ELSEVIER

Catalysis Today 76 (2002) 301–315

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Recent developments in the coupling of photoassisted and aerobic biological processes for the treatment of biorecalcitrant compounds

Victor Sarria [a], Sandra Parra [a], Nevenka Adler [a], Paul Péringer [a],
Norberto Benitez [b], César Pulgarin [a],*

[a] *Institute of Environmental Science and Technology, Laboratory of Environmental Biotechnology,*
Swiss Federal Institute of Technology (EPFL), CH-1015 Lausanne, Switzerland
[b] *Departamento de Química, Facultad de Ciencias, Universidad del Valle, A.A. 25360 Cali, Colombia*

Abstract

A general strategy to develop combined photochemical and biological system for biorecalcitrant wastewater treatment is proposed. For the development of this strategy, the following points were taken into account: the biodegradability of initial solutions, the operation mode of the coupled reactor, the chemical and biological characteristics of the phototreated solutions, the evaluation of different photoassisted advanced oxidation processes, the optimal conditions of both photochemical and biological processes, and the efficiency of the coupled reactor.

The strategy to couple photochemical and biological processes is illustrated by case studies of four different biorecalcitrant pollutants. Three kinds of combined systems were developed using either photo-Fenton, Fe^{3+}/UV, or TiO_2 supported on glass rings for the photocatalytic pretreatment and in all cases immobilized biomass for the biological step. The advantages of the each coupled system are discussed and beneficial effects of such two-step treatments were found. However this strategy is not a universal solution. Chemical, biological, and kinetic studies must be always carried out to ensure that the photochemical pretreatment increase the biocompatibility of the treated wastewater. Some field experiments using solar reactor indicated that a coupled photochemical–biological treatment system at pilot scale is a possible way to achieve the complete mineralization of the biorecalcitrant pollutants.

Keywords: Advanced oxidation processes; Integrated chemical and biological treatment; Photochemical treatment; Process integration; Wastewater treatment

---

1. Introduction

Advanced oxidation processes (AOP) are very promising methods for the remediation of contaminated ground, surface, and wastewaters containing non-biodegradable organic pollutants [1,2]. The most commonly used AOP utilize H_2O_2, O_3, or O_2 as the oxidant. These involve the generation of the hydroxyl radical ($^{\bullet}OH$) that is a reactive intermediate and has a high oxidation potential. This hydroxyl radical attacks organic molecules by abstracting a hydrogen atom or by adding to the double bonds. Organic molecules are then transformed to more oxidized intermediates, carbon dioxide and water. An important drawback of these AOP is that their operational costs are relatively high

---

* Corresponding author. Tel.: +41-21-693-47-20;
fax: +41-21-693-47-22.
E-mail address: cesar.pulgarin@epfl.ch (C. Pulgarin).

0920-5861/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0920-5861(02)00228-6

compared to those of biological treatments, which are, at present, the cheapest and the most compatible with the environment. However, the use of AOP as a pretreatment step to enhance the biodegradability of wastewater containing recalcitrant or inhibitory compounds can be justified if the resulting intermediates are easily degradable in a further biological treatment.

Previous studies have attempted the strategy of combine chemical and biological processes to treat contaminants in wastewater. These studies, extensively reviewed by Scott and Ollis [3,4] suggest potential advantages of this strategy for water treatment. Recently, very interesting coupled systems have been proposed to treat different kinds of industrial wastewaters such as effluents from alkaline fruit cannery, textile industry, dyehouse liquors, olive mill, polyester resin production, among others. The proposed systems include up-flow anaerobic sludge blanket (UASB) pretreatment followed by H_2O_2 and/or ozonation [5], a sequencing batch cycle, which implies a biological anoxic decolorization, followed by an aerobic mineralization combined with an ozonation of organic metabolites [6], Fenton's reagent—aerobic biological treatment [7], ozonation—biological treatment [8–10]. All these processes are characterized by the utilization of sequential batch reactors at laboratory scale treating volumes between 1 and 3 l. Special attention is done by Ollis [11] to kinetic studies and engineering models of integrated chemical and biological oxidation of wastewaters, in order to impulse the practical application and design of these systems.

The first coupled flow system was developed in our laboratory using Fenton reaction as pretreatment step [12–15].

At present, excluding one of our recent publications [16], there are no published reports of combined systems using iron(III) and TiO_2-photoassisted reactions as pretreatment processes. The iron(III)/light system is developed as an alternative to the use of photo-Fenton as pretreatment since addition of H_2O_2 is avoided. The advantages of the TiO_2-photoassisted system are that the catalyst can be reused and that the pH of the solution remains at neutral values [16]. The photo-Fenton reaction instead, renders the phototreated solution acidic making neutralization necessary [14].

The main aim of this paper is to propose a general strategy that can be used to develop a combined photoassisted AOP and biological process for biorecalcitrant wastewater treatment. To illustrate this strategy we shall present the examples of model substances degradation: (a) *p*-nitrotoluene-*ortho*-sulfonic acid (*p*-NTS), which is a pollutant coming from manufacture of dyes, surfactants and brighteners; (b) metobromuron (MB) and isoproturon (IP), two of the most used herbicides in Europe; (c) 5-amino-6-methyl-2-benzimidazolone (AMBI), a precursor of dyes industry. Three kinds of combined systems are developed using in all cases immobilized biomass for the biological step and either photo-Fenton, or Fe^{3+}/UV, or TiO_2 supported on glass rings for the photocatalytic pretreatment.

For the development of the coupled strategy, the following points were taken into account: the biodegradability of initial solutions, the operation mode of the coupled reactor, the chemical and biological characteristics of the photo pre-pretreated solutions, the evaluation of different photoassisted AOP, the optimal conditions of the individual processes and the efficiency of the coupled reactor. Finally, the feasibility of coupling a photoreactor with a biological system at field pilot scale is also discussed.

2. Experimental

2.1. Materials

All chemicals were used as received without further purification. MB ($C_9H_{11}BrN_2O_2$), IP ($C_{12}H_{18}N_2O$), and *p*-NTS ($C_7H_7NO_5S$) were obtained from Ciba, Monthey-Switzerland, AMBI ($C_8H_9N_3O$) was a gift from Rohner, Basel, Switzerland. $FeCl_3{\cdot}6H_2O$ and H_2O_2 (30%, w/w) analysis grade (p.a.) were from Fluka, and TiO_2 was from Degussa P-25, mainly anatase with a surface area of $50\,m^2\,g^{-1}$. The chemicals for high performance liquid chromatography (HPLC) analysis were obtained from Fluka. Milli-Q water was used throughout for the preparation of aqueous solutions and as a component of the mobile phase, water-acetonitrile (HPLC grade) in HPLC analysis. The phototreated solutions were neutralized by means of NaOH. Neutral pH of the solutions was maintained during the biological treatment by adjusting with HCl or NaOH.

