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# Kinetic modelling of TOC removal by $H_2O_2/UV$ , photo-Fenton and heterogeneous photocatalysis processes to treat dye-containing wastewater

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Abstract Wastewater from textile manufacturing introduces recalcitrant organic compounds, such as dyes and toxic by-products into the environment, where advanced oxidation processes are used to treat toxic and non-biodegradable organic pollutants which cannot be removed by traditional methods. H<sub>2</sub>O<sub>2</sub>/UV, photo-Fenton and heterogeneous photocatalysis (TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV) processes were used, and the effect of the hydraulic retention time on total organic carbon (TOC) removal was evaluated by fitting the analytical data for the three processes to different kinetic models. The high correlation between empirical and modelled data was accomplished with a pseudo-first-order model for the three processes ( $R^2 = 0.9823 \pm 0.017$ ). Mineralisation, decolourisation and disinfection of textile wastewater were investigated with laboratory-scale experiments for each process. Data showed that when 5 g/L  $H_2O_2$  was used, heterogeneous photocatalysis was the most effective method for the removal of TOC (94.55 %). With respect to colour, all three processes achieved nearly 100 % removal (99.6, 99.3 and 99.9 % at 120 min for the H<sub>2</sub>O<sub>2</sub>/UV, photo-Fenton and  $TiO_2/H_2O_2/UV$  processes, respectively).

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## Introduction

Effluents from the textile industry contain toxic compounds, most of which are not biodegradable (Ledakowicz and Gonera 1999). The discharge of coloured effluents from textile mills into the environment is undesirable, not only because of their colour, but also due to the large variety of raw materials and reagents as well as high levels of organic compounds, whose breakdown products are toxic and/or mutagenic (Weisburger 2002; Blanco et al. 2012). The elevated levels of coloured products and toxic chemicals introduced into the environment are not easily eliminated by conventional treatments (Garcia et al. 2009; Verma et al. 2012). So, the use of a technology, such as advanced oxidation processes (AOPs), capable of removing broad ranges of contaminants is necessary (Prato-Garcia and Buitrón 2013).

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 (Mantzavinos and Psillakis 2004). The effects of AOPs have been studied for different kinds of wastewater (Agustina et al. 2005; Sillanpää et al. 2011; Choi et al. 2013; Del Moro et al. 2013) and are a good option for the removal of persistent pollutants when conventional processes are not enough (Moreira et al. 2005). In addition, due to high disinfection efficiency, the AOPs are considered a good treatment against most viruses, bacteria and protozoa (Guo et al. 2009; Rubio et al. 2013). The most common method used to control the quality of water is Escherichia coli (Pitkänen et al. 2007). These processes can



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be classified as heterogeneous or homogeneous, and the homogeneous processes are further subdivided into processes that use energy and processes that do not use energy (Poyatos et al. 2010). AOPs generate hydroxyl free radicals (OH) which have a very high oxidation potential and can destroy organic pollutants, resulting in complete mineralisation (Del Moro et al. 2013). The radicals are produced from oxidising agents such as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), often combined with metallic or semiconductor catalysts and UV radiation (Homem and Santos 2011).

Among the AOP methods, the use of ultraviolet radiation in the presence of  $H_2O_2$  is a very promising technique for removing toxic organics from water (Aleboyeh et al. 2005). The advantages of the UV/ $H_2O_2$  process include a wide range of applications for the degradation of pollutants such us dyes, phenols and pesticides, with an accelerated rate of oxidation, disinfection potential and thorough mineralisation of pollutants in wastewater (Cao and Mehrvar 2011). This system has been applied to the degradation of several azo dyes from industrial wastewater, suggesting its use as an effective method for the treatment of dye-contaminated wastewater (Zuorro et al. 2013).

Photo-Fenton is another AOP which can be used for the treatment of textile wastewater and dyes and can completely decolourise water and partially mineralise dyes (Lucas and Peres 2006). The mixture of ferrous sulphate and  $H_2O_2$  generates OH radicals which are capable of oxidising organic pollutants in wastewater (Sivakumar et al. 2013), and the additional formation of hydroxyl radicals could be increased with UV light. In this way, the concentration of Fe<sup>2+</sup> is increased and the overall reaction is accelerated (Modirshahla et al. 2007). As dye concentration increases, it is necessary to increase the concentration of both Fe<sup>2+</sup> and peroxide to ensure the presence enough OH radicals to degrade the organic matter (Arslan-Alaton et al. 2009; Prato-Garcia and Buitrón 2013).

