conditions. Ertugay and Acar [33] achieved 94% decolourisation of Blue 71 azo dye with 3 mg/L Fe^{2+} and 125 mg/L H_2O_2 after a hydraulic retention time (HRT) of 20 min. Núñez et al. [34] demonstrated that the optimal dosing of Fe^{2+} and H_2O_2 for the decolourisation of synthetic wastewater with Procion Red H-E7B and Cibacron FN-R was 10 and 100 mg/L, respectively.

One of the most promising AOPs is TiO_2 photocatalysis [15]. This process is a technology with key advantages such us the lack of mass transfer limitations, operation under ambient conditions and the possible use of solar irradiation; moreover, the catalyst itself is inexpensive and readily available [12]. TiO_2 is widely used in AOPs because it is a non-toxic photocatalyst, and is biologically and chemically inert [35,36]; however, several studies have shown that TiO_2 can be used like a bactericide [37–40] and some effects on health and the environment related to TiO_2 nanoparticles have been described [41]. n-TiO_2 could be damaging towards *Bacillus subtili* and *Escherichia coli* due to the production of reactive oxygen species [42]. The process can easily decolourise and considerably reduce the organic load of dyehouse and related effluents [12]. With this photocatalyst, Prieto et al. [43] achieved maximum colour removal in 55 min of operating time. They used a synthetic textile effluent with a mix of six commercial dyes at an alkaline pH. With the same HRT, Mahmoodi et al. [44] achieved 100% removal of Direct Red 80 dye at neutral pH and with 300 mg/L H_2O_2.

The aim of this research was to evaluate the effect of H_2O_2 on the toxic characteristics of textile wastewater polluted with non-biodegradable dye using a Microtox bioassay with *Vibrio fischeri* after treatment with three different AOPs, i.e. H_2O_2/UV, photo-Fenton and heterogeneous photocatalysis (TiO_2/H_2O_2/UV). Total organic carbon (TOC) and colour removal efficiency were also studied in each case.

2. Materials and methods

2.1. Description of the photoreactor

The experiments were carried out in a batch reactor with a total volume of 800 mL. The reactor was composed of a cylindrical quartz glass with a 150-W medium-pressure mercury lamp and a quartz glass inside it. The reactor was covered with an opaque material to avoid interference from external radiation, and was placed on a magnetic stirrer in order to provide complete mixing. The temperature was controlled to compensate for heat produced by the lamp. The temperature was controlled with a cooling, tube maintaining it at a constant temperature of 25 ± 0.5˚C. Fig. 1 shows a schematic diagram of the UV Consulting Pesch® laboratory-scale photoreactor used in the present research.

2.2. Experimental procedure

The composition of the wastewater solution was similar to that proposed by Gil Rodríguez [45] for 1 L of water: 750 mg of glucose monohydrate, 750 mg of L-glutamate monohydrate sodium, 1.12 g of PO_4H_2 K, 1.06 g of PO_4HK_2, 100 mg of $MgSO_4{\cdot}7H_2O$, 20 mg of $Cl_3Fe{\cdot}6H_2O$ and 100 mg of $CaCl_2$ were included, and 500 mg of a synthetic dye mixture was added. In all cases, the pH of the wastewater was adjusted to pH 3 using sulphuric acid (10%). The solution was stirred for 24 h to ensure all reagents were completely dissolved.

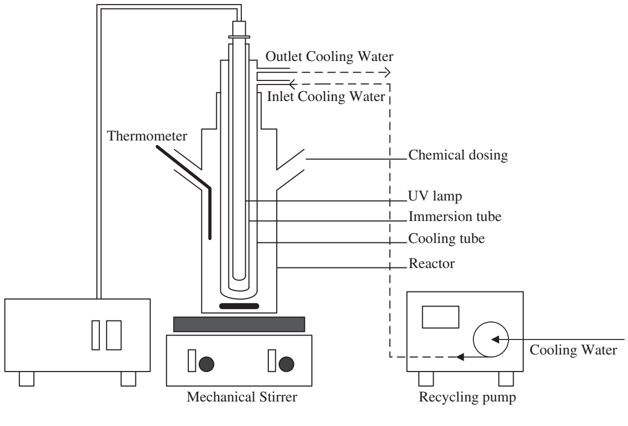

Fig. 1. Diagram of the photoreactor.

