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Degradation of Procion Red H-E7B reactive dye by coupling a photo-Fenton system with a sequencing batch reactor

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Abstract

A bench-scale study combining photo-Fenton reaction with an aerobic sequencing batch reactor (SBR) to degrade a commercial homo-bireactive dye (Procion Red H-E7B, 250 mg l^{-1}) was investigated. The photo-Fenton process was applied as a pre-treatment, avoiding complete mineralisation, just to obtain a bio-compatible water able to be treated by means of the SBR in a second step. In this sense, different Fenton reagent concentrations were assessed by following dye solution biodegradability enhancement (BOD_5/COD), as well as the toxicity (EC_{50}), DOC, colour ($Abs_{543.5}$) and H_2O_2 evolution with photo-Fenton irradiation time. Obtained pre-treated solutions were biologically oxidized in a SBR containing non-acclimated activated sludge. Different hydraulic retention time (HRT) in the bioreactor were tested to attain the maximum organic load removal efficiency. Best results were obtained with 60 min of 10 mg l^{-1} Fe(II) and 125 mg l^{-1} H_2O_2 photo-Fenton pre-treatment and 1 day HRT in SBR.

Keywords: Textile reactive dye; Advanced oxidation processes; Photo-Fenton reaction; Biodegradability enhancement; Sequencing batch reactor; Organic removal

1. Introduction

The textile industry daily consumes large quantities of water in dyeing and finishing processes. Generated effluents are characterized by a high content of suspended solids and heavy metals, high temperature, unstable pH, elevated chemical oxygen demand and the presence of chlorinated organic compounds, surfactants and colour [1]. The substantial amount of dyes, especially reactive dyes, used in the dyeing stage of textile manufacturing supposes an increasing environmental threat due to its refractory nature. 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.

At present, several methods have been developed to treat dye wastewater. Physicochemical treatments such as coagulation/flocculation, flotation, membrane processes or activated carbon adsorption are common practices [2–5], but they are quite inefficient and result in a phase transfer of pollutants, leaving the problem unsolved. On the other hand, single biological treatments, the most economical and environmentally friendly ones, are not a suitable alternative when working with toxic and/or non biodegradable wastewaters [6]. In fact, most of disposed dyes are of non-biodegradable nature and standard biological treatment of their coloured effluents is not effective [7].

Therefore, destructive treatment methods for the remediation of recalcitrant or hazardous pollutants are currently under investigation. In this direction, *Advanced Oxidation Processes* (AOPs), based on the generation of highly reactive hydroxyl radicals ($HO^{\bullet}$, $E = 2.8$ V versus NHE) as primary oxidant, appear as the emerging alternatives for the organic pollutants abatement [8]. Among them, the *Fenton* and *photo-Fenton* type reactions are very promising since they achieve high reaction yields with a low treatment cost [9]. Fenton and photo-Fenton methods have been successfully applied to treat reactive dyes [10,11] as well as textile effluents [12,13].

In the accepted mechanism of *Fenton* reaction [14], hydroxyl radicals ($HO^{\bullet}$) are generated by interaction of H_2O_2 with ferrous

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salts [reaction (1)]:

$$\mathrm{Fe(II)} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe(III)} + \mathrm{HO^\bullet} + \mathrm{HO^-}$$
$$k = 76.51\,\mathrm{mol^{-1}\,s^{-1}} \quad (1)$$

Then, Fe(III) can be reduced by reaction with exceeding H_2O_2 to form again ferrous ion and more radicals. This second process is called *Fenton-like*, is slower than Fenton reaction and allows Fe(II) regeneration giving place to a catalytic mechanism [reactions (2)–(4)]:

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

$$\mathrm{FeOOH^{2+}} \rightarrow \mathrm{HO^\bullet}_2 + \mathrm{Fe(II)} \quad k = 2.7 \times 10^{-3}\,\mathrm{s^{-1}} \quad (3)$$

$$\mathrm{Fe(III)} + \mathrm{HO^\bullet}_2 \rightarrow \mathrm{Fe(II)} + \mathrm{O_2} + \mathrm{H^+}$$
$$k < 2 \times 10^3\,\mathrm{l\,mol^{-1}\,s^{-1}} \quad (4)$$

Degradation of the organic pollutants in the *Fenton* reaction can increase in presence of an irradiation source (*photo-Fenton* reaction). In this case, the regeneration of Fe(II), with production of new $HO^\bullet$ radicals, follows a photoreduction process [reactions (5) and (6)]:

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

$$\mathrm{FeOH^{2+}} \xrightarrow{h\upsilon} \mathrm{Fe(II)} + \mathrm{HO^\bullet} \quad \lambda = 410\,\mathrm{nm} \quad (6)$$

Since the reaction requires radiations up to 410 nm [15], photo-Fenton reaction offers the possibility to be driven under solar irradiation, becoming a cost-effective process [16,17]. Nevertheless, Fenton and photo-Fenton methods have some drawbacks: necessity of pH changes, sludge generation and, mainly, high operational costs due to the chemical reagents consumption. In this sense, chemical oxidation alone can often be prohibitive for wastewater treatment.

Recently, several studies have proposed the combination of single AOP and biological treatments to avoid the drawbacks of each other [18–22]. With this aim, the AOP is performed as a first step to just enhance the biodegradability and generate a new effluent able to be treated in a biological plant, while reducing operational costs.

The biological treatment is carried out in a sequencing batch reactor (SBR). There are large facilities incorporating the SBR design, mainly because of its simplicity, flexibility of operation, as well as cost effectiveness [23,24]. In this sense, SBR is considered an attractive alternative to conventional biological wastewater treatment systems, but with a unique tank for reaction and sedimentation stages. Therefore, in a controlled time sequence, usually SBR-type bioreactors operate under five defined phases: filling, aeration-reaction, activated sludge settling, draw and idle. With respect to applications, SBRs have been successfully employed in the biodegradation of both municipal and industrial wastewaters [25], as well as for the degradation of textile wastewaters in combined systems [18].