The use of  $TiO_2$  in AOPs is of great interest due to its high photocatalytic activity, lack of toxicity, biological and photochemical stability in aqueous solutions and its chemically inert nature (Herrmann 1999; Pekakis et al. 2006; Sakkas et al. 2009). Heterogeneous photocatalytic processes, which degrade contaminants by the generation hydroxyl radicals using a catalyst (TiO<sub>2</sub>), an oxidant (H<sub>2</sub>O<sub>2</sub>) and UV radiation, are advantageous due to the lack of mass transfer limitations, operation at ambient conditions and the possible use of solar irradiation (Pekakis et al. 2006).

AOPs can be mathematically modelled at several different levels dependent upon the kinetic pathways, reaction rate constants, structure of the model pollutant, type of catalyst and the presence of UV light, computer resources and the modelling objectives (Crittenden et al. 1999; Kusic et al. 2009). The models can optimise the dosage of



hydrogen peroxide and catalyst (Fe<sup>2+</sup>, TiO<sub>2</sub>) in order to avoid the loss of these reagents (Santos et al. 2010).

The aim of the present research was to study TOC degradation in dye-containing wastewater by three different AOPs and to compare systems over time. This research was carried out in Granada (Spain). Seven kinetic models of organic matter removal were studied for  $H_2O_2/UV$ , photo-Fenton and heterogeneous photocatalysis at different  $H_2O_2$  concentrations in order to understand the behaviour of the different processes. Moreover, biological control and colour analysis were done to study effluent water quality for each system using dye-containing wastewater.

## Materials and methods

### Experimental procedures

UV oxidation of textile wastewater adjusted to pH 3 with 10 % sulphuric acid was carried out in a batch laboratoryscale UV Consulting Peschl® photoreactor (López-López et al. 2013) at 25  $\pm$  0.5 °C with continuous agitation for 120 min. López-López et al. (2013) studied the use of AOP for removal of water polluted, and from these results, it was necessary to analyse the effect of the catalysts for this kind of water. H<sub>2</sub>O<sub>2</sub> was used at 0.25, 0.5, 1, 2 g/L (Schrank et al. 2007) and 5 g/L to study the behaviour with an excess of oxidant for the three processes (López-López et al. 2013). Samples were collected from the photoreactor every 15 min (Bali et al. 2004; Schrank et al. 2007), and samples from the heterogeneous photocatalysis process were filtered through a 0.45-µm Millipore filter to remove particles of  $TiO_2$  (Alaton et al. 2002). The amount of catalysts used were 40 mg/L of Fe<sup>2+</sup> and 200 mg/L of TiO2 (Kang et al. 2000; Fatta-Kassinos et al. 2011).

# Physical and chemical determinations

Colour measurements were carried out according to UNE-EN ISO 7887:1994. Absorbance measurements were recorded at 436, 525 and 620 nm using a He $\lambda$ ios  $\gamma$  spectrophotometer (ThermoSpectronic), pH using a pH meter (Crison pH 25<sup>®</sup>) and TOC measurements were determined using a Formarcs <sup>HT</sup> TOC/TN Analyser by oxidative combustion at 950 °C.

## Microbiological determinations

Coliform bacteria ferment lactose and produce acid after 24–48 h at 37 °C, while faecal coliform bacteria ferment lactose and produce acid and gas after 24 h at 44 °C. Material was 0.45- $\mu$ m–filtered, and the filter membranes were plated onto Endo Agar (Difco<sup>TM</sup> Manual) at pH

 $7.5 \pm 0.2$  (APHA 2012). The samples were incubated for 24 h, and colonies were used to estimate total and faecal coliforms (CFU/100 mL) present in samples.

# Statistical analysis

Data were analysed using IBM SPSS Statistic 20. ANOVA was evaluated using Tukey's honestly significant difference (HSD) to obtain a homogeneous subset of data with a confidence interval of 95 % ( $\alpha = 0.05$ ).

## Kinetic modelling

Table 1 shows the kinetic models applied to TOC concentration. For each model studied in this research were evaluated the process time, oxidant concentration and the process. The kinetic models used by López-López et al. (2013) were used to compare the effect of the different effluent and dyes. The models described by Taylor et al. (1995) and Calero et al. (2011) were checked in order to facilitate comparison with previously published data. Data were fitted to the different models, minimising the sum of squares error (SSE) between empirical and modelled data. The removal capacity at equilibrium was initialised in the maximum removal concentration during the test. The iterative method was finished when no differences in the SSE were obtained.