The reactor was filled with wastewater, which was kept under constant agitation by the magnetic stirrer in order to achieve a high contact surface with the UV light. The oxidant (H_2O_2) and the catalysts (Fe^{2+} and TiO_2) were added when the temperature was constant at 25 ± 0.5˚C. Samples were taken every 15 min through a tap and the experiments lasted 2 h [17,18,46]. The samples with TiO_2 were filtered through a 0.45-μm Millipore filter to remove the particles. The toxic properties, TOC and colour were analysed. In all processes studied, the H_2O_2 doses used were 0.25, 0.5, 1, 2 and 5 g/L (7, 15, 29, 59 and 147 mM, respectively) similar to the concentration tested in other research [18] in order to compare the effect of the concentration of H_2O_2 in the processes. The doses of Fe^{2+} and TiO_2 were 40 and 200 mg/L, respectively [47,48]. In addition to comparing the studied processes, measurements were taken using a control sample which was prepared without dye.

2.3. Toxicity measurements

The toxicity of the textile wastewater was determined using a Microtox® Model 500 Analyser, which utilises freeze-dried luminescent bacteria (*Vibrio fisheri*) as the test organism. The test system is based on the principle that bacterial luminescence is directly related to cell respiration, and on any inhibition of cellular activity caused by toxicity results in a reduction in the degree of luminescence [49]. The light emitted by the bacteria was measured after 5 min of contact time. Toxicity was expressed as toxicity units, TU = 100/EC_{50}, where EC_{50} is defined as the effective concentration of the toxicant, expressed as a percentage relative to the original sample strength, that causes a 50% reduction in the light output of the test organisms during the designated time interval [49,50].

2.4. Physical and chemical determinations

The colour measurements were determined according to UNE-EN ISO 7887:1994. The absorbance measurements at 436, 525 and 620 nm were taken using a Heλios γ spectrophotometer (ThermoSpectronic). The pH was determined using a pH meter (Crison pH 25).

TOC analysis was used to follow the degree of mineralisation during the different wastewater treatments. The TOC was determined using a Formarcs TOC/TN Analyser by oxidative combustion at 950°C.

2.5. Statistical analysis

The statistical analysis of data was done using IBM SPSS Statistic 20. The ANOVA test used was the honestly significant difference (HSD) test of Tukey to obtain a homogeneous subset of data. The ANOVA test was done with a confidence interval of 99% ($\alpha = 0.01$).

3. Results and discussion

3.1. Effect of dye, H_2O_2 and catalysts on toxicity of H_2O_2/UV, photo-Fenton and heterogeneous photocatalysis processes

As the presence of H_2O_2 influences the toxicity of the sample [51,52], toxicity analyses were carried out based on the concentration of H_2O_2. In Fig. 2, the toxicity values obtained for each of the processes tested according to the different H_2O_2 concentrations and constant Fe^{2+} and TiO_2 concentrations are shown to analyse the parameter of toxicity caused by the dye. Independently of the oxidant concentration, lower toxicity was detected in the sample without colour and catalyst and higher toxicity was found in the samples with Fe^{2+} and colour, whereas the samples with dye only and with TiO_2 and dye presented the same values of toxicity. It was observed that when the concentration of H_2O_2 increased, the toxicity of the sample increased. An average increase of 4.99 ± 1.48%, 27.4 ± 3.24%, 39.16 ± 5.64%, 53.40 ± 4.15% and 59.39 ± 4.67% was found with 0.25, 0.5, 1, 2 and 5 g/L of H_2O_2, respectively. As can be seen in Fig. 2, for the wastewater before oxidation, the dye had a toxic effect on the bacterium *V. fisheri*; the toxicity of the water without the dye was lower than the others at all H_2O_2 concentrations, with a value of 0.24% in the sample without peroxide. Whether different concentrations of dye can make a sample toxic was determined and it was suggested that toxicity was due to the presence of dye. In a study by Vajnhandl and Le Marechal [53], with an initial concentration of the azo dye Reactive Black 5 of 20 mg/L and a sonochemical process, no toxicity was detected; however, Gottlieb et al. [54], using the same concentrations as in the present research (500 mg/L), toxicity was detected after hydrolysis. Both catalysts presented a different performance in relation to the toxicity with the method used. On the one hand, the TiO_2 catalyst is inert in the method to measure the toxicity used, imparting no additional toxicity to the influent (Fig. 2), as reported by Medana and Sakkas [35,36]. On the other hand, the presence of Fe^{2+} in the influent increased the toxicity of the samples.

