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Study of kinetic parameters related to the decolourization and mineralization of reactive dyes from textile dyeing using Fenton and photo-Fenton processes

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Abstract

The decolourization and mineralization of two reactive azo dyes, Procion Red H-E7B (CI Reactive Red 141) and Cibacron Red FN-R (CI Reactive Red 238), under Fenton's and photo-Fenton's conditions have been investigated. Some parameters, like temperature, initial concentrations of Fe(II) and H_2O_2 and the use of natural or artificial light were evaluated aiming to find the optimal conditions to promote the efficient degradation of the dyes. The experimental results showed that the Fenton's process run under solar light was the most effective. Pseudo-first order degradation rate constants were obtained from batch experimental data. It is suggested that Fenton's and photo-Fenton's type reactions are viable techniques for the treatment of such types of reactive dyes, according to the high levels of colour, aromatic content (UV_{254}) and DOC removal.

Keywords: Reactive azo dyes; Fenton's process; Photo-Fenton's process; Solar light; Kinetics; Decolourization and mineralization

1. Introduction

Textile dyeing and finishing processes produce large quantities of wastewater that is highly coloured and contains large concentrations of organic matter [1], which is difficult to treat via classical methods. Apart from the aesthetic problems created when coloured effluents reach the natural water currents, dyes strongly absorb sunlight, thus impeding the photosynthetic activity of aquatic plants and seriously threatening the whole ecosystem [2].

Reactive azo dyes are of non-biodegradable nature and direct biological treatment of the coloured effluents is not effective [3]. Therefore, it is necessary to find an effective method of wastewater treatment, both in terms of limited water recourses management and the need for nature preservation. In this direction, *Advanced Oxidation Processes (AOPs)*, based on the generation of highly reactive hydroxyl radicals ($HO^{\bullet} + H^+ + e^- \rightarrow H_2O$, $E^0 = 2.8$ V versus NHE) as primary oxidant, appear as the emerging alternatives for the organic pollutants abatement [4]. Among them, Fenton's and photo-Fenton's type reactions are very promising since they achieve high reaction yields with a low treatment cost [5]. These AOPs have been successfully applied to treat reactive dyes [6−8] as well as textile effluents [9−11].

Fenton's and *photo-Fenton's* reactions are AOPs where oxidant species are generated from hydrogen peroxide and Fe(II)/Fe(III) as a catalytic couple. In Fenton's reaction [12], ferrous salts react with hydrogen peroxide to generate the hydroxyl radicals as follows (reaction (1)):

$$\mathrm{Fe(II)} + H_2O_2 \rightarrow \mathrm{Fe(III)} + HO^{\bullet} + HO^- \quad k = 76.5\ \mathrm{L\,mol^{-1}\,s^{-1}} \tag{1}$$

Then, Fe(III) can be reduced by reaction with exceeding H_2O_2 to form again ferrous ion and more radicals. This second

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process is called Fenton's-like [13], is slower than Fenton's reaction and allows Fe(II) regeneration giving place to a catalytic mechanism (reactions (2)–(4)):

$$\mathrm{Fe(III)} + \mathrm{H_2O_2} \leftrightarrows \mathrm{FeOOH^{2+}} + \mathrm{H^+} \quad K_{\mathrm{eq}} = 3.1 \times 10^{-3} \tag{2}$$

$$\mathrm{FeOOH^{2+}} \rightarrow \mathrm{HO_2^{\bullet}} + \mathrm{Fe(II)} \quad k = 2.7 \times 10^{-3}\ \mathrm{s^{-1}} \tag{3}$$

$$\mathrm{Fe(III)} + \mathrm{HO_2^{\bullet}} \rightarrow \mathrm{Fe(II)} + \mathrm{O_2} + \mathrm{H^+} \quad k < 2 \times 10^{3}\ \mathrm{L\,mol^{-1}\,s^{-1}} \tag{4}$$

The rate of contaminants degradation can be considerably increased via photochemical reaction in the photo-Fenton's process [13,14]. In this case, the regeneration of Fe(II), with production of new $HO^{\bullet}$ radicals, follows a photoreduction process (reactions (5) and (6)):

$$\mathrm{Fe(III)} + \mathrm{H_2O} \rightarrow \mathrm{FeOH^{2+}} + \mathrm{H^+} \tag{5}$$

$$\mathrm{FeOH^{2+}} \xrightarrow{h\nu} \mathrm{Fe(II)} + \mathrm{HO^{\bullet}} \quad \lambda \leq 410\ \mathrm{nm} \tag{6}$$

Fenton's and photo-Fenton's type reactions offer successful pollutant removal with relatively low operational costs [5] and with the possibility of efficient sun radiation exploitation [15].