## **Results and discussion**

One of the most important aspects to consider in the treatment of a textile wastewater was colour removal. Comparison of the different processes indicated there were no statistically significant differences, as colour removal at high concentrations of  $H_2O_2$  was nearly complete. Evolution of the colour removal rate for the three processes is shown in Fig. 1, and slightly better colour removal was obtained with  $H_2O_2/UV$  and  $TiO_2/H_2O_2/UV$  processes with 0.5–5 g/L of oxidant. However, only with 0.25 g/L of  $H_2O_2$  the better colour removal rate was obtained with photo-Fenton and homogeneous photocatalysis.

At low concentrations of  $H_2O_2$  used in the  $H_2O_2/UV$  process, the rate of colour removal was relatively constant at 90 min for 0.25 g/L (47.4 %) and 75 min with 0.5 g/L (82.2 %) (Fig. 1a). When TiO<sub>2</sub> was used as the catalyst (Fig. 1c) at the same concentrations, colour removal rates were higher, but the reaction rate remained approximately constant (77.6 and 85 % for 0.25 and 0.5 g/L of  $H_2O_2$ , respectively). However, when Fe<sup>2+</sup> was used as the catalyst, the reaction rate was about constant at 60 min for 0.25 and 0.5 g/L oxidant but colour removal rates were reduced (65.3 and 70.6 %, respectively).

 Table 1
 Kinetic equations

Model	Equation	Parameters
Pseudo-first order	$C_{t} = C_{0} - (C_{e} * (1 - e^{-k*t}))$	<i>C</i> <sub>0</sub> : initial TOC concentration (mg/L)
Pseudo-second order	$C_t = C_0 - \frac{t}{\left(\frac{1}{h} + \frac{t}{C_c}\right)}$	$C_t$ : TOC concentration at any time, $t$ , (mg/L)
Zero order $C_t = C_0 + k_0 * t$ First-order $\ln(C_t) = \ln(C_0) + k1 *$ Second-order $\frac{1}{C_t} = \frac{1}{C_0} + k_2 * t$ Third-order $\frac{1}{C_t^2} = \frac{1}{C_0^2} + k_3 * t$ Elovich-type $C_t = C_0 + \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta}$	$C_{t} = C_{0} + k_{0} * t$ $\ln(C_{t}) = \ln(C_{0}) + k1 * t$ $\frac{1}{C_{t}} = \frac{1}{C_{0}} + k_{2} * t$ $\frac{1}{C_{t}^{2}} = \frac{1}{C_{0}^{2}} + k_{3} * t$ $C_{t} = C_{0} + \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t)$	C <sub>e</sub> : the removal capacity at equilibrium (mg/L) t: time of process (min) k: overall rate constant α: initial TOC concentration rate
		(mg/L min) $\beta$ : removal constant (mg/L) $h = k^*C^2$



Fig. 1 Colour removal as a function of time at different concentrations of  $H_2O_2$ : 0.25 (*square*), 0.5 (*triangle*), 1 (*multi symbol*), 2 (*dash line*) and 5 (*circle*) g/L for **a**  $H_2O_2/UV$ , **b** photo-Fenton, and **c** heterogeneous photocatalysis



At high concentrations of  $H_2O_2$ , the rate of colour removal was constant both in the heterogeneous photocatalysis and without catalyst at 1–5 g/L  $H_2O_2$  over 60 min and colour removal rates were nearly 100 % (Fig. 1a, c). However, for the photo-Fenton process, lower removal rates of 87.2, 91.0 and 93.3 % for 1, 2 and 5 g/L peroxide, respectively, were seen at 120 min. These rates were lower than those reported by Elmorsi et al. (2010) for photo-Fenton treatment of the Mordant red 73 dye, where 99 % decolourisation was seen within 15 min.

When compared to other methods, the photo-Fenton process yielded a greater colour removal (Fig. 1b) at 15 min for all  $H_2O_2$  concentrations due to the presence of the Fe<sup>2+</sup> catalyst, which accelerated the reaction compared to the TiO<sub>2</sub> catalyst or no catalyst. When 0.25 and 0.5 g/L  $H_2O_2$  were used, colour removal was constant at 60 min for photo-Fenton process.