Accordingly, it is clear from the above discussion that SBR is an appropriate alternative in the combined AOP-biological treatment of the wastewaters studied here. In the present work, a representative reactive dyestuff employed in cellulosic fibre dyeing (Procion Red H-E7B) is taken as a model compound. The paper aims at more efficient use of chemical oxidants to carry out the photo-Fenton pre-treatment. In this sense, an important indicator of the pre-treatment effectiveness will be the increase of the biodegradability under minimum Fenton reagent doses. Subsequently, different photo-treated dye solutions will be fed to the SBR to evaluate the best photo-Fenton conditions. Moreover, the hydraulic retention time needed to obtain maximum organic load removal in the bioreactor is studied.

2. Experimental

2.1. Synthetic dye solution

A commercial homo-bireactive azodye, Procion Red H-E7B (C.I. 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 250 mg l^{-1}, a value that is among typical dye concentrations in real textile wastewaters [26]. 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 AOP operation.

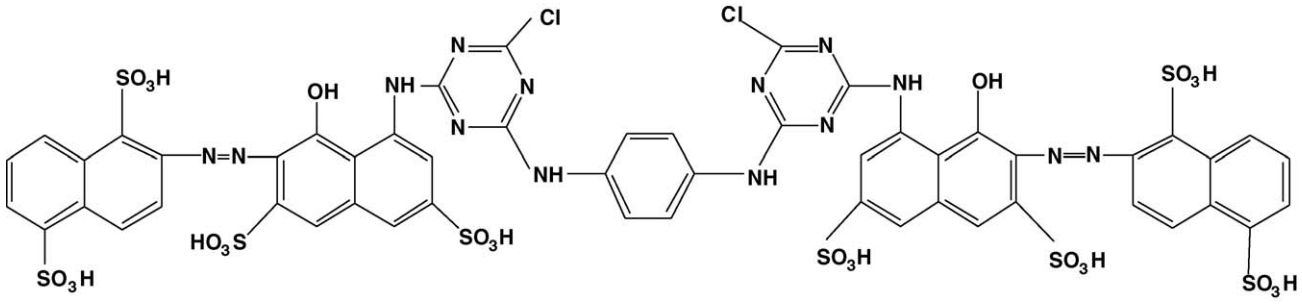

Fig. 1. Chemical structure of Procion Red H-E7B.

2.2. Photo-Fenton 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%.

2.3. Photo-chemical reactor

Photo-Fenton oxidation was carried out using a cylindrical Pyrex thermostatic cell of 300 ml of capacity ($T = 23 \pm 1\,^{\circ}C$), equipped with a magnetic stirrer to provide good mixing with the defined Fenton reagent inside the reactor. The dye solution volume was 250 ml. A 6 W Philips black light fluorescent lamp, which basically emits at 350 nm, was used as artificial light source. The intensity of the incident light, measured employing an uranyl actinometer, was 1.38×10^{-9} Einstein s^{-1}.

2.4. SBR biomass

The bioreactor was seeded with activated sludge coming from the recirculation stage of a municipal Wastewater Treatment Plant, WWTP, in Manresa (Catalonia, Spain). The biomass population of the collected activated sludge, usually expressed as volatile suspended solids (VSS, $g\,l^{-1}$) [27], fluctuated within the range 2.85–4.94 $g\,l^{-1}$. Then, to perform every experiment with approximately the same initial cells concentration, the SBR was seeded by diluting the original activated sludge to a VSS value of 1 $g\,l^{-1}$.

2.5. SBR set-up and operation conditions

The biological treatment system was composed of a 2 l aerobic bench-scale sequencing batch reactor, equipped with an air diffuser and agitation. The operating liquid volume was 1.5 l. Temperature was maintained under room conditions, between 21 and 23 °C, while keeping the concentration of dissolved oxygen (DO, $mg\,l^{-1}$ O_2) not lower than 3 $mg\,l^{-1}$ O_2. Fresh biomass was used for the performance of each run.

The SBR operation strategy was as follows: once the hydraulic retention time was fixed, the bioreactor was fed with the required sample volume during the filling stage. At the end of the aeration-reaction period, the agitation and the airflow were switched off to allow to settle the activated sludge for 1 h. Afterwards, the corresponding volume of treated solution was decanted from the supernatant during the draw step, according to the defined HRT. Finally, the reactor was fed with the same volume of fresh solution and the aeration-agitation turned on again. This process was repeated cycle by cycle as many times as necessary to allow cells acclimation and/or to obtain repetitive results.

Daily analyses carried out were VSS, DO, dissolved organic carbon (DOC, $mg\,l^{-1}$ C) (influent and effluent samples content) and pH adjustment between 6.5 and 7.5 if necessary. Suitable proportions of essential biological nutrients ($MgSO_4$, $CaCl_2$, NH_4Cl and NaH_2PO_4 buffer at pH 7) were also added to the solution [28].

2.6. Chemical assays

The UV/vis-absorption spectra were recorded by using a Shimatzu UV-1603 double beam spectrophotometer in the 200–700 nm range. The maximum absorption in the visible region ($\lambda_{max} = 543.5$ nm) was taken as an estimation of the dye presence in solution. DOC was determined with a Shimadzu TOC-V_{CSH} analyser with a solution of potassium phthalate as standard of calibration. Chemical oxygen demand (COD, $mg\,l^{-1}$ O_2) was assessed by the closed reflux colorimetric method with a HACH DR/2000 spectrophotometer [28]. H_2O_2 consumption was tested by the potassium iodide titration method [29]. Accordingly, correction was made in the COD measurement for residual H_2O_2 [30]. Determination of total suspended solids (TSS, $g\,l^{-1}$) and volatile suspended solids (VSS, $g\,l^{-1}$) was carried out gravimetrically following Standard Methods recommendations [28].