In this work, we explore Fenton's reactions with and without the use of radiation (natural or artificial), to perform efficiently the decolourization and degradation of organic matter present in two synthetic reactive azo dye solutions, namely Procion Red H-E7B and Cibacron FN-R. The aim of this study is to examine in detail the role of a set of selected parameters (pH, temperature, initial concentrations of Fe(II) and H_2O_2 and the use of natural or artificial light). Special care was taken in the determination of kinetic parameters like rate constants and half-life times for both dyes. Evidences based on the obtained results suggest that the reactive azo dye solutions studied can be treated using Fenton's reactions.

2. Materials and methods

2.1. Synthetic dye solutions

A commercial homo-bireactive azo dye, Procion Red H-E7B (CI Reactive Red 141, empirical formula $C_{52}H_{34}O_{26}S_8Cl_2N_{14}$), composed of two monochlorotriazine reactive groups, was supplied by DyStar and used as received without any purification. The chemical structure of the dye is shown in Fig. 1. The initial concentration of Procion Red H-E7B for all the experiments was 100 mg L^{-1}, a value that is among typical dye concentrations in real textile wastewaters [16]. In order to simulate batch-dyeing conditions, the dye was hydrolysed, by adjusting the pH of synthetic solutions to 10.6, followed by heating to 80 °C for 6 h. Finally, the hydrolysed dye solutions were stored at 4 °C after pH adjustment between 2.8 and 3.0, being ready for Fenton's and photo-Fenton's operation.

A commercial hetero-bireactive azo dye, Cibacron Red FN-R (C.I. Reactive Red 238, empirical formula $C_{29}H_{15}ClFN_7O_{13}S_4Na_4$, 944.2 g mol^{-1}) was supplied by CIBA and used as received without further purification. The chemical structure was confidential and not available. The initial Cibacron Red FN-R concentration for all the experiments was 100 mg L^{-1}. In order to simulate batch-dyeing conditions, the dye was hydrolysed by adjusting the pH of synthetic solutions to 10.6, followed by heating to 60 °C for 1 h. Finally, pH of the hydrolysed dye solutions was adjusted between 2.8 and 3.0 (the optimum pH for photo-Fenton process) and stored at 4 °C until Fenton's and photo-Fenton's operation.

2.2. Chemicals for pH adjustment

For the pH adjustment, concentrated reagent grade sulphuric acid and sodium hydroxide solutions (Panreac) were used. All solutions were prepared with deionised water obtained from a Millipore Milli-Q system.

2.3. Fenton's and photo-Fenton's oxidation reagent

The hydroxyl radical, $HO^{\bullet}$, was generated in situ by the addition of the following reagents in aqueous media: hydrogen peroxide, H_2O_2, Panreac, 33% w/v and ferrous sulphate, $FeSO_4 \cdot 7H_2O$, Merck, 99.5%.

2.4. Reactors and light sources

Fenton's and photo-Fenton's oxidation was carried out using a cylindrical Pyrex thermostatic cell of 150 mL of capacity. The reaction mixture inside the cell, consisting of 100 mL of dye sample (100 mg L^{-1}) and the precise amount of Fenton's reagent, was continuously stirred with a magnetic bar and the temperature fixed at the required level (298, 313 or 333 K at ±1 K). A 6 W Philips black light fluorescent lamp, which basically emits at 350 nm, was used as artificial light

