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Environmental assessment of different photo-Fenton approaches for commercial reactive dye removal

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Abstract

An environmental study using life cycle assessment (LCA) has been applied to three bench-scale wastewater treatments for Cibacron Red FN-R hetero-bireactive dye removal: artificial light photo-Fenton process, solar driven photo-Fenton process and artificial light photo-Fenton process coupled to a biological treatment. The study is focused on electricity and chemicals consumption, transports and atmosphere and water emissions generated by the different processes involved. Results show that the artificial light photo-Fenton process is the worst treatment in terms of environmental impact. On the other hand, both solar driven and coupled to biological photo-Fenton processes reduce significantly the environmental damage, although none can be identified as the best in all impact categories. The major environmental impact is attributed to the H_2O_2 consumption and to the electrical energy consumption to run the UVA lamp. An economic analysis of the different photo-Fenton processes has also been performed and the results are discussed together with those obtained from the environmental assessment.

Keywords: Textile reactive dye; Photo-Fenton's oxidation; Sunlight; Biological treatment; Life cycle assessment; Economic study

1. Introduction

Reactive dyes have been identified as the most environmental problematic compounds in textile dye effluents [1]. Therefore, in the last decade, attention has been focused on the development of new treatment technologies that leads to complete destruction of the dye molecules. Among these treatments, advanced oxidation processes (AOPs) are a powerful alternative to conventional treatment methods for wastewater decontamination [2]. These treatments are based on the in situ generation of highly reactive hydroxyl radicals as a primary oxidant species ($HO^{\bullet}$). These radicals are high oxidant species ($E = 2.8$ V versus NHE) that are able to mineralise almost all recalcitrant organic compounds under mild experimental conditions. Among the considered AOPs, the Fenton and photo-Fenton type reactions are very promising since they achieve high reaction yields with a low treatment cost [3]. In Fenton reaction, hydroxyl radicals are generated by interaction of H_2O_2 with ferrous salt in aqueous media. The rate of contaminant degradation is considerably increased via photochemical reaction in the photo-Fenton process. Moreover, since the reaction requires radiations up to 410 nm [4], photo-Fenton reaction offers the possibility of sunlight exploitation.

On the other hand, AOPs are currently being object of the development for new application areas. When working with toxic or non-biodegradable wastewaters, AOPs are employed as a pre-treatment of standard biological treatments. Complete mineralisation is avoided in the chemical process, being the goal the generation of a new biocompatible effluent [5,6]. In any case, every strategy must be developed paying special attention to its potential environmental impact. In this way, environmental factors must be taken into account for the most suitable water treatment technique selection.

In this paper, a representative commercial hetero-bireactive dye, 250 mg/l Cibacron Red FN-R, is taken as a model compound for the environmental impact assessment of different lab-scale wastewater treatments. The photo-Fenton reaction, under

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both artificial and solar irradiation, is applied as a single process to degrade the pollutant. In another scenario, just partially photo-treated dye solution was subsequently submitted to an aerobic sequencing batch reactor (SBR), that is an efficient alternative to conventional biological systems for a wide variety of model pollutants and real wastewaters biodegradation [7].

The life cycle assessment (LCA) tool, according to ISO 14.040 Standard [8], is applied to carry out the environmental impact evaluation. Four distinguishable phases constitute the LCA sequence: (1) goal and scope, in which the purpose, scope, main hypothesis and data quality are defined, (2) inventory analysis, in which data are collected in order to quantify the inputs and outputs of the system, (3) impact assessment, where potential environmental impacts are identified and characterised, and (4) interpretation, in which the results of the inventory analysis and impact assessment are discussed in the light of the goals set in the beginning of the study, identifying the areas for environmental improvement of the system under study.

Finally, an economic study based on adding the costs of all chemicals and energy consumption through the life cycle of the different treatments has also been considered and discussed together with the environmental assessment.

2. Materials and methods

2.1. Synthetic dye solution

A commercial hetero-bireactive azodye, Cibacron Red FN-R (C.I. Reactive Red 238, $C_{29}H_{15}ClFN_7O_{13}S_4Na_4$) was supplied by CIBA and used as received without further purification. The initial Cibacron Red FN-R concentration for all the experiments was 250 mg/l. 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 for AOP operation. The dissolved organic carbon (DOC) of the synthetic effluent was 79.46 ± 1.34 mg/l C and the BOD_5/COD index was 0.02 ± 0.02 ($n = 3$, $\alpha = 0.05$).