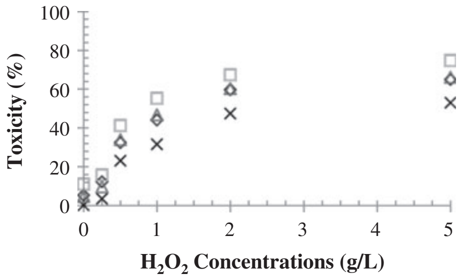

Fig. 2. Toxicity values of the influent without and with the different doses of H_2O_2 tested before the radiation expressed as a percentage for each AOP tested: influent without colour (×), coloured influent (◊), coloured influent with Fe^{2+} (□) and coloured influent with TiO_2 (Δ).

The toxicity analysis for each of the four samples is shown in Fig. 2. It was observed that, on the one hand, the toxic effect of the dye increased with the concentration of H_2O_2, as can be seen by the difference between the two curves when the H_2O_2 is increased. This could have occurred if the peroxide hydrogen reacted with the dye. On the other hand, in relation to the catalyst, regardless of the oxidant concentration, TiO_2 did not increase the toxicity of water. However, the toxicity from iron was relatively constant regardless of the concentration of peroxide, as the samples with Fe^{2+} showed an average increase in toxicity to 7.77 ± 2.77%. Considering the above results, the addition of H_2O_2 to relatively non-toxic water makes the wastewater toxic [52]. Increasing the concentration of the oxidant (2–5 g/L) in both the heterogeneous photocatalysis and H_2O_2/UV processes presented similar toxicity. With 1 g/L at 60 min, there were differences, but at 120 min, the same toxicity was seen. At a concentration of 0.250.5 g/L with the catalyst, the water was less toxic than without a catalyst. However, at higher H_2O_2 concentrations (1–5 g/L), the toxicity of Fe^{2+} was affected, and the toxicity increased in relation to heterogeneous photocatalysis and processes without a catalyst. At low concentrations of the oxidant, the photo-Fenton process removed more toxicity with respect to the process without a catalyst, but no more than with TiO_2. The increased toxicity in the photo-Fenton process was greater when the concentrations of H_2O_2 increased.

Fig. 3 shows the effect of Fe^{2+} in the process, regardless of the yields of TOC and colour removal, with unfavourable behaviour concerning toxicity. The difference between the values obtained with the catalyst (Fe^{2+}) and without the catalyst was always

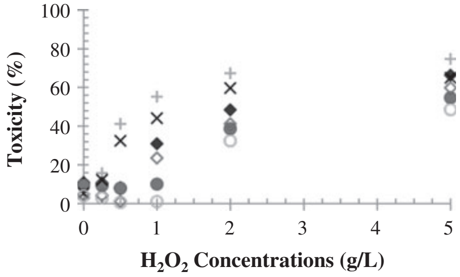

Fig. 3. Effect of Fe^{2+} on the toxicity values of the wastewater: 0 min with Fe^{2+} (+), 60 min with Fe^{2+} (♦), 120 min with Fe^{2+} (•), 0 min without the catalyst (×), 60 min without the catalyst (◊) and 120 min without the catalyst (○).