The evolution of the TOC removal rate over time is shown in Fig. 2 for H<sub>2</sub>O<sub>2</sub>/UV (a), photo-Fenton (b) and heterogeneous photocatalysis processes (c). The data indicated TOC removal values increased with time for all concentrations of H<sub>2</sub>O<sub>2</sub>, while removal rates increased with H<sub>2</sub>O<sub>2</sub> concentration independent of time. TOC removal rate was different for each process. The operative variable affected the efficiency of the process due to the fact that TOC removal did not show statistically significant differences in the ANOVA test (p value > 0.05). Under the operative conditions studied, heterogeneous photocatalysis had the highest efficiencies. For the photo-Fenton process, TOC removal increased in relation to H<sub>2</sub>O<sub>2</sub>/UV but did not reach the values obtained with TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV reported by Riga et al. (2007), where heterogeneous photocatalysis was used at pH 3, 1 g/L TiO<sub>2</sub> and 0.5 %  $H_2O_2$ .

At low concentrations of hydrogen peroxide, higher TOC removal efficiencies were achieved with the heterogeneous process than for photo-Fenton and  $H_2O_2/UV$ . Using TiO<sub>2</sub> as the catalyst (Fig. 2c) at 0.25 and 0.5 g/L  $H_2O_2$ , TOC removal was 46.81 and 73.85 % at 120 min, respectively. When Fe<sup>2+</sup> was used as the catalyst at 0.25 and 0.5 g/L peroxide (Fig. 2b), TOC removal was 28.73 and 58.35 % at 120 min, respectively, and 9.44 and 27.56 % without a catalyst (Fig. 2a). These data indicated that the catalysts improved the efficiencies of the reactions.

At high concentrations of  $H_2O_2$  (1–5 g/L), the behaviour was similar to that seen at low concentrations. TOC removal rates were higher for the TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV process, while the photo-Fenton process rate was slightly higher than the H<sub>2</sub>O<sub>2</sub>/UV process rate. At 120 min with 1, 2 and 5 g/L of H<sub>2</sub>O<sub>2</sub>, TOC removal rates were 84.83, 87.80 and 94.55 %, respectively, for process catalysed with TiO<sub>2</sub>. Similar values (85 %) of TOC removal were reported by Lee et al. (2007) for dye-contaminated wastewater using 1.82 g/L of TiO<sub>2</sub>, 0.98 g/L of H<sub>2</sub>O<sub>2</sub> and a 20-min reaction



Fig. 2 TOC removal as a function of time at different concentrations of  $H_2O_2$ :0.25 (*square*), 0.5 (*triangle*), 1 (*multi symbol*), 2 (*dashed line*) and 5 (*circle*) g/L for **a**  $H_2O_2$ /UV, **b** photo-Fenton, and **c** heterogeneous photocatalysis

time. However, for photo-Fenton and  $H_2O_2/UV$  processes carried out at 1, 2 and 5 g/L  $H_2O_2$ , TOC removal rates were 69.93, 82.95, 91.42 % and 65.41, 77.86, 84.90 %, respectively. Elmorsi et al. (2010) reported 65 % mineralisation of Mordant red 73 dye within 3 h using the  $H_2O_2/UV$  process, while photo-Fenton treatment was more efficient, yielding 85 % mineralisation over the same 3-h period.

With respect to the effect of reaction time on TOC removal (Fig. 2), data indicated statistically significant differences within the first 15 min between TiO<sub>2</sub> (39.44 %) and Fe<sup>2+</sup> (11.60 %) catalysed and uncatalysed (11.31 %) processes, independent of oxidant concentration. For a 45-min reaction time with 2 and 5 g/L H<sub>2</sub>O<sub>2</sub>, TOC removal rates were higher for the H<sub>2</sub>O<sub>2</sub>/UV process (53.67 and 69.79 %) than photo-Fenton (51.73 and 66.88 %), which could be attributed to an optical shield effect by the catalyst to high concentrations of peroxide.

Kinetic modelling was used to compare and predict the behaviour of the each system, where mathematical models for the three processes at five different peroxide concentrations were analysed to compare empirical and theoretical values for TOC over time. Figure 3 shows the TOC values for the  $H_2O_2/UV$  (a, d, g, j and m), photo-Fenton (b, e, h, k, n) and TiO\_2/H\_2O\_2/UV processes (c, f, i, l,

o) at  $H_2O_2$  concentrations of 0.25 g/L (a, b, c), 0.5 g/L (d, e, f), 1 g/L (g, h, i), 2 g/L (j, k, l), and 5 g/L (m, n, o).