2.1.1. Photo-Fenton oxidation

Photo-Fenton oxidation was conducted in a thermostated ($T = 23 \pm 1$ °C) well-stirred cylindrical Pyrex cell of 300 ml of capacity (78.54 cm^2 surface). The dye solution volume was 250 ml. Analytical grade hydrogen peroxide (33% w/v, Panreac) and $FeSO_4 \cdot 7H_2O$ (99.5%, Merck) were used as received to generate hydroxyl radical ($HO^\bullet$) in aqueous solution. A 6 W Philips black light fluorescent lamp, situated over the reactor, was used for artificial light photo-Fenton experiments. The intensity of the incident UVA light, measured employing a luminometer, was 0.6 mw/cm^2. Solar light experiments were performed during sunny days of July at Universitat Autònoma de Barcelona (45 m a.s.l., 41°30′N, 2°6′E).

2.2. Biological treatment

The biological treatment system was composed of a 2 l aerobic bench-scale sequencing batch reactor (SBR), equipped with an air diffuser and agitation. The activated sludge, coming from a municipal wastewater treatment plant (WWTP) in Manresa (Catalonia, Spain), was initially around 0.6 g/l of volatile suspended solids (VSS) concentration. The operating liquid volume was 1.2 l and the hydraulic retention time was 24 h. Temperature remained stable and close to room conditions, between 21 and 23 °C. The concentration of dissolved oxygen (DO) was kept above 3 mg/l O_2. Daily analyses of VSS, DO and DOC were carried out, and pH adjustment between 6.5 and 7.5 was done if necessary. Suitable proportions of nutrients ($MgSO_4$, $CaCl_2$, NH_4Cl and NaH_2PO_4 buffer at pH 7) were also added to the solution [9].

2.3. Analysis

DOC was determined with a Shimadzu TOC-V_{CSH} analyser. Chemical oxygen demand (COD, mg/l O_2) was assessed by the closed reflux colorimetric method with a HACH DR/2000 spectrophotometer [9]. H_2O_2 consumption was tested by the potassium iodide titration method [10]. Accordingly, correction was made in the COD measurement for residual H_2O_2 [11]. Determination of total suspended solids (TSS, g/l) and VSS was carried out gravimetrically [9]. The measurement of biochemical oxygen demand for 5 days (BOD_5, mg/l O_2) was performed by means of a mercury-free WTW 2000 Oxytop thermostated at 20 °C. Ammonium ion concentration was determined by *Nessler* colorimetric assay [9].

2.4. Life cycle assessment methodology

The environmental impact assessment is focused on the following small-scale wastewater treatments: artificial light photo-Fenton process (scenario 1), solar driven photo-Fenton process (scenario 2) and artificial light photo-Fenton process coupled to a biological treatment (scenario 3). The DOC parameter has been used as indicator of pollutant removal.

A preliminary optimisation study to degrade Cibacron Red FN-R reactive dye was carried out by testing the following Fenton reagent dose: 10 mg/l Fe (II) combined with 125, 250 and 500 mg/l of H_2O_2, and 20 mg/l Fe (II) combined with 250 and 500 mg/l H_2O_2 concentrations [12]. The best experimental conditions that give rise to a more efficient dye degradation were 20 mg/l Fe (II) and 500 mg/l H_2O_2, which lead to a maximum mineralisation level (around 80–90% of the initial DOC) after relatively short irradiation times (Fig. 1). These conditions were used for single photo-Fenton processes (scenarios 1 and 2). On the other hand, when the photo-Fenton oxidation was just applied as a pre-treatment (scenario 3), the H_2O_2 dose was reduced in order to soften the chemical consumption. In this way, 20 mg/l Fe (II) and 250 mg/l H_2O_2 were enough to bio-compatibilize the effluent. After an irradiation time of 90 min, with just 49.6% mineralisation and 21 mg/l remaining H_2O_2, BOD_5/COD ratio went from 0.02 ± 0.02 up to 0.36 ± 0.05 ($n = 3$, $\alpha = 0.05$) (Fig. 2), close to 0.4, which is the characteristic value for completely biodegradable wastewaters [13]. Afterwards, the aerobic SBR treatment was performed until achieving 80% global