2.7. Biological assays

Residual hydrogen peroxide was removed from the solution with *Catalase* (2350 U mg^{-1}; Sigma), according to the following specifications: 1 U destroys 1 μmol min^{-1} of hydrogen peroxide at pH 7 and temperature 25 °C. Fe ion (mainly Fe(III)) was precipitated before the assays by increasing the pH. The toxicity was assessed using the Biotox® technique. According to the sample preparation procedure prior to the Biotox® test, the pH of the solutions was adjusted to 7 and solid sodium chloride was added in order to adjust salinity to 2%.

The test is based on the determination of the acute toxicity that the sample has on the marine photobacteria *Vibrio fischeri*. The toxicity is quantified as the relative decrease of the photobacteria light emission with respect to a sample control that only contains the dilution medium, i.e. sodium chloride, 2% (w/v). The analysis generates the EC_{50} parameter (the concentration of toxicant that causes a 50% decrease of light emission), which is determined by interpolation from a series of dilutions of the original toxicant sample that have been in contact with the photobacteria during 30 min. A graph is plotted with the *x*-axis containing % DOC (compared to the total DOC content of the initial sample) and the *y*-axis displays the inhibition percent. EC_{50} values were expressed as percentage of DOC of the original sample. When the DOC of the original samples were lower than the EC_{50}, these values were given as >100%. Phenol and glucose solutions were used as standard toxic and non toxic samples to check the technique suitability.

The measurement of biochemical oxygen demand for 5 days (BOD_5, $mg\,l^{-1}$ O_2) was performed by means of a mercury-free WTW 2000 Oxytop thermostated at 20 °C. When BOD_5 determination took place during the photo-treatment stage, due to the toxic character of hydrogen peroxide, its removal with the precise amount of SO_3^{2-} [31] was found to be necessary.

The Zahn–Wellens test was carried out under conditions close to those of a conventional municipal wastewater treatment plant. Activated sludge coming from the Manresa WWTP was used to prepare the 0.2 $g\,l^{-1}$ of TSS required in the test specifications [32].

The experimental set-up to perform the short-term respirometry test was composed of a closed and thermostatic 250 ml respirometer ($T = 25 \pm 1\,^{\circ}C$), connected to a dissolved oxygen-meter (Model 407510, EXTECH), an air diffuser and a mechanical stirrer. Results were determined as specific oxygen uptake rate (OUR, $g\,O_2\,g^{-1}$ VSS min^{-1}) of the sample, while biodegradability was estimated by comparing the oxygen demand (OD, $g\,O_2\,g^{-1}$ VSS) within the first 2 h of reaction with the oxygen demand of an acetic acid solution (OD_{st}, $g\,O_2\,g^{-1}$ VSS), a completely biodegradable standard with the same COD than the sample.

3. Results and discussion

3.1. Untreated wastewater characteristics

The parameters employed to characterize the wastewater were the DOC, colour ($Abs_{543.5}$), acute toxicity (EC_{50}) and BOD_5/COD index and OD/OD_{st} as biodegradability indicators. Their values in the original dye solution are shown in Table 1. The absorption spectrum of the dye has a large band centred at 543.5 nm, responsible of the red colour of the solution.

As seen in Table 1, it is noticeable the low biodegradability of the synthetic textile wastewater, expressed as a BOD_5 to COD ratio. This relation shows that only a 10% of the chemically oxidable fraction is able to be biologically oxidised as well. Apart from the BOD_5 to COD estimation, the Zahn–Wellens test was carried out to investigate the potential of a biological treatment as a single process to remove the reactive dye. As it has been mentioned before, the experiment takes place under conditions close to those of a conventional WWTP, using non-acclimated activated sludge as inoculum. Two concentrations of dye (125 and 250 $mg\,l^{-1}$) were tested in order to discover if any toxicity effect was present. Obtained results clearly reveal that the biodegradability associated to both concentrations of Procion Red H-E7B is almost negligible (Fig. 2). The activated sludge has not removed any DOC within the 28 days of contact, with no sign of adaptation. This behaviour contrasts with the experiment performed with ethylene glycol, a completely biodegradable standard, which achieved an 85% of biodegradation under the same conditions in just 4 days. Once the 28 days period was completed, ethylene glycol was added to the dye solutions to discard a possible inhibition caused by the sample (data not shown). Again, the standard was consumed in few days, demonstrating that the biomass was still active or not inhibited.

Table 1
Chemical characterisation of 250 $mg\,l^{-1}$ hydrolysed Procion Red H-E7B in the synthetic textile effluent

DOC ($mg\,l^{-1}$ C)	44.96 ± 1.55[a]
EC_{50} ($mg\,l^{-1}$ C)	>44.96[b]
BOD_5 ($mg\,l^{-1}$ O_2)	12 ± 2[a]
COD ($mg\,l^{-1}$ O_2)	115 ± 2[a]
BOD_5/COD	0.10 ± 0.02[a]
OD/OD_{st}	0.04

[a] $n = 3$, $\alpha = 0.05$.
[b] $EC_{50} > 100\%$.

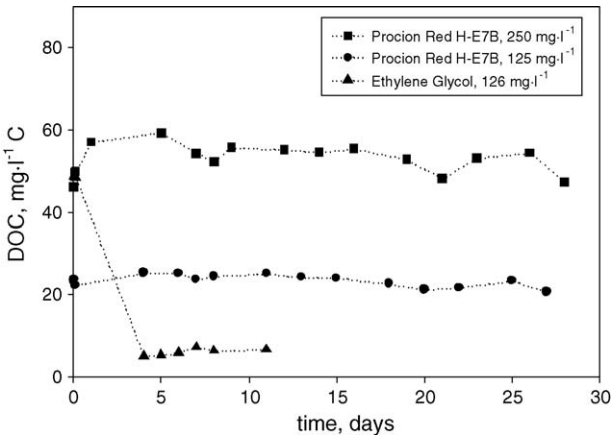

Fig. 2. Zahn–Wellens assay. DOC evolution of hydrolysed Procion Red H-E7B solutions (250 and 125 $mg\,l^{-1}$) and the biodegradable standard ethylene glycol (126 $mg\,l^{-1}$).