2.2. Coupled photochemical–biological flow reactor

The coupled photochemical–biological system used for the total mineralization of biorecalcitrant compounds has been designed and constructed in our laboratory (Fig. 1). The biological reactor shown at the right hand side of Fig. 1, was coupled with one of the two possible photochemical reactors: the coaxial or the coiled one as shown in the left hand side of Fig. 1. The coaxial reactor was used for heterogeneous phase reactions using TiO_2 supported on glass rings, while the coiled reactor was used for experiments in homogeneous phase via photo-Fenton reaction.

2.2.1. Coiled photochemical reactor

In the coiled photochemical reactor shown in Fig. 1, the pollutant solution circulates through an 8 mm diameter glass spiral of about 20 m long. A 400 W, 40 cm long, medium-pressure Hg-lamp is positioned in such a way that its center line passes through the axis of the coiled reactor. The predominant radiation is at 366 nm with output equivalent to ∼15 W. It has been taken care that all photons are absorbed in the optical thickness of the coiled reactor since the scattering effects are less significant in a reacting medium having a

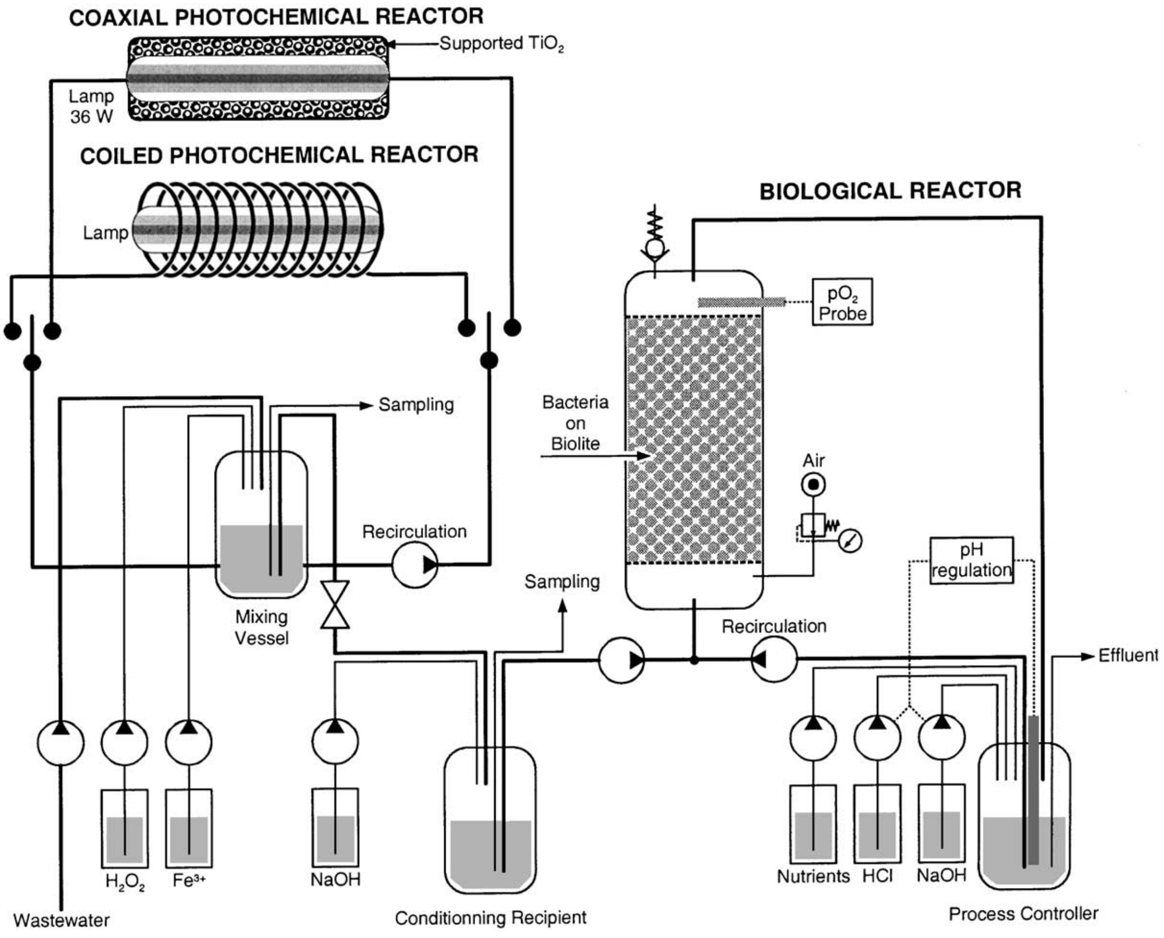

Fig. 1. Scheme of the coupled photochemical–biological flow reactor.

high optical absorption. The reactor was designed for different flow rates, organic loads, recirculation, and oxidant addition rates. The reactor mixing-vessel has a volume of 1 l. The runs were carried out at room temperature. Eight hundred milliliters of the pollutant solution was fed into the system from a 20 l reservoir and H_2O_2, and Fe^{3+} solutions were automatically added by means of peristaltic pumps into the mixing-vessel. The solution is continuously or in batch mode recirculated at 22 l h^{-1} through the illuminated part of the reactor. In order to prepare the phototreated water for biological treatment, the solution is neutralized at the photoreactor outlet, into the conditioning recipient.

2.2.2. *Coaxial photocatalytic reactor*

Titanium dioxide supported on glass rings (4 mm length, 4 mm internal diameter) was employed in the coaxial photocatalytic reactor as shown in Fig. 1. Immobilization of the catalyst was performed by the Laboratory of Renewable Resources of the University of Concepción, Chile [17,18]. A Philips 36 W (1.20 m long and 26 mm in diameter, TLD 36 W/08) black actinic light source is employed for irradiation in such a way that its center passes through the axis of the reactor. The lamp radiation has a λ-distribution between 330 and 390 nm centered at 366 nm. The reactor has a total volume of 1.5 l where 0.8 l were illuminated. The runs were carried out at room temperature. The pollutant solution is fed into the system from a 20 l reservoir and is continuously recirculated at 90 l h^{-1} by means of a peristaltic pump through the illuminated part of the reactor. Samples were taken from a mixing-vessel sampling port. The glass rings impregnated of TiO_2 float freely in the space between the light source tube and the outer wall of the jacketed reactor. During the photocatalytic experiments, the coaxial reactor is covered with an aluminum-coated parabolic device to avoid loss of light by reflecting it through the bulk of the solution. To prepare the effluent for the biological treatment, a conditioning recipient is available between the photocatalytic and the biological reactor, in which, the pH of the phototreated solution can be automatically neutralized, if necessary, by means of NaOH.

2.2.3. *Biological reactor*

The fixed bed reactor (FBR) shown on the right hand side of Fig. 1 consists of a column of 1 l of capacity containing biolite colonized by activated sludge from a municipal wastewater treatment plant (Vidy, Lausanne, Switzerland). The effluent of the photochemical step is circulated through the column at 6 l h^{-1}, which operates as an up-flow reactor. The pH is controlled and adjusted at 7. The required nutrients N, P, K, and oligoelements for the bacterial activity were also added. The aeration is about 150 l h^{-1} and the O_2 concentration is measured by means of an O_2 probe on the top of the column.