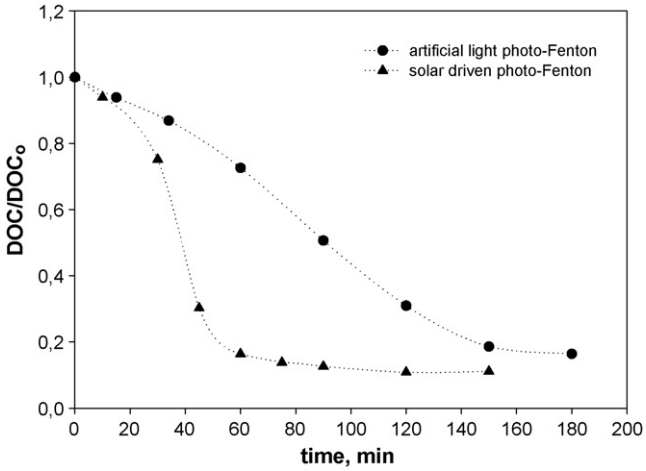

Fig. 1. DOC/DOC$_o$ evolution vs. time for 250 mg/l Cibacron Red FN-R degradation with artificial and solar light photo-Fenton reaction: 20 mg/l Fe (II), 500 mg/l H_2O_2, pH 3 and T = 23 °C.

DOC removal (accumulated in the chemical plus biological stages).

The functional unit (the unit of service to which the environmental burdens must be referred) has been defined as "the removal of 80% DOC from 1.2 l of 250 mg/l Cibacron Red FN-R synthetic effluent". To achieve this % DOC elimination, single artificial light and solar driven photo-Fenton processes required 150 and 50 min of treatment periods, respectively (Fig. 1). Residual hydrogen peroxide concentrations of 19 mg/l were found at the end of both experiments.

The flow diagrams and boundaries considered to perform the LCA are shown in Figs. 3 and 4. The inputs and outputs included are: (i) the electricity consumption by the different processes involved, including extraction of resources, transport and energy conversion, (ii) the chemicals consumption, including extraction of resources, production of the corresponding chemicals and the different transport steps, and (iii) the air and water emissions generated through the considered scenarios. The construction and the end-of-life of each system have not been considered.

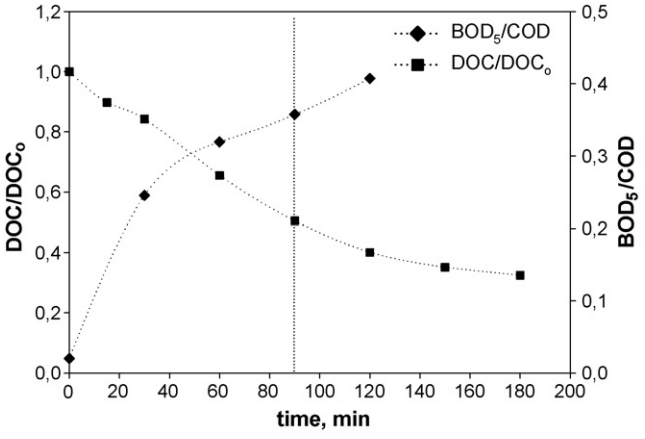

Fig. 2. DOC/DOC$_o$ and BOD$_5$/COD evolution vs. time for 250 mg/l Cibacron Red FN-R degradation with artificial light photo-Fenton reaction: 20 mg/l Fe(II), 250 mg/l H_2O_2, pH 3 and T = 23 °C.

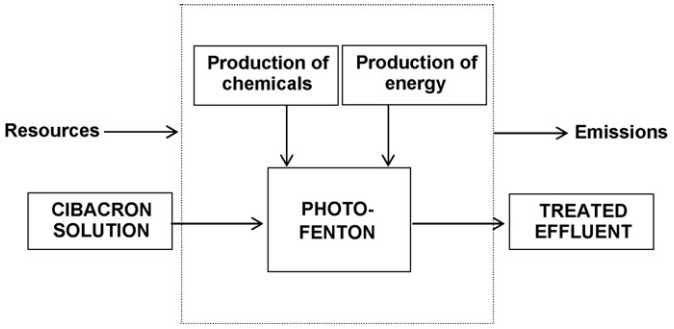

Fig. 3. Simplified flow diagram and system boundaries for scenarios 1 and 2.

The main environmental burdens associated to the defined systems and referred to the functional unit have been inventoried. The sources and quality of the data handled in this assessment, mostly obtained from Ecoinvent database version 1.1 [14,15], are detailed in Table 1.The main hypothesis assumed in the inventory phase of the LCA are the following: as a general consideration, those inputs, outputs or processes common to all the evaluated scenarios have been excluded, i.e., auxiliary reagents consumption for pH adjustments or residual iron sludge recovery for disposal.