In order to compare the different models, the "best-fit" model was determined by the high correlation coefficient



Fig. 3 TOC removal of  $H_2O_2/UV$  process with 0.25 g/L (a), 0.5 g/L (d), 1 g/L (g), 2 g/L (j) and 5 g/L (m), photo-Fenton process with 0.25 g/L (b), 0.5 g/L (e), 1 g/L (h), 2 g/L (k) and 5 g/L (n) and TiO\_2/H\_2O\_2/UV process with 0.25 g/L (c), 0.5 g/L (f), 1 g/L (i), 2 g/L (l) and 5 g/L (o) at different empirical and model values: empirical

values (diamond), zero order (solid line), first order (dotted line), second order (dashed line), third order (single dotted dashed line), pseudo-first order (double dotted dashed line), pseudo-second order (small dashed line), Elovich (large dashed line)



Table 2 Correlation rates between the empirical and theoretical data of seven kinetics models for each process

Process	H <sub>2</sub> O <sub>2</sub> (g/L)	$R^2$						
		Zero order	First order	Second order	Third order	Pseudo-first order	Pseudo-second order	Elovich-type equation
H <sub>2</sub> O <sub>2</sub> /UV	0.25	0.9179	0.9256	0.9326	0.9391	0.9856	0.9736	0.8715
	0.5	0.9508	0.9651	0.9727	0.9743	0.9755	0.9522	0.7577
	1	0.9804	0.9663	0.9075	0.8168	0.9274	0.8923	0.3155
	2	0.9273	0.9803	0.8736	0.6930	0.9809	0.9523	0.3807
	5	0.9041	0.9945	0.8474	0.6639	0.9945	0.9890	0.5696
Photo-Fenton	0.25	0.8520	0.8894	0.9182	0.9394	0.9763	0.9441	0.8549
	0.5	0.9136	0.9672	0.9770	0.9500	0.9802	0.9068	0.6501
	1	0.9250	0.9882	0.9866	0.9308	0.9955	0.9890	0.6491
	2	0.8670	0.9792	0.9787	0.8935	0.9947	0.9869	0.6799
	5	0.8197	0.9686	0.9654	0.8554	0.9934	0.9844	0.7899
Heterogeneous photocatalysis	0.25	0.9460	0.9794	0.9913	0.9864	0.9928	0.9917	0.8483
	0.5	0.8437	0.9413	0.9873	0.9846	0.9802	0.9909	0.9728
	1	0.7507	0.9348	0.9460	0.9900	0.9809	0.9942	0.9963
	2	0.6773	0.8720	0.9904	0.9760	0.9871	0.9954	0.9905
	5	0.6106	0.8515	0.9978	0.9747	0.9892	0.9975	0.9699

Table 3 Kinetic constant of pseudo-first order

Process	$\mathrm{H_2O_2}\;(\mathrm{g/L})$	Pseudo-first order		
		C <sub>e</sub> (mg/L)	k (min <sup>-1</sup> )	
H <sub>2</sub> O <sub>2</sub> /UV	0.25	43.57	5.71E-03	
	0.5	104.31	7.09E-03	
	1	115.73	1.51E-02	
	2	147.06	1.85E-02	
	5	155.36	2.11E-02	
Photo-Fenton	0.25	77.25	1.25E-02	
	0.5	131.56	1.69E-02	
	1	149.01	1.97E-02	
	2	152.23	2.17E-02	
	5	177.70	2.95E-02	
Heterogeneous photocatalysis	0.25	98.10	1.29E-02	
	0.5	158.59	2.99E-02	
	1	169.36	3.75E-02	
	2	171.17	4.46E-02	
	5	177.90	8.23E-02	

between empirical and theoretical data (López-López et al. 2013) (Table 2). The correlation rate changed from 0.3155 using an Elovich-type equation to 0.9978 using a second-order model. To choose the better fit, all correlation rates were considered globally, and the Elovich-type equation and zero order were rejected due the lowest correlation rates ( $R^2$  lower than 0.9). Although the average  $R^2$  value was higher than 0.9, the third-order model was rejected because it had a correlation rate lower than 0.7 for certain



 $H_2O_2$  concentrations (0.6930 and 0.6639 at 2 and 5 g/L of  $H_2O_2$ , respectively, for the  $H_2O_2/UV$  process).

