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Supported Fe/C and Fe/Nafion/C catalysts for the photo-Fenton degradation of Orange II under solar irradiation

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Abstract

The physicochemical properties and photocatalytic behavior of Fe/C and Fe/Nafion/C fabrics have been investigated under laboratory conditions (small vial, artificial light) and in large-scale photo-reactors under sunlight to achieve low-cost decontamination of textile and agro-chemical industry effluent wastewater. Fe-ions deposited onto chemically treated C fabrics or encapsulated in Nafion thin films cast directly onto the carbon fabrics are efficient in decomposing H_2O_2 used as an oxidant in the photo-assisted abatement of non-biodegradable azo-dyes used in textiles. The Orange II taken as a model pollutant quickly fades under solar irradiation even at an initial pH 6. This range of pH is not possible with the homogeneous photo-Fenton process. In contrast, the use of supported catalysts on C fabrics allows the costly pH adjustment to be avoided. This makes catalyst recovery and economical decontamination of wastewater containing non-biodegradable pollutants possible.

Keywords: Photo-Fenton; Solar photo-reactor; Compound parabolic collector (CPC); Flat-type reactor; Orange II

1. Introduction

The degradation of aromatics, pesticides, herbicides and other bio-recalcitrant compounds in industrial waste waters can be efficiently achieved by means of oxidative radicals generated in the Fenton [1,2] and photo-assisted Fenton reaction [3–6]. However, the removal of Fe-ions from the system at the end of the treatment by precipitation is costly in terms of chemicals and manpower. These drawbacks can be avoided by immobilizing Fe-ions on a suitable non-corrosive substrate like Nafion [7] or onto chemically treated C fabrics [8].

However, any suitable support anchoring Fe-ions to catalytically decompose H_2O_2 has to meet several criteria to catalyse the degradation process: (a) the substrate has to be resistant to the oxidative radicals produced by the Fenton reagent in solution, (b) the fixed iron-ions cannot leach out into the solution and (c) the degradation of the pollutant has to proceed with acceptable kinetics. These criteria are met by:

(a) iron clusters deposited on the chemically modified surface of C fabrics [8];
(b) Nafion perfluorinated membranes or films cast onto glass fibers [9] or C fabrics [11] chemically resistant to the highly oxidative $OH^\bullet$ radicals, in which case, the iron-exchanged clusters (mainly Fe^{3+}) have to be electrostatically bound to the sulfonic groups in Gierke cages (30–50 Å size) [10].

In this study, C fabrics on which Fe catalysts are chemically anchored on a C surface or immobilized in the thin Nafion films cast onto the C-fibers are used for the abatement of Orange II, a non-biodegradable azo-dye found in textile industry effluents. The objectives of this work are: (a) to

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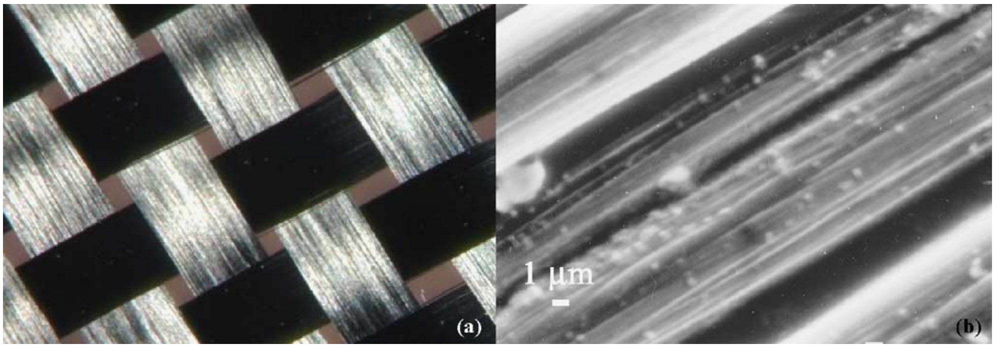

Fig. 1. Microscopic images of C fabrics: (a) optical microscopy before the chemical treatment and (b) scanning electron microscope image after the deposit of Fe clusters.

prepare and study the activity of various supported Fe catalysts by testing various experimental parameters in a solar simulator (Suntest lamp) under laboratory conditions, (b) to compare the activity of the most active supported catalysts (Fe/Nafion/C and Fe/C) for large-scale applications (solar radiation, various pH values, large photo-reactors) with respect to the results obtained under the same experimental conditions (pollutant, H_2O_2, pH, . . .) with the homogeneous Fenton and photo-Fenton processes, (c) to design and construct a new flat-type photo-reactor, better adapted to the use of catalysts supported on C fabrics, (d) to compare the performances of a flat-type reactor and the CPC photo-reactors used so far to perform homogeneous photo-Fenton degradation under solar illumination of model azo-dyes up to bio-compatible pH values, since the pH of textile waste water containing dyes is in the range of pH 7–9 and (e) to estimate the cost of decontamination for each type of treatment.