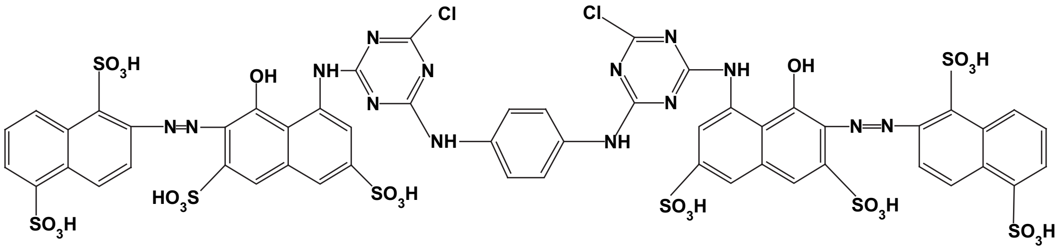

Fig. 1. Chemical structure of Procion Red H-E7B.

source, when working under photo-Fenton's conditions. The intensity of the incident light, measured employing a uranyl actinometer, was 1.38×10^{-9} Einstein s^{-1}.

When experiments were performed using solar light, the temperature rose from 30 to 40 °C. The yearly averaged solar energy between 300 and 400 nm hitting the earth's surface in the south of Spain is ca. $3-4 \times 10^{-3}$ W cm^{-2} [17].

2.5. Chemical assays

The UV/vis-absorption spectra were recorded by using a Shimadzu UV-1603 double beam spectrophotometer in the 200–700 nm range. As we can see in Fig. 2, the absorption spectra of the Procion Red H-E7B is characterised by two main bands, one in the visible region ($\lambda_{max} = 543.5$ nm) and the other in the UV region ($\lambda_{max} = 289.0$ nm). In the absorption spectra of Cibacron Red FN-R, there are also two main bands, one in the visible region ($\lambda_{max} = 542.5$ nm) and the other in the UV region ($\lambda_{max} = 286.5$ nm). For both dyes, also an important band is at 254 nm (aromatic content).

DOC was determined with a Shimadzu TOC-V_{CSH} analyser with a solution of potassium phthalate as standard of calibration.

H_2O_2 consumption was tested by the potassium iodide titration method [18].

3. Results and discussion

3.1. Evaluation of kinetic parameters

The kinetics of Fenton reaction can be quite complex because of the larger number of steps involved [14]. The general elementary rate law for reaction of a target organic compound (RH) can be written as follows:

$$-\frac{dC_{RH}}{dt} = k_{HO}C_{HO^\bullet}C_{RH} + \sum_i K_{ox_i}C_{ox_i}C_{RH} \qquad (7)$$

where ox_i represents oxidants other than $HO^\bullet$ that may be present, such as ferryl. Hydroxyl radical is usually regarded as the sole or most important reactive species. Then:

$$-\frac{dC_{RH}}{dt} = k_{HO}C_{HO^\bullet}C_{RH} \qquad (8)$$

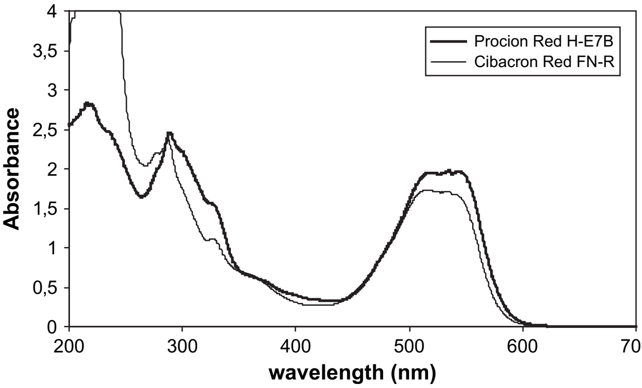

Fig. 2. Absorption spectra of hydrolysed Procion Red H-E7B (100 mg/L) and hydrolysed Cibacron FN-R (100 mg/L), before treatment; pH = 3.