2.3. *Chemical and biological analysis*

Dissolved organic carbon (DOC) measurements were performed using a TOC analyzer (Shimadzu, model 5050A) with a solution of potassium phthalate as the calibration standard. Chemical oxygen demand (COD) was carried out via a Hach-2000 spectrophotometer using dichromate solution as the oxidant in strong acid media. HPLC was carried out in a Varian 9065 unit provided with a Varian 9012 solvent delivery system, an automatic injector 9100, and a Varian ProStar variable (200–400 nm) diode array detector 9065 Polychrom. A reverse phase Spherisorb silica column ODS-2 and acetonitrile/water as mobile phase were used to run the chromatography in gradient mode. The signals for IP, MB, *p*-NTS, and AMBI were detected at 254, 246, 275 and 302 nm, respectively. Concentrations of H_2O_2 were determined by the Merckoquant® peroxide analytical test strips and by permanganate titration in acid medium. The inorganic ions were followed by flow injection analysis (FIA).

Biological oxygen demand (BOD_5) measures were made by means of an Hg free WTW 2000 Oxytop unit thermostated at 20 °C. The Zahn–Wellens Test [19] was used for determination of inherent biodegradability. The toxicity was assessed using the Microtox® test system. This test was carried out using a Microtox model 500 analyzer, which is a laboratory-based temperature controlled photometer (15–27 °C) that maintains the luminescent bacteria reagent and test samples at the appropriate test temperature. This self-calibrating instrument measures the light production from the luminescent bacteria reagent. The sample toxicity is determined by measuring the effective concentration at which 50% of the light is lost due to compound toxicity (EC_{50}).

3. Results

3.1. Biodegradability of pollutant compounds

Due to the high cost of photochemical treatments, it must be first confirmed that target pollutants are definitively non-biodegradable since for biodegradable compounds, classical biological treatments are, at present, the cheapest and the most environmentally compatible.

The biodegradability of the studied pollutants (*p*-NTS, MB, IP, and AMBI) is practically zero. The Zahn–Wellens test, which is carried out in conditions similar to those of a wastewater treatment plant using activated sludge, shows that these pollutants are not degraded even during 50 days.

The biodegradability of the compounds was also tested in batch mode using an FBR. This test was negative even under theoretically favorable conditions such as the presence of co-substrates and adapted bacteria, strict control of pH, temperature, and aeration. In this biological reactor, urban and industrial activated sludge were used in different aerobic culture media. Three methods were used to follow the test: (a) respirometric measurements with an O_2 probe in the inlet and outlet of the FBR, (b) determination of compounds concentration by HPLC, and (c) measurements of DOC as a function of time.

3.2. The photo-Fenton reaction as pretreatment process

Photodegradation of *p*-NTS, MB, IP, and AMBI were carried out using the coiled reactor operated in semi-continuous mode. The coupled reactor operates in semi-continuous mode when the photochemical step treats the pollutant solution in short-duration batch cycles providing phototreated water to continuously feed the biological reactor. This mode was chosen since it gave better results comparing with the continuous mode. These two operation modes were compared by studying the efficiency of the photochemical, biological, and overall treatments of a *p*-NTS solution [13]. The main parameter affecting the performance of the photoreactor in continuous mode are related to the very low pollutant concentration that can be treated and the high concentration of H_2O_2 remaining in the phototreated solution, which are inhibitory for bacteria. The semi-continuous mode was then applied to overcome this inconveniences.

In this section, the strategy to couple photochemical and biological treatments is shown for the mineralization of the *p*-NTS, MB and IP using the Fenton reaction as pretreatment step.

3.2.1. p-NTS

The coupled reactor was operated in semi-continuous mode, as explained above, the photochemical step treats the *p*-NTS solution in short-time batch cycles providing phototreated water to continuously feed the biological reactor. The *p*-NTS solution (1.0 g *p*-NTS l^{-1}) was recirculated from the mixing-vessel into the reactor at 22 l h^{-1}. Hydrogen peroxide (300 μl, 30%) was added every 5 min and different Fe^{3+} concentrations were tested obtaining the best degradation rate at a Fe^{3+} concentration of 75 mg l^{-1}.

3.2.1.1. Chemical and biological characteristics of the phototreated p-NTS solution. To ensure that the photochemical process can be used as a pretreatment for a biological process, it is very important to gather information concerning the chemical nature of the intermediates formed during the photo-pretreatment, as well as the evolution of the toxicity and biodegradability. Fig. 2 shows the evolution of these parameters for *p*-NTS degradation in batch mode in the presence of H_2O_2 and Fe^{3+}.

Fig. 2a shows that in less than 5 min of photochemical treatment, the *p*-NTS was completely eliminated from the solution. HPLC scanning by a diode array detector revealed the presence of aromatic and aliphatic degradation by-products [14]. The aromatic intermediates detected attained a maximum concentration within 5 min and were totally degraded within 20 min.

The average oxidation state (AOS) of the solution is shown at the right hand side axis of Fig. 2a as a function of the photo-pretreatment time. These values were estimated according to the following equation [3]:

$$\text{Average oxidation state} = 4\frac{\text{DOC} - \text{COD}}{\text{DOC}} \quad (1)$$

where DOC and COD are expressed in moles of C l^{-1} and moles of $O_2\,l^{-1}$, respectively. AOS takes values between +4 for CO_2, the most oxidized state of C and

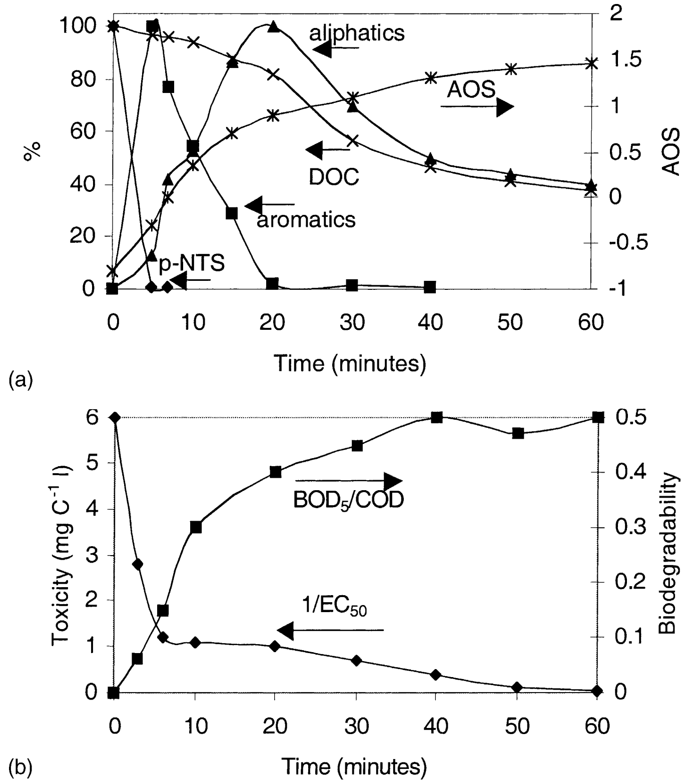

Fig. 2. Phototreatment of a *p*-NTS solution by Fenton reaction. (a) Relative concentration of *p*-NTS, aliphatics, and aromatics intermediates. *p*-NTS, 330 mg C l^{-1}; H_2O_2, 300 ml every 5 min; Fe^{3+}, 75 mg l^{-1}. The AOS evolution is shown using the right hand side axis. (b) Evolution of toxicity and biodegradability of the phototreated solution of *p*-NTS as a function of time.