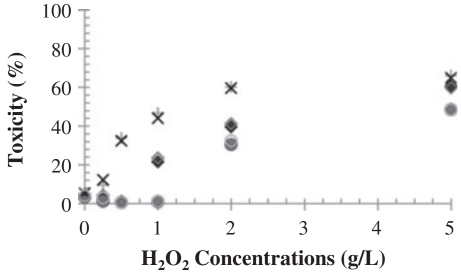

Fig. 4. Effect of TiO_2 on the toxicity values of the wastewater: 0 min with TiO_2 (+), 60 min with TiO_2 (♦), 120 min with TiO_2 (•), 0 min without the catalyst (×), 60 min without the catalyst (◊) and 120 min without the catalyst (○).

positive, showing an average toxicity value of 7.13 ± 1.72%. It was observed that, at low concentrations of H_2O_2, toxicity decreased at 60 min and was close to 0 in the case of using no catalyst. However, at concentrations above 1 g/L of the oxidant, the toxicity of the samples was higher. This could be due to H_2O_2—which is primarily responsible for toxicity—that was not consumed in the process. Therefore, there is a peroxide hydrogen concentration at which toxicity is minimal; this concentration was in the range of 0.25–1 g/L.

The effect of TiO_2 as a catalyst in AOPs is shown in Fig. 4. As stated above, TiO_2 is inert [35,36] and not toxic in the method used here, so no statistical differences in toxicity at 0 min were observed between the samples with and without this catalyst. However, some nanoparticles of TiO_2 may be toxic for other micro-organisms due to the production of reactive oxygen species [42]. A range of concentrations of H_2O_2 (0.25–1 g/L) showed that the presence of TiO_2 reduced the toxicity of the influent water at 120 min. The assays at the same time, with concentrations greater than 1 g/L, showed greater toxicity than the untreated wastewater. On average, there was an improvement in toxicity of 7.3 ± 5.9% in the process using a catalyst (TiO_2), reaching in some cases an improvement of up to 15%. For example, at 60 min with 1 g/L of H_2O_2, the toxicity with the catalyst was 53.84% vs. 46.61% obtained without the catalyst, while at 120 min with 0.25 g/L of H_2O_2, the toxicity using the catalyst was 86.99% compared to 75.54% with no catalyst. As shown by Kim et al. [55], TiO_2 photocatalysis with UV-B photolysis is the most effective method to remove toxic derivatives in water.

3.2. *Effect of H_2O_2/UV, photo-Fenton and heterogeneous photocatalysis on TOC removal*

The values obtained for TOC and colour removal as a function of HRT are shown in Figs. 5 and 6,

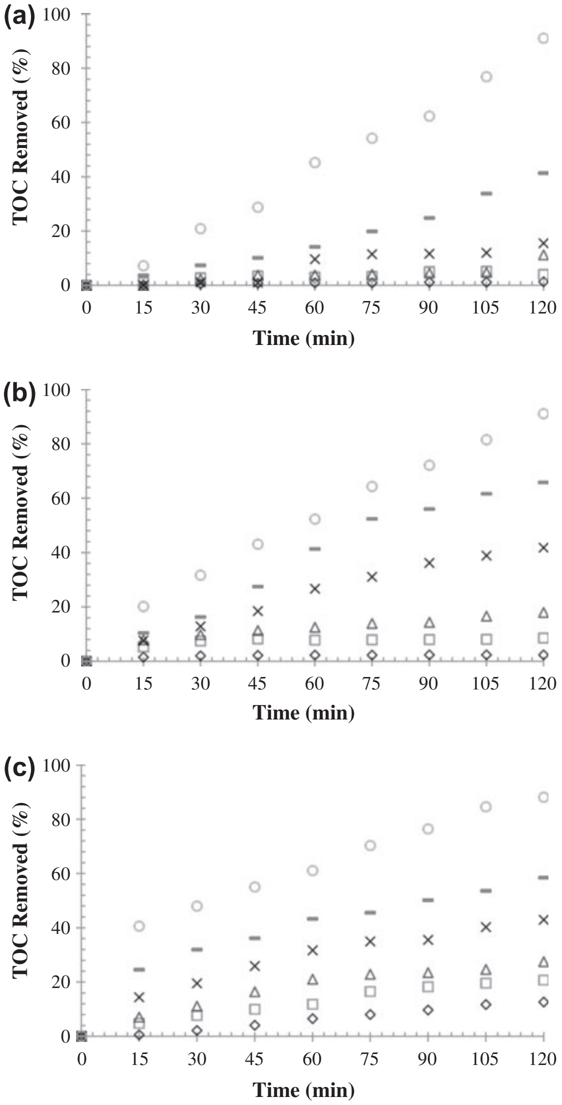

Fig. 5. TOC removal as a function of HRT at different concentrations of H_2O_2: 0 (◊), 0.25 (□), 0.5 (Δ), 1 (×), 2 (–) and 5 (○) g/L for (a) H_2O_2, (b) photo-Fenton, and (c) heterogeneous photocatalysis.