2.4.1. Photo-Fenton process

(1) The energy used to run the black light has been assumed to be electricity delivered from the European grid. In order to consider operational conditions similar to those employed in a full-scale photochemical reactor, 100% efficiency has been considered. This implies to assume that all the UV-photons emitted by the lamp reach the solution. In the laboratory set-up, this efficiency has been calculated to be only around 0.8% (0.6 mW/cm^2 UVA light measured by the luminometer multiplied by the 78.54 cm^2 photo-reactor surface).
(2) H_2O_2 and $FeSO_4$ are assumed to be produced in Spain and delivered from the supplier to the site by 16 t-trucks over a 50 km distance.
(3) It is assumed that residual H_2O_2 is totally decomposed after each photo-Fenton process.
(4) CO_2 emissions have been estimated from DOC mineralised by chemical oxidation.
(5) Residual DOC, COD and ammonium ion content have been considered for final effluent impact assessment.

Table 1
Summary of data used in the inventory phase of the LCA

Dataset
Electricity, low voltage, production UCTE, at grid/UCTE S [28]
Hydrogen peroxide, 50% in H_2O, at plant/RER S [29]
Iron sulphate, at plant/RER S [28]
Quicklime, milled, packed, at plant/CH S [30]
Acrylonitrile, at plant/RER S [31]
Heat diesel B250 [25]
Transport, lorry 16 t/CH S [32]

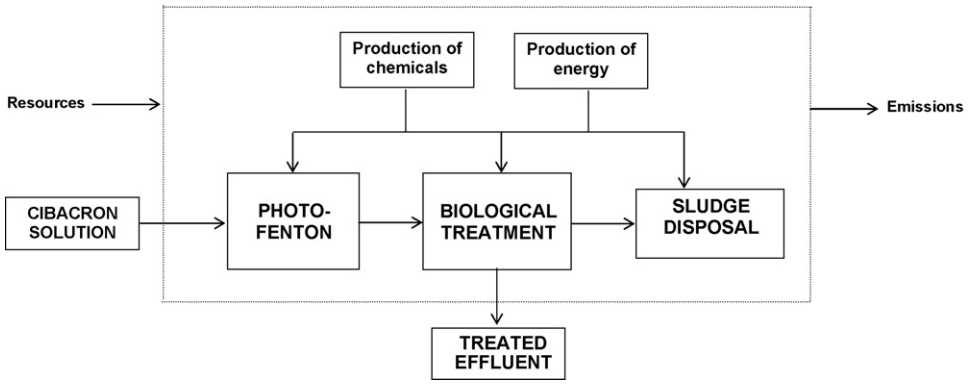

Fig. 4. Simplified flow diagram and system boundaries for scenario 3.

2.4.2. Biological treatment

(1) It is considered that the bench-scale sequencing batch reactor behaved as a real conventional biological treatment process. A municipal WWTP with a 0.76 VSS/TSS ratio is chosen as a model for the estimation, assuming an excess sludge production of 0.55 mg VSS per mg COD consumed [16].
(2) External electricity consumption for mechanical aeration equipment has been considered. In this way, the figure 1.5 kg O_2/kWh [17] has been taken into account. The consumed oxygen, required for nitrification and organic matter oxidation processes, has been determined from removed COD in the bioreactor (34 mg per functional unit) minus the COD fraction assimilated by biomass for cells grown, quantified as 1.42 mg COD per mg VSS of sludge production [16].
(3) The CO_2 emissions have been determined from oxygen requirements, considering that O_2 is mainly employed to oxidise organic substrate.
(4) It is considered a subsequent sludge treatment system composed of several independent unit processes [18]: thickening, dewatering and stabilisation processes. By means of this treatment, a dewatered sludge with 31% final dry matter content (DM) is obtained. About 50 kWh of electricity and 4 kg of polymers are considered to be consumed at the thickening and 40 kWh and 5 kg of polymer at dewatering per ton of DM of sludge. On the other hand, 200 kg lime per ton of DM of sludge is needed for stabilisation while 5 kWh of electricity is consumed for pumping and mixing it [18].
(5) It is assumed that solid residues from exceeding sludge management are finally deposited at landfill. The main environmental emissions from landfill (leachate and landfill gas) are calculated according to the ORWARE (Organic Waste Research) theoretical model [19,20]. By means of this model, the air/water/land distribution of different elements present at landfill is obtained, considering a period of 100 years for biochemical stabilisation after anaerobic sludge digestion. An input to the model is the sludge composition: $C_8H_{15}O_4N$ (typical municipal WWTP sludge, [21]), which is anaerobically degraded according to reaction (1) [21].