−4 for CH_4, the most reduced state of C. In Fig. 2a, a significant increase of AOS was not observed after about 20 min of phototreatment, suggesting that the chemical nature of intermediates does not vary considerably after 20 min of reaction. Furthermore, the AOS value at the plateau after 50 min (average 1.5) is characteristic of very oxidized and biocompatible aliphatic compounds like oxalic acid.

The chemical features described above were validated by the related decrease of the toxicity and increase of biodegradability of the phototreated *p*-NTS solution. As shown in Fig. 2b, the reduction of toxicity reflects the abatement of *p*-NTS in 6 min. A slower decrease was subsequently observed until complete disappearance of toxicity in 50 min. The toxicity control during phototreatment revealed that intermediates more toxic than *p*-NTS did not develop during the photoassisted pretreatment process.

Although the *p*-NTS toxicity is relatively low, the most undesirable property of the *p*-NTS is its recalcitrance to biodegradation leading to potential chronic effects in natural environment. The beneficial effect of a short phototreatment, on the biodegradability of the *p*-NTS solution is shown in Fig. 2b. After 20 min of phototreatment (20% of mineralization), the BOD_5/COD ratio, representative of biodegradability, surpasses the value 0.4, which is the threshold for a wastewater to be considered easily biodegradable.

3.2.1.2. Efficiencies of the coupled system. As indicated above, the *p*-NTS solution becomes biocompatible after 30 min of phototreatment in batch mode when the *p*-NTS is completely degraded and the AOS of the intermediates does not change significantly any longer. In this sense, the coupled system can be better used to attain the total mineralization of the solution since the high energy consumption required to reach good levels of mineralization with single photochemical reactor makes it not attractive from an economical point of view.

The coupled photochemical–biological reactor is operated at five different phototreatment times: 50, 70, 95, 110, and 125 min (corresponding to the following flow rates, respectively, 0.96, 0.68, 0.50, 0.44, and $0.38\,\mathrm{l\,h^{-1}}$). The *p*-NTS solution is phototreated in a batch mode, as explained before, and when the chosen time is attained, the solution passes to the conditioning recipient, where it is neutralized. The phototreated solution is then led to the biological reactor in a continuous mode.

Fig. 3 shows the energy consumption and the percentage of DOC removed in the photochemical, the biological, and the whole coupled process as a function of phototreatment time.

From results presented in Fig. 3, it can be concluded that the most suitable conditions for the coupled treatment are obtained when the phototreatment time is short enough to achieve a cost-effective process together with high biological and overall efficiencies. At longer phototreatment times, the photochemical efficiency is improved by the unnecessary photodegradation of substances biologically degradable while the biological and the overall efficiencies remain almost invariable, which implies higher energy consumption without beneficial effects.

3.2.2. *MB and IP herbicides*

The photodegradation conditions, via photo-Fenton reaction, of these herbicides were optimized [14]. It was found that the optimal concentrations of Fe^{3+} and H_2O_2 were 1.0 and $25.0\,\mathrm{mmol\,l^{-1}}$, respectively. Before sending the effluent to the biological system, the biocompatibility of the treated solutions was determined as a function of the phototreatment time.

3.2.2.1. *Chemical and biological characteristics of the phototreated solutions.*

Fig. 4 shows the evolution of the concentration of the initial compound, aromatic, and aliphatic intermediates, as well as the DOC, toxicity and ions during the phototreatment of an MB (Fig. 4a and b) and IP (Fig. 4c and d) solutions using photo-Fenton pretreatment as a function of time.

Fig. 4a shows the HPLC measurements of MB degradation, where it can be seen that in less than 20 min of photochemical treatment the initial compound disappears from the solution. The scanning by a diode array detector revealed the existence of aromatic and aliphatic degradation by-products. The aromatic intermediates attained a maximum concentration within 1 h, remaining constant for about 6 h after which it started to decay, coinciding with an increase of aliphatic intermediates. Analysis of Br^- in solution (Fig. 4b) shows that approximately 80% of the bromine bound to organic carbon has been liberated after 1 h and remains constant during the phototreatment. The Br^- evolution is consistent

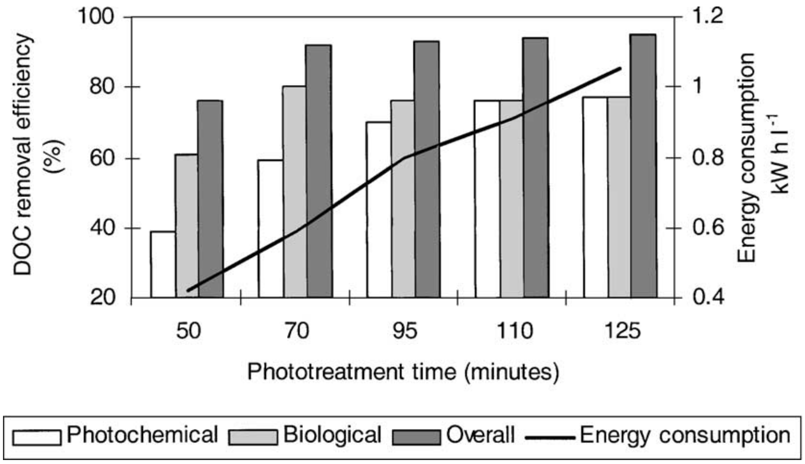

Fig. 3. DOC remotion by photochemical, biological, and coupled (overall) treatment of *p*-NTS. The consumed energy for the photochemical step is represented on the right-side axis.