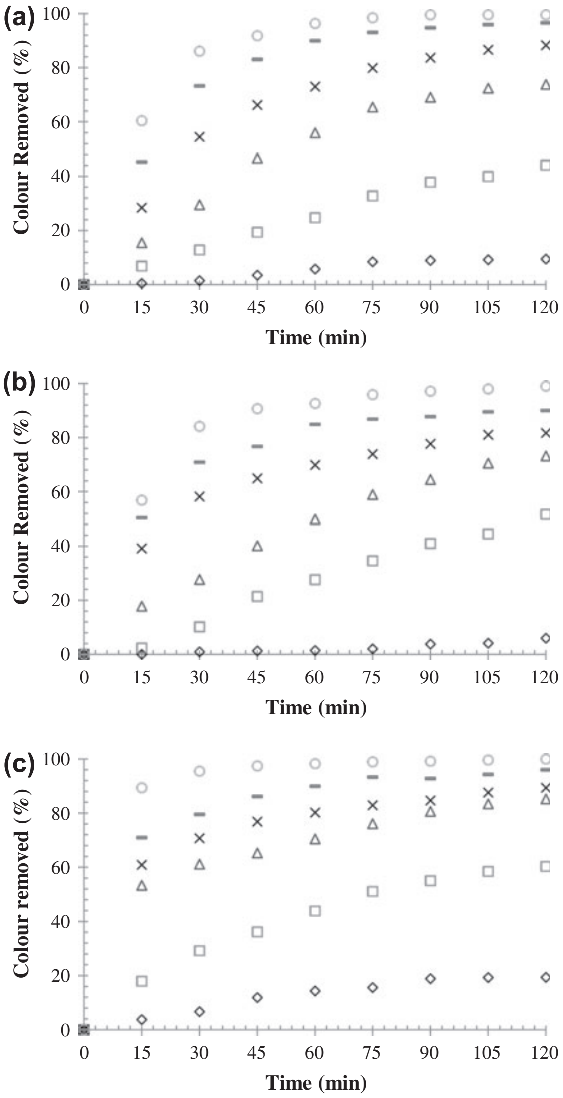

Fig. 6. Colour removal as a function of HRT at different concentrations of H_2O_2: 0 (◇), 0.25 (☐), 0.5 (Δ), 1 (×), 2 (–) and 5 (○) g/L for (a) H_2O_2, (b) photo-Fenton, and (c) heterogeneous photocatalysis.

respectively. In both figures, it can be seen that TOC and colour removal increased with time in each process at all concentrations of hydrogen peroxide. In each process for TOC and colour removal, the removal increased with increasing H_2O_2 concentration at all time points.

In general, for TOC removal at the same concentrations of H_2O_2 and the same operating conditions with the heterogeneous photocatalysis process, a better TOC removal rate was obtained than with the other processes. Zhang et al. [56] obtained TOC removal close to 100% with 1 g/L TiO_2 and 100 mg/L H_2O_2. The addition of Fe^{2+} in the photo-Fenton process led to an increase of the TOC removal rate in relation to the H_2O_2/UV process, although this increase was not as high as that seen with the H_2O_2/TiO_2/UV process.

At low concentrations of H_2O_2, there were no differences in the TOC removal rate over time. The rate of TOC removal was constant from 30 min as can be seen in the process with Fe^{2+} using 0.25 and 0.5 g/L of H_2O_2 (Fig. 5(b)) and without a catalyst (Fig. 5(a)) with the same H_2O_2 concentrations. This trend was seen in both the photo-Fenton and H_2O_2/UV processes when using 0.25 and 0.5 g/L of the oxidant. The TOC removal rates for photo-Fenton at these concentrations were 8.15 and 18.00%, respectively, at 120 min, and for the H_2O_2/UV process, the TOC removal rates were 4.26 and 5.05%, respectively, at the same time point. In both processes, the TOC removal rate was stable after 75 min of HRT. In relation to the TiO_2/H_2O_2/UV process (Fig. 5(c)) at higher concentrations and later time points, there was greater TOC removal.