First- and pseudo-first-order models were exponential functions, while second-order and pseudo-second-order models were hyperbolical functions (Fig. 3). Regarding the geometrical sense of the different equation, both first-order and second-order models can describe the TOC removal and so both pseudo-orders too. Both curves (pseudo-firstorder and pseudo-second-order) were tested in these processes with good fit. Crittenden et al. (1999) used a pseudofirst-order kinetic model for H<sub>2</sub>O<sub>2</sub>/UV processes in a mixed batch reactor and Kusic et al. (2009) tested an exponential model for dye degradation kinetics using dark- and photo-Fenton type processes. Ho et al. (2000) used a pseudosecond-order rate equation to describe the kinetic sorption of divalent metal ions, while Lan et al. (2008) and Lucas et al. (2009) used the second-order model to describe reaction kinetics in an ozonation system.

Although the four models chosen (zero order, second order, third order and Elovich-type equations) could be used to represent/compare the processes, the model with the greatest correlation was the pseudo-first-order model with an average  $R^2$  value of 0.9823 (López-López et al. 2013). The kinetic constants of this model for each H<sub>2</sub>O<sub>2</sub> concentration are shown in Table 3. Both  $C_e$  and k increased with the H<sub>2</sub>O<sub>2</sub> concentration as reported by Elmorsi et al. (2010), where removal capacity of the system was higher when oxidant concentration was elevated, which were seen for each process for different conditions.

Independent of concentration, the most efficient process for the conditions tested was heterogeneous photocatalysis (Fig. 2), which had a higher TOC removal rate and capacity (Fig. 3). The lowest TOC removal rates were obtained with the  $H_2O_2/UV$ , which showed the lowest kinetic constants for the conditions evaluated. A comparison between the processes was possible by using the kinetic constants (Table 3), which are analysed one by one and finally they are compared together.

The rate of removal k was similar for the H<sub>2</sub>O<sub>2</sub>/UV and photo-Fenton processes, especially at higher oxidant concentrations, though the rates were lower than when  $TiO_2$ was used as catalyst, indicating the fastest process was heterogeneous photocatalysis. These rates ranged from  $5.71^{\ast}10^{-3}\ \text{min}^{-1}$  for  $H_2O_2/UV$  at the lowest  $H_2O_2$  concentration and  $8.23*10^{-2}$  min<sup>-1</sup> for heterogeneous photocatalysis at 5 g/L of oxidant, which were similar to values reported by Elmorsi et al. (2010) for dye decolourisation in water using H<sub>2</sub>O<sub>2</sub>/UV and photo-Fenton treatment, and Maldonado et al. (2007) in a study comparing  $TiO_2$  and Fenton plus photo-Fenton in a solar pilot plant. Karci et al. (2012) reported a similar order for the kinetic constants indicating pollutants were most rapidly degraded by photo-Fenton process followed by H<sub>2</sub>O<sub>2</sub>/UV, which were similar to values for the present study. The values of this research were slightly lower than values obtained by Arslan et al. (2000) using a photo-Fenton process to treat simulated dye effluents. On the other hand, the differences observed in removal capacity between catalysts were not significant, though these two processes with catalysts had a higher  $C_{\rm e}$ value. Considering both constants, although the TOC removal at 120 min was similar for  $TiO_2$  and  $Fe^{2+}$ , in the first case, the reaction took place before removing higher TOC content in the first minutes (Fig. 2), and so the lowest volume of reactor will be correspond to the heterogeneous photocatalysis.

#### Conclusion

Data obtained for  $H_2O_2/UV$ , photo-Fenton and heterogeneous photocatalysis (TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV) at H<sub>2</sub>O<sub>2</sub> concentrations between 0.25 and 5 g/L used to treat wastewater contaminated with dye yielded the following conclusions:

Colour removal by higher  $H_2O_2$  concentrations was 99.6, 99.3 and 99.9 % at 120 min for the  $H_2O_2/UV$ , photo-Fenton and TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV processes, respectively, being the colour removed before in the photo-Fenton process although the removal was lower.

The most effective method for TOC removal was heterogeneous photocatalysis (94.55 %) using 5 g/L of  $H_2O_2$ , while photo-Fenton and  $H_2O_2/UV$  processes removed

91.42 and 84.9 %, respectively, at the same concentration of oxidant.

The pseudo-first-order model for the three processes indicated the highest correlation between empirical and modelled data, suggesting this model could be used to design AOPs. The rate constants increased with  $H_2O_2$ concentration and indicated heterogeneous photocatalysis was the most rapid way to remove TOC removal at the same  $H_2O_2$  concentration.

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