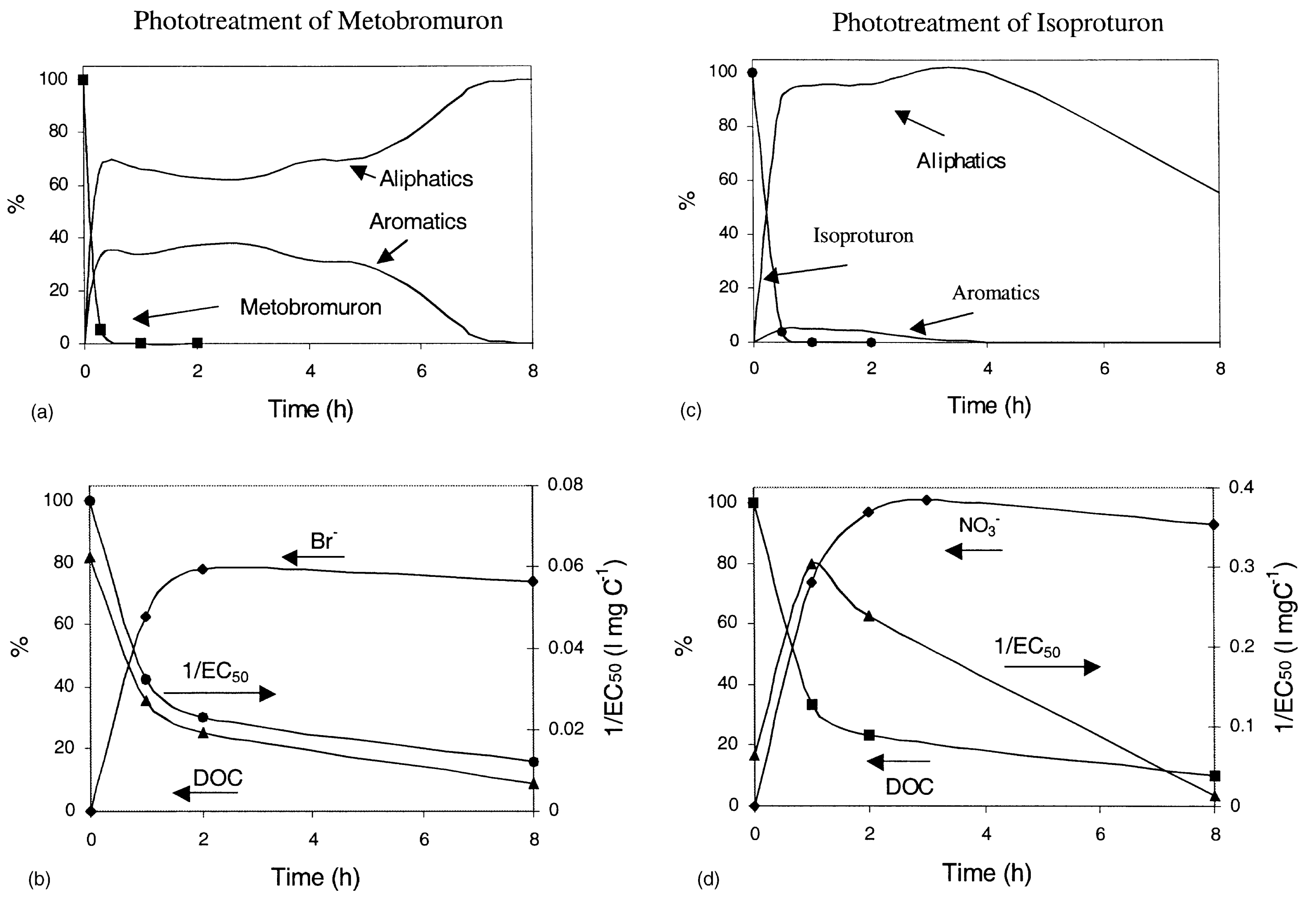

Fig. 4. Phototreatment of an MB (a), (b) and IP (c), (d) solutions using photo-Fenton pretreatment. (a) and (c) represent, respectively, the relative concentration of the initial compound, aromatic, and aliphatic intermediates for MB (0.93 mmol l^{-1}) and IP (0.21 mmol l^{-1}). (b) and (d) show the evolution of DOC, ions (Br^- for MB and NO_3^- for IP), and toxicity, expressed as $1/EC_{50}$, during the same phototreatment as a function of time. H_2O_2, 25.0 mmol l^{-1}; Fe^{3+}, 1.0 mmol l^{-1}.

with the MB degradation, but its final concentration (~54.0 mg Br^- l^{-1}) does not correspond to the theoretical stoichiometric value (74.0 mg Br^- l^{-1}). Thus, the degradation of MB should be leading to the formation of bromide intermediates, which were photo-recalcitrant in the tested conditions. The DOC evolution indicates a very slow mineralization rate after 2 h of treatment (Fig. 4b).

A biocompatibility study (toxicity and biodegradability tests) shows that, the solution resulting from the MB photodegradation is not appropriate for a biological treatment. During the photodegradation, even if the toxicity (expressed as $1/EC_{50}$ in Fig. 4b) is reduced together with the reduction of DOC, the ratio BOD_5/COD (representative of the biodegradability) does not vary significantly, having values of 0.0 and 0.1 before and after the treatment. As a reference, this parameter for municipal biodegradable wastewater is around 0.4. The FBR is also used to evaluate the biodegradability of the solution resulting from the MB phototreatment with no biodegradation observed. From these results it can be conclude that, even if the bromo-aliphatic compounds remaining in the solution after 8 h of phototreatment are non-toxic, they remain highly biorecalcitrant.

The same analyses were made for the IP degradation. In this case, the ratio BOD_5/COD was found to be 0.0 before phototreatment and increased up to 0.65 after pretreatment. Fig. 4c and d shows the results obtained by HPLC analysis as well as the evolution of NO_3^-, DOC, and toxicity.

A very high toxicity increase is observed at the beginning of the treatment, followed by a sharp decrease (Fig. 4d). This indicates that at the beginning of the photo-pretreatment there is formation of intermediates, which are more toxic than the initial compound. Toxicity evolution is related to the formation and degradation of intermediates. Fig. 4c shows first that the occurrence of aliphatic intermediates goes together with the abatement of IP and secondly, that the aromatic compounds were rapidly degraded coinciding with the decrease of toxicity. The NO_3^- ion (Fig. 4d) reaches the stoichiometric value (25.8 mg NO_3^- l^{-1}, corresponding to 100%) in about 2 h of treatment after which there will be no nitro compounds in solution. The evolution of DOC shows that the mineralization is about 90% after 8 h of treatment.

The chemical features described above, validated by the concomitant toxicity decrease and biodegradability increase of the treated IP solution, suggest that the photo-Fenton process is a promising pretreatment method. Therefore, a photochemical–biological coupled flow treatment can be applied for the complete mineralization of this compound.

3.2.2.2. Efficiencies of the coupled reactor. The coupled system, using the coiled photoreactor was tested for the degradation of an IP solution (0.8 l). This herbicide was chosen because in contrast to MB, the biocompatibility of its photodegraded solution has been proved. As in the case of *p*-NTS, the coupled system is operated in semi-continuous mode using a photo-Fenton reaction as pretreatment.

During the phototreatment, the AOS of the treated solution was calculated according to Eq. (1). The AOS attained a plateau after approximately 30 min reaching a value close to 2. These results suggest that after this time the chemical nature of the intermediates does not vary any more. Biodegradability and toxicity tests performed during a photodegradation run in batch mode show that the resulting solution becomes biocompatible when the DOC gets constant and after the total depletion of H_2O_2. The DOC evolution in this batch system seems to be directly correlated with AOS evolution. Consequently, when the stabilization of these parameters is reached, the phototreated solution may be considered as biocompatible. The AOS stabilization is reached after 30 min of the phototreatment when 50–65% of DOC is mineralized.

At this stage of the treatment the pH of the solution is around 3.0, which is automatically neutralized at the outlet of the photoreactor in order to prepare the solution for the biological treatment. During the biological process the pH is maintained between 6.5 and 7.5.

The evolution of the initial compound and its degradation intermediates is followed by HPLC during the whole process. It is observed that at 30 min, the phototreatment depleted IP up to 97% producing aromatic and aliphatic by-products. After 60 min of phototreatment, the IP was degraded while aromatic and aliphatic by-products were detected. After the biological process there are no substances detected by HPLC. The effective total mineralization is verified by DOC measurements.