Considering that the concentration of reactive species must reach quickly a stationary-state regimen during the process, and provided that $C_{HO^\bullet}$ can be considered constant, the rate law for the degradation process can be treated as being pseudo-first order, in terms of consumption of the target organic compound. We have

$$-\frac{dC_{RH}}{dt} = k_{app}C_{RH} \qquad (9)$$

and, by integration, we obtain:

$$\ln C_{RH} = \ln C_{(RH)_0} - k_{app} \times t \qquad (10)$$

A plot of $\ln C_{RH}$ versus time generated a straight line with a negative slope. The slope of this line corresponds to the apparent rate constant value for the degradation of the organic target compound.

In our case, we follow the rate of decolourization of the dye ($\lambda = 543.5$ nm for Procion Red H-E7B and 542.5 nm for Cibacron Red FN-R) and also the rate of aromatic content removal ($\lambda = 254$ nm for both dyes). Consequently, Eq. (10) was converted to:

$$\ln A = \ln A_0 - k_{app} \times t \qquad (11)$$

where k_{app} is the apparent rate constant, t is the reaction time and A_0 and A are the initial and final absorbance values of the dye solution, respectively. As indicated in several papers [2,7,19–23] decolourization and aromatic content removal kinetics of most dyes can be safely treated using a pseudo-first order rate law, based on the steady-state approximation, as it will be the case of our studied dyes (Procion Red H-E7B and Cibacron Red FN-R).

The following parameters were evaluated aiming to find the optimal conditions to promote the degradation of both dyes: temperature, pH, concentration of Fe(II) and H_2O_2. For temperature, we choose room temperature (25 ± 1 °C). The pH in the initial assays was defined as being 3, since it has been reported that Fenton's reactions occur efficiently at pH in a range between 2.9 and 3.5 [13,24–26].

For Fe(II) and H_2O_2 concentrations, different molar ratios were tested, taken into account previous work [8,27,28] and the fact that, for mineralization, a good level of hydrogen peroxide is thought to be ca. 1–2 times the stoichiometric requirements [25] (1 g COD = 0.03125 mol oxygen = 0.0625 mol hydrogen peroxide).

For a fixed Fe(II) concentration (0.18 mM) [8], the following H_2O_2 concentrations were tested: 50, 100, 150, 250, 500 and 1000 mg L^{-1} (1.47, 2.94, 4.41, 7.35, 14.7 and 29.4 mM). For Procion Red H-E7B decolourization and aromatic content removal (UV_{254}), the best H_2O_2 concentration can be taken as 100 mg L^{-1} (2.94 mM). At these conditions, the time needed to reduce to half the initial colour of the dye was $t_{1/2} = 2.55$ min with a $k_{app} = 0.2713$ min^{-1} (Fig. 3). The time needed to reduce to half the initial aromatic content (UV_{254}) of the dye was

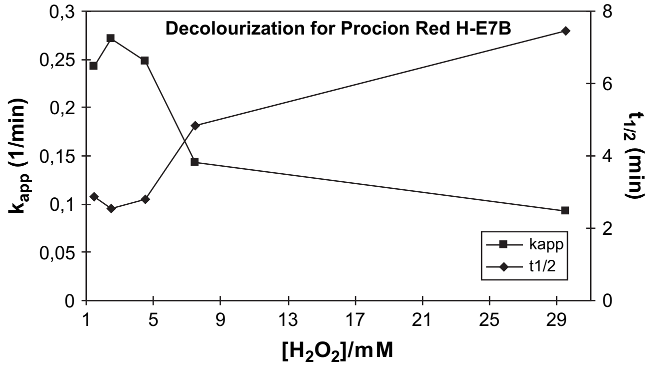

Fig. 3. Effect of the initial H_2O_2 concentration on the apparent rate constant (k_{app}) and half-life time ($t_{1/2}$) for the decolourization of Procion Red H-E7B ([Fe(II)] = 10 ppm (0.18 mM); pH = 3; $T = 25 \pm 1$ °C).

$t_{1/2} = 113.6$ min with a $k_{app} = 0.0061$ min^{-1} (Fig. 4). At these optimal conditions, the molar ratio H_2O_2/Fe(II) was 16.3.