With the highest concentrations of H_2O_2 (1–5 g/L), the behaviour of the three processes changed. At these concentrations, in all cases, the TOC removal increased with time. For the TiO_2/H_2O_2/UV process, TOC removal was somewhat higher than with the Photo-Fenton process, which was higher than the process without a catalyst (Fig. 5). At high concentrations of peroxide, there were no differences between the photo-Fenton and heterogeneous photocatalysis processes in relation to TOC removal. It can be seen that, at 120 min with concentrations of 1 and 2 g/L, TOC removal rates of 41.83 and 65.81% for photo-Fenton and 42.92 and 68.41% for heterogeneous photocatalysis, respectively, were obtained. However, for the H_2O_2/UV process, and the same concentrations, the TOC removal rates were 19.86 and 41.39%, respectively. At the highest concentrations of H_2O_2 for each process, an average of 89.48 ± 4.16% TOC removal was obtained, which went up to 94.09% TOC removal with the TiO_2/H_2O_2/UV process.

3.3. *Effect of H_2O_2/UV, photo-Fenton and heterogeneous photocatalysis on colour removal*

In relation to colour removal, some differences were observed compared to TOC removal. With the heterogeneous photocatalysis and H_2O_2/UV processes, better colour removal was seen than with the Photo-Fenton process. At low concentrations of H_2O_2, there were no differences in the colour removal rate over time, as with TOC removal.

The rate of colour removal was constant without a catalyst (Fig. 6(a)) at 0.25 g/L of H_2O_2 from 90 min. This could be due to the fact that this low concentration of H_2O_2 was consumed in the initial period, and so more time was not required in the process. This trend was shown both in the photo-Fenton and H_2O_2/UV processes when using 0.25 g/L of the oxidant. The colour removal rates for photo-Fenton at 0.25 g/L H_2O_2 was 51.66% at 120 min, and for the H_2O_2/UV process, colour removal was 44.15%. Prato-Garcia and Buitrón [14] obtained 97% colour removal after 60 min of decolourisation for a mixture of azo dyes with the photo-Fenton process using 400 and 20 mg/L of H_2O_2 and Fe^{2+}, respectively. In relation to the TiO_2/H_2O_2/UV process (Fig. 6(c)), at higher concentrations and later time points, there was greater colour removal.

Colour removal increased over time with the highest concentrations of H_2O_2 (1–5 g/L). However, for the TiO_2/H_2O_2/UV and H_2O_2/UV processes, this was somewhat higher than for the photo-Fenton process. It can be seen that at 120 min with concentrations of 0.5–2 g/L, colour removal rates of 73.87, 88.34 and 96.6% for H_2O_2/UV and 85.20, 89.34 and 98.32% for heterogeneous photocatalysis, respectively, were obtained. In the photo-Fenton process at the same concentrations, colour removal was 73.16, 81.66 and 89.97%, respectively. Schrank et al. [18] obtained only 52% Vat Green 01 dye removal with the H_2O_2/UV process and 0.5 g/L of H_2O_2. Finally, at 120 min with 5 g/L of H_2O_2 for all three processes, close to 100% colour removal was obtained.

3.4. Evolution of TOC and colour removal during H_2O_2/UV, photo-Fenton and heterogeneous photocatalysis

In order to analyse the performance of each process, a statistical analysis of the TOC and colour removal in relation to time was performed. The ANOVA test of the efficiency of each process was done in two ways: to analyse the process in relation to the H_2O_2 concentration independently of time, and considering time as a factor. Tables 1 and 2 show the average, maximum and minimum values of TOC and colour removal based on the ANOVA test in relation to the concentration of H_2O_2 and time, respectively. The homogeneous subsets of the HSD of Tukey are shown as the superscript of the median value in both tables.