As a complementary assay, respirometric measurements where made to provide more information about biomass activity during the reactive dye biodegradation. In agreement with BOD_5/COD and Zahn–Wellens biodegradability tests, short-term respirometry test declares the non biodegradability of untreated wastewater (Table 1, OD/OD_{st} index).

Finally, results from the acute toxicity assessment of the dyestuff by means of Biotox® assay show that EC_{50} was greater than 100% or >44.96 $mg\,l^{-1}$ C (Table 1). This means that the concentration present in solution did not cause the 50% inhibition of the bacteria. It should be noted that toxicity assays could be distorted due to disturbances in luminescence measurements caused by intensive coloured dye solutions. In this case, it was necessary to take into account the lost of light due to absorption just applying a correction factor previously determined for every sample dilution.

Based on the above results, we conclude that Procion Red H-E7B is a non toxic but non biodegradable reactive dye. No aerobic biological treatment would be effective enough to remove the pollutant. Therefore, it could be a suitable compound to carry out the photo-Fenton reaction and biological treatment coupling strategy.

3.2. Photo-Fenton reaction as a pre-treatment process and biodegradability enhancement

The photo-Fenton process was applied in order to improve the dye solution biodegradability, avoiding complete mineralisation, as a previous step of an ensuing biological treatment. In this sense, preliminary experiments were firstly carried out to find suitable ferrous salt and hydrogen peroxide doses needed to biocompatibilize the synthetic wastewater with a second SBR stage.

An extended study about optimisation of Procion Red H-E7B reactive dye oxidation with photo-Fenton reaction has been previously reported elsewhere by our group [33]. Based on those findings, few Fenton reagents doses were tested in the present work (a serial of three experiments): 5 $mg\,l^{-1}$ Fe(II) and 125 $mg\,l^{-1}$ H_2O_2, 10 $mg\,l^{-1}$ Fe(II) and 125 $mg\,l^{-1}$ H_2O_2, 10 $mg\,l^{-1}$ Fe(II) and 250 $mg\,l^{-1}$ H_2O_2. Fig. 3 shows

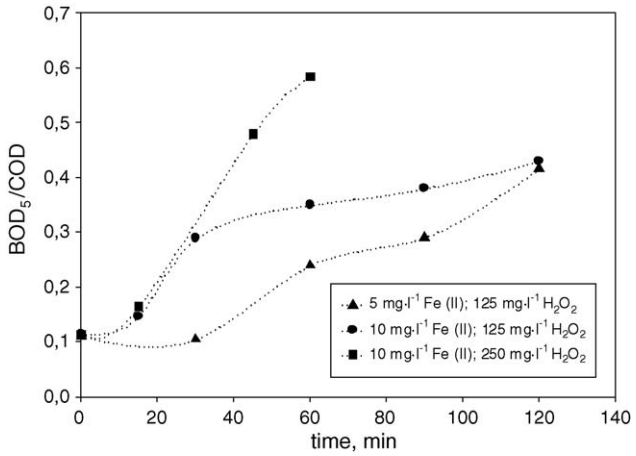

Fig. 3. Evolution of BOD_5/COD ratio vs. irradiation time at different Fenton reagent doses for hydrolysed Procion Red H-E7B, 250 mg l^{-1}, pH 3 and $T = 23\,^{\circ}C$.

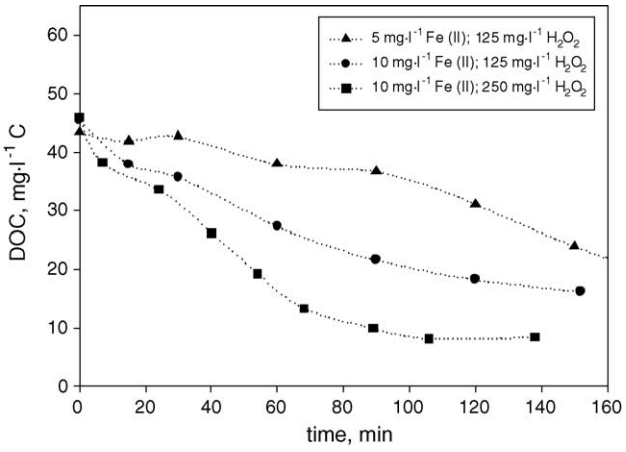

Fig. 5. Evolution of DOC vs. irradiation time at different Fenton reagent doses for hydrolysed Procion Red H-E7B, 250 mg l^{-1}, pH 3 and $T = 23\,^{\circ}C$.

the biodegradability evolution of every assessed condition, expressed as BOD_5 to COD index. Contaminants with a ratio of $BOD_5/COD \geq 0.4$ are generally accepted as biodegradable, while those with ratios situated among 0.2 and 0.3 units result partially biodegradable. Apart from biodegradability enhancement, residual H_2O_2 is also a key parameter to decide the suitable irradiation time when photo-Fenton reaction is employed as a previous step, before the biological treatment. It should be minimum and, due to its associated bactericide potential, eliminated prior feeding the bioreactor [34]. Fig. 4 shows its evolution. Finally, the concentration of DOC was also monitored during the course of photo-Fenton oxidation, and is represented in Fig. 5.