2. Experimental

2.1. Preparation of supported catalysts

2.1.1. Fe^{3+}/C (Tex 66)

Large pieces (14 cm × 100 cm or 40 cm × 90 cm) of fibrous active carbon Tex 66 C fabrics made of thin C fibers (7 μm in diameter woven in 1.3-mm thick bundles, spaced 0.3-mm apart, as shown in the optical microscope image in Fig. 1a), were boiled in HNO_3 (22%) for 2 h and then washed repeatedly with deionized water. The number of active sites introduced by the HNO_3 treatment was estimated to be around 8×10^{20} sites/m^2, considering 1 g of C fabric with an area of 0.24 m^2/g titrated by 4.1 mol HNO_3.

Next, the chemically treated C fabrics were introduced in a solution 1 M of $Fe(NO_3)_3$ for 2 h, rinsed and dried in air. The size of the Fe clusters deposited on the C fibers ranges between 0.2 and 1 μm, as shown in the scanning electron micrograph (SEM) given in Fig. 1b.

2.1.2. Fe/Nafion/C (Tex 66)

C fabrics Tex 66 (large 14 cm × 100 cm or 40 cm × 90 cm pieces) thoroughly washed with water, alcohol and then dried, were impregnated with a solution of Nafion perfluorinated ion-exchange resin (5%) in a mixture of alcohols (50%) and water (45%) purchased from Aldrich, following the technique described in [11]. The Nafion/C (Tex 66) pieces were then heated overnight at 110 °C to evaporate solvents and to cast the Nafion thin films. Next, Fe ions were introduced into the Nafion Gierke cages by ion exchange with an aqueous solution of $Fe_2(SO_4)_3$ for 16 h, after which the supported Fe/Nafion/C catalysts were carefully washed with distilled water and kept in water to avoid drying out the Nafion thin films which could then become loosened from the C fibres. On the SEM image (Fig. 2a), some of the Nafion films often

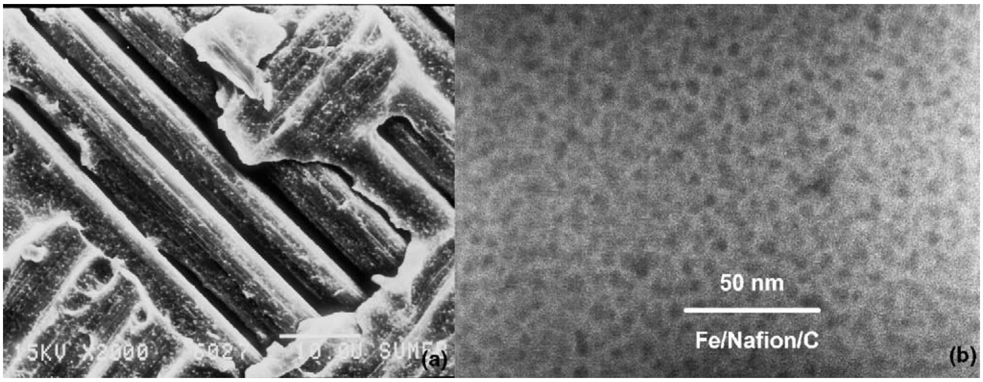

Fig. 2. Morphology of Fe/Nafion/C fabrics: (a) Nafion thin films observed by SEM and (b) Fe clusters observed by TEM.