For hydrogen peroxide concentrations below 100 mg L^{-1} (2.94 mM) worse results were obtained. Concretely, the worst results were obtained when 50 mg L^{-1} (1.47 mM) H_2O_2 was used. As we can see in the results shown in Figs. 3 and 4, at this concentration level, insufficient oxidant is available to destroy the dye. On the other hand, a further increase in oxidant concentration slows down the degradation process, because hydrogen peroxide in excess acts as hydroxyl-radical scavenger as shown by the following kinetic equation [10]:

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad k = 2.7 \times 10^{7}\ \mathrm{L\,mol^{-1}\,s^{-1}} \tag{12}$$

Moreover, some competitive reactions could take place [29]:

$$2HO^{\bullet} \rightarrow H_2O_2 \tag{13}$$

For Cibacron Red FN-R, the best H_2O_2 concentration can be taken as 250 mg L^{-1} (7.35 mM), because higher H_2O_2 concentrations than 250 ppm (7.35 mM) don't give better results. At these conditions, the time needed to reduce to half the initial colour of the dye was $t_{1/2} = 16.19$ min with a $k_{app} = 0.0428$ min^{-1} (Fig. 5). The time needed to reduce to half the initial aromatic content (UV_{254}) of the dye was $t_{1/2} = 103.4$ min with a $k_{app} = 0.0067$ min^{-1} (Fig. 6). At these optimal conditions, the molar ratio H_2O_2/Fe(II) was 40.8.

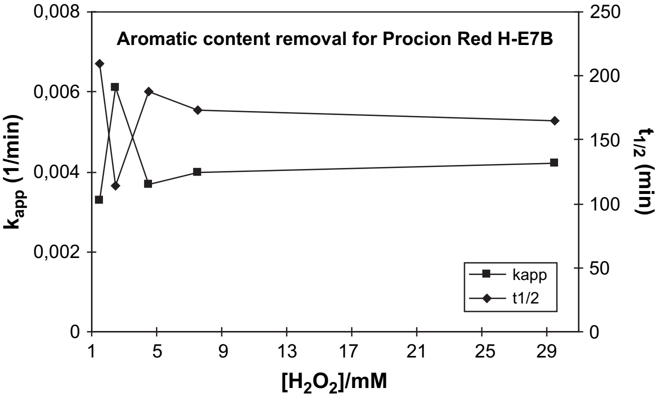

Fig. 4. Effect of the initial H_2O_2 concentration on the apparent rate constant (k_{app}) and half-life time ($t_{1/2}$) for the aromatic content removal of Procion Red H-E7B ([Fe(II)] = 10 ppm (0.18 mM); pH = 3; $T = 25 \pm 1$ °C).

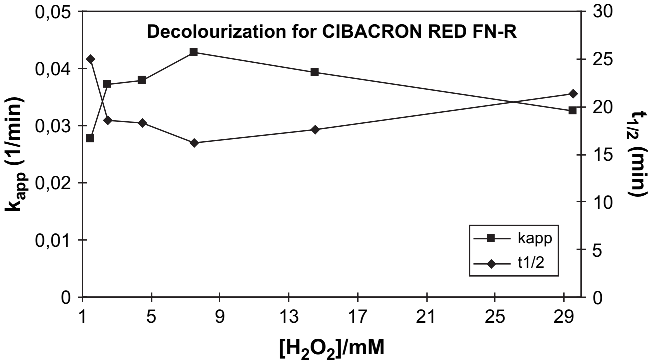

Fig. 5. Effect of the initial H_2O_2 concentration on the apparent rate constant (k_{app}) and half-life time ($t_{1/2}$) for the decolourization of Cibacron Red FN-R ([Fe(II)] = 10 ppm (0.18 mM); pH = 3; $T = 25 \pm 1$ °C).

On the other hand, assuming an Arrhenius dependence of temperature, k can be expressed as:

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

where A is the preexponential factor (s^{-1}), E_a is the apparent activation energy (kJ/mol), R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature (K); temperature values tested were 298, 313 and 333 K.

The Arrhenius plot showing ln k versus 1/T is in Fig. 7. From this plot we obtain $E_a = 1.26$ kJ mol^{-1} for Procion Red H-E7B and $E_a = 1.09$ kJ mol^{-1} for Cibacron Red FN-R. We should note that these E_a values are very similar. However, these E_a values were obtained under optimal doses of Fenton's reagent for the dyes, viz. molar ratio H_2O_2/Fe(II) = 16.3 for Procion Red H-E7B and molar ratio H_2O_2/Fe(II) = 40.8 for Cibacron Red FN-R.