As the reaction proceeded, for every tested condition, solutions suffered a biodegradability increase achieving BOD_5 to COD ratios around 0.4. However, necessary irradiation time differ for each initial pair of Fenton reagent concentrations. The highest one, 10 mg l^{-1} Fe(II) and 250 mg l^{-1} H_2O_2, was able to reach the 0.58 units within 60 min of reaction. Nevertheless, it could be notice that an unnecessary mineralisation had taken place with this too high H_2O_2 dose (65% DOC removal, Fig. 5). On the other hand, the experiments with the lower concentration

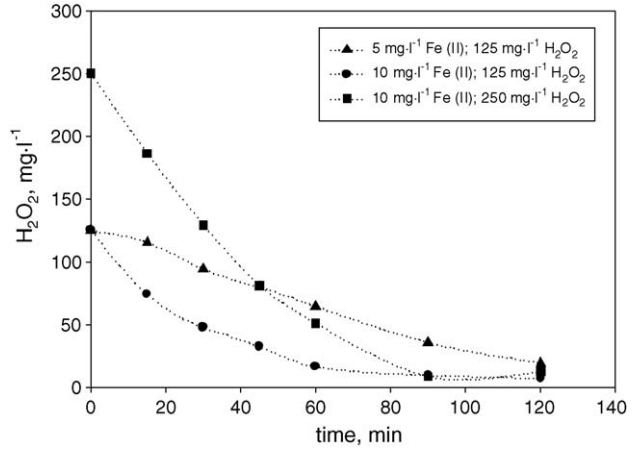

Fig. 4. Evolution of H_2O_2 vs. irradiation time at different Fenton reagent doses for hydrolysed Procion Red H-E7B, 250 mg l^{-1}, pH 3 and $T = 23\,^{\circ}C$.

(125 mg l^{-1}) required longer irradiation times as a compensation but, in both cases, high enough BOD_5/COD values were obtained along with lower mineralisation and, in the case of 10 mg l^{-1} of iron(II), with smaller remaining hydrogen peroxide levels (Figs. 4 and 5). According to the above argument, we conclude that 10 mg l^{-1} Fe(II) and 250 mg l^{-1} H_2O_2 would be the optimum concentration to complete mineralise the studied dye, but not for a partial degradation desired when using photo-Fenton as a pre-treatment. In fact, theoretical stoichiometric hydrogen peroxide required to complete oxidize the dye is 245 mg l^{-1} (1 g COD = 0.0312 mol oxygen = 0.0625 mol hydrogen peroxide). Consequently, this concentration is too high to be considered for AOP and biological coupling applications. In contrast, smaller Fenton reagent doses (5 mg l^{-1} Fe(II), 125 mg l^{-1} H_2O_2 and 10 mg l^{-1} Fe(II), 125 mg l^{-1} H_2O_2) seem to be appropriate to just enhance biodegradability to high enough levels. On the other hand, longer irradiation times will not be a drawback since the final goal of photo-Fenton reaction application is the use of solar light. Sunlight can give better results when compared with the performance of some artificial sources and, as discussed in the Section 1, with the possibility of low cost applications. In fact, the beneficial use of solar light has been already proved by our group for the removal of colour, aromatic compounds (Abs_{254}) and dissolved organic carbon of different commercial reactive dyes, such as Procion Red H-E7B [35].

Furthermore, when treating textile dyestuffs with biological processes, it has been reported that a narrow relationship exists between colour and non biodegradability [36]. In fact, single conventional biological treatment plants are not suitable methods for decolourising textile wastewaters. Based on this affirmation, it seemed possible to obtain bio-treatable solutions once the colour had disappeared. If we compare the BOD_5 to COD index evolution (Fig. 3) with absorbance data (Fig. 6), it is noticeable that biodegradability improves as solution colour disappears. Finally, it should be pointed out that this biodegradability enhancement was also exhibited in short-term respirometry measurements. For instance, consumed oxygen within the first 2 h of respirometry increased for all pre-treated solutions

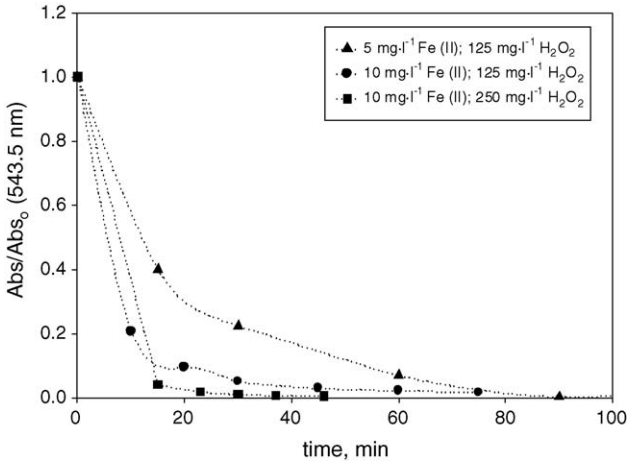

Fig. 6. Evolution of colour vs. irradiation time at different Fenton reagent doses for hydrolysed Procion Red H-E7B, 250 mg l^{-1}, pH 3 and $T = 23\,^{\circ}C$.

tested, even taking into account that COD decreases during the pre-treatment.

It may be possible that, while initial reactive dye was degraded, some other compounds with more inhibitor effect than the parent compound were formed. In this sense, apart from biodegradability measurements, acute toxicity after 30, 60 and 120 min of irradiation with the 5 mg l^{-1} Fe(II), 125 mg l^{-1} H_2O_2 and 10 mg l^{-1} Fe(II), 125 mg l^{-1} H_2O_2 photo-Fenton conditions was assessed. As happened with the untreated solution (Table 1), EC_{50} values were larger than the DOC content at every measurement time ($EC_{50} > 100\%$). There was no evidence of toxic by-products development during the photo-Fenton process. Therefore, the coupling of photo-Fenton with a biological treatment was presumably not conditioned by the possible toxic nature of reactive dye intermediates generated in the first step.

3.3. Aerobic SBR

Since the irradiated solution was in the acid pH range (2.8–3.0), it was neutralised with sodium hydroxide prior feeding into the SBR. Moreover, any residual hydrogen peroxide was quenched with an excess of sodium sulphite to avoid further reactions and to prevent its bactericide effect inside the bioreactor [31]. The remaining sulphite was removed by bubbling O_2. Taking into account such precautions, photo-treated Procion Red H-E7B samples could be introduced into the biological system.