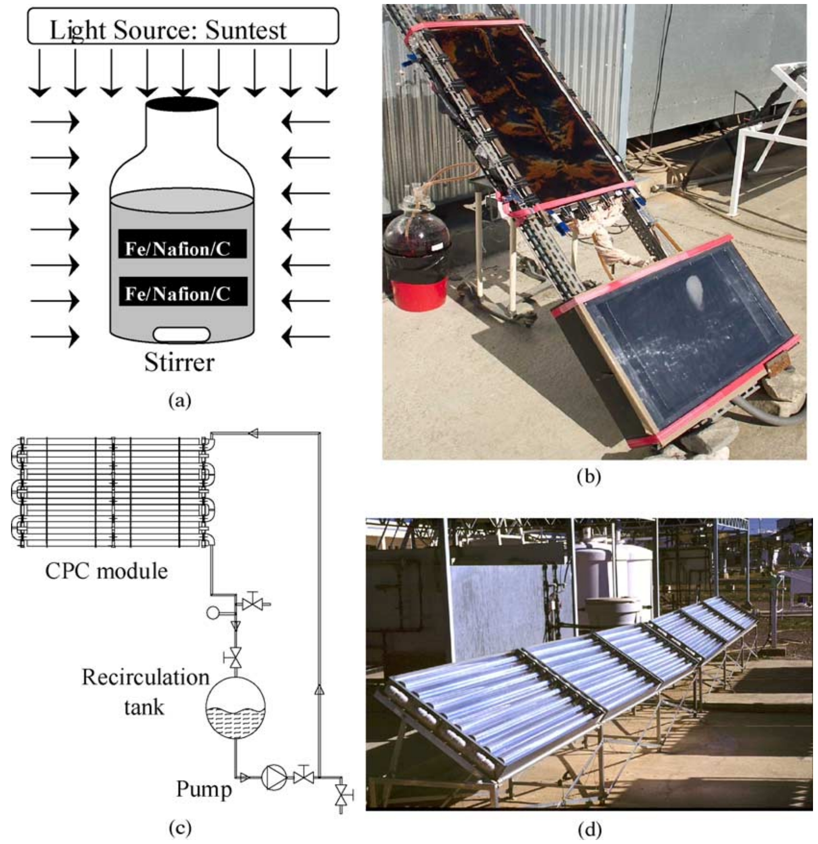

Fig. 3. Experimental set-up used: (a) static reactor in solar box; (b) flat-type photo-reactor under solar irradiation; (c) schematic drawing of the CPC photo-reactors containing supported catalysts; (d) photo of the CPC field at the PSA.

deposited at the intersections of C fibers can be seen, while the TEM image (Fig. 2b) shows well dispersed iron clusters ranging from 3.5 to 5 nm in diameter, most of them 4.76 nm.

2.2. Photo-reactors under artificial or solar irradiation

(a) The Suntest solar simulator has a wavelength distribution with about 7% of the photons between 290 and 400 nm and between 400 and 800 nm as in the solar spectrum. The photocatalytic activity of small sheets (4 cm × 14 cm) of Fe/C or Fe/Nafion/C supported catalysts were evaluated in 70-ml cylindrical reaction vessels (Fig. 3a).

(b) The flat-type stainless steel reactor tilted at 37° (Fig. 3b) allowed a piece of supported catalyst (80 cm × 40 cm) to be inserted before covering tightly with 4-mm-thick float glass. Two special devices, placed at the reactor inlet and outlet, were used to ensure a homogeneous, laminar flow by means of a centrifugal pump circulating 20 l of water through a 12-l reservoir and a large glass flask in which reactants have been added. The value of the flow rate was 1.5 l/min. The 4-cm thick reservoir, painted black, was placed in an insulated, wooden box, also painted black, and covered with a 4-mm pane of glass to ensure collection of the infrared solar radiation and obtain, by the greenhouse effect, a temperature increase in the circulating liquid.

(c) *The CPC reactors* installed at the PSA (Almeria, Spain) consist of 24 glass tubes horizontally mounted above compound parabolic collectors (CPC) on a fixed platform tilted 37° (local latitude) (Fig. 3c) and connected in series so that water flows directly from one to another and finally to a large glass flask. Only six tubes, and a total volume of 11 l were used in this case, with two long pieces (7 cm × 100 cm or 8 cm × 150 cm) of the supported catalyst firmly attached around an inner glass tube closed at the bottoms before being placed in two of the CPC tubes (Fig. 3d). Experiments started with the collectors covered for the time necessary (30 min) to introduce chemicals (excepted H_2O_2) and ensure homogenization of the solution throughout the system. Then peroxide was introduced and the reactor left covered at least 30 min (up to 180 min) more before exposing it to the sunlight. Then the cover was removed and the samples were collected at predetermined times, e.g., every 5–60 min depending on the degradation rate.