To start the coupled photochemical–biological flow process, sequential batches of the phototreatment were carried out every 60 min, which corresponds to an input flow rate of 0.8 l h^{-1}. This flow rate was maintained during at least 3 days after reaching steady state to check up the stability of the system during a long time period. In this coupled system, 100% of the initial concentration of IP and 95% of DOC were removed.

3.2.3. AMBI: photo-Fenton reaction vs. Fe(III)/light system as pretreatment processes

Among AOP, the iron photoassisted system Fe(III)/light is a potential wastewater treatment process. In such system, instead of H_2O_2 as in photo-Fenton reaction, O_2 is used as the main oxidizing agent. Previous investigations have shown that irradiation by UV/visible light, Fe(III) salts can promote the photooxidation of organic compounds [20–24]. The agent responsible for these reactions could be hydroxyl radical formed by photochemical dissociation of Fe(III)-hydroxy complex, $Fe(OH)^{2+}$. The reaction can be simply expressed as follows [25]:

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH^{\bullet} \quad (2)$$

We have studied this system as a pretreatment step for the mineralization of AMBI [26]. It was observed that the iron photoassisted process, in 5 h, could remove 100% of the initial AMBI contained in wastewater. Complete mineralization is not attained but this fact in not considered as a disadvantage since DOC remaining in solution is biodegradable and the complete mineralization can be achieved by a biological treatment. In these conditions, a flow system coupling Fe(III)/light oxidation process with a biological system for the treatment of AMBI was developed.

The coupled reactor was operated in a semi-continuous mode. The optimal pretreatment time was 5 h obtaining the best compromise between the shortest photochemical pretreatment and the highest biological and overall efficiency.

Using the photo-Fenton reaction as a pretreatment step (with H_2O_2), the solution becomes biocompatible after 2 h reaching 65% of mineralization and total elimination of AMBI. The effectiveness of both Fe(III)/light and photo-Fenton systems as pretreatments, of the biological process, and the whole system are illustrated in Fig. 5. It is clear that the addition of H_2O_2 increases the photodegradation rate and efficiency of the photochemical reactor but in both cases almost the same global efficiency was reached (∼90%). The contribution of the biological

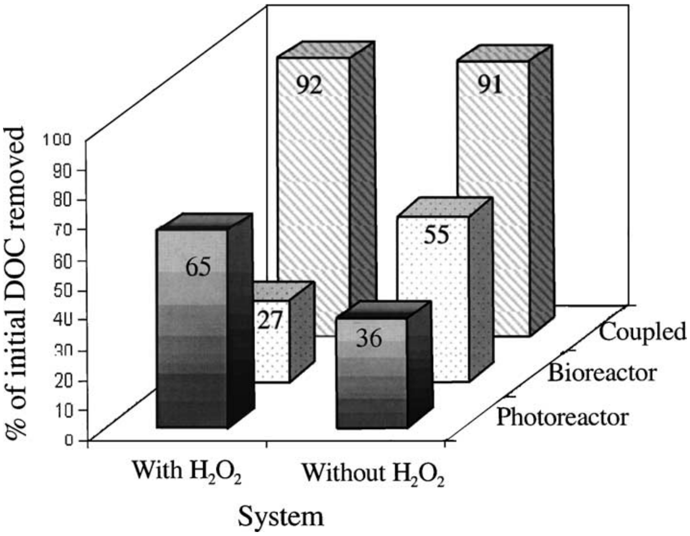

Fig. 5. Percentage of the initial DOC removed by the individual and the whole coupled system in the photochemical–biological flow reactor treating AMBI. Phototreatment times were 2 and 5 h with and without H_2O_2, respectively. In both the cases AMBI was completely eliminated in the photoreactor.

treatment is more important for the mineralization of the phototreated solution of AMBI using the system Fe(III)/light as pretreatment than for the solution resulting after the photo-Fenton treatment. It is an indication that H_2O_2 help to degrade in shorter time AMBI and biocompatible by-products. From the economical point of view, the photo-Fenton reaction as pretreatment is more interesting since the required phototreatment time is shorter but the Fe(III)/light system is the most environmental compatible. A more detailed research has to be carried out to try to reduce the residence time of this last system.

3.3. Supported TiO_2 photocatalytic system as pretreatment process

The advantages of using supported TiO_2 for the photochemical stage of the coupled process are (i) the catalyst can be reused, (ii) the pH of the solutions remains neutral, and (iii) H_2O_2 is not necessarily required for the reaction. In this way, the phototreated solution is ready to be biologically treated when it is biocompatible. This process is illustrated in the present section by mineralization an IP solution. The coaxial reactor described in Section 2 was used (Fig. 1). The photodegradation kinetics of IP employing either suspended or supported TiO_2 were very similar indicating that the activity of the TiO_2 was not reduced when it is immobilized on an inert surface of the glass rings used in this work. In addition, after 300 h of experiments using the same single batch of impregnated glass rings it was verified that the activity of the supported TiO_2 was not affected.

In both the suspended and the supported systems, the total elimination of IP is reached in approximately 2 h of phototreatment, whereas the mineralization reached in the same time is only about 20% measured by DOC.

Biocompatibility of the photochemically treated solution was studied to be sure that this process could be used as a pretreatment. The system presents the same kind of toxicity profile as in the case of photo-Fenton treatment with a high toxicity increase at the beginning of the treatment, followed by a sharp decrease. After 2 h of phototreatment, toxicity is as low as that of the initial compound and NO_3^- ion concentration reaches a stoichiometric value of 24.8 mg NO_3^- l^{-1}, corresponding to 100% of IP degradation.

The ratio BOD_5/COD (representative of the biodegradability) is found to be zero before phototreatment and it increases after 1 h up to 0.65, a value of high biodegradable wastewaters.

The coupled photochemical coaxial–biological flow reactor was used operating in semi-continuous mode, where 100% of the initial IP concentration and 65% of DOC were removed.

3.4. General strategy for the coupling photochemical and biological treatments

We developed a general strategy that can be used to develop a combined photoassisted AOP and biological process for biorecalcitrant wastewater treatment (Fig. 6). For the treatment of a particulate pollutant, this general way have sometimes to be adapted in order to get water quality that will fulfil the local and other legislation requirements at the lowest financial cost.

Due to the high cost of photochemical treatments, as a first step it must be confirmed that target pollutants are definitively non-biodegradable since for biodegradable compounds, classical biological treatments are, at present, the cheapest and the most environmentally compatible.

In coupled systems, the AOP pretreatment is meant to modify the structure of pollutants by transforming them into less toxic and easily biodegradable intermediates, which allows the subsequent biological degradation to be achieved in a shorter time and in a less expensive way.

The solution resulting from the phototreatment stage is considered to be biologically compatible after the elimination of (i) the initial biorecalcitrant compound, (ii) the inhibitory and/or non-biodegradable intermediates, and (iii) the residual H_2O_2, or other inhibitory electron acceptors, whenever they are utilized for the phototreatment.