3.3.1. Preliminary run

In order to guarantee the cells viability and to estimate the lower residual DOC that could be achieved within the SBR system, this was initially fed with a completely biodegradable wastewater and a 10 day HRT cycle was carried out. This blank run was performed before every cycle of SBR experiments with municipal wastewater coming from the WWTP, a water characterised by an average DOC of 50 mg l^{-1} C and COD of 210 mg l^{-1} O_2.

During this preliminary run, almost complete DOC removal was observed in every experiment, with a constant residual value of 11.87 ± 1.54 mg l^{-1} C corresponding to the metabolites released by the biomass. In addition, along this period, cells were adapted to the experimental laboratory conditions such as temperature, oxygen flow and manipulation, and the VSS content stabilised along every preliminary run around 0.85 g l^{-1}.

3.3.2. Effect of different photo-Fenton pre-treatments and HRT

After the preliminary run, a set of four different hydraulic retention times (10, 4, 2 and 1 days) were tested. The duration of the HRT may determine the grade of organic load removal achieved, expressed as DOC in this study. For the same experimental conditions, at least three cycles were carried out in order to obtain reproducible results. The HRT = 10 days experiment was run only twice because the residual DOC stabilized within 2 cycles.

The pretended goal was, after determining BOD_5/COD ratios of the pre-treated samples and choosing different HRT, to attain maximum DOC removal with residual DOC values close to those obtained in each previous blank run (biomass metabolites). A summary of the characteristics of the influent sample and the performance of the SBR is presented in Tables 2 and 3. Initially, an irradiation time of 60 min for a 10 mg l^{-1} Fe(II), 125 mg l^{-1} H_2O_2 photo-Fenton process was chosen to generate the feed of the bioreactor. The resulting solution was slightly yellow, without trace of red colour and with a 0.35 ± 0.05 BOD_5/COD ratio (Table 2). The mineralisation during the pre-treatment was 39%, with a small remaining H_2O_2 of 16.5 mg l^{-1}. The DOC content of the SBR influent was 26.90 ± 0.55 mg l^{-1} C.

Table 2
Summary of experimental results for the 10 mg l^{-1} Fe(II), 125 mg l^{-1} H_2O_2 conditions in photo-Fenton process and SBR coupling system

Pre-treatment (min)	Initial DOC[a] (mg l^{-1} C)	BOD_5/COD[b]	EC_{50} (mg l^{-1} C)	HRT, days	Cycles	OLR (mg l^{-1} day^{-1} C)	Residual DOC[a] (mg l^{-1} C)	SBR % DOC removal
60	25.60 ± 0.47	0.35 ± 0.05	>25.60[c]	10	2	2.560	12.82 ± 0.63	49.1
60	28.39 ± 0.01	0.35 ± 0.05	>28.39[c]	2	5	14.20	14.51 ± 0.36	48.9
60	27.79 ± 0.81	0.35 ± 0.05	>27.79[c]	1	15	27.79	13.23 ± 0.36	52.4
30	38.65 ± 0.33	0.29 ± 0.02	>38.65[c]	2	3	19.32	25.71 ± 1.37	33.4
30	37.58 ± 0.47	0.29 ± 0.02	>37.57[c]	4	3	9.395	23.99 ± 0.75	36.2

[a] Replicate data have been determined with a minimum of 5 values and $\alpha = 0.05$.
[b] $n = 3$, $\alpha = 0.05$.
[c] $EC_{50} > 100\%$.

Table 3
Summary of experimental results for the 5 mg l^{-1} Fe(II), 125 mg l^{-1} H_2O_2 conditions in photo-Fenton process and SBR coupling system

Pre-treatment (min)	Initial DOC[a] (mg l^{-1} C)	BOD_5/COD[b]	EC_{50} (mg l^{-1} C)	HRT (days)	Cycles	OLR (mg l^{-1} day^{-1} C)	Residual DOC[a] (mg l^{-1} C)	SBR % DOC removal
60	38.17 ± 1.01	0.25 ± 0.03	>38.17[c]	2	8	19.08	24.81 ± 0.86	35.0
60	38.12 ± 0.84	0.25 ± 0.03	>38.12[c]	4	3	9.53	24.13 ± 0.56	37.2

[a] Replicate data have been determined with a minimum of 5 values and $\alpha = 0.05$.
[b] $n = 3$, $\alpha = 0.05$.
[c] $EC_{50} > 100\%$.

At the beginning, an HRT = 10 days was fixed to insure a reaction period long enough to determine the maximum biodegradation percentage. As a result, a 49.1% DOC removal was obtained along the whole biological run, with no need of acclimation period (percent of reduction calculated from influent DOC). The attained residual DOC, 12.82 ± 0.63 mg l^{-1} C, coincided with the remaining content previously determined in the blank run. It should to be remarked that this residual DOC value settles the lowest threshold of DOC removal. However, obtained results showed that it may be possible to reduce the HRT without renouncing to attain maximum biodegradation. A low and stable residual DOC is reached after 2 days in the first SBR cycle. Cycle time duration corresponding to 2 and 1 day were consequently tested. From Table 2 it is noticeable that when HRT decreases, it increases the steady-state organic loading rate (OLR, mg l^{-1} day^{-1} C). Moreover, it should be pointed out that, for the three studied experiments, initial VSS level decreased until a stabilized value, just when % DOC removal became stable (see Fig. 7).

As predicted, organic load removals for HTR = 2 and 1 day show similar efficiencies than for HRT = 10 days, but making necessary an acclimation period of 2 and 4 days, respectively. Nevertheless, since minimum SBR cycle time duration is to be accomplish, 1 day cycle was chosen as the suitable HRT for a 60 min, 10 mg l^{-1} Fe(II), 125 mg l^{-1} H_2O_2 photo-Fenton pre-treatment. Afterwards, SBR process was continued for 15 cycles to check that SBR worked under steady conditions (Fig. 7). On average, residual DOC was 13.23 ± 0.36 mg l^{-1} C after the fourth cycle, with no more than 4.74% fluctuation in DOC values, while VSS remained stable around 0.41 g l^{-1}. The DOC removal rate was 14.85 mg l^{-1} day^{-1} C. In those steady-state conditions, daily BOD_5 to VSS ratio was 0.04 mg O_2 mg^{-1} VSS. Finally, once the 15 days of operation were over, a blank run (by adding biodegradable municipal wastewater as influent to the adapted biomass) was performed to ensure that the remaining biomass was able to reduce DOC to a residual value around 12 mg l^{-1} C.