$$C_8H_{15}O_4N + 3H_2O \rightarrow 4.5CH_4 + 3.5CO_2 + NH_3 \quad (1)$$

The model considers that leachate generated at landfill is treated biologically and that recovered biogas (99% both CO_2 and CH_4, [22]) is totally burned in a torch. It is assumed a 50% of capture efficiency for biogas [23] and 90% for leachate [24]. Fugitive biogas and leachate reach atmosphere and aquatic media, respectively. Considered removal yields for captured leachate in subsequent biological treatment are 90% for both COD and BOD_7 [22] and 80% for $N–NH_4^+$ [23]. Atmosphere emissions and the management of sludge generated at leachate treatment have been excluded from the inventory.

With respect to the energy requirements, 1.8 l diesel consumption per ton of fresh sludge is considered for machinery operation at landfill [22]. The energy consumption (electricity) for leachate treatment has been quantified as a function of the BOD_7 and NH_4^+ eliminated, following the ORWARE methodology. The electricity consumption for biogas pumping is considered to be 0.013 kWh/m^3. It has been determined indirectly from BUWAL 250 database [25], which gives 1.35 kWh/t of residue that produces 200 m^3 of biogas (from which 53% of biogas is captured). Inventory data for inorganic compounds and energy requirements at landfill resulting from calculations are shown in Table 2.
(6) All reagents used have been supposed to be produced in Spain and delivered by 16 t-trucks. The assumed distance for lime and polymer employed in biological sludge disposal processes was 50 km. The average distance for the sludge transport between the municipal WWTP and the landfill site has also been considered to be 50 km.
(7) Residual DOC, COD, ammonium and nitrate ions content in the treated effluent have been considered for final effluent impact assessment. Nitrate concentration has been estimated considering that all disappeared NH_4^+ (5.4 mg per functional unit, minus the N fraction assimilated by biomass for cells grown quantified according to a $C_8H_{15}O_4N$ VSS sludge composition) was completely oxidised to NO_3^- through aerobic biodegradation.

In Table 3 data concerning energy, chemicals consumption, and generated emissions per functional unit for every considered scenario are summarized.

Table 2
Inventory for WWTP sludge (31% DM) deposited at landfill per functional unit

Inputs	
Transport	
Truck 16 t (t km)	4.97×10^{-6}
Energy	
Diesel (l)	1.72×10^{-7}
Electricity (kWh)	4.35×10^{-9}
Outputs[a]	
Atmosphere emissions	
CH_4 (mg)	2.27
CO_2 (mg)	25.4
NH_3 (mg)	0.01
NO_x (mg)	0.09
Water emissions	
COD (mg)	0.05
NH_4^+ (mg)	0.45
NO_3^- (mg)	1.90

[a] Outputs related chemicals and energy consumed are not included here, but in corresponding life cycle inventory dataset.

The impact assessment for each wastewater treatment was carried out considering the following potential environmental impacts categories included in the CML 2000 method [26]: abiotic resource depletion (ARD), global warming potential (GWP), ozone depletion potential (ODP), human toxicity potential (HTP), freshwater aquatic toxicity potential (FATP), marine aquatic ecotoxicity potential (MAEP), terrestrial ecotoxicity potential (TEP), photochemical oxidation potential (POP), acidification potential (AP) and aquatic eutrophication potential (AEP).

Table 3
Energy usage, chemicals consumption and generated emissions per functional unit for considered scenarios (excluding landfill inventory)

	Scenario 1	Scenario 2	Scenario 3
Inputs			
Grid electricity (kWh)	6.28×10^{-4}		3.84×10^{-4}
H_2O_2 50% (mg)	1200	1200	600
Truck 16 t (t km)	5.94×10^{-5}	5.94×10^{-5}	2.97×10^{-5}
$FeSO_4$ (g)	0.065	0.065	0.065
Truck 16 t (t km)	3.25×10^{-6}	3.25×10^{-6}	3.25×10^{-6}
CaO (mg)			4.92
Truck 16 t (t km)			2.46×10^{-7}
Acrylonitrile (mg)			0.22
Truck 16 t (t km)			1.11×10^{-8}
Outputs[a]			
Atmosphere emissions			
CO_2 (mg)	287.5	280.9	170.5
Water emissions			
COD (mg)	46	42	36
DOC (mg)	16.93	18.74	19.94
NH_4^+ (mg)	7.16	4.79	1.76
NO_3^- (mg)			12.50

[a] Outputs related chemicals and energy consumed are not included here, but in corresponding life cycle inventory dataset.