2.3. Analysis

Ferrous sulphate $FeSO_4{\cdot}7H_2O$, ferric sulphate or ferric nitrate and sulphuric acid were analytical grade (Merck). Orange II was also obtained from Merck. Hydrogen peroxide (30%, w/v) was technical grade. Total organic carbon (TOC) was measured with a Shimadzu TOC 5050 analyser with an ASI 5000 auto sampler. The pH of the solution was measured with a glass electrode. Orange II concentrations were determined by photometric measurement (at 486 nm) using a Unicam-2 spectrophotometer.

2.4. Evaluation of solar radiation

The experiments were performed with the same type of catalyst, pollutant and experimental conditions (pH) as in the CPC reactors and sampling was done at the same time in order to obtain comparable results despite variation in solar illumination due to cloud passage. The effect of the change in solar power input was calculated [12] taking into account the incident radiation continuously monitored by radiometers and the ratio between the geometric area of the supported catalyst and the irradiated volume of the liquid contained in the photo-reactor.

As mentioned above, solar ultraviolet radiation (UV) is an important parameter for the correct treatment of data obtained from solar photocatalytic experiments. A global-UV radiometer (KIPP&ZONEN, model CUV3) with typical sensitivity of 264 $\mu V\ W^{-1}\ m^2$, placed on a horizontal platform, provides data in terms of UV solar power incident per unit area ($W\ m^{-2}$). The amount of energy collected by the reactor (per unit of area) from the start up of the experiment until each sample is:

$$Q_{\mathrm{UV},n} = Q_{\mathrm{UV},n-1} + \Delta t_n \overline{\mathrm{UV}}_{\mathrm{G},n}, \quad \Delta t_n = t_n - t_{n-1} \qquad (1)$$

where t_n is the experimental time of the sample irradiation, $\overline{\mathrm{UV}}G, n$ the average during Δt_n and $Q_{\mathrm{UV},n}$ is the accumulated energy (per unit of area, kJ/m^2).

3. Results and discussion

3.1. Suntest lamp irradiation experiments

Fig. 4 shows the abatement (measured by spectrometry, Abs maximum 486 nm, as the decrease in color due to the rupture of the –N=N– bond) of Orange II on Fe/C or Fe/Nafion/C fabrics under artificial (Suntest) light irradiation in the presence of H_2O_2 at different initial pH.

The results of the degradation of Orange II in the presence of H_2O_2 under Suntest lamp irradiation at different pH show that the decomposition of Orange II takes place in a wide pH-range: about 85% of the initial Orange II disappears on Fe/C and 100% on Fe/Nafion/C even at initial pH 9. This represents a considerable improvement over the results obtained previously with the Fe^{3+}/Nafion systems [7]. Indeed, the mineralization of Orange II under Suntest irradiation on Fe/Nafion was observed to proceed up to pH 4.7 and to reach less than ~50%. Therefore, the immobilized Fe/C and Fe/Nafion/C systems tested in this study avoid the costly initial acidification needed to treat many effluents from the textile industry in the range of pH 7–8 where Fenton or photo-assisted Fenton homogeneous treatments are currently employed [2,6]. This acidification is more costly than the energy and oxidant used in Fenton degradation [2].

The drop in pH occurring when the reaction is starting at the initial pH values of 6 or 9 (Fig. 4a and b) is due to two factors: (a) during mineralization of Orange II, predominantly NH_4^+ and HSO_4^- have been reported as the inorganic species formed [3,6] and (b) the formation of intermediate Fe-complexes consisting of Fe-chelates leads to the formation of carboxylic acids during the degradation of Orange II. Oxalic, formic, acetic acids and also smaller concentrations of other acids have been reported [7,8]. The pK_a of these acids correspond to the solution pH (between 3 and 4) found at the end of degradation as shown in Fig. 4. The degradation of Orange II involves the formation of Fe-organic complexes:

$$[\mathrm{RCOO{-}Fe}]^{2+} + h\nu \rightarrow [\mathrm{R}^{\bullet}] + \mathrm{CO_2} + \mathrm{Fe}^{2+} \qquad (2)$$

where the LMCT (ligand-to-metal charge transfer) complex in Eq. (2) is the precursor step responsible for the TOC decrease. This process would proceed concomitantly with the radical reaction under Suntest lamp.

$$\mathrm{RH} + \mathrm{HO}^{\bullet}(\mathrm{HO_2}^{\bullet}) \rightarrow [\mathrm{R}^{\bullet}] + \mathrm{RHOH\ or\ H_2O} \qquad (3)$$