Statistically significant differences in relation to the concentration were obtained in the TOC and colour removal rates, as shown by the superscripts in Table 1. A similar TOC removal rate, independent of time, was obtained with a low concentration of H_2O_2 using TiO_2 as the catalyst, e.g. with 0.25 g/L H_2O_2 using TiO_2, the TOC removal rate was 13.87%, similar to the TOC removal rate of Fe^{2+} with 0.5 g/L of H_2O_2 (13.03%). This fact can be observed in the statistical analysis with the same superscript in these conditions. Indeed, the maximum average TOC removal rate with TiO_2 (66.22%) was higher than that obtained with Fe^{2+} (56.68%) and without a catalyst (47.7%). The same effect was seen in relation to colour removal, as the best removal rate was obtained with TiO_2 as the catalyst. As shown in Table 1, using TiO_2 as the catalyst with 1 g/L H_2O_2, the colour removal rate (79.11%) was similar to the rate obtained with 1 g/L H_2O_2 and Fe^{2+} (79.60%), both belonging to the homogeneous subsets D, E and F. The same effect was shown with 2 and 5 g/L H_2O_2 with TiO_2 and Fe^{2+}, respectively, obtaining colour removal rates of 88.12 and 89.26%.

Table 1
Average, minimum and maximum values of the TOC removal rate (a) and colour removal rate (b) from the ANOVA test in relation to the concentration of H_2O_2, independent of time

Concentration (g/L)	H_2O_2/UV		Photo-Fenton		Heterogeneous Photocatalysis	
TOC (%)						
0	0.86^{A}	(0.14–1.26)	$2.20^{A, B}$	(1.53–2.35)	$6.43^{A, B, C}$	(1.69–9.72)
0.25	$3.40^{A, B}$	(0.66–5.62)	$7.54^{A, B, C}$	(5.31–8.15)	$13.87^{A, B, C}$	(5.69–20.68)
0.5	$4.47^{A, B}$	(1.06–9.24)	$13.03^{A, B, C}$	(7.65–18.00)	$19.50^{A, B, C, D}$	(9.07–27.49)
1	$8.98^{A, B, C}$	(1.66–15.58)	$26.81^{B, C, D, E}$	(8.53–41.83)	$30.74^{C, D, E}$	(14.41–42.92)
2	$19.45^{A, B, C, D}$	(3.71–41.39)	$41.41^{D, E, F}$	(10.40–65.81)	$44.18^{D, E, F}$	(24.50–68.41)
5	$47.70^{E, F}$	(7.21–86.03)	56.68^{F}	(20.13–88.32)	66.22^{F}	(40.55–94.09)
Colour (%)						
0	5.94^{A}	(0.53–9.46)	2.45^{A}	(0.00–6.00)	13.67^{A}	(3.71–19.30)
0.25	$27.35^{A, B}$	(6.93–44.15)	$29.18^{A, B}$	(2.39–51.66)	$43.97^{B, C}$	(17.85–60.30)
0.5	$53.60^{B, C, D}$	(15.58–73.87)	$50.32^{B, C}$	(17.77–73.16)	$71.90^{C, D, E, F}$	(53.34–85.20)
1	$70.10^{C, D, E, F}$	(28.48–88.34)	$68.28^{C, D, E}$	(39.16–81.66)	$79.11^{D, E, F}$	(60.89–89.34)
2	$84.02^{E, F}$	45.30–96.60	$79.60^{D, E, F}$	(50.36–89.97)	$88.12^{E, F}$	(70.94–98.32)
5	$91.49^{E, F}$	(60.48–99.56)	$89.26^{E, F}$	(56.85–98.99)	97.24^{F}	(89.32–100.00)

Note: A, B, C, D, E and F shows the homogenous subset of ANOVA, the groups with different superscripts presented statistically significant differences.

Table 2
Average, minimum and maximum values of the TOC removal rate (a) and colour removal rate (b) from the ANOVA test in relation to time, independent of the concentration of H_2O_2