2.5. Economic study

An economic study has been performed for the three reactive dye treatments on the basis of the previously defined functional unit. The same boundaries than in the LCA are considered, taking into account chemical and energy costs employed during operation phases. All other running costs and capital investments are excluded.

3. Results and discussion

Table 4 shows the characterised values obtained for the different environmental impacts and the considered scenarios. Relative scores are represented graphically in Fig. 5, in which the highest environmental impact is set to 100% for each category. In view of this, scenario 1 is the wastewater treatment with a major global impact on the environment, with highest scores for every considered impact indicator (Table 4). However, when the photo-Fenton process is applied as a pre-treatment of a secondary biological treatment (scenario 3), impacts decrease considerably achieving around 45% reduction for most categories (Fig. 5). Fig. 6 exhibits, for single (a) and combined (b) artificial light photo-Fenton processes, the relative contributions to the impact categories of the different stages of the life cycle: H_2O_2 and iron sulphate production and consumption, associated transports, biological treatment and sludge management (without WWTP emissions), grid electricity production and use, and finally emissions from chemical and biological oxidation steps. In both cases, the major impact contribution is attributed to H_2O_2 consumption, followed by the electricity requirements of the UVA lamp. It is worth to note that, for both scenarios, air and water emissions have an important effect on AEP due to NH_4^+ and NO_3^- ions content; also it is significant the contribution to GWP due to the CO_2 emitted during chemical and biological stages. Finally, the reagents transport effect and iron salt consumption are not considered important since together represent less than 5% in all categories. From manifested similarities of both scenarios contributions profiles, it could be stated that the

Table 4
Characterisation of the different environmental impacts for considered scenarios

Category	Unit	Scenario 1	Scenario2	Scenario 3
ARD	kg Sb	8.1×10^{-6}	5.6×10^{-6}	4.4×10^{-6}
GWP	kg CO_2	1.3×10^{-3}	9.7×10^{-4}	8.2×10^{-4}
ODP	kg CFC 11	7.9×10^{-11}	6.5×10^{-11}	4.2×10^{-11}
HTP	kg 1,4-D[a]	2.4×10^{-3}	2.2×10^{-3}	1.2×10^{-3}
FATP	kg 1,4-D[a]	1.7×10^{-4}	1.5×10^{-4}	8.8×10^{-5}
MAEP	kg 1,4-D[a]	4.9×10^{-1}	2.6×10^{-1}	2.7×10^{-1}
TEP	kg 1,4-D[a]	1.1×10^{-5}	4.7×10^{-6}	6.3×10^{-6}
POP	kg C_2H_4	1.8×10^{-7}	1.0×10^{-7}	1.2×10^{-7}
AP	kg SO_2	4.3×10^{-6}	2.4×10^{-6}	2.5×10^{-6}
AEP	kg PO_4^{3-}	3.7×10^{-6}	2.8×10^{-6}	2.8×10^{-6}

ARD, abiotic resource depletion; GWP, global warming potential; ODP, ozone depletion potential; HTP, human toxicity potential; FATP, freshwater aquatic toxicity potential; MAEP, marine aquatic ecotoxicity potential; TEP, terrestrial ecotoxicity potential; POP, photochemical oxidation potential; AP, acidification potential; AEP, aquatic eutrophication potential.

[a] 1,4-Dichlorobenzene.

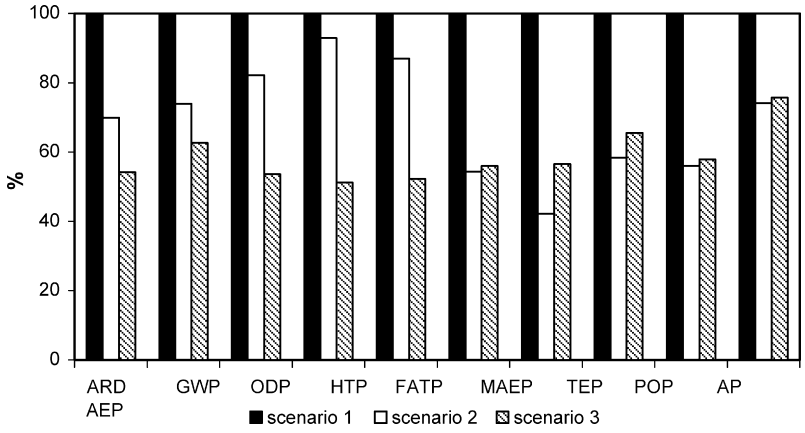

Fig. 5. Characterisation values of the different environmental impacts for considered scenarios.