4. Comparison of different Fenton's and photo-Fenton's processes

Once optimal doses of Fenton's reagent have been established and kinetic parameters obtained, the presence of an

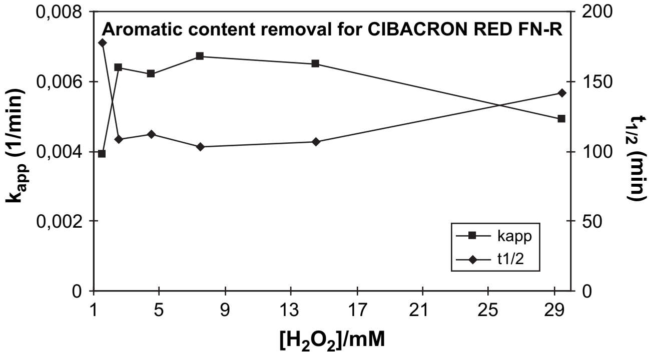

Fig. 6. Effect of the initial H_2O_2 concentration on the apparent rate constant (k_{app}) and half-life time ($t_{1/2}$) for the aromatic content removal of Cibacron Red FN-R ([Fe(II)] = 10 ppm (0.18 mM); pH = 3; $T = 25 \pm 1$ °C).

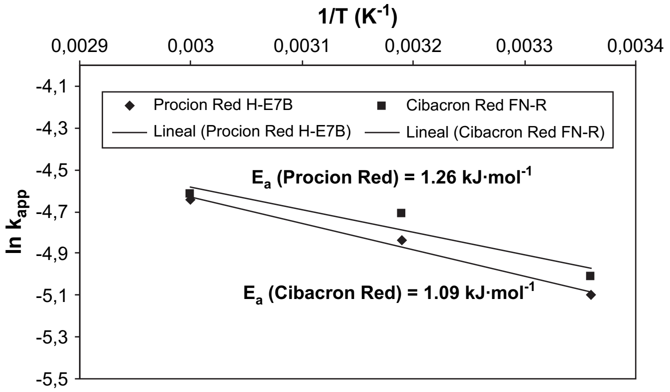

Fig. 7. Arrhenius plot for pseudo-first order rate constants calculated for both dyes at optimal Fenton's reagent doses.

irradiation source was tested. We tested an artificial light, a 6 W Philips black light fluorescent lamp which basically emits at 350 nm, and solar light. At his point, the analytical parameters UV_{254} (aromatic content) and DOC (dissolved organic carbon) were followed.

Although attempts to monitor colour removal were also carried out, the disappearance was too fast in presence of light. Light can play two different roles that will lead to an improvement of the reaction yields: (a) it drives photo-Fenton's reaction, producing extra hydroxyl radicals and the recovery of Fe(II) needed in Fenton's reaction. The photo-Fenton's reaction may involve photolysis of ferric ion (reaction (6)) or photolysis of Fe(III)–peroxy complexes or any of their potential intermediates [30]. (b) It can drive ligand to metal charge transfer in the potentially photolabile complexes formed by Fe(III) and organic compounds, a process that has been well proven for the complexes formed between Fe (III) and the carboxylic acid moiety [31].

For 90 min treatment and optimal Fenton's reagent doses, the results obtained for both dyes under different Fenton's and photo-Fenton's processes are shown in Figs. 8 and 9. The best results were obtained under solar light conditions, because solar light has the largest fraction of photons with the energy needed to drive photoreactions involved in the present reactive system. This fact opens up the possibility of extended low cost applications. For Procion Red H-E7B, a 100% DOC removal and more than 80% UV_{254} removal is obtained after 90 min treatment. For Cibacron Red FN-R the results were 100% DOC removal and more than 70% UV_{254} removal. For both dyes, it has to be pointed out that the remaining absorption at 254 nm was due to the residual H_2O_2 present in the effluent and the presence of several complexes of iron that absorb photons of this wavelength.