Many other parameters such as Orange II and H_2O_2 concentrations, light intensity, etc., have been tested under laboratory conditions for Fe/C [8] and Fe/Nafion/C [11] supported catalysts, which allows their large-scale optimization under sunlight. In these latter works, it was shown that the photocatalysis mediated by both supported catalysts increased with the applied light intensity and reaction temperature [8,11]. The activation energy of the Orange II discoloration was determined to be 10.4 kcal/mol for the Fe/C catalyst [8] and 9.8 kcal/mol for the Fe/Nafion/C catalyst [11]. The Fe/C catalyst surface was shown by infrared spectroscopy (IR) not to block during the reaction due to the adsorption of initial or intermediate products during Orange II decomposition and the oxidation state of the Fe was observed to remain constant during the long-term reactor operation indicating a stable catalyst performance [8]. The Fe/Nafion/C catalyst in the presence of H_2O_2 under solar simulated light transformed the totally non-biodegradable Orange II into a bio-compatible material with a very high BOD_5/COD value [11].

3.2. Experiments performed with the flat-type photoreactor under solar irradiation

The performance of the flat-type reactor with a large, 40 cm × 80 cm sheet of Fe/Nafion/C fabric is shown in Fig. 5.

The results obtained for the discoloration of Orange II (absorption maximum, 486 nm) and its mineralization (TOC) as a function of light energy Quv are quite close when the initial pH is 3 or 4. Complete discoloration, i.e.,

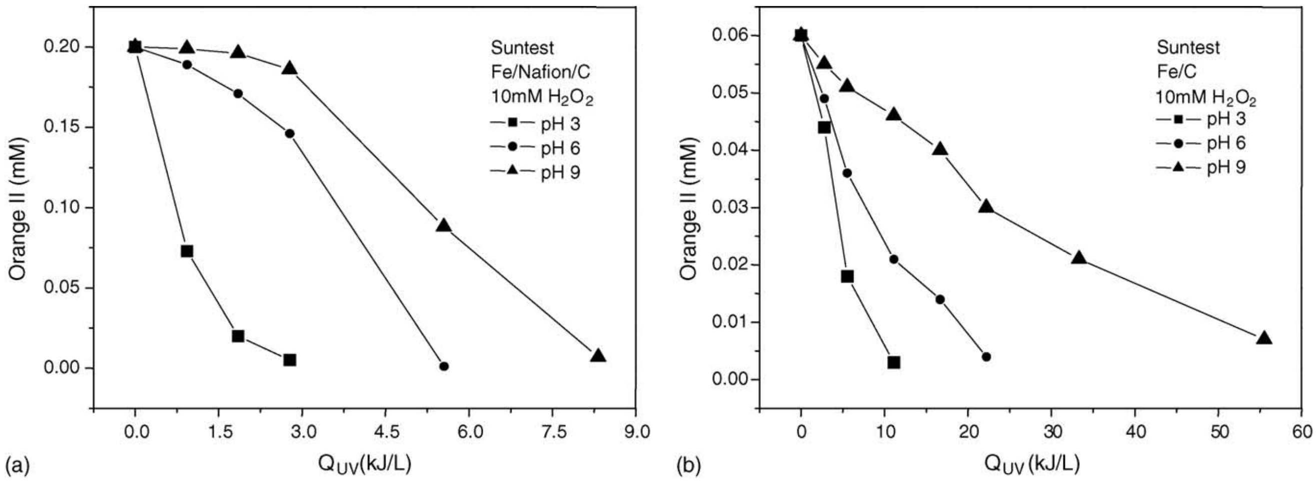

Fig. 4. Effect of pH on abatement of solutions of 0.2 and 0.06 mM Orange II: (a) Fe/Nafion/C fabrics and (b) Fe/C fabrics under Suntest lamp irradiation (80 mW/cm^2).

complete abatement of the bio-recalcitrant compound was quickly reached (Fig. 5a), but only 30% mineralization was attained after 3 h under solar irradiation. Nevertheless, if the intermediates are non-toxic, total mineralization by photo-Fenton or by any other physico-chemical method is unnecessary, because a biological treatment, which is by far less expensive, can then be applied. A careful diagnosis of the toxicity of the compounds formed during the intermediate decontamination steps is crucial [12] before coupling physico-chemical and biological treatments.