chemical stage in the combined treatment supposes the main impact, since the biological treatment and subsequent processes only slightly contribute (12–17%) to the GWP, POP and AEP categories. Therefore, it becomes evident that the lower H_2O_2 concentration and the shorter irradiation time employed in the artificial light photo-Fenton pre-treatment are the main factors responsible of the impact scores reduction presented in Table 4 for scenario 3.

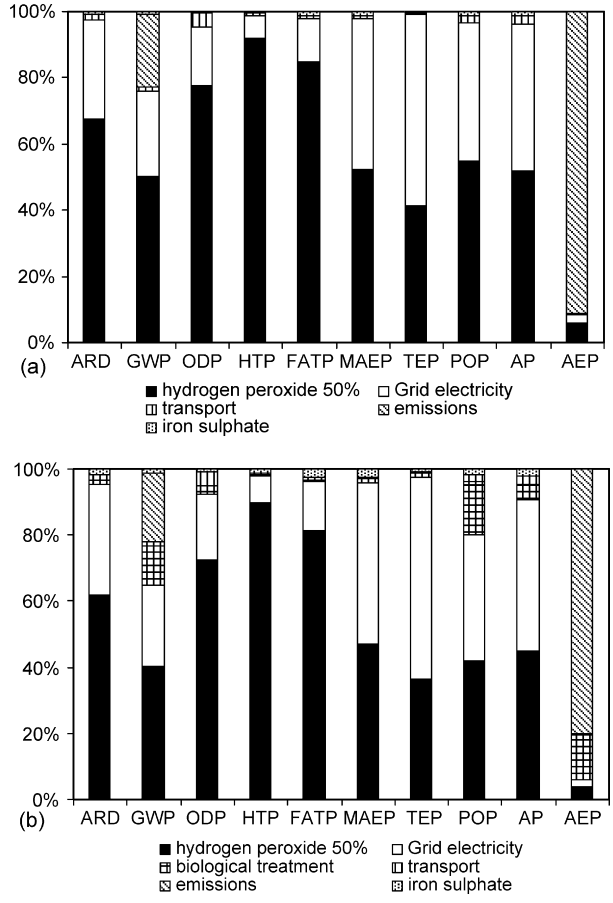

Fig. 6. Relative contributions to the respective impact categories of the different stages of the life cycle for scenarios 1 (a) and 3 (b).

The characterised values for the different environmental impact categories are also reduced when no artificial UVA light is employed (scenario 2) (Table 4). Since there is no use of electricity from the grid, environmental impacts are directly associated with the production of hydrogen peroxide, whose contribution supposes more than 93% for most categories (data not shown). It should be noted that, apart from the impact reduction attainment, solar light gives more efficient dye degradation than artificial light (Fig. 1). This higher efficiency observed with the use of sunlight is basically due to the higher number of photons between 300 and 400 nm arriving to the earth surface in Spain [27] (estimated around 3–4 mW/cm^2).

When comparing scenario 2 with the artificial light photo-Fenton process coupled to the biological treatment (scenario 3), it is difficult to distinguish which treatment would be more environmentally friendly since data notably vary depending on the category considered (Fig. 5). Solar driven photo-Fenton process offers better results than the coupled system for MAEP, TEP, POP, AP and AEP. This behaviour can be attributed to the major electricity contribution to these impact categories (Fig. 6). However, since electricity does not suppose a large burden for the rest of indicators (as H_2O_2 does), solar driven photo-Fenton impacts are not further reduced and the coupled system becomes more environmentally benign. In any case, obtained results allow concluding that both, scenarios 2 and 3, are more environmentally friendly alternatives than artificial light photo-Fenton process.