These requirements, together with information concerning the evolution of toxicity and biodegradability of the phototreated solutions, allow the determination of an optimal phototreatment time, which corresponds to the best cost-efficiency compromise. The phototreatment time must be as short as possible to avoid a high electricity consumption, which

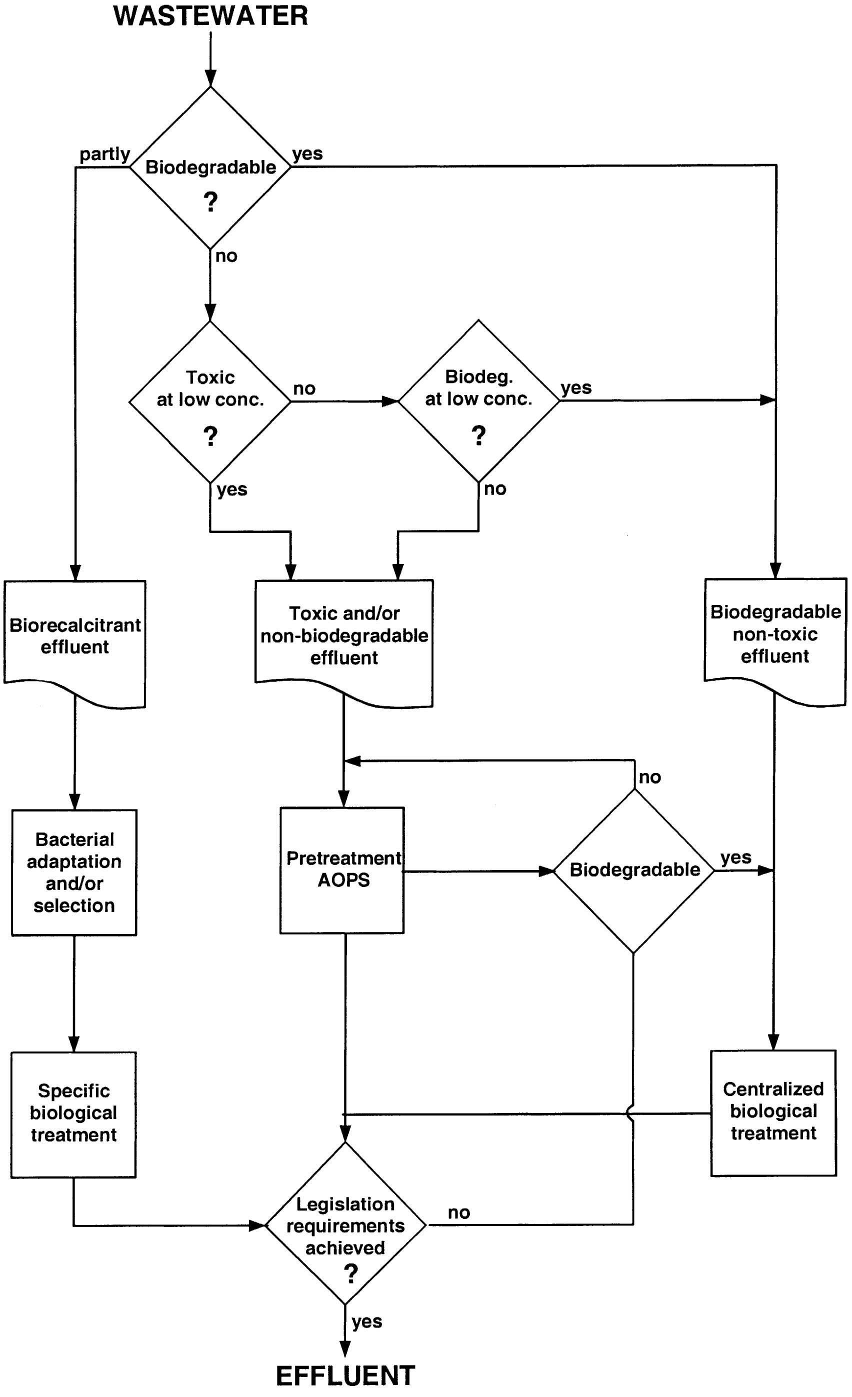

Fig. 6. General strategy of wastewater treatment.

represents about 60% of the total operational cost when using electric light sources [12]. However, if the fixed pretreatment time is too short, the intermediates remaining in solution could still be structurally similar to initial biorecalcitrant compounds and therefore, non-biodegradable. Furthermore, at short phototreatment time, the residual H_2O_2 concentration or other oxidant may be high enough to inhibit the biological stage of the coupled reactor. Chemical, biological, and kinetic studies must always be carried out to ensure that the photochemical pretreatment induces beneficial effects on the biocompatibility of the treated wastewater.

3.5. Perspectives for the coupling of photochemical and biological processes at field pilot scale

Direct solar light is promising and economically attractive source of UV irradiation, which has been applied in combination with oxidants and catalyst for the complete mineralization of a wide range of organic pollutant in water [27,28]. We have performed a series of experiments in order to find out whether photo-AOP using solar reactors, could be coupled with a biological system.

The efficiency of the solar photocatalytic treatment of IP based on the photo-Fenton system and TiO_2 photocatalysis was compared using a compound parabolic collector (CPC) at the Plataforma Solar de Almeria, Spain [16]. Even if the photo-Fenton reaction was the most efficient process for the mineralization of the IP solution, both homogeneous and heterogeneous photocatalysis are considered as suitable methods to reach the complete decay of IP in the solution. When IP is totally eliminated, the residual DOC remaining in the phototreated solution is biodegradable. Therefore, the complete mineralization can be achieved in a further biological treatment.

Interesting results were obtained using suspended TiO_2-photoassisted process since this catalyst is not sacrificed and can be separated from the treated water. This is very important when an industrial application is contemplated since TiO_2 is recycled and clean treated water could be drained away. Different procedures of filtration or sedimentation have been published for this purpose [29,30].

These encouraging results as well as those concerning the using immobilized TiO_2 (lab scale) open new possibilities for the coupling of TiO_2-photoassisted and biological processes, at pilot scale, employing supported TiO_2 and bacteria. The main advantage of this fixed system is that a separation procedure of the catalyst is not necessary rendering simpler and more economic the operation of both reactors.

4. Conclusions

A general strategy that can be used to develop a combined photoassisted AOP–biological process for biorecalcitrant wastewater treatment was proposed. For the development of this strategy, the following points need to be considered: the biodegradability of initial solutions, the operation mode of the coupled reactor, the chemical and biological characteristics of the photo pre-pretreated solutions, the evaluation of different photoassisted AOP, the optimal conditions of the individual processes and the efficiency of the coupled reactor.

The application of this strategy was illustrated using four different model substances. All this pollutants were determined to be non-biodegradable by the Zahn–Wellens biodegradability test and in an FBR under theoretically favorable conditions.

Three kinds of combined systems were developed using in all cases immobilized biomass for the biological step and either photo-Fenton, or Fe^{3+}/UV, or TiO_2 supported on glass rings for the photocatalytic pretreatment.