Therefore, for treatment cost estimates (see Table 1), we have used the amount of light energy (Quv) needed for the discoloration of Orange II. As shown in Table 1, in contrast to the CPC photo-reactors, the flat-type reactor is an ‘‘academic model’’ the cost of which is relatively high (€2550/m^2) and thus only a qualitative cost estimate can be made. However, compared to the average cost (€3000/m^3) of the treatment of industrial wastewater, the solar treatment performed with the flat-type reactor (to be optimized before large-scale construction) is only €12.5/m^3.

3.3. Experiments performed with the CPC photo-reactors under solar irradiation

Most homogeneous photo-Fenton processes performed so far at the PSA (Spain), have used the whole CPC solar field shown in Fig. 4c. In this case, only two CPC tubes contained supported Fe/C and Fe/Nafion/C catalysts and, in order to compare their performance, with those of the homogeneous photo-Fenton, another experiment was performed under the same conditions (Orange II and H_2O_2 concentrations, pH, solar irradiation, etc.). The results are shown in Fig. 6.

Both Fe/C and Fe/Nafion/C catalysts were found to need more light energy (Quv) for the discoloration of Orange II (Fig. 7a) and its mineralization (Fig. 7b) than the

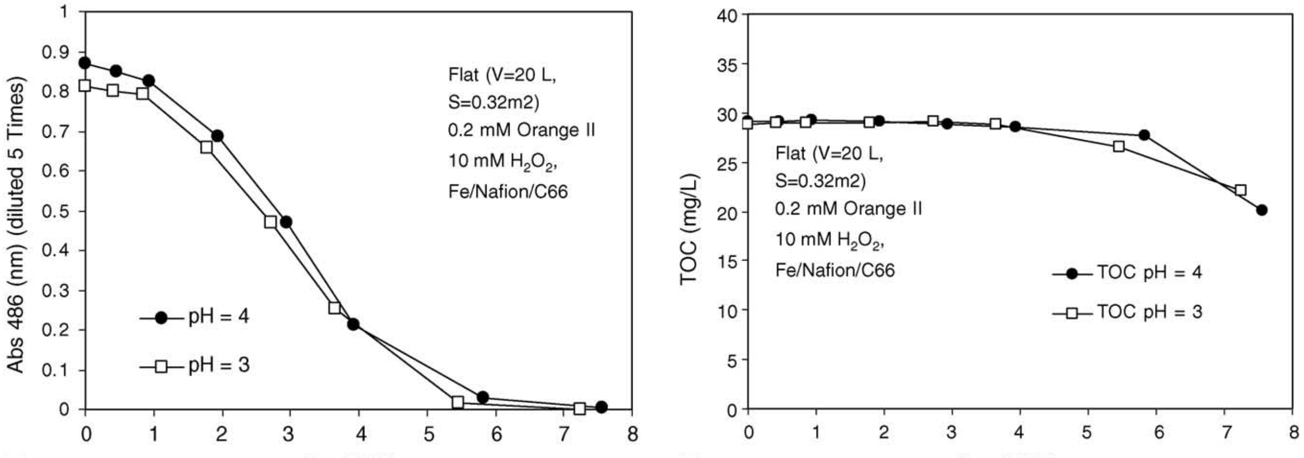

Fig. 5. Flat-type photo-reactor containing solutions at initial pH 3 or 4 under sunlight: Orange II (a) discoloration and (b) mineralization.

Table 1
Cost estimate for water treatment with photo-Fenton in CPC and flat photo-reactors

	CPC fixed	CPC homogeneous	Flat fixed
Common input data			
Yearly working days (days)	365	365	365
Average of useful hours (h)	12	12	12
Availability factor (%)	80	80	80
Effective yearly operating hours (h)	3504	3504	3504
UV global radiation (W_{uv}/m^2)	18.6	18.6	18.6
Total collector area (m^2)	40.6	20.5	23.5
Solar collector cost (€/m^2)	1000	1000	2550
Cost of H_2O_2 (30%) (€/kg)	0.31	0.31	0.31
Cost of $Fe_2(SO_4)_3$ (€/kg)	–	1	–
Cost of H_2SO_4 (96%) (€/kg)	1	1	1
Cost of NaOH (€/kg)	–	1	–
Cost of tank and recirculation pump for Fe recovering (€)	–	700	–
Cost of Fe/Nafion/C (€/m^2)	130	–	130
Cost estimation for 1000 m^3/year			
Direct cost			
Total collector cost (€)	40600	20500	52875
Fe recovering (€)	0	700	
Fixed catalyst (€)	5280	0	3055
Total direct cost (€)	45880	21200	55930
Indirect cost			
Contingencies (12% TD) (€)	5506	2544	6712
Spare parts (1% TD) (€)	459	212	559
Total capital required (TCR) (€)	51845	23956	63201
Annual cost (€/year)			
Capital (13% of the TCR) (€/year)	6740	3114	8216
Consumables (€/year)	1100	2850	1100
Operation and maintenance (5% TCR) (€/year)	2592	1198	3160
Total annual cost (€/year)	10432	7162	12476
Treatment cost (€/year m^{-3})	10.43	7.16	12.48