The considered wastewater treatments have also been assessed from an economic point of view. Employed unitary prices and cost per functional unit of the different inputs are shown in Tables 5 and 6, respectively. Fig. 7 displays the overall costs as a percentage of the most expensive treatment. From Table 6 and Fig. 7, it can be stated that the artificial light photo-Fenton process is the most expensive treatment. When carrying out the treatment under solar irradiation or coupled to an ensuing biological process, the estimated relative cost decreased in a 13 and 44%, respectively, being the combined system the cheaper option. A reduction of H_2O_2 dosage and electricity consumption for UVA irradiation (which contribute in an 81% and 14% cost for scenario 1, respectively) in favour of the biological treatment are the major cause since biological and sludge management

Table 5
Unitary costs considered for economic study

Product	Price (€)	Source
Electricity (kWh)	0.07	[33]
H_2O_2 50% (kg)	0.22	Hera-Segasa S.L. Barcelona, Spain
$FeSO_4$ (kg)	0.25	Albaida Recursos Naturales y Medio Ambiente S.L. Almería, Spain
Landfill (kg)	0.07	[34]
CaO (kg)	0.09	DSM-Deretil, Almería, Spain
Polymer (kg)	2.69	DSM-Deretil, Almería, Spain; Hera-Segasa S.L. Barcelona, Spain

Table 6
Economic cost per functional unit of the different inputs for considered scenarios

	Cost (€)		
	Scenario 1	Scenario 2	Scenario 3
Electricity	4.4×10^{-5}		2.7×10^{-5}
H_2O_2 50%	2.6×10^{-4}	2.6×10^{-4}	1.3×10^{-4}
$FeSO_4$	1.6×10^{-5}	1.6×10^{-5}	1.6×10^{-5}
Landfill			6.8×10^{-6}
CaO			4.4×10^{-7}
Polymer			5.9×10^{-7}
Total	3.2×10^{-4}	2.8×10^{-4}	1.8×10^{-4}

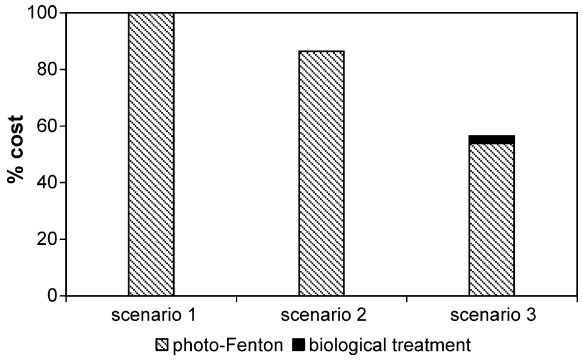

Fig. 7. Relative economic cost per functional unit for considered scenarios.

processes just suppose a 4.5% of the global combined treatment cost (Fig. 7).

In view of this, considering both environmental and economic data to decide about the suitability of the studied wastewater treatments, the best environmental/cost option seems to be the coupling of artificial light photo-Fenton process and biological treatment (scenario 3). On the other hand, artificial light photo-Fenton treatment appears as the worst option in both assessments mainly due to the high hydrogen peroxide and energy demand, in this order.

4. Conclusions

A LCA study has been performed to determine the environmental suitability of three small-scale wastewater treatments for Cibacron FN-R reactive dye removal: artificial light photo-Fenton process, solar driven photo-Fenton process and artificial light photo-Fenton process coupled to a biological treatment.

The artificial light photo-Fenton process is the most environmentally harmful treatment, mainly due to H_2O_2 consumption which presents the higher environmental impact and scores for almost all the categories considered. The electricity requirements for UVA light irradiation appear in a second place. Finally, as in the other considered scenarios, air and water emissions generated during dye oxidation have an important effect on AEP and GWP indicators while iron salt consumption and chemicals transport to the treatment plant barely contribute in a representative way.

When artificial light photo-Fenton reaction is applied as a biological pre-treatment, H_2O_2 dose and electricity consumption are significantly reduced giving place to around 45% diminution for most environmental impact categories. However, both continue to be the highest burdens of the combined process. In contrast, the biological stage becomes environmentally advantageous since it just contributes with small quantities (among 12–17%) in GWP, POP and AEP indicators. When comparing it with the solar driven photo-Fenton process, no clear preferences can be drawn from all impacts categories. Although using solar energy as a source of photons avoids electricity consumption, it just gives better environmental benefits than the combined system in five categories from the 10 evaluated since it maintains a large H_2O_2 consumption. On the other hand, from the economic point of view, the coupled process appears to be better achieving a 44% cost diminution with respect to the most expensive one, in front of the 13% reduction attained with the solar assisted process.

As a final remark, and taking these results as starting point, it is predictable that a solar driven photo-Fenton process coupled to a biological treatment would be the best economic and environmental option to remove Cibacron FN-R hetero-bireactive dye from textile effluent.

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