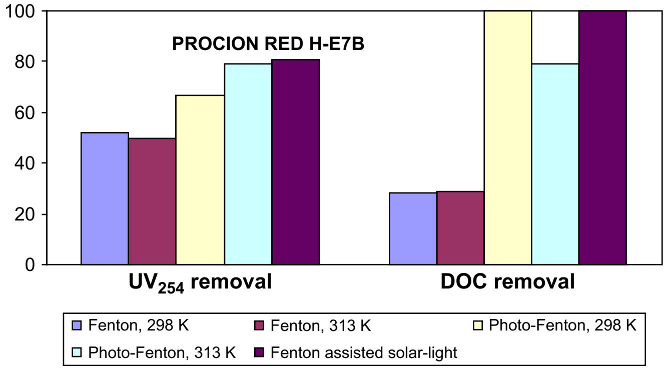

Fig. 8. DOC and UV_{254} removal for Procion Red H-E7B, after 90 min of treatment, under different Fenton's and photo-Fenton's processes ([Fe(II)] = 10 ppm (0.18 mM); $[H_2O_2]$ = 100 ppm (2.94 mM); pH = 3; $T = 25 \pm 1$ °C).

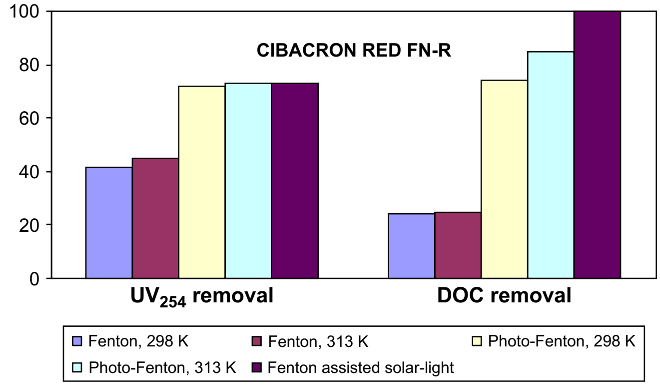

Fig. 9. DOC and UV_{254} removal for Cibacron Red FN-R, after 90 min of treatment, under different Fenton's and photo-Fenton's processes ([Fe(II)] = 10 ppm (0.18 mM); $[H_2O_2]$ = 250 ppm (7.35 mM); pH = 3; $T = 25 \pm 1$ °C).

5. Conclusions

The Fenton's process for both dyes was found to follow pseudo-first order kinetics in the range of operating conditions studied. For Procion Red H-E7B decolourization and aromatic content removal (UV_{254}), the best Fenton's reagent conditions were: $[H_2O_2] = 100\ \mathrm{mg\ L^{-1}}$ (2.94 mM) and $[Fe(II)] = 10\ \mathrm{mg\ L^{-1}}$ (0.18 mM). At these conditions, the time needed to reduce to half the initial colour of the dye was $t_{1/2} = 2.55$ min with a $k_{app} = 0.2713\ \mathrm{min^{-1}}$. The time needed to reduce to half the initial aromatic content (UV_{254}) of the dye was $t_{1/2} = 113.6$ min with a $k_{app} = 0.0061\ \mathrm{min^{-1}}$. For Cibacron Red FN-R, the best Fenton's reagent conditions were: $[H_2O_2] = 250\ \mathrm{mg\ L^{-1}}$ (7.35 mM) and $[Fe(II)] = 10\ \mathrm{mg\ L^{-1}}$ (0.18 mM). At these conditions, the time needed to reduce to half the initial colour of the dye was $t_{1/2} = 16.19$ min with a $k_{app} = 0.0428\ \mathrm{min^{-1}}$. The time needed to reduce to half the initial aromatic content (UV_{254}) of the dye was $t_{1/2} = 103.4$ min with a $k_{app} = 0.0067\ \mathrm{min^{-1}}$. Moreover, the degradation of both dyes was always greater under the presence of a source of light. Concretely, under solar light conditions a 100% DOC removal was obtained for both dyes.

Acknowledgements

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