homogeneous photo-Fenton performed with only two CPC tubes and 0.3 mM Fe ions, but no separation and recovery of catalyst was necessary for them. A comparison of the treatment cost of the supported catalysts and the cost of the homogeneous photo-Fenton performed under the same experimental conditions is therefore of interest. The following points were considered:

(a) Treatment volume of 1000 m^3 of wastewater (V_W) with 0.2 mM of Orange II per year.

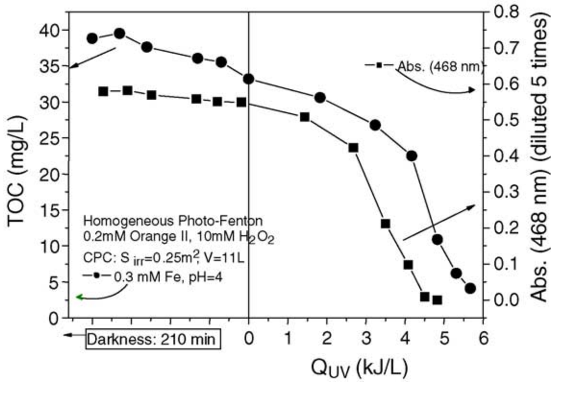

Fig. 6. Orange II abatement under solar irradiation in homogeneous photo-Fenton.

(b) To treat 11 l of wastewater until total discoloration of Orange II, the accumulated energy necessary in the CPC reactor is about 4.8 kJ/l (Fig. 6) with the homogeneous system and about 9.5 kJ/l with heterogeneous system (Fig. 7), and to treat 20 l of wastewater, the accumulated energy necessary in the flat reactor is about 5.5 kJ/l (Fig. 5).

(c) The average UV global radiation during operating hours in Almería is 18.6 W_{UV}/m^2 with an irradiation time of 12 sunny hours per day.

(d) The CPC collector cost is €1000/m^2 (based on the Albaida Project 2004 set-up) and the flat reactor cost is €2550/m^2.This includes collectors, glass tubes, piping, pump, control system, engineering, radiometer, etc. It does not include civil works, water or electricity, consumables, etc.

(e) The total collector area needed (A_C) may by found by:

$$A_C = \frac{Q_{UV} \times V_W}{\Delta t_n \times \overline{UV}_{G,n}} \tag{4}$$

To treat 1000 m^3 of wastewater per year, 20.5 m^2 of illuminated reactor are needed in the homogeneous CPC system, 40.6 m^2 in the fixed CPC system and 23.5 m^2 in the flat system. Taking into account these results and, by ana-