The chemical and biological characteristics of phototreated solutions were studied, in order to be able to determine the shortest time when the photochemical pretreatment reduces the anti-physiological properties of pollutant to permit transfer of phototreated wastewater to a biological treatment. Toxicity and biodegradability analyses of the phototreated solutions of *p*-NTS, MB, and IP show that the solution resulting from the photodegradation of MB is not biocompatible, while the photodegraded solution of *p*-NTS and IP are biologically compatible and their complete mineralization can be performed by biological process.

The coupling of a photochemical and biological flow reactor was operated in semi-continuous mode for the total mineralization of a *p*-NTS and IP solutions. This mode of operation was chosen since it gave better results comparing with the continuous mode.

The coupled photochemical and biological flow system was efficient for the mineralization of *p*-NTS and IP solutions. The primary degradation efficiency expressed as percentage of IP and *p*-NTS removed was 100% and the mineralization efficiency was 95% for both the substances.

A coupled photoreactor system using Fe(III)/light and immobilized activated sludge culture, was developed and tested for the treatment of AMBI solutions. The pretreatment system was able to remove the biorecalcitrant compound and produce biocompatible intermediates, which is completely mineralized by the biological system. The coupled reactor was operated in a semi-continuous mode and an optimal pretreatment time of 5 h was found. At this moment the best compromise between the shortest photochemical pretreatment and the highest biological and overall efficiency was reached.

Fe(III)/light pretreatment was compared with the well know photo-Fenton system Fe^{3+}/H_2O_2/light as a pretreatment in the coupled reactor. For both the compared systems the same global efficiency of the coupled reactor was achieved (90% of DOC removed). Nevertheless the Fe(III)/H_2O_2/light system is 2.5 times more efficient that the Fe(III)/light system, regarding pretreatment time.

The third coupled system developed used TiO_2 supported on glass rings in the photocatalytic coaxial reactor and fixed bed bacteria on biolite. These fixed components render coupled technology for the treatment of wastewater more economic and simpler.

The field experiments under direct sunlight using a CPC reactor demonstrate that the solar photocatalytic treatment is effective for the purification of water contaminated by herbicides and other biorecalcitrant substances. They are also adequate to attain the state of biocompatibility of the phototreated solutions required for further biological treatment. These results indicate that a coupled photochemical–biological treatment system at pilot scale is a possible method to achieve the complete mineralization of the biorecalcitrant pollutants.

Acknowledgements

This work was supported by the OFES contract no. 01.0199 within the 'Improving Human Potential—Access to Research Infrastructures' program of the European Community EU: HPRI-CT-99-00013. We are pleased to thank the Swiss Academy of Engineering Sciences (SATW) and the Colombian Institute for the Science and Technology Development "Francisco José de Caldas"—COLCIENCIAS for the doctoral grant to V. Sarria, and S. Parra, respectively. We wish to express our gratitude to the "Projet environnement EPFL-UNIVALLE". We tank Dr Sixto Malato of the Plataforma Solar de Almeria (PSA) for his help throughout the work.

References

[1] D.F. Ollis, H.A. Ekabi, Photocatalytic Purification and Treatment of Water and Air, EDS, Elsevier, Amsterdam, 1993.
[2] D. Blake, Bibliography of work on the heterogeneous photocatalytic removal of hazardous compounds from water and air, Update no. 3 to January 1999, NREL/TP-570-26797, National Technical Information Service (NTIS), US Department of Commerce, Springfield, VA, 1999.
[3] J.P. Scott, D.F. Ollis, Environ. Prog. 14 (1995) 88.
[4] J.P. Scott, D.F. Ollis, J. Adv. Oxid. Technol. 2 (1997) 374.
[5] G.O. Sigge, T.J. Britz, P.C. Fourie, C.A. Barnardt, R. Strydom, Water Sci. Technol. 44 (2001) 69–74.
[6] R. Krull, D.C. Hempel, Water Sci. Technol. 44 (2001) 85.
[7] G. Bertanza, C. Collivignarelli, R. Pedrazzani, Water Sci. Technol. 44 (2001) 109.
[8] J. Beltrán-Heredia, J. Torregrosa, J. García, J.R. Dominguez, J.C. Tiern, Water Sci. Technol. 44 (2001) 103.
[9] Y. Zeng, P.K.A. Hong, D.A. Wavrek, Water Res. 34 (2000) 1157.
[10] S. Ledakowicz, M. Solecka, R. Zylla, J. Biotechnol. 89 (2001) 175.
[11] D.F. Ollis, Water Sci. Technol. 44 (2001) 117.
[12] J. Bandara, C. Pulgarin, P. Peringer, J. Kiwi, J. Photochem. Photobiol. A 111 (1997) 253.
[13] C. Pulgarin, M. Invernizzi, S. Parra, V. Sarria, R. Polania, P. Peringer, Catal. Today 54 (1999) 341.
[14] S. Parra, V. Sarria, S. Malato, P. Peringer, C. Pulgarin, Appl. Catal. B 27 (2000) 153.
[15] V. Sarria, S. Parra, M. Invernizzi, P. Péringer, C. Pulgarin, Water Sci. Technol. 44 (2001) 93.
[16] S. Parra, S. Malato, C. Pulgarin, Appl. Catal. B 36 (2002) 131.
[17] M.C. Yeber, J. Freer, J. Baeza, H.D. Mansilla, TiO_2 and ZnO thin film formation on glass, in: Proceedings of the Second International Conference on Advanced Wastewater Treatment Recycling and Reuse, September 1998, Milan, Italy.
[18] M.C. Yeber, J. Rodriguez, J. Freer, N. Durán, H.D. Mansilla, Chemosphere 41 (2000) 1193.
[19] OECD, Guidelines for Testing of Chemicals, vol. 2, Test 302B, 1996.

[20] R.A. Larson, M.B. Schlauch, K.A. Marley, J. Agric. Food Chem. 39 (1991) 2057.

[21] D. Nansheng, F. Tao, T. Shizhong, Chemosphere 33 (1996) 547.

[22] P. Mazellier, M. Sarakha, M. Bolte, New J. Chem. 23 (1999) 133.

[23] G. Mailhot, A. Asif, M. Bolte, Chemosphere 41 (2000) 363.

[24] M. Rodriguez, N. Abderrazik, S. Contreras, E. Chamarro, J. Gimenez, S. Esplugas, Appl. Catal. B 37 (2002) 131.

[25] B.C. Faust, J. Hoigne, Atmos. Environ. A 24 (1990) 79.

[26] V. Sarria, M. Deront, P. Péringer, C. Pulgarin, Appl. Catal. B, 2002, in press.

[27] S. Malato, J. Blanco, C. Richter, P. Fernandez, M.I. Maldonado, Solar Energy Mater. Solar Cells 64 (2000) 1.

[28] S. Malato, J. Caceres, A. Agüera, M. Mezcua, D. Hernando, J. Vial, A.R. Fernández-Alba, Environ. Sci. Technol. 35 (2001) 4359.

[29] J. Blanco, S. Malato, F.J. De las Nieves, P. Fernández, Sedimentation method for colloidal semiconductor particles, EU Patent P9 902 508 (1999).

[30] W. Xi, S.-U. Geissen, Water Res. 35 (2001) 1256.