The next step of the study was to try to reduce the pre-treatment irradiation time of photo-Fenton process, by maintaining the same Fenton reagent dose, in order to evaluate the pre-treatment duration effect. In this sense, it should be pointed out that pre-treatment times beyond 60 min were not considered since this was enough to obtain an effluent that can be completely degraded in the biological reactor. With this aim, some new SBR runs were performed with a pre-treatment irradiation time of 30 min (Table 2). This time reduction involves an increase in organic carbon load to an average concentration of 37.91 ± 0.42 mg l^{-1} C, a remaining H_2O_2 of 47.6 mg l^{-1} and a 0.29 ± 0.02 BOD_5/COD ratio (Table 2). As a difference with the 60 min one, this influent was characterised by a visible slight brown colour. A 2 day HRT was fixed as starting point. As it can be seen in the table, an increase of the remaining DOC takes place when comparing with the 60 min experiment under the same conditions. The obtained residual DOC was 25.71 ± 1.37 mg l^{-1} C, far away from the 14.51 mg l^{-1} C value. In any case, good performance of the SBR was observed since operating parameters were properly maintained throughout each run. The VSS

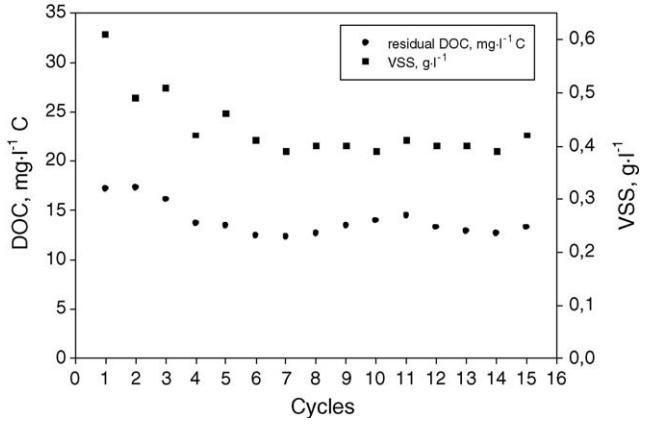

Fig. 7. VSS evolution and final DOC concentration for the 60 min, 10 mg l^{-1} Fe(II) 125 mg l^{-1} H_2O_2 photo-Fenton pre-treatment and 1 day HRT SBR cycle.

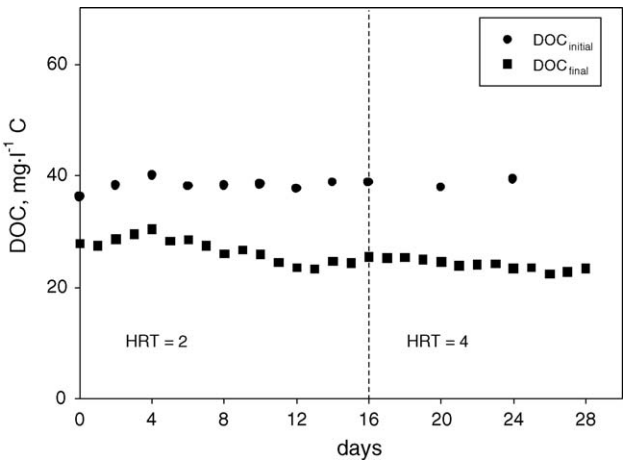

Fig. 8. Initial and final DOC for the 60 min, 5 mg l^{-1} Fe(II), 125 mg l^{-1} H_2O_2 photo-Fenton conditions and SBR coupling system. HRT = 2 and 4 days.

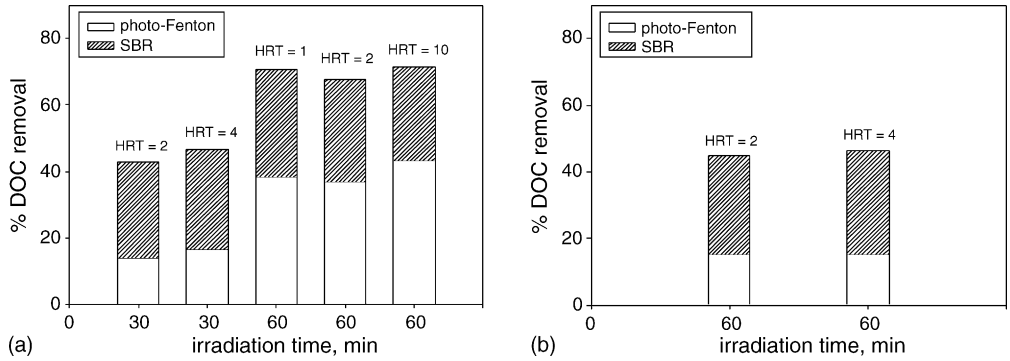

Fig. 9. % DOC removal in photo-Fenton pre-treatment and SBR coupling system as a function of pre-treatment irradiation time and HRT: (a) 10 mg l^{-1} Fe(II), 125 mg l^{-1} H_2O_2; (b) 5 mg l^{-1} Fe(II), 125 mg l^{-1} H_2O_2.

arrived to a steady-state while final DOC fluctuated slightly from cycle to cycle. In an attempt to ascertain if there was any chance to improve the situation, an increase of the bioreactor cycle time from 2 to 4 days was probed. However, in spite of extending the reaction period, the bioreactor response showed a similar behaviour. Moreover, data reveal that a 1 day HRT in the SBR would give the same remaining DOC. Therefore, biodegradability of 30 min pre-treated reactive dye was not high enough, while hydraulic retention time did not seem to influence the removal percentage values. In conclusion, sample irradiation for 60 min under 10 mg l^{-1} Fe(II), 125 mg l^{-1} H_2O_2 photo-Fenton pre-treatment conditions proves to be necessary to generate an effluent able to be completely biodegraded in the SBR.