Time (min)	H_2O_2/UV		Photo-Fenton		Heterogeneous Photocatalysis	
TOC (%)						
15	2.86	(0.66–7.21)	10.40	(5.31–20.13)	18.84	(5.69–40.55)
30	7.27	(1.81–20.87)	15.61	(7.46–31.66)	23.81	(8.62–47.94)
45	10.21	(2.45–28.81)	21.60	(7.65–43.09)	28.65	(9.92–54.95)
60	15.22	(3.05–45.25)	28.12	(7.82–52.32)	33.74	(11.73–61.05)
75	18.62	(3.33–54.19)	33.92	(7.89–64.31)	38.00	(16.50–70.29)
90	21.89	(5.02–62.36)	37.33	(8.03–72.09)	40.94	(18.25–76.35)
105	26.76	(5.26–76.88)	41.35	(8.05–81.51)	44.49	(19.53–84.49)
120	31.57	(5.62–86.03)	44.42	(8.15–88.32)	50.72	(20.68–94.09)
Colour (%)						
15	31.35	(6.93–60.48)	33.30	(2.39–56.85)	58.47	(17.85–89.32)
30	51.27	(12.84–86.12)	50.21	(10.21–84.08)	67.17	(29.17–95.44)
45	61.49	(19.44–91.86)	58.76	(21.43–90.62)	72.32	(36.13–97.35)
60	68.03	(24.75–96.40)	64.96	(27.61–92.55)	76.49	(43.80–98.20)
75	73.95	(32.82–98.44)	70.01	(34.63–95.89)	80.41	(51.05–98.90)
90	76.99	(37.90–99.53)	73.59	(40.98–97.09)	82.41	(55.01–99.15)
105	78.90	(39.95–99.53)	76.69	(44.51–97.98)	84.63	(58.43–99.58)
120	80.51	(44.15–99.56)	79.09	(51.66–98.99)	86.63	(60.30–100.00)

In relation to time (Table 2), no statistically significant differences were found due to the fact that the range of concentrations tested (0.25–5 g/L) provided similar values at each time point. However, the descriptive statistics for time allowed us to compare the processes with and without the catalyst and to show the effect of time for each catalyst. As has been said previously, the use of TiO_2 as the catalyst was more efficient than the use of Fe^{2+}.

As shown in Table 2, TOC removal with Fe^{2+} was similar without a catalyst at least 30 min earlier, e.g. at 15 min with Fe^{2+} and at 45 min without the catalyst, the removal rates were 10.40 and 10.21%, and at 45 min with Fe^{2+} and at 90 min without catalyst similar rates were obtained (21.60 and 21.89%, respectively). The same effect was shown using TiO_2 as the catalyst although the time point was later; a similar rate was obtained at 15 min with TiO_2 and at 75 min without a catalyst (18.84 and 18.62%, respectively). Comparing the use of the two catalysts in relation to colour removal, TiO_2 presented better behaviour that Fe^{2+}; a similar removal rate was obtained 15 min earlier with TiO_2 after the first 45 min. Differences in the rate of colour removal were not seen when using of Fe^{2+} as catalyst in comparison to the conventional process. Therefore, in relation to TOC removal, the use of a catalyst allows a reduction in the HRT of the process of at least 30 min with Fe^{2+} and 45 min with TiO_2, without a reduction in the TOC removal rate. For colour removal with TiO_2, the HRT was reduced by 15 min in relation to the use of Fe^{2+} as the catalyst or without a catalyst.

4. Conclusions

Given the results obtained in a photoreactor plant after the treatment of textile wastewater with H_2O_2/UV, photo-Fenton and heterogeneous photocatalysis (TiO_2/H_2O_2/UV), the following conclusions were drawn:

- Dye increases the toxicity of the influent by 10.41 ± 4.18%, but AOP technology removed the colour totally; and therefore, the toxicity from the dye was also removed.
- H_2O_2 increased the toxicity of the effluent. After 120 min of AOP, the toxicity of the treated wastewater was higher than the initial water without H_2O_2 when the concentration of H_2O_2 was greater than 1 g/L, and so it is not recommended to operate the AOP process with a concentration higher than this.
- The use of a catalyst improved AOP technology by reducing the HRT of the process by at least 30 min with Fe^{2+} and 45 min with TiO_2 without reducing the TOC removal rate, and so the volume of the process will be lower.

- The colour removal increased with the peroxide concentration in all processes. There were no differences between the use of Fe^{2+} and without a catalyst; however, with respect to TiO_2, the HRT was reduced to 15 min without a decrease in the colour removal rate, so the use of a system with TiO_2 may reduce the operative volume of the process.

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