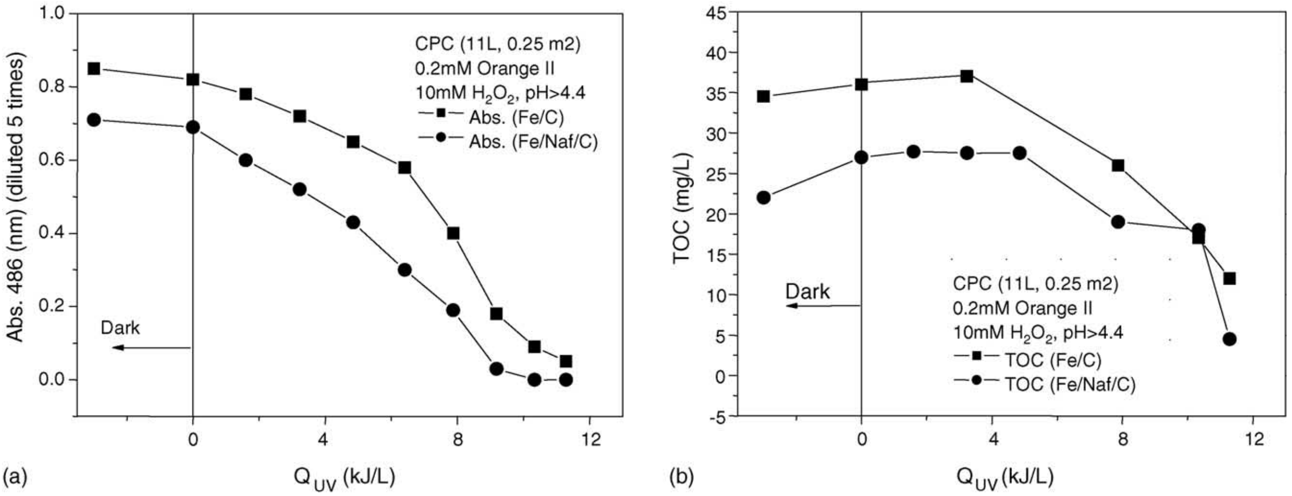

Fig. 7. Comparison of Fe/C and Fe/Nafion/C supported catalysts introduced in two CPC tubes: (a) absorbance and (b) TOC.

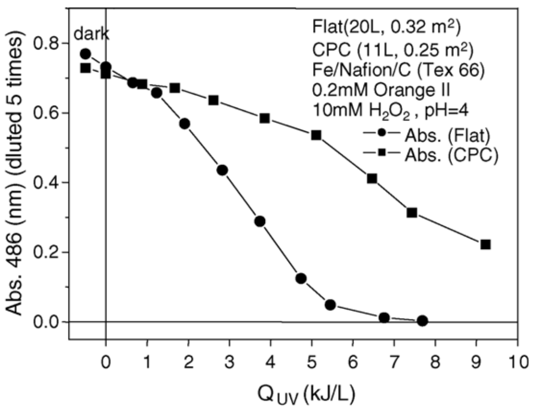

Fig. 8. Comparison of performance of the flat-type reactor and two CPC tubes containing Fe/Nafion/C fabrics.

logy to [13], a cost estimate is made as shown in Table 1. Total annual costs were calculated with an interest rate of 13% over a 15-year period. The treatment cost was estimated to be €7.2/m^3 for the homogeneous CPC system, €10.4/m^3 for the fixed CPC system and €12.5/m^3 for the flat system.

From these results, it appears that, although the cost of treatment with the supported catalysts in CPC tubes is more expensive than the homogeneous process, it is still far below the cost of €3000/m^3 for other physico-chemical treatment processes.

However, it is not easy to insert the supported catalysts in the CPC tubes and requires too much manpower. The flat-type reactors, in which the supported catalysts can be easily inserted, do not need reflecting collectors and, under the same experimental conditions, show better performance (Fig. 8). Our goal is thus to optimize the size, geometry, flow conditions and the temperature increase in this reactor design by taking advantage of the greenhouse effect to enhance the reaction rate.

4. Conclusions

The results obtained are: (a) the C fabrics are suitable for anchoring Fe-ions because these C-structured fabrics are resistant to the oxidative radicals produced by the Fenton reagent in solution, (b) the fixed iron-ions, either attached to the surface of chemically modified C fabrics, or embedded in Gierke cages in thin Nafion films cast onto C fabrics, that do to not leach out into the solution after repeated photo-Fenton processes, (c) the degradation of Orange II chosen as the model pollutant for textile industry effluents was found to proceed with acceptable kinetics even at neutral pH, (d) activity of Fe/C catalysts is comparable to that of Fe/Nafion/C catalysts and thus the expensive Nafion monomer used to prepare Nafion thin films cast onto C fibers is avoided, (e) the flat-type photo-reactor tested at pilot plant scale showed better performance than the CPC photo-reactors currently used at the PSA, Almería, in Spain and (f) the total investment and water treatment cost for the decontamination of the industrial effluent was carefully estimated, showing that supported Fe catalysts on C fabrics can be used advantageously for homogeneous Fenton and photo-Fenton.

The academic research with C fabrics inserted both in small vials and in large photo-reactors opens up the application of solar energy in low-cost treatment of industrial effluents containing bio-recalcitrant pollutants from the textile and agro-chemical industry. Now, more R&D is needed to improve the design of the flat-type photo-reactor for coupling with low-cost biological treatment.

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