Finally, a pair of SBR runs coupled to the 5 mg l^{-1} Fe(II), 125 mg l^{-1} H_2O_2 photo-Fenton process were assessed (Table 3). To establish time-comparable conditions to the ones presented above, the irradiation pre-treatment time chosen was 60 min. At that point, Procion Red H-E7B intermediates were characterized by a 0.25 ± 0.03 BOD_5/COD index, slight brown colour, 64.6 mg l^{-1} of non-reacted H_2O_2 and a substrate concentration of 38.15 ± 0.64 mg l^{-1} C. As previously stated, HRT of tested bio-treatment cycles were, initially, 2 days and extended later to 4 days to discard any HRT limitation in the DOC percent reduction (Fig. 8). Table 3 clearly reveals that, although DOC removal of both tested runs was not high, it was neither affected by the HRT. In fact, Fig. 8 exhibits that, as happened with the 30 min, 10 mg l^{-1} Fe(II) and 125 mg l^{-1} H_2O_2 pre-treatment, 24 h SBR cycle would be time enough to reach the same final DOC content. Residual values for 2 and 4 days runs were 24.81 ± 0.86 and 24.13 ± 0.56 mg l^{-1} C, respectively.

With regard to VSS evolution, it should be pointed out that the bioreactor did not manage to work under stable operation until the fourth cycle of the 2 days HRT experiment. During the first cycles bacteria experimented a slight adaptation until stable VSS and reproducible final DOC values were achieved. Due to this behaviour, and proceeding in a different way with respect to the other SBR experiments, biomass was reused from one run to the other to avoid such acclimation period.

It is noteworthy that this set of experiments showed a similar biodegradation percent than the 30 min of irradiation, 10 mg l^{-1} Fe(II), 125 mg l^{-1} H_2O_2 photo-Fenton pre-treatment. Although with Fe(II) concentration of 5 mg l^{-1}, the ratio BOD_5/COD is not close to 0.4, it seems reasonable that longer irradiation times (more than the 1 h tested) would eventually produce a biodegradable solution, an interesting possibility taking into account the potential use of sunlight in the photo-Fenton reaction.

In summary, studied AOP and SBR coupling show higher degradation efficiencies when working under the 10 mg l^{-1} Fe(II), 125 mg l^{-1} H_2O_2 photo-Fenton pre-treatment conditions. This DOC removal efficiency was affected by the irradiation time, being significantly higher in the case of 60 min. Fig. 9 compares the DOC removal of all the studied runs, taking into account the percentage of mineralisation reached by the coupling of both stages. Under most favourable conditions a 71% removal with respect to the initial DOC in coloured dye solution was obtained. This percentage dropped around 45% in the other combined treatments. Finally, it is remarkable that the residual DOC values oscillated around 12 mg l^{-1} C, setting a lower threshold for DOC removal.

With regard to the hydraulic retention time effect, no remarkable differences in DOC removal were found between different assessed cycle times. For instance, the 60 min of 10 mg l^{-1} Fe(II), 125 mg l^{-1} H_2O_2 photo-Fenton pre-treatment, the most effective one, allowed to reduce HRT from 10 to 1 day without lost of biodegradability (Fig. 9). This fact let us to conclude that SBR efficiency is not time dependent over 1 day HRT. Nevertheless, the SBR behaviour when reducing the hydraulic retention time below 24 h has not been studied, being not possible to discard an HRT effect below this cycle time duration.

4. Conclusions

Results have demonstrated that photo-Fenton reaction can be successfully used as a pre-treatment process to biocompatibilize Procion Red H-E7B reactive dye solutions. With partial oxidation run under mild conditions, dye solution became decolourised and more biodegradable, as well as non toxic. Photo-treated solutions were subsequently biodegraded in an aerobic sequencing batch reactor working under different hydraulic retention times.

Best pre-treatment results were obtained with 60 min of photo-Fenton irradiation time and 10 mg l^{-1} Fe(II), 125 mg l^{-1} H_2O_2 of initial reagents concentrations. At these conditions, BOD_5/COD index went from 0.10 up to 0.35 units just with

39% mineralisation and 16.5 mg l^{-1} of residual H_2O_2. On the other hand, data comparison for every tested HRT in SBR shows that the biological process efficiency appeared to be independent of the changes carried out in the cycle time duration. Therefore, 1 day (the minimum one tested) was chosen as the suitable HRT for SBR operation. Low residual DOC values obtained were close to those previously obtained in a blank run, assuming complete biodegradability. In addition, a good performance of the bioreactor was observed since operating parameters (VSS and residual DOC content) were properly maintained within each experiment.

On the other hand, when trying to reduce the 10 mg l^{-1} Fe(II) and 125 mg l^{-1} H_2O_2 photo-Fenton process duration from 60 to 30 min, it was not possible to attain enough biodegradation percentage levels, showing that photo-treated water was not biodegradable enough to feed the SBR. The same behaviour was observed in the 60 min, 5 mg l^{-1} Fe(II) and 125 mg l^{-1} experiment. In any case, results exhibit that DOC removal was not conditioned by the studied HRT.

In summary, the use of photo-Fenton type reactions as a pre-treatment allows the SBR system to remove Procion Red H-E7B reactive dye from aqueous solution, fact which improves the low success of aerobic biological removal of dye colour. Moreover, it should be pointed out that, taking the studied artificial light photo-Fenton process as starting point, more favourable results are expected when using solar light, both in terms of photo-Fenton pre-treatment effectiveness as well as energy